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TITLE STUDIES ON THE ELECTROCHEMICAL REDUCTION AND THE PHOTOLYSIS OF PHENACYL 'ONIUM SALTS AND RELATED COMPOUNDS

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STUDIES ON THE ELECTROCHEMICAL REDUCTION AND THE PHOTOLYSIS OF PHENACYL 'ONIUM SALTS AND RELATED COMPOUNDS.

A Thesis Submitted to the Council for National Academic Awards in Partial Fulfilment of the Regulations for the Degree of Doctor of Philosophy.

By

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STUDIES ON THE ELECTROCHEMICAL REDUCTION AND THE PHOTOLYSIS OF PHENACYL 'ONIUM SALTS AND RELATED COMPOUNDS.

D. Fonseca

Abstract

The electrochemical reduction of a series of quaternary phenacylammonium and tertiary phenacylsulphonium salts in aqueous solution at a mercury cathode has been investigated using polarography, coulometry, titrimetry and product analysis methods. The relatively small effect of p-ring substituents, quantified by a Hammett analysis indicate that the keto group has a predominating effect on the ease of reduction. The same effect also reduces the effect of ligands on the reaction. The only mechanism which can account for these results is the reductive cleavage in aqueous solution involving a two-electron transfer from the electrode to the salt substrate: all attempts to find evidence for one-electron transfer steps by studying the effect of applied potential and temperature gave negative results. These results are in marked contrast to those of benzyl dialkylsulphonium salts. Mechanisms have been put forward to account for these differences and those of the related phenacylamines and sulphides.

A polarographic study of dimethylphenacylsulphonium bromide and trimethylphenacylammonium bromide has been considered to ascertain the rates of reaction and activation energies for the reduction of these salts.

(2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide and (2-phenyl-2-oximinoethyl)trialkylammonium salts have been prepared and their electrolytic reduction studied for the first time. These compounds reduce similarly to the phenacyl salts: two-electron reduction of the C-X bond precedes other reductions. However, in alkaline solution chemical reaction may intervene.

A limited study of the photolysis of (2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide and its O-methyl ether has been carried out. The reaction mechanisms have not been fully established but homolysis of the C-S bond appears to be predominant. However there is much evidence for secondary photochemical processes involving initial reaction products. (2-phenyl-2-oximinoethyl) trimethylammonium bromide was inert to the same photochemical conditions.

ACKNOWLEDGEMENTS

I wish to express my sincere thanks and gratitude to Mr. H. Williams and Dr. J. V. Westwood for their supervision, encouragement, valuable comments and discussions during the preparation of this thesis.

I would like to acknowledge the co-operation of all the teaching and technical staff of the School of Chemistry, City of London Polytechnic, with special reference to B. Saunderson for the glc/ms and micro-analyses and to my friends and colleagues for their moral support and assistance.

To My

FAMILY

For Their Support

Moral Courage

And

Patience

CONTENTS

ELECTROCHEMISTRY

PHOTOCHEMISTRY

Chapter 1

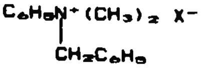
Introduction: Electrochemical reduction of 'onium salts(1.1)

The reduction of ammonium and sulphonium salts has been carried out by a number of methods. The present researches concern the electrochemical reduction of some phenacylammonium and sulphonium salts. This introduction gives a general survey of previous electrochemical studies on the 'onium salts of nitrogen and sulphur and concludes with the statement concerning the purpose and scope of the present studies.

Quaternary ammonium salts

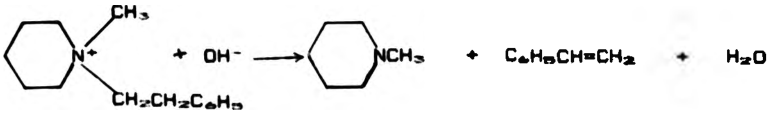
The electrochemical reduction of quaternary ammonium salts has been known for over seventy years(1.2).

eg. $C_6H_5N^+(CH_3)_3\ X^- \xrightarrow{\text{Pb cathode/(H}^+\text{)}} C_6H_6 + N(CH_3)_3$



$$C_6H_5N^+(CH_3)_2(CH_2C_6H_5)\ X^- \xrightarrow{\text{Pb cathode/(H}^+\text{)}} (CH_3)_2NC_6H_5 + C_6H_5CH_3$$

Where a β-hydrogen is available, sometimes the major product is the alkene, due to an elimination side reaction(1.2).



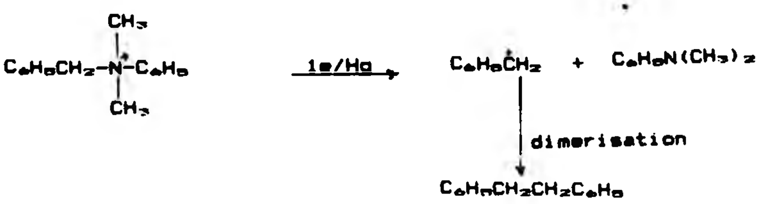
The ring opening of N,N-dialkyltetrahydroquinolinium salts by sodium amalgam was also brought about by electrochemical reduction(1.4).

Reductive cleavage at a mercury cathode was said to be "cleaner" than the use of amalgams. Using mixed ligand salts the following ease of ligand cleavage was established as:

$N^+\!-CH_2C_6H_5 \;>\; N^+\!-CH_2-CH{=}CH_2 \;>\; N^+\!-C_6H_5 \;>\; N^+\!-CH_3$

This order, which was also found from the results of chemical reduction using sodium and lead/sodium parallels the relative stabilities of the ligand groups.

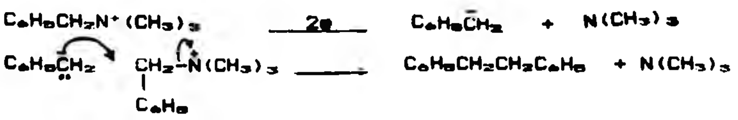
All the above reactions were carried out in protic solvents and are consistent with two-electron reduction, but there is strong evidence that one-electron reduction can occur in aprotic solvents such as dimethylformamide and N,N-dimethylacetamide(1.5). Thus electrolysis of benzyldimethylanilinium bromide gives rise to bibenzyl, a process which can be formulated as follows.



$$C_6H_5CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-C_6H_5 \xrightarrow{1e/Hg} C_6H_5\dot{C}H_2 + C_6H_5N(CH_3)_2$$

$$C_6H_5\dot{C}H_2 \xrightarrow{\text{dimerisation}} C_6H_5CH_2CH_2C_6H_5$$

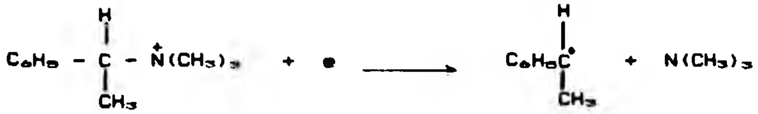
This result in itself is not conclusive for a one-electron reduction, insofar as a two-electron reduction to give a carbanion, followed by an SN2 reaction could account for the formation of bibenzyl.



$$C_6H_5CH_2N^+(CH_3)_3 \xrightarrow{2e} C_6H_5\bar{C}H_2 + N(CH_3)_3$$

$$C_6H_5\ddot{C}H_2 \quad \underset{C_6H_5}{CH_2}-\overset{+}{N}(CH_3)_3 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + N(CH_3)_3$$

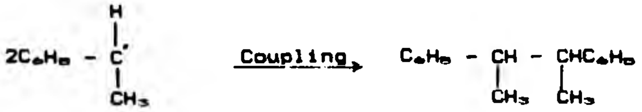
However, a similar reduction of chiral D-α-phenylethyltrimethylammonium nitrate, gave results much more consistent with a radical mechanism than a SN2 process(1.6).



$$C_6H_5-\overset{H}{\underset{CH_3}{C}}-\overset{+}{N}(CH_3)_3 + e \longrightarrow C_6H_5\overset{H}{\underset{CH_3}{C^{\bullet}}} + N(CH_3)_3$$

Planar or configurationally

labile radical



$$2C_6H_5-\overset{H}{\underset{CH_3}{C^{\bullet}}} \xrightarrow{\text{Coupling}} C_6H_5-\underset{CH_3}{CH}-\underset{CH_3}{CH}C_6H_5$$

Mixture of meso and

dl stereoisomers

Two-electron reduction to give the carbanion, followed by an SN2 reaction should give a mixture of the meso compound and one of the enantiomers. However it could not account for the racemic butane product.

In a related study, Mayell and Bard investigated the mercury cathodic reduction of benzyldimethylanilinium bromide in water, acetonitrile and dimethylformamide(1.7). The polarography showed only two-electron reduction waves, but reduction at controlled potential gave evidence for one electron reduction.

Whereas in water the only hydrocarbon product was toluene; in the aprotic solvents a mixture of toluene and bibenzyl was obtained. A coulometric study gave a value corresponding to 1.4 electron transfer. This result is consistent with concurrent one- and two-electron reduction processes giving 60% bibenzyl. They found that the dimer fraction increased with increasing concentration of the salt and also increased with lowering of the temperature. When the salt was reduced in acetonitrile solvent in the micro- cavity of an e.s.r. spectrometer, signals ascribed to radicals were obtained. However they had difficulty in reproducing this experiment.

They put forward the following scheme to account for these results:

$$C_6H_5N^+(CH_3)_2CH_2C_6H_5 \quad + \quad e \longrightarrow C_6H_5N(CH_3)_2 \quad + \quad C_6H_5\dot{C}H_2$$

$$C_6H_5\dot{C}H_2 \quad + \quad H_2O \longrightarrow C_6H_5CH_3 \quad + \quad \dot{O}H$$

$$C_6H_5\dot{C}H_2 \quad + \quad CH_3CN \longrightarrow C_6H_5CH_3 \quad + \quad \dot{C}H_2CN$$

$$2C_6H_5\dot{C}H_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5$$

$$\dot{O}H \quad + \quad e \longrightarrow OH^-$$

$$\dot{C}H_2CN \quad + \quad e \longrightarrow \bar{C}H_2CN$$

They considered that an alternative scheme for the formation of toluene by the transfer of a second electron to the benzyl radical was less satisfactory :

$$C_6H_5\dot{C}H_2 \quad + \quad e \longrightarrow C_6H_5\bar{C}H_2 \xrightarrow{H_2O} C_6H_5CH_3$$

This reluctance to accept a scheme involving the benzylcarbanion gives rise to a number of problems discussed more fully below. It becomes even more difficult to reject the anion hypothesis when reduction of the salt in protic solvents, such as water or methanol were shown to give only toluene and no dimer. Reviewing this work

Horner proposed a scheme involving adsorbed species(1.8).

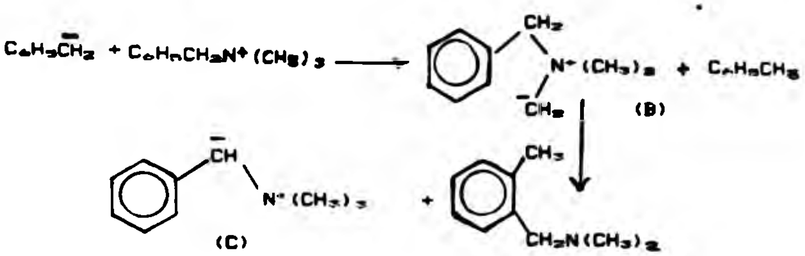
$$R_4N^+ + e \longrightarrow (R_4N)^{\bullet}_{ads.} \longrightarrow R_3N + R^{\bullet}_{ads.}$$

$$R^{\bullet}_{ads.} + e + H^+ \longrightarrow RH$$

A study by Dubois et alia of the reduction of a number of quaternary alkylammonium salts in hexamethylphosphorotriamide solution at platinum electrodes gave surprising results(1.9). Although the coulometry indicated a one electron transfer process, no dimer product was found except in the case of benzyltrimethylammonium perchlorate and even in this case the yield of bibenzyl was only 13%. The main product was toluene (45%) but there was also a large amount of rearrangement product, O-methylbenzyldimethylamine (32%). This rearrangement is formally similar to the Sommelet - Hauser reaction and they formulated an ionic mechanism(1.10).

$$C_6H_5CH_2N^+(CH_3)_3 + e \longrightarrow \underset{(A)}{\left(C_6H_5CH_2N^+(CH_3)_3\right)^{\bullet}} \longrightarrow C_6H_5\overset{\bullet}{C}H_2 + N(CH_3)_3$$

$$C_6H_5\overset{\bullet}{C}H_2 + e \longrightarrow C_6H_5\bar{C}H_2$$



It is interesting that this mechanism postulates the transfer of a "second" electron to the benzyl moiety, but stoichiometrically preserves the net overall one-electron transfer because the formation of ylid and rearrangement product is not an electrochemical reaction. The carbanion (C) is a more stable carbanion intermediate, when one considers the relative acidities of the CH_2 and CH_3 group hydrogens, but the rearrangement presumably goes via the less stable ylid (B).

They also stated without detail that the radical (A) may rearrange to the product plus a hydrogen atom which could react with a benzyl radical.

They reported that in dimethylformamide solvent the product was toluene, no bibenzyl or O-methylbenzyldimethylamine was formed and concluded that in this solvent the toluene must arise from the benzyl anion which presumbly would require the coulometry to correspond with a net two- electron process. In a later paper(1.11) the same group reported that their experimental coulometry results were unable to distinguish unambiguously between the one- and two-electron transfer mechanism, but because of the results of Finkelstein et alia(1.8) and Mayell and Bard(1.7) discussed earlier in this account they preferred the radical mechanism, and formulated the toluene to arise from reaction with water.

$$C_6H_5\dot{C}H_2 + H_2O \longrightarrow C_6H_5CH_3 + \dot{O}H$$

$$4\dot{O}H \longrightarrow O_2 + 2H_2O$$

$$O_2 + e \longrightarrow \bar{O}_2$$

Since all their yields are reported as "electron yields", based on an assumed one- or two-electron transfer mechanism, it is difficult to properly understand what the figures imply. For example, the reduction of the benzyl salt in dimethylformamide and dimethylsulphoxide gives only toluene and this is reported as an "electric yield" of 45%. If this means that of the total number of coulombs passed, only 45% can be accounted for by the formation of toluene, assuming a one-electron reduction, then what reduction processes are responsible for the remaining 55% coulomb total ?. Their results can be accommodated by the following scheme, involving net two-electron reduction, either in a single step or by two successive one-electron steps.

a) $C_6H_5CH_2N^+(CH_3)_3 + 2e \longrightarrow C_6H_5\bar{C}H_2$

b) $C_6H_5CH_2N^+(CH_3)_3 + e \longrightarrow (C_6H_5CH_2N^+(CH_3)_3)^{\bullet}$

$$\begin{array}{lllll} (C_6H_5CH_2N^+(CH_3)_3)^{\bullet} & + & e \longrightarrow C_6H_5\bar{C}H_2 & + & N(CH_3)_3 \\ \quad\downarrow & & & & \\ (CH_3)_3N & + & C_6H_5\dot{C}H_2 \xrightarrow{e} C_6H_5\bar{C}H_2 & & \\ C_6H_5\bar{C}H_2 & + & H_2O \longrightarrow C_6H_5CH_3 & + & OH^- \end{array}$$

This mechanism would account for 90% of the current passed. If the electrolysis ceased after 45% yield of toluene, one is faced with the question why. One possibility is the chemical reaction between the benzyl carbanion and the ammonium salt.

$$C_6H_5\bar{C}H_2 + C_6H_5CH_2N^+(CH_3)_3 \longrightarrow C_6H_5CH_3 + C_6H_5\bar{C}HN^+(CH_3)_3$$

This mechanism accounts for both the yield of toluene and the disappearance of half the salt by a purely chemical reaction to give the non reducible ylid. The reason for dealing with these latter reports in such detail is to draw attention to the current practice for regarding electron transfer processes as of necessity going through one- electron stages, even in cases where there is no experimental evidence for this. There may be a strong theoretical reason for believing that electrons can only be transferred singly, but in practical chemistry we must be mindful of observational criteria(1.12). This is of particular relevance to the systems we have been studying and this will be taken up again in the later discussion.

Sulphonium Salts

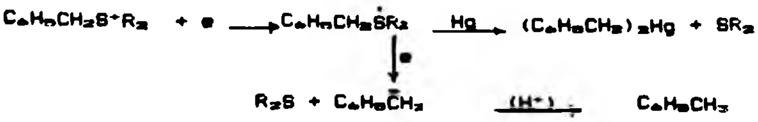
The reduction of sulphonium salts has been reviewed by Grimshaw(1.13). Early polarographic studies by Colichman and Love(1.14) led to the two-electron reduction mechanism.

$$R_3S^+ \xrightarrow{2e} R_2S + \bar{R}: \xrightarrow{H^+} R{-}H$$

Some years later Lüttringhaus and Machatzke(1.15) investigated the polarography of a large number of sulphonium salts in connection with some cytostatic effect studies and concluded that the two electrons were transferred in different steps.

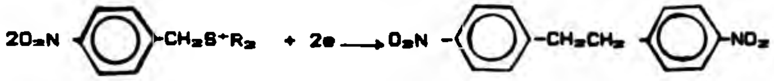
$$R_3S^+ + e \longrightarrow R_3\dot{S} \longrightarrow R_2S + \dot{R} \xrightarrow{e} \bar{R} \xrightarrow{(H^+)} R{-}H$$

The evidence for this scheme is not unambiguous and the work was not complemented by coulometry and product analysis studies. Settineri et alia, in a number of patents, on the electrolysis of sulphonium salts containing benzyl ligands, provided evidence, mainly from the reaction product, for one-electron reductions in aqueous solutions(1.16). Recently Parmar, in a careful study of the reduction of sulphonium salts having benzyl ligands, provided convincing evidence for the existence of the radical $R_3\dot{S}$ as an intermediate and made a careful study of the effect of temperature and cathode potential on the product distribution(1.17). Parmar's results were rationalised in the following scheme.



$$\begin{tikzcd}[column sep=small] C_6H_5CH_2S^+R_2 + e \arrow[r] & C_6H_5CH_2\dot{S}R_2 \arrow[r, "Hg"] \arrow[d, "e"] & (C_6H_5CH_2)_2Hg + SR_2 \\ & R_2S + C_6H_5\bar{C}H_2 \arrow[r, "(H^+)"] & C_6H_5CH_3 \end{tikzcd}$$

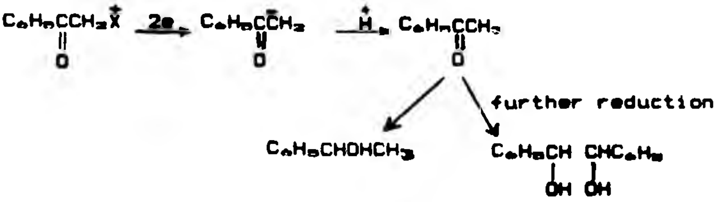
Parmar found only one example of dimerisation, namely



Considerable attention was given to Parmar's results in the present investigation: this is taken up again in the discussion of the present investigation.

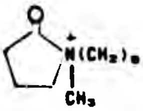
Electrochemical reduction of phenacyl 'onium salts

Zuman and Horak(1.18) studied the polarographic reduction of some phenacylammonium salts. These salts reduced essentially by the same mechanism; a two-electron first reduction relating to the cleavage of the C-X bond, followed by a second step concerned with the reduction of the ketone formed. The latter reduction varied with the pH of the solution in both reduction potential and the number of electrons transferred. (This second reduction is of minor importance in the present investigation, in so far as it is a reduction of the product carbonyl compound rather than the 'onium salt).



In acid solutions the first step was pH dependent. These workers also reported studies on the related ammonium salts listed in table 1.1 .

Table 1.1

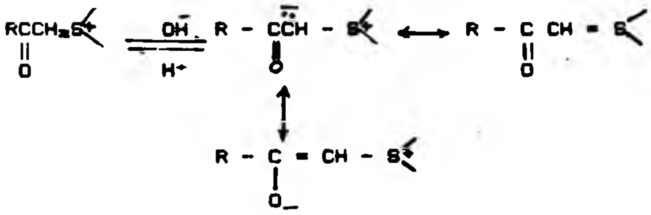
		pH	3.3	6.4	9.4	10.2
 $C_6H_5COCH_2\overset{+}{N}(CH_3)_2(CH_3)$	I^-	$E_{1/2}$ (-V)	0.79	0.90	0.99	0.99
		pH	4.0	6.3	7.0	10.4
 $CH_3COCH_2\overset{+}{N}(CH_3)_2(CH_3)$	I^-	$E_{1/2}$ (-V)	1.18	1.25	1.27	1.28
		pH		6.4	8.3	10.1
	I^-	$E_{1/2}$ (-V)		1.30	1.31	1.31
		pH	3.1	6.2	8.8	10.4
 $C_6H_5COCH_2\overset{+}{N}(CH_3)_2(H)$	I^-	$E_{1/2}$ (-V)	0.90	1.01	1.11	1.21
		pH		6.3	7.8	10.4
 $CH_3COCH_2\overset{+}{N}(CH_3)_2(H)$	I^-	$E_{1/2}$ (-V)		1.41	1.45	1.57

These results show clearly that the phenacyl group enhances the ease of reduction more than the acetyl and cyclopentanoyl groups. As shown in the table, these studies included hydroiodide salts of amines, as well as quaternary ammonium salts. Whereas the quaternary salt reduction is independent of pH at the higher pH's, the amine salts are converted to the much less reducible amines. The polarographic studies were complemented by some controlled potential electrolysis and the carbonyl compound (acetophenone) resulting from the first reduction step was identified through its 2,4-dinitrophenylhydrazone derivative and by glc studies and the comparison of the polarography with that of an authentic sample of acetophenone. From differences in wave height dependence of acetophenone and the products in the polarographic reduction, these authors suggested that the primary product of reduction was the enol rather then the keto isomer.

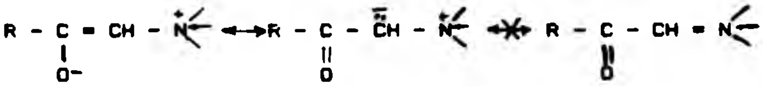
Zuman and Tang(1.19) studied the polarographic reduction of butylmethylphenacylsulphonium perchlorate in some detail with essentially the same result as for the quaternary phenacylammonium salts except that

a) the sulphonium salt reduced at a significantly lower $E_{1/2}$ value than the phenacylammonium salt, and

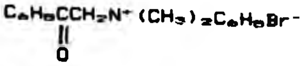
b) the sulphonium salt became markedly pH dependent above pH 7. The pH dependence was related to the higher acidity of the sulphonium salt, the ylid being stabilised by the sulphur atom.

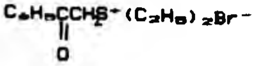


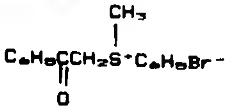
In fact the phenacylsulphonium salt underwent reversible conversion to ylid with aqueous alkali i.e. normal acid-base behaviour and this was used to evaluate the pKa of the sulphonium salt. We confirmed this behaviour with related sulphonium salts in the present investigation. In the ammonium ylid, carbon-nitrogen double bond formation is not energetically feasible and must be responsible for the much lower acidity of the quaternary phenacylammonium salts in aqueous solution.



As observed with the ammonium salts the difference in pH dependence of the polarographic wave height (diffusion current) of an authentic sample of acetophenone and the second wave reduction of the phenacylsulphonium salt led these workers to suggest that the primary electrode reduction product was the enol form of acetophenone. The same authors also investigated the nature of a round shaped streaming maximum observed when the above salt was reduced in pH 8-12 region. They showed that it differed from most commonly known catalytic and streaming maxima and they suggested that possibly the conjugate ylid base, present in alkaline solution, may be involved. These studies by Zuman et alia overlapped a similar investigation of Saveant(1.20) who published a preliminary account of his work which essentially confirmed Zuman's polarographic study on the phenacylsulphonium salt. Saveant later published the results of the detailed study on the electrochemical reduction of the following phenacyl 'onium salts(1.21).

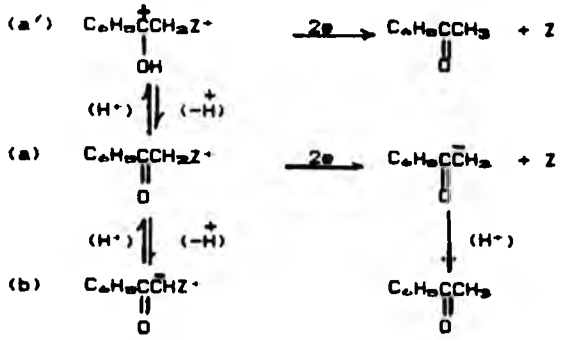

$C_6H_5\underset{\underset{O}{\|}}{C}CH_2N^+(CH_3)_2C_6H_5Br^-$


$C_6H_5\underset{\underset{O}{\|}}{C}CH_2S^+(C_2H_5)_2Br^-$


$C_6H_5\underset{\underset{O}{\|}}{C}CH_2\overset{\overset{CH_3}{|}}{S^+}C_6H_5Br^-$

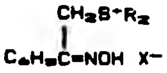
He confirmed the difference in pH dependence of the sulphonium salt and the ammonium salt and used a spectral method to investigate the acid-base behaviour of the salts. The considerable difference between the spectra of the sulphonium salts in acid and alkaline solutions was consistent with appreciable electron delocalisation in the ylid, as described earlier. From the acid-base titration he was able to determine the pKa value of the sulphonium salts, which he compared with values of pKa obtained from $E_{1/2}$ versus pH curve from polarographic measurements. Since we did similar studies in the present investigation, this is discussed later. Saveant also carefully examined the phenomenon of the streaming maximum reported by Zuman. He complemented the polarographic and acid-base results with electrocapillary studies. He found that the abnormal wave maximum occurs as soon as the pH becomes greater then the pKa and concluded that it was concerned with a kinetic current on the electrode surface, the chemical reaction being the recombination of the ylid adsorbed on the surface with a proton to form the sulphonium salt. This surface reaction appears to be accompanied by convection currents at the electrode surface and this agitation causes departure from the normal quiescent diffusion conditions of polarography, thus contributing to the maximum. The adsorption-desorption of the ylid on the surface is also important and is sensitive to suppressant (e.g. gelatine).

In the present investigation suppressant was used throughout and no instances of maxima were observed. Saveant suggested that the differences in adsorbtion of the ammonium and the sulphonium salts made it difficult to compare their half wave potentials as a function of their structures, even where they are most comparable i.e. in the region where they are pH independent. He also looked for one-electron transfer steps by polarography in dimethylformamide and like Mayell and Bard, obtained the same negative results. However, he pointed out that their reaction scheme was only one possible scheme and suggested that intervention by the electrode metal cannot be ruled out. He put forward the following scheme to account for his results and stated that the importance of the various stages depended on the acidity of the solution and the adsorbtion phenomena intervening with species (a) and (b).

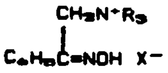


In later studies by Saveant and Andrieux(1.22) on phenacyl compounds such as phenacylamines, sulphides and ethers, evidence for one- and two-electron reduction was obtained. These results are examined in relation to our studies in the discussion.

Because the present work included a study on the phenacyloximino 'onium salts of general structure:



$$C_6H_5\overset{\displaystyle CH_2S^+R_2}{\overset{|}{C}}{=}NOH\ X^-$$



$$C_6H_5\overset{\displaystyle CH_2N^+R_3}{\overset{|}{C}}{=}NOH\ X^-$$

and there are no known electrochemical studies of this class of compounds, the following section is a summary of previous work on the cathodic reduction of oximes.

Electrochemical reduction of Oximes

The carbon-nitrogen analogue of the carbonyl group is the imine $>C{=}NH$ group. Imines are not all that accessible and are often readily hydrolysed. It was therefore decided to investigate the oxime analogues of the phenacyl 'onium salts. The electrochemical reduction of the oximes has been investigated by a number of workers and was reviewed by Lund(1.23). Because of the amphoteric nature of the oxime group the reduction is more complex than observed for the carbonyl group and the process is more pH dependent. Generally, oximes can be reduced in acid solution and much less so in alkaline solution. A scheme proposed for the reduction in acid solution involves the conjugate acid of the oxime.

$$\begin{tikzcd}
RR'C{=}NOH + H^+ \arrow[r, shift left=0.5ex, harpoon] & (RR'C{=}NOH)H^+ \arrow[l, shift left=0.5ex, harpoon] \arrow[d, "2e + 2H^+"] \\
RR'CH\overset{+}{N}H_3 & RR'C{=}N^+H_2 + H_2O \arrow[l, dash, "2e + 2H^+"']
\end{tikzcd}$$

Protonation of the oxime can occur at the oxygen or nitrogen atom giving rise to two isomeric conjugate acids

$$RR'C{=}N^+H{-}OH \qquad RR'C{=}N{-}\overset{+}{O}H_2$$

Both species will be present in unequal amounts; the nitrogen atom will probably be the more basic. Both species will be more readily reduced than the neutral oxime, but at present it is not known whether one or both isomers are involved in the reduction. It was earlier thought that the reduction went via the hydroxylamine group.

$$RR'CH{=}NOH + 2e + 2H^+ \longrightarrow RR'CH_2{-}NHOH$$

However when the hydroxylamine was submitted to the same reduction conditions it was not reduced. Therefore another species must be involved in the reduction and it was suggested that the imine was the initial reduction product(1,24).

$$(RR'C{=}NOH)H^+ + 2e + 2H^+ \longrightarrow RRC{=}N^+H_2 + H_2O$$

The imine intermediates are generally not isolable or even detectable by polarography; presumably they are at least as readily reducible as their precursor. However Lund found that 1,4 dihydroxybenzophenone oxime gave a two wave polarogram and controlled reduction at the potential corresponding to the first wave plateau gave the imine, which was isolated as its hydrochloride(1.28). This imine was investigated polarographically and shown to have a $E_{1/2}$ 0.15V more negative than that of the oxime.

Lund found that benzaldoxime is reducible to the hydroxylamine in alkaline solution at pH's as high as 12.8 in yields up to 42%.

The mechanism for this reduction is not clear. It was suggested that the reduction may go via an oxime tautomer X or Y.

$$C_6H_5CH{=}N^+H{-}O^- \qquad C_6H_5CH_2N{=}O$$

(X) (Y)

However the lack of H/T exchange at the CH group of benzaldehyde oxime when this substance was refluxed in an alkaline ethanol solution enriched with C_2H_5OT argues against the presence of Y(1.26).

In general the oxime is more readily reduced at the mercury cathode than the corresponding carbonyl compound, the $E_{1/2}$ value of the latter being approximately 0.2V more negative than those of the oximes. This may be due to the much weaker C=N bond compared with the C=O bond.

Table 1.2

Bond	Bond energy(1.27) (KJ mole^{-1})
C=N	≈ 575
C-N	≈ 295
C=O	≈ 735
C-O	≈ 370

In view of the fact that in the present study it was found that reduction of the phenacyloximesulphonium salts caused initial cleavage of the C-X bond and not reduction of the oxime group (this occurred at a more negative potential) further discussion of the reduction of the oxime group will be omitted.

Parallel behaviour of the reduction of α-bromoacetophenone oxime is described with that of the oxime 'onium salts in the discussion (page 210). However, as in the case of the phenacyl 'onium salts, electrochemical reduction of the corresponding oxime salts lead to the cleavage of the C-X bond and not reduction of the oxime group. In fact there was an almost parallel set of results for the oxime salts as for the phenacyl salts.

The reduction of phenacyl 'onium compounds by chemical methods had already been studied in this laboratory and these compounds were, therefore, of particular interest in the electrochemical study of reduction. Despite the detailed studies of Zuman and Saveant on these systems, there was scope for further work, e.g. on the influence of ligands and the effect of ring substituents. Following more recent studies on the effect of applied potential and temperature on the control of one- and two-electron transfer studies with benzylsulphonium salts, there was the need to search for further evidence for the one-electron reduction of phenacyl 'onium salts.

While the differing ease of reduction of ammonium and sulphonium salts has been correlated with $E_{1/2}$ values, no activation energy or reaction rate studies have been reported. The present studies include an investigation of this problem. The field was also widened to include an investigation of hitherto unreported phenacyloximinosulphonium and ammonium salts.

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Chapter 2

2.1 POLAROGRAPHY

(The theory of the polarographic technique)

Polarography constitutes a unique type of electrolysis in that it involves the study of current-voltage relationships at the dropping mercury electrode (DME). The DME consists of droplets of mercury emerging regularly from the end of a fine capillary tube and continuously exposing a fresh mercury surface to the electrolyte, thus preventing the accumulation of any products of electrolysis at the electrode. This is a polarisable electrode; such an electrode by definition is one which may adopt any potential (over two volts in aqueous solutions) applied to it with no change in the current flow. The other electrode is often a large unpolarised pool of mercury. The potential of this type of electrode is constant but depends on the composition and nature of the electrolyte in contact with it and is now often replaced by electrodes such as the saturated calomel electrode (SCE) whose potential is constant and independent of the nature of the electrolyte in contact with the DME.

The results obtained with the DME have a high degree of reproducibility since the mercury surface is renewed with each drop and there is no accumulation of decomposition products at the electrode surface. Mercury is relatively inert and has a high over-voltage towards hydrogen which allows the method to be used in alkaline solutions. There are a few disadvantages in using the DME, however, particularly its small anodic working range (+0.4 volts vs SCE), but most of the substances that concern us here are reduced at potentials more negative than the mercury dissolution potential. Dissolved oxygen is reduced in two sluggish stages at cathodic potentials, but these are eliminated by flushing the working solution with nitrogen. Mercury has a slight vapour pressure at room temperature and hence can prove to be a health hazard, but sensible precautions make its use quite safe.

2.1.A. POLAROGRAPHIC CURRENTS

The currents which flow depend on factors given below, under controlled circumstances: these can be used for qualitative and quantitative analyses. However, the current-voltage curves (C-V curves) can be of considerable value in the study of the mechanisms of electrode reactions and it is this aspect which is of importance in the present study.

During electrolysis two main types of process are involved. These are:

(1) mass transfer processes i.e. processes involved in bringing the electroactive species to the electrode surface;

(2) processes occurring at the surface of the electrode. These include adsorption, electron interchange and desorption of products, etc.

(1) The mass transfer processes involved in bringing the electroactive species to the electrode surface include the following:

(a) **Migration:** This is an electrical field effect arising from the applied potential and also depends upon the charge carried by an electroactive species and upon its transference number. The migration effect, and hence the migration current, depends on the presence of other electrolytes. This is clearly undesirable, but the migration rate can be suppressed by having present with the species under study, an excess of a 'supporting' or 'indifferent' electrolyte, normally 50 to 100-fold in excess of the electroactive component of the solution. Supporting electrolytes serve as current carriers and by virtue of being in large excess, cause the migration effect of the test species to be so small as to be insignificant and thus effectively reduce its transference number to zero.

(b) **Diffusion:** This is a non-electrical effect and depends on the natural rate of diffusion of the species, whether charged or uncharged, to the electrode. It is governed by the concentration of the species and the temperature. The magnitude of the diffusion current depends upon the usual factors of diffusion, namely the concentration gradient at the electrode-surface interface; the temperature and the viscosity of the solution; the size and drop rate of the mercury drop; and the number of electrons involved in the reduction.

(c) **Convection:** Any mechanical, thermal or deliberate stirring of the solution will increase the rate of deposition. However, it is difficult to stabilise this effect with the DME, and accordingly it is eliminated using quiescent conditions to avoid convection.

(2) Processes at the electrode are more difficult to quantify. Each process involves an activation energy barrier. If all the energy barriers are small the process becomes a reversible one. However, complications can occur due to strong adsorption leading to an adsorption current or, alternatively, special secondary chemical processes occur at the electrode causing a kinetic current. Fortunately, none of these complications occur in the present studies so that diffusion remains the most important process.

A potential is applied across the dropping mercury electrode and the reference electrode (SCE) and is increased in a stepwise manner. A very small current flows, called the residual current, until the decomposition potential of the reducible species is reached. A steep rise in current is now observed for a small increase in potential, eventually levelling out in a plateau. This limiting current at the plateau is called the diffusion current and is denoted by id. The current-voltage (C-V) curve is called the 'polarogram' and has the appearance as shown in Fig.(2.1). The original development of this technique was due to Heyrovsky(2.1). Since the rate of reduction increases with the applied potential, a point is eventually reached at which the ions are reduced as fast as they can arrive at the electrode surface by the diffusion process. Fig.(2.2) gives a planar representation of this process in the vicinity of the electrode.

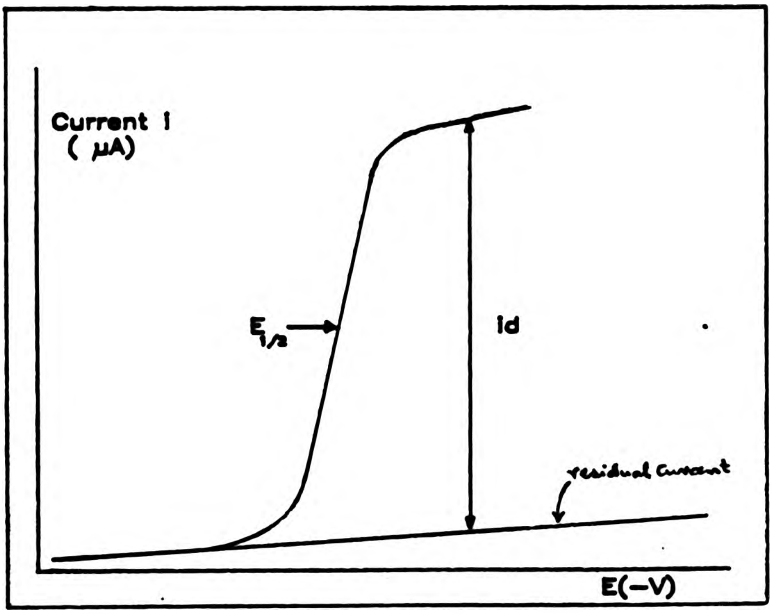

Fig. 2.1. Essential features of a current-voltage curve known as a "Polarogram" or "Polarographic Wave".

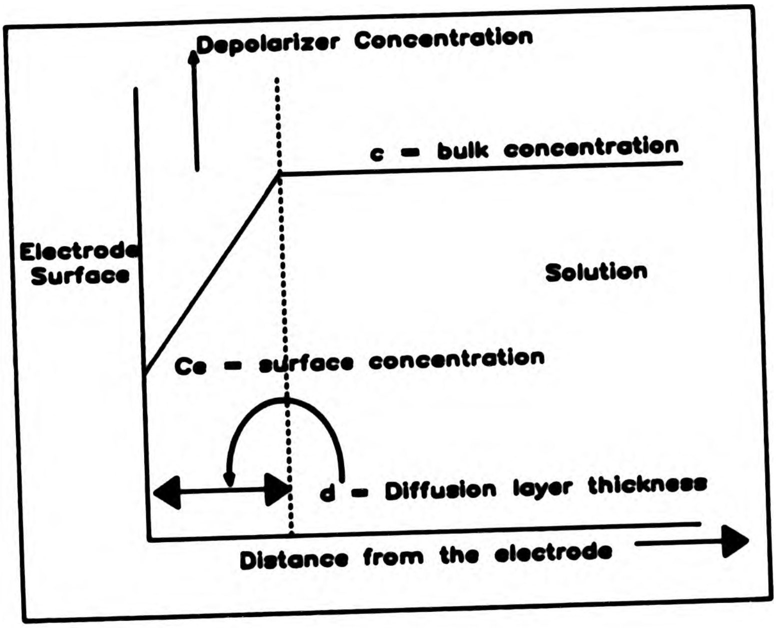

Fig. 2.2. Concentration gradient at a planar electrode.

A complex mathematical study of the polarographic wave by Ilkovic(2.2) lead to an equation for a diffusion controlled process in the form:

$$id = 0.732nFCD^{1/2}m^{2/3}t^{1/6} \qquad (2.1)$$

where,

n is the number of electrons invoved in the reduction or oxidation process

C is the concentration of the electroactive species in moles cm^{-3}

D is the diffusion coefficient in $cm^{2}sec^{-1}$

m is the weight of mercury flowing through the capillary in $gsec^{-1}$

t is the drop time in seconds

id is the diffusion current in amperes

F is the Faraday, 96,500 coulombs

The above equation was modified by Lingane and Loveridge(2.3) in the form:

$$\begin{array}{rcl} & : & \\ & : & \\ id = 607nCD^{1/2} & : & m^{2/3}\,t^{1/6} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.2) \\ & : & \\ \text{solution} & : & \text{electrode} \\ \text{factors} & : & \text{factors} \end{array}$$

where,

c is in millimoles per litre (mm $litre^{-1}$)

m is in milligrams per second (mg sec^{-1})

id is in microamps (μA) and is the mean current

Analysis of the terms in equation (2.2) shows that there are solution factors and electrode factors. Using constant electrode conditions i.e. m and t are kept constant, then id is proportional to c. However, if the solution factors are maintained constant then,

$$id = \text{constant}.\ m^{2/3}\, t^{1/6} \qquad (2.3)$$

If the drop rate is changed by altering the height of the mercury reservoir h, then the time for the drop to fall is inversely proportional to h. Also, the amount of mercury, m flowing through the capillary per second is proportional to h. Substituting these quantities for m and t in equation (2.2) which is

$$id = \text{constant}.\ m^{2/3}\, t^{1/6}, \text{ gives}$$
$$id = \text{constant}.\ h^{2/3}.h^{-1/6}$$
$$= \text{constant}.\ h^{1/2}$$
$$\text{i.e.}\quad id \propto h^{1/2}$$

Thus the criteria that $id \propto c$ and $id \propto h^{1/2}$ are used to confirm that the process at the electrode is diffusion controlled. Indeed these criteria are always applied to check that there are no complications from adsorption or kinetic effects.

Residual current (i_r)

There is, however, a further current flow which occurs and which cannot be eliminated. This arises from the fact that a new mercury surface is continually being presented to the solution as the drops grow and fall. This surface acquires a charge by the alignment of ions at its surface.

It corresponds to the charging of a condenser and is often termed the charging or residual current. It increases steadily as the applied voltage is increased and causes the polarogram to be 'tilted' as shown in figure (2.1). It is essentially a non-faradaic current since no electron transfer occurs across the double layer.

As the concentration of the active species decreases so id decreases but i_r does not so that the lower practical limit of id above i_r is reached at approximately 10^{-5}M. The upper limit is reached at approximately 10^{-2}M by the need to supress the migration effect.

In practice therefore, polarography is conveniently operated within the range of 10^{-3}M to 10^{-4}M

Since the surface area of the mercury drop alters appreciably over its lifetime, there is variation of current over this time which would produce a polarogram with a saw- edge shape. Moreover, a recording instrument cannot follow these fluctuations precisely. Fortunately this phenomenon can be damped by a high capacity condenser across the recording system which greatly increases its time constant, giving a reasonable step with a small ripple on its upper surface.

The drop time is controlled by a reservoir of mercury to be within the range of 3-7 seconds per drop. If less than this the drops are falling rapidly enough to produce a convection effect. If it is more than this it is approaching the time constant of the recording system and the damping circuit becomes offset.

2.1.B. Polarographic potentials

The potential corresponding to the mid-point of the wave where the current is exactly one-half of the maximum value (id/2) is known as the 'half-wave potential', $E_{1/2}$ as shown in Fig. (2.1). Heyrovsky and Ilkovic(3,4) showed that for a reversible process the current i at any point on the wave could be related to the applied potential E and $E_{1/2}$ by the equation

$$E = E_{1/2} + (2.303RT/nF) \times \log i/(id-i) \quad .... \quad (2.4)$$

A plot of log i/(id-i) vs E(-V) thus gives a graph as shown Fig. (2.3) below.

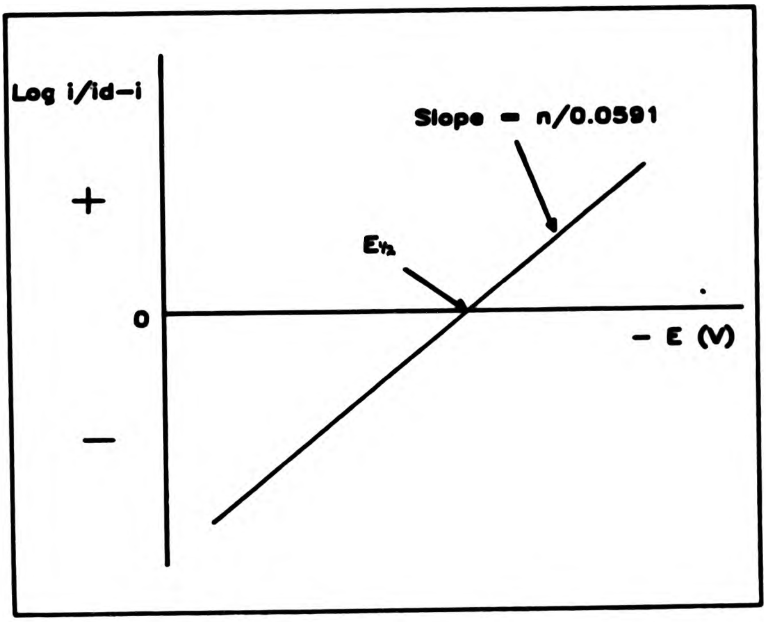

Fig 2.3 Logarithmic Analysis

The process is termed the logarithmic analysis of the wave. The value of this graph is that it gives an accurate value for $E_{1/2}$ and also the value of n can be derived from the slope.

Since most processes are not reversible, equation (2.4) cannot be applied directly. However, an equation was derived which is similar in form to equation (2.4) except that it contains the term α, the transfer coefficient.

$$E = E_{1/2} + (2.303RT/\alpha nF) \times \log i/(id-i) \quad \ldots\ldots\ldots\ldots \quad (2.5)$$

From the slope given by the logarithmic analysis of the irreversible process the value of αn may be determined. It is possible to solve for n provided the value of α is known. Frequently, however, this is not known so that other procedures are adopted. The value of n may be determined from the Ilkovic equation. The value m can be measured by weighing 50 drops of mercury flowing through a capillary at a fixed height of mercury head; the time t and id can be measured directly for a fixed concentration C; n can now be solved if D is known. The basic problem is to find D. A method in common use is to obtain the value of D for a species of similar molecular weight and this will usually be sufficient to enable n to be evaluated to the nearest whole number. However, the most satisfactory approach is to carry out a coulometric study of the reduction process. This is discussed later.

2.1.C. The effect of pH

Organic reduction processes in aqueous solutions may involve the participation of protons (H^+), due to the consumption of protons during the reduction process, either before, during or after electron transfer. Considerable changes in pH may occur at the electrode surface which can lead to the formation of new species depending on the acid-base nature of the substrate and this can give rise to wave distortion and even to additional waves, it is therefore customary to work in buffers of fixed pH which maintain a constant pH at the electrode surface. The type and concentration of the buffer may affect the wave profile and also the $E_{1/2}$ value.

For reversible organic reductions which are pH dependent, $E_{1/2}$ changes with pH as follows:

$$dE/dpH = -m/n\ (0.0591) \text{ per pH unit at } 25^\circ C \quad \ldots\ldots. \quad (2.6)$$

Where m is the number of protons.

For irreversible processes equation (2.6) includes αn (instead of just n) and becomes:

$$dE/dpH = -m/\alpha n\ (0.0591) \text{ per pH unit at } 25^\circ C$$

A plot of $E_{1/2}$ against pH gives a linear relationship and has a slope of $-2.303mRT/\alpha nF$ for an irreversible reduction process. Sometimes however, a change of slope occurs indicating that the nature of the electrode process changes as the potential changes.

Complications

Aqueous solutions containing dissolved oxygen undergo reduction at the DME giving two waves within the normal working voltage range, the first arising from the reduction of oxygen to hydrogen peroxide,

$$O_2 \longrightarrow H_2O_2$$

and the second for the reduction of hydrogen peroxide to water,

$$H_2O_2 \longrightarrow H_2O$$

This dissolved oxygen is removed by degassing the solution with nitrogen. It can also be eliminated by the use of sulphite in alkaline solutions although this can cause complications at lower pH values.

In some cases a maximum (i.e. formation of a peak on the current-voltage curve) instead of a well defined plateau occurs which can make the evaluation of id difficult and sometimes impossible. This effect arises due to the strong adsorption of the species on the electrode surface and is accompanied by rapid streaming of the electrolyte past the drop. This indicates that normal diffusion effects are not operative and a convection effect is also present and is causing the rapid rise in current.

Elimination of this phenomenon is usually achieved by use of a maximum suppressor. Several substances have been used for this, but are often effective over a narrow potential range. However, gelatine at 0.01% has been shown to be effective over a wide range of voltage. It appears to prevent adsorption effects without interfering with the normal diffusion process.

Normal conditions for using polarography.

A summary of the conditions required for normal polarographic studies are as follows:

1. The electroactive species should be of concentration 10^{-3} to 10^{-4} M
2. An indifferent electrolyte must be present in the amount 50 to 100 times that of the test species. KCl is often used, but if the $E_{1/2}$ is subject to variations with pH, then a buffer solution is usually adequate.
3. Dissolved oxygen is removed preferably by a stream of nitrogen over a period of 8-10 minutes.
4. If a maximum occurs then the solution should contain a maximum suppressor and for this purpose gelatine (0.01%) is usually used. However, additions are avoided if unnecessary.
5. The drop time should lie between 3 and 7 seconds per drop.
6. Electrolysis is carried out in quiescent conditions.

2.1.D. Determination of the rate constant (Ke°) for a slow electrode (irreversible) process from polarographic data (Koutecky method).

The wave analysis has produced a series of αn values for the phenacylsulphonium and ammonium salts which suggest that the reductions are irreversible processes. A measure of the degree of irreversibility is given by the standard reaction rate constant for the reduction process, Ke°. In a series of papers, Koutecky derived equations relating to these processes(2.5, 2.6, 2.7, 2.8). These equations are rather complex and difficult to apply, but by making certain simplifying assumptions, such as that the rate constant for the oxidation process is negligible and the polarographic drop time does not affect the rate constant or the diffusion coefficient, etc., Koutecky derived a relatively simple equation which allows an approximate value of Ke° to be evaluated. This is expressed as:

$$E_{1/2} = E^{\circ} + \frac{2.303\ RT}{\alpha nF} \log 0.886\ Ke^{\circ} \ (t/D)^{1/2} \ \ldots\ldots \quad (2.7)$$

where, t = droptime is secs.

D = Diffusion Coefficient in $cm^{2}sec^{-1}$

E°= standard redox potential; assuming a reversible process this is constant.

The importance of this equation is that $E_{1/2}$ depends on t. Accordingly if values of $E_{1/2}$ are studied at various drop times using the same solution cell set up and capillary, the evaluation of Ke° is possible.

As E° is not known, we can evaluate Ke° from two values of $E_{1/2}$ and t.

Suppose we consider the $E_{1/2}$ values at two drop times t_1' and t_1'' say $E_{1/2}'$ and $E_{1/2}''$ respectively, and make t_1' and t_1'' sufficiently different to be significant; then from the equation (2.7):

$$E_{1/2}'' - E_{1/2}' = \Delta E_{1/2} = \frac{2.303RT}{\alpha nF} \log 0.886\, Ke^\circ \left[(t_1''/D)^{1/2} - (t_1'/D)^{1/2}\right]$$

or,

$$\Delta E_{1/2} = \frac{2.303\ RT}{\alpha nF} \log Ke^\circ + \frac{2.303\ RT}{\alpha nF} \log 0.886 + \frac{2.303\ RT}{\alpha nF} \log \left[(t_1''/D)^{1/2} - (t_1'/D)^{1/2}\right]$$

at 25°C,

$$\Delta E_{1/2} = \frac{0.0591}{\alpha n} \log Ke^\circ + \frac{0.0591}{\alpha n} \log 0.886 + \frac{0.0591}{\alpha n} \log \left[(t_1''/D)^{1/2} - (t_1'/D)^{1/2}\right].$$

or,

$$\log Ke^\circ = \frac{\alpha n \Delta E_{1/2}}{0.0591} - \log 0.886 - \log\left[(t_1''/D)^{1/2} - (t_1'/D)^{1/2}\right] \qquad \ldots\ldots (2.8)$$

Experimentally it is possible to determine all the parameters in the above equation and hence calculate the value of $\log Ke^\circ$.

2.1.E. Determination of activation energy for an irreversible electrode process (Vlcek method).

A method for determining the activation energy was developed by Vlcek(8,9) as follows:

The rate constant Ke (cm.s^{-1}) at potential E for an irreversible process may be expressed as

$$Ke = A \exp -Q/RT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.9)$$

where,

Q is the real activation energy at potential E

A is the frequency factor.

The activation energy depends on the potential according to

$$Q = Q^{\circ} + \alpha nF\eta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.10)$$

where,

Q° = activation energy at the standard potential and the over-voltage $\eta = E - E^{\circ}$

α is the transfer coefficient

n is the number of electrons involved at the electrode.

For a completely irreversible process(2.5, 2.6),

$$i/(id-i) = 0.866\ Ke\ (t_1/D)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.11)$$

where,

i denotes the current at a given potential E.

In this equation t_1 and D are also functions of temperature.

The variation of the diffusion coefficient with temperature has been expressed by Temkin(2.10) in the form:

$$D = D_O \exp(-Q_D\ /RT) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.12)$$

where,

Q_D is the activation energy of the diffusion process.

By substituting the value of Ke from equation (2.9) in equation (2.11), we obtain:

$$i/(id-i) = 0.886\ A(t_1/D)^{1/2}\exp((Q - {}^{1}\!/\!_{2}Q_D)/RT) \quad \ldots\ldots\ldots \quad (2.13)$$

which on taking logs and rearranging gives:

$$\log i/(id-i) = \log A^1 - ((Q - {}^{1}\!/\!_{2}Q_D)/2.303\ RT) \quad \ldots\ldots \quad (2.14)$$

A^1 is the apparent frequency factor which contains all the temperature independent terms. From equation (2.14) the value of $Q - \frac{1}{2}Q_D$ can be directly calculated from the dependence of log i/(id - i) on 1/T.

The value of Q obtained from equation (2.14) refers to a fixed potential. In order to compare the activation energy of several substances having different $E_{1/2}$ values, the value of Q has to be referred to a common reference potential(2.11).

For the determination of Q, the value of Q_D must be known. This may be determined from the dependence of the diffusion current (id) on temperature.

The value of Q thus obtained is a measure of the structural changes in the depolariser during the acceptance of the electrons and the frequency factor is a characteristic of the orientation of the species at the electrode surface(2.9).

The plot of half-wave potential vs temperature in most cases gives a straight line whose slope is proportional to the frequency factor. In some cases a non-linear dependence(2.12) of $E_{1/2}$ on T is observed. Such behaviour is attributed to a change in reaction mechanism with temperature.

2.2 COULOMETRY

Introduction

The number of electrons involved in a polarographic reduction step can be calculated using the Ilkovic equation.

$$id = 607\ ncD^{1/2}\ m^{2/3}\ t^{1/6}$$

However, the basic problem is to find the value of D, the diffusion coefficient. It can be obtained from experiments using a diffusion cell; if the species is an ion it can be evaluated from measurements on ionic conductance or by comparing the diffusion coefficients of species having similar molecular weight and shape. These methods, however, can be time consuming and are not always accurate.

Another method used for determining the value of n is to obtain the slope of the wave given by plotting E against log (id-i)/i. A straight line is usually obtained for both reversible and irreversible processes. In the former case, the slope corresponds to an integral value of n and in the latter to a non-integral value of αn and the general lack of knowledge of information on α is the chief drawback of this method.

Coulometry is the most useful method for determining the value of n. It involves electrolysis on a 'micro' scale using large area electrodes. Where reduction processes are concerned, mercury is ideal as the cathode because of its chemical stability and high over-voltage. Since both current and voltage are adjustable, it is essential that one parameter is kept fixed. Thus coulometry at constant current or constant voltage is used, although the application is very different in each case. Constant current can be used where the process can be applied easily and reversibly,

$$\text{e.g. } Fe^{3+} + e \rightleftharpoons Fe^{2+}$$

and where changes of voltage over a range do not induce a further electrode process. In these cases the complete electrolysis can be carried out. The method is a highly accurate one.

In many cases, however, this procedure is not practical since difficulties arise from the drift of potential that occurs during depletion of the test species. If another process can occur close to the one of interest, the current would arise from the two processes to varying extents. Accordingly the process of constant potential electrolysis is employed and the quantity of electricity measured by a coulometer in the circuit. This coulometer can be a cell involving silver electrodes with silver nitrate as the electrolyte which gives fairly accurate readings, or less accurately, by a copper/acidified copper sulphate solution or an iodine coulometer. However, it is now possible to measure accurately with an electronic coulometer. Such a device was used in the present study. The potential applied is predetermined by polarography and corresponds to some point on the plateau of the wave. However, this is not the potential applied across the cell as it would be in polarography. This is because in polarography the value of i is in µA so that the ir drop across the cell is very small. In coulometry where i may be 100mA or more, the ir drop across the cell is considerably greater. To overcome this difficulty, a third electrode is introduced. Normally a saturated calomel electrode (SCE), this reference electrode is set up close to the working electrode (the cathode). The potential between the working electrode and the reference electrode is maintained constant, corresponding to the plateau value. This is achieved by a potentiostat which controls the potential between the cathode and the reference electrode.

2.2.A. Determination of the value of n

From the total amount of species present and the number of coulombs consumed, the number of electrons (n) can be calculated. As this is a 'macro' method, analysis of the solution after electrolysis can lead to identification and quantitative estimation of the products and hence establish the net reaction occuring during electrolysis.

Since the current falls exponentially as shown in Fig. (2.4), there is no advantage in attempting a complete electrolysis.

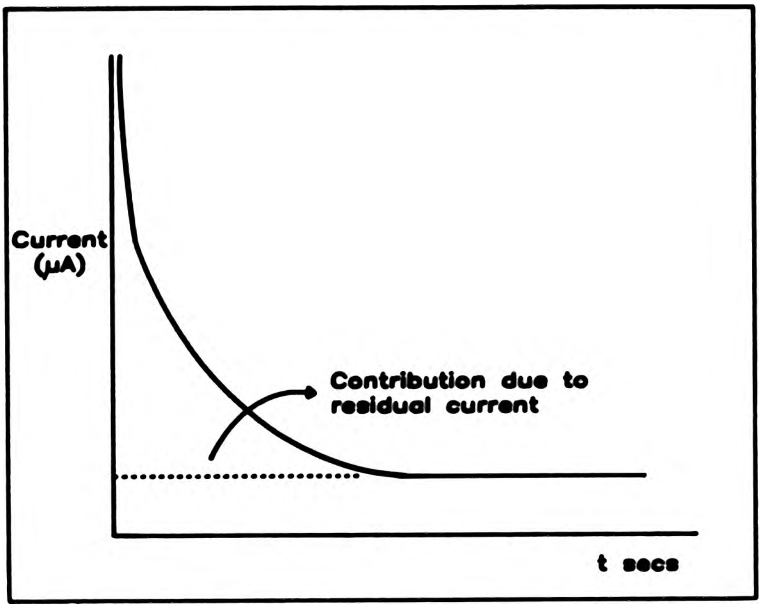

Fig. 2.4. Graph of decrease of electrolysis current with time in controlled potential electrolysis.

Termination is made after a reasonable period, when the current is mainly due to a residual current and a correction is made for this involving the residual current and the total time. This is then substracted from the total number of coulombs to obtain that for the species under investigation.

The theoretical number of coulombs for a 'one-electron' process can be obtained as follows:-

In $50cm^3$ of 10^{-2} molar solution there are

$(50 \times 10^{-2})/1000 = 5 \times 10^{-4}$ moles

For 1 mole reduction 96,500 coulombs are required.

Therefore $50cm^3$ of $10^{-2}M$ will require

$5 \times 10^{-4} \times 96{,}500$ coulombs = 48.25.

In an unknown case, if the total coulombs minus that due to the background = true count, then the number of electrons involved in the electrolysis, n = (true count)/(theoretical count for a one-electron process).

For a straight forward reduction in a single process, n will come out close to a whole number. If, however, there is a participation of another process at the chosen potential, then a non-integral value may be obtained. Indeed, there is some evidence that the variation of n can occur in the region of a polarographic wave with some benzylsulphonium salts.

2.2.B. Determination of reaction parameters.

In coulometry, electrolysis is carried out under stirred conditions, where diffusion control is no longer operative and quiescent conditions do not prevail. Under such conditions we can regard the process to be a rate process which is temperature dependent and some form of Arrhenius equation will apply:

i.e. $$k = Ae^{-\xi/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.15)$$

where,

k is the rate constant

ξ is a type of activation energy

Comparing the rates k_1 and k_2 at temperatures T_1 and T_2, then,

$$\ln \frac{k_2}{k_1} = \xi/R \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.16)$$

where, k_2 is the rate constant at temperature T_2

k_1 is the rate constant at temperature T_1

In the first instance of electrolysis, the current measures the rates so that it is possible to write:

$$\ln \frac{i_{o2}}{i_{o1}} = \frac{\xi}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.17)$$

where initial rates, i_{o2} and i_{o1} are taken since depletion of the concentration of the substrate soon occurs and thus i values decrease quickly as shown by Fig. (2.5).

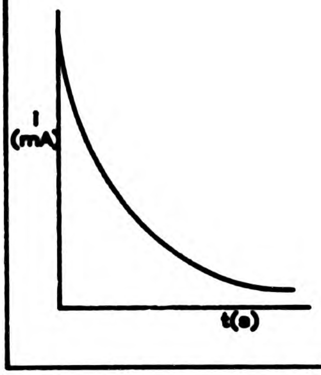

Fig. 2.5.

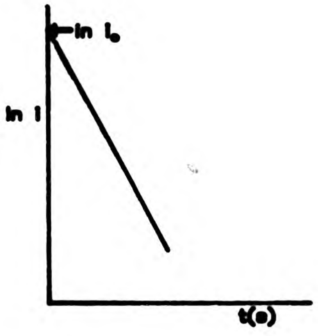

Fig. 2.6.

A problem may arise in satisfactorily determining i_o due to some fluctuation in the current values. Since the decrease in i occurs exponentially, one can, as an alternative, plot $\ln i$ vs t and extrapolate back to $t=0$ (Fig. 2.6). Since the graph is linear, this procedure is usually considered to be more satisfactory. It also gives direct values for equation (2.16).

We are thus in a position to evaluate activation energies, ξ , for the phenacylsulphonium and phenacylammonium compounds. However, an interpretation of its meaning is needed. Each of these compounds involves an overall activation energy barrier, say Q_1 (for S compounds) and Q_2 (for N compounds). The absolute values of Q_1 and Q_2 cannot be determined, but we can say something about the applied potentials used to reduce the barrier and allow the processes to occur at a certain rate.

Consider the models given for sulphonium compounds (Fig. 2.7) and ammonium compounds (Fig. 2.8). In general the ammonium salts are more difficult to reduce than the sulphonium salts, and models are put forward to give a qualitative interpretation of the difference.

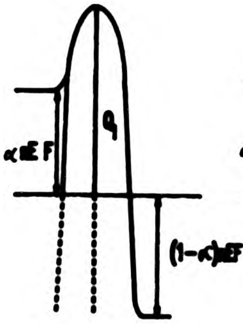

Fig. 2.7.

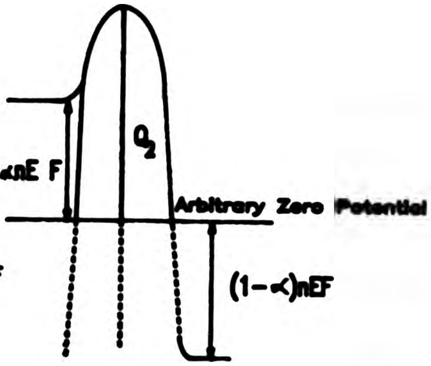

Fig. 2.8.

In these models the contribution of the applied potentials in reducing the forward barriers are given by the αnEF values.

Now experiment shows that for a potential at which the sulphonium compounds reduce at a reasonable rate, there is no measureable reduction of the ammonium compounds.

Models 2.7 and 2.8 are thus unsuitable for any interpretation of ξ. A more realistic comparison is given in Figs. (2.9) and (2.10).

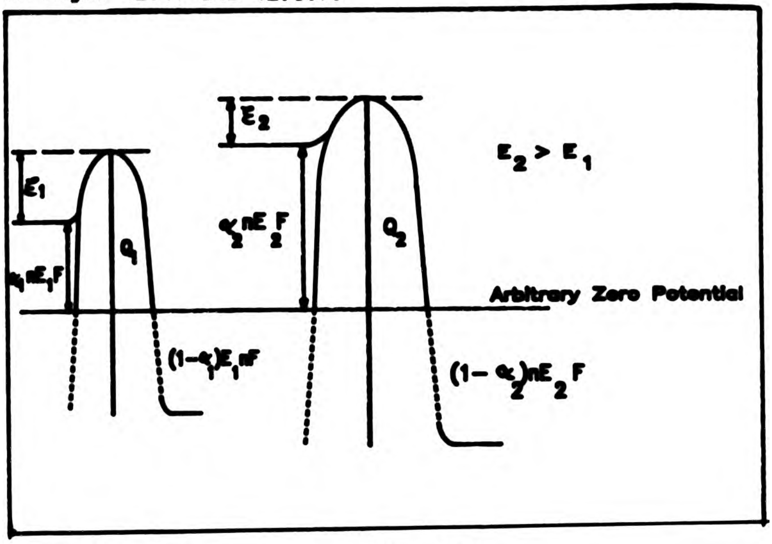

Fig. 2.9. Fig. 2.10.

Here, the potentials E_1 and E_2 are those applied to obtain the current values, i_{o1} and i_{o2}. An interesting result of this is that although $Q_2 > Q_1$, it does not follow that $\xi_2 > \xi_1$. In fact, the reverse may be the case. It is suggested, however, that we may obtain a measure of the difference in overall activation energy $\Delta Q = Q_2 - Q_1$ from the relationship:

$$\begin{aligned} \Delta Q = Q_2 - Q_1 &= (\xi_2 + \alpha_2 nE_2F) - (\xi_1 + \alpha_1 n E_1F) \\ &= (\xi_2 - \xi_1) + (\alpha_2 nE_2F - \alpha_1 nE_1F) \\ &= (\xi_2 - \xi_1) + Fn(\alpha_2 E_2 - \alpha_1 E_1) \end{aligned}$$

F and n are constants.

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Chapter 3

Equipment used for electrochemical studies

A. Polarography

Apparatus: The polarographic curves were obtained manually using a precision potentiometer (Wier 403D) and a sensitive Scalamp galvanometer (Pye Ltd., Cambridge). The polarograms were also recorded automatically on a P04 Radiometer Polariter (Copenhagen, Denmark). A Kalousek vessel(3.1) with a separated saturated calomel electrode (SCE) was used. The capillary used had the following constants:

flow of mercury rate, m = 2.5 mg/sec
drop time, t = 2.9 sec
mercury pressure, h = 65 cm

All the values of half-wave potentials ($E_{1/2}$) are expressed against the saturated calomel electrode (SCE).
The pH values of buffer solutions were checked using a pH meter (Pye, Unicam) with a glass electrode (Pye, Ingold).

Experimental measurements

Details are given of the procedures used to determine

(a) half-wave potentials,
(b) mass flow rate and
(c) drop time.

(a) Half-wave potentials.

In order to study the effects of (i) ligands, (ii) p-substituents, (iii) pH and temperature changes, determination of $E_{1/2}$ was necessary and this was determined by the direct method and by logarithmic analysis.

(b) Mass flow rate ofmercury (m).

Kolthoff and Lingane(3.2) suggest that the mass of mercury flowing per second should be determined by allowing the mercury to flow into an electrolyte solution under the influence of the applied potential corresponding to the region where the diffusion starts. The amount of mercury flowing in time 't' is collected and weighed directly after the mercury has been completely dried.

(c) Drop-time (t).

This was determined using the method of Koltoff and Lingane(3.3, 3.4). The mercury was allowed to flow into a solution under the influence of the applied potential corresponding to the diffusion plateau. The time was recorded for a specific number of drops by means of a stop watch.

B. Coulometry

The cell used for coulometry and preparative scale reduction was of the divided type and is described in detail on page 119 and is shown in Fig.(4.25) (page 120).

The potentiostat used for fixed potential reduction was a TA 251 Ministat and a Wenking SS 170 coulomb integrator (Linton Instrumentation, Harlow).

Additional Instrumental Equipment

Chromatograms were obtained on a Pye 104 series gas-liquid chromatograph (glc) with a nitrogen flow rate of 40cm^3/minute linked to a Servoscribe mkII integrator, using a silar 5cp column. The Pye 304 chromatograph was also used with a SE 30 capilliary column and a hydrogen flow rate of 2cm^3/minute. The flame ionisation detector was used.

Nuclear magnetic resonance (nmr) proton spectra were determined on a Jeol 60MHz spectrometer chemical shifts are given in values with tetramethylsilane (tms) as the internal standard.

Carbon-13 (C) spectra were recorded using a Jeol 100MHz Fourier transform spectrometer.

Mass spectra were recorded on the Jeol JMS-DX300 low/high resolution spectrometer. The column used in the GC/MS determinations was silar 5cp.

Ultra-Violet spectra (UV) was determined on a Unicam SP1800 spectrometer using $1cm^3$ quartz cells.

Infra-Red spectra (IR) of solids were determined as nujol-mulls, and liquids as thin films on either a Perkin-Elmer 237 grating spectrophotometer or a Perkin-Elmer 298 spectrophotometer.

Melting points were determined on an Electrothermal melting point apparatus.

References

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Chapter 4

4.A. The preparation of 'onium salts and some 'onium amine salts

4.A.1. Preparation of sulphonium salts

These compounds were prepared by reaction of the phenacyl bromide with the appropriate sulphides in alcohol or alcohol-ether solutions. These reactions were often exothermic. The solutions were left for a few hours during which time some solid usually precipitated. Excess anhydrous ether was added to complete the precipitation of the salt. The solution was filtered and the solid was washed with ether and recrystallised from ethanol. Where the salt was deliquescent, the filtration was carried out under nitrogen using a Schlenk filter.

The general reaction may be represented as:

$$C_6H_5COCH_2\ Hal + R_2S \longrightarrow C_6H_5COCH_2S^+R_2Hal^-$$

Preparation of dimethylphenacylsulphonium bromide

Phenacyl bromide (10g, 0.05mole) was dissolved in ethanol (30cm^3), a slight excess of dimethyl sulphide (3.5g, 0.056mole) was added and the mixture was left to stand at room temperature for 1-2 hours. An excess of sodium dried ether was added to complete the precipitation. The solid was filtered off and recrystallised from ethanol.

Similar derivatives were prepared by the same method, where R was C_2H_5, C_3H_7, C_4H_9, $(CH_2)4$ cyclic and $(CH_2)5$ cyclic. Melting points and elemental analyses are given in Tables 4.1 and 4.2.

The following table lists the phenacyl sulphonium salts prepared.

Table 4.1 $C_6H_5COCH_2S^+R_2Br^-$

R	m.p.(°C)	lit.m.p.(°C)	yield(%)	ref.
CH_3	147	148,149	90	4.1, 4.2
C_2H_5	92-3		87	
C_3H_7	95-6		88	
C_4H_9	80-2		87	
$(CH_2)_4$(cyclic)	123-4		92	
$(CH_2)_5$(cyclic)	116-8		90	

Elemental analyses for the above compounds are given in Table (4.2).

Table 4.2 $C_6H_5COCH_2S^+R_2Br^-$ Elemental analyses

R	FOUND		CALCULATED	
	%C	%H	%C	%H
CH_3	45.9	4.97	45.98	4.98
C_2H_5	49.85	6.15	49.83	6.23
C_3H_7	52.8	6.58	53.0	6.63
C_4H_9	55.51	7.67	55.49	7.72
$(CH_2)_4$(cyclic)	50.2	5.17	50.20	5.23
$(CH_2)_5$(cyclic)	51.72	5.64	51.83	5.65

Preparation of aryl substituted sulphonium salts

Para-substituted phenacylsulphonium salts were synthesised using the appropriate substituted phenacyl bromide and dimethylsulphide. The following compounds were prepared.

Table 4.3. $p\text{-}XC_6H_4COCH_2S^+(CH_3)_2Br^-$

X	m.p.(°C)	lit.value (°C)	yield(%)	ref.
Cl	128-9	128-30	85	4.3
Br	133	135-6	83	4.3
CH_3O	132		80	
NO_2	120	123-5	87	4.4

4.A.2. Preparation of Ammonium salts

Phenacyltrialkylammonium salts were prepared from phenacyl bromide and tertiary amines. The reactions were significantly faster than for the phenacylsulphonium salts, due to the greater nucleophilicity of the amines over the sulphides.

a) Trimethylphenacylammonium bromide

Phenacyl bromide (10g.,0.05 mole) was dissolved in warm ethanol (30cm^3) and a slight excess of an aqueous alcoholic solution of trimethylamine was added.

Slight warming of the resulting solution was detected followed by precipitation of the salt. Sodium-dried ether was added and the white precipitate was filtered off and recrystallised from absolute alcohol and dried under vacuum. The salt was non-deliquescent.

Table 4.4

m.p.(°C)	lit.value (°C)	yield(%)	ref.
205	207	89.0	4.5

b) <u>Triethylphenacylammonium bromide.</u>

This was synthesised by the same method using triethyl amine. The reaction was slower than with trimethylamine and the mixture was kept overnight. Earlier experiments had shown that the precipitate was deliquescent and it was therefore filtered off using a Schlenk filter under an atmosphere of nitrogen. The salt was recrystallised from ethanol.

Table 4.5

m.p.(°C)	lit.value (°C)	yield(%)	ref.
68-70	69-71	85	4.5

c) Preparation of oxime 'onium salts

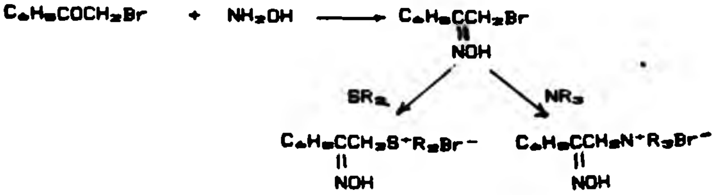
(i) Direct method

$C_6H_5COCH_2S^+R_2Br^- + NH_2OH \longrightarrow C_6H_5C(NOH)CH_2S^+R_2Br^-$

Dimethylphenacylsulphonium bromide salt (1g, 0.0038 mole) was dissolved in 2M ethanoic acid/sodium ethanoate buffer (5cm^3). To this was added hydroxylamine hydrochloride (0.14g, 0.002 mole). No apparent change was observed, either of the mixture warming up or any sign of precipitate, and although the mixture was kept for several days; addition of ether did not precipitate a solid. Similarly the preparation of the trimethylphenacylammonium bromide was attempted without success.

(ii) Indirect method

Since the above direct method was unsuccessful, the oxime of the α-bromoacetophenone was first prepared and to this was added the dialkylsulphide or trialkylamine to give the corresponding salt.



$$C_6H_5COCH_2Br + NH_2OH \longrightarrow C_6H_5C(=NOH)CH_2Br$$

$$C_6H_5C(=NOH)CH_2Br \xrightarrow{SR_2} C_6H_5C(=NOH)CH_2S^+R_2Br^-$$

$$C_6H_5C(=NOH)CH_2Br \xrightarrow{NR_3} C_6H_5C(=NOH)CH_2N^+R_3Br^-$$

(iii) Preparation of 1-bromo-2-phenyloximinoethane

Phenacyl bromide (10g., 0.05 mole) was added to methanol (40cm^3) and warmed on a water bath to ensure complete dissolution. To this solution aliquots of an aqueous methanol solution (16cm^3 50/50 v/v) containing hydroxylamine hydrochloride (10.5g., 0.15 mole) was added. The mixture was shaken vigorously for 20 minutes then allowed to stand until precipitation occurred, normally between 1-2 hours. The precipitate was filtered and recrystallised from cyclohexane. See Table 4.6.

Table 4.6

m.p.(°C)	lit. m.p. (°C)	yield(%)
90-92	89.5	82

Elemental analysis:

Calculated:	C 44.86%	H 3.74%	N 6.55%
Found:	C 45.02%	H 3.97%	N 6.65%

(iv) Preparation of (2-phenyl-2-oximinoethyl)-dimethylsulphonium bromide.

Dimethyl sulphide (1.35g., 0.022 mole) was added to a solution containing phenacyl bromide oxime (4.6g., 0.021 mole) in alcohol (5cm^3) and left for one hour. Sodium dried ether was added and the white precipitate formed was filtered off and washed with ether and recrystallised from ethanol.

Table 4.7

m.p.(°C)	yield(%)
106-107	94

Using the same method but with different sulphides, a number of (2-phenyl-2-oximinoethyl)dialkylsulphonium salts were prepared. See Table 4.8.

Table 4.8 $C_6H_5CNOHCH_2S^+R_2Br^-$

R	m.p.(°C)	yield(%)
CH_3	105-6	94
C_2H_5	98-100	84
C_3H_7	94-5	86
C_4H_9	80-2	90
$(CH_2)_4$(cyclic)	124-6	90
$(CH_2)_5$(cyclic)	90-2	92

Elemental analysis of the above compounds is given in Table (4.9)

Table 4.9

R	FOUND			CALCULATED		
	C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
CH_3	43.76	5.17	5.12	43.48	5.11	5.07
C_2H_5	50.66	6.10	5.06	50.5	6.33	4.93
C_3H_7	49.99	6.50	4.30	50.9	6.67	4.24
C_4H_9	52.87	7.30	3.76	53.3	7.22	3.88
$(CH_2)_4$(cyclic)	48.10	5.26	4.98	47.68	5.30	4.64
$(CH_2)_5$(cyclic)	49.88	5.92	4.75	49.37	5.70	4.43

d) Preparation of (2-phenyl-2-oximinoethyl)trimethylammonium bromide.

Trimethylamine (1.8g., 0.03 mole, 33% solution in alcohol) was added to a solution containing phenacylbromide oxime (2.14g., 0.01 mole) in methanol ($5cm^3$). The reaction was initially vigorous. After one hour the sticky mass was worked up with excess anhydrous ether and the solid filtered off under nitrogen using a Schlenck filter.

The same method as above with triethylamine gave (2-phenyl-2-oximinoethyl)triethylammonium bromide. See Tables 4.10 and 4.11.

Table 4.10

Compound	m.p.(°C)	yield(%)
$C_6H_5CNOHCH_2N^+(CH_3)_3Br^-$	143-5	90
$C_6H_5CNOHCH_2N^+(C_2H_5)_3Br^-$	153.0	85

Table 4.11 Elemental analysis

	FOUND			CALCULATED		
	C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
$C_6H_5CNOHCH_2N^+(CH_3)_3Br^-$	48.25	5.23	10.16	48.35	5.13	10.26
$C_6H_5CNOHCH_2N^+(C_2H_5)_3Br^-$	53.41	7.53	8.99	53.33	7.30	8.88

The structures of the oxime 'onium salts follow from the method of preparation and their ^1H nmr spectra and elemental analysis.

Table 4.12 ^{1}H nmr shifts of (2-phenyl-2-oximinoethyl)-sulphonium salts

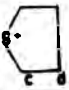
	values (ppm)					
	a	b	c	d	e	f
$C_6H_5CNOHCH_2S^+(CH_3)_2Br^-$ a b c	7.61(um)	4.77(s)	2.97(s)			
$C_6H_5CNOHCH_2S^+(CH_2CH_3)_2Br^-$ a b c d	7.59(um)	4.71(s)	3.38(q)	1.42(t)		
$C_6H_5CNOHCH_2S^+(CH_2CH_2CH_3)_2Br^-$ a b c d e	7.59(um)	4.80(s)	3.32(m)	1.81(m)	0.99(t)	
$C_6H_5CNOHCH_2\overset{+}{S}(CH_2CH_2CH_2CH_3)_2Br^-$ a b c d e f	7.61(um)	4.76(s)	3.36(t)	1.78(m)	1.41(m)	0.89(m)
$C_6H_5CNOHCH_2S^+$  Br^- a b c d	7.60(um)	4.65(s)	3.57(um)	2.35(um)		
* $C_6H_5CNOHCH_2S^+$  Br^- a b c d e	7.60(um)	4.58(s)	3.52(bm)	2.34(bm)		

Table 4.13 ^{1}H nmr shifts of (2-phenyl-2-oximinoethyl)-ammonium salts.

	values (ppm)			
	a	b	c	d
$C_6H_5CNOHCH_2N^+(CH_3)_3Br^-$ a b c	7.62(bs)	4.53(s)	3.11(s)	
$C_6H_5CNOHCH_2N^+(CH_2CH_3)_3Br^-$ a b c d	7.6(s)	4.38(s)	3.38(q)	1.22(t)

* There are anomalies in the ^{1}H nmr spectrum and the elemental analysis of this compound, hence its structure is provisional.

Table 4.14 ^{1}H nmr shifts of acetophenone oxime and phenacyl bromide oxime

	values (ppm)		
	a	b	c
$C_6H_5CNOHCH_3$ a b c	7.40(um)	9.30(bs)	2.31(s)
$C_6H_5CNOHCH_2Br$ a b	7.42(um)	4.42(s)	

Chemical shifts are given in δ values with sodium trimethylsilylpropanesulphonate as the internal standard; splitting patterns are designated as:
s, singlet; d, doublet; t, triplet; q, quartet; bs, broad singlet; m, multiplet; um, unresolved multiplet.

Preparation of 2-phenyl-2-O-methyloximinoethane.

The method described by Karabotsos was used(4.6).

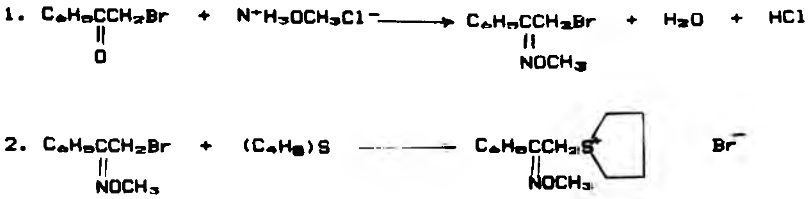
Acetophenone (3.0g, 0.025 mole) in ethanol (5cm^3) was put in a 100cm^3 round-bottom flask. O-Methylhydroxylamine hydrochloride (3.0g) was dissolved in water (10cm^3) and to this was added sodium acetate trihydrate (5.0g). This solution was added to the acetophenone solution and refluxed for one hour. Sufficient alcohol was added to the boiling mixture until the solution was clear. This was refluxed for 24 hours. The solution was cooled to room temperature and extracted with ether (3 X 25cm^3). The ether solution was washed with sodium carbonate (2 X 10cm^3) then with water (1 X 10cm^3) and dried over magnesium sulphate. The ether was removed by distillation and the residue examined by nmr. (See Table 4.15.) Yield = 91.3%

Table 4.15

	values
^{1}H nmr	2.10 (S,3H) 3.94 (S,3H) 7.25 - 7.59 (m,5H)
^{1}H nmr Lit.$^{(4.7)}$	2.19 (S,3H) 3.98 (S,3H) 6.86 - 7.96 (m,5H aromatic)

Preparation of (2-phenyl-2-O-methyloximinoethyl) tetramethylenesulphonium bromide.

This involved two stages, firstly the preparation of 1-bromo-2-phenyl-2-O-methyloximinoethane and this compound was used in the preparation of the above salt.



1. $C_6H_5\underset{\underset{O}{\|}}{C}CH_2Br + N^+H_3OCH_3Cl^- \longrightarrow C_6H_5\underset{\underset{NOCH_3}{\|}}{C}CH_2Br + H_2O + HCl$

2. $C_6H_5\underset{\underset{NOCH_3}{\|}}{C}CH_2Br + (C_4H_8)S \longrightarrow$

1. Preparation of 1-bromo-2-phenyl-2-O-methyloximinoethane

Phenacyl bromide (5.0g) was dissolved in warm ethanol (10cm³) and a solution of O-methylhydroxylamine hydrochloride (5.0g, 0.06 mole) in aqueous ethanol (5cm³, 50:50 v/v) was added in aliquots with stirring. The mixture was allowed to stand overnight and the oily liquid product formed was extracted with ether (3 X 25cm³) and dried over anhydrous magnesium sulphate. After filtering, the ether was removed on a rotary evaporator. The crude product (78%) was used in the next step.

2. (2-phenyl-2-O-methyloxminoethyl)tetramethylene-sulphonium bromide

The crude product from the previous step was reacted with a small excess of tetrahydrothiophene as described for the preparation of the oxime salt (page 59).

% yield	mp (°C)
60	90 - 91

Table 4.16 Elemental Analysis

	Calculated %	Found %
C	49.52	49.84
H	5.71	5.78
N	4.44	4.38

4.B. Electrolysis experiments

4.B.1. Phenacyl 'onium salts

Tests to establish that the reduction processes are diffusion controlled

i) Effect of concentration on the diffusion current

Solutions of 'onium salts of known concentration and containing 0.01% gelatine solution as maxima suppressor were placed in a Kalousek cell and degassed for five minutes. The height of the mercury column was fixed and polarogram recorded.

Results. (See Table 4.17).

Height of mercury column = 60cm
Rate of mercury flow = 1.6mg sec^{-1}
Drop time = 4.0 sec
Supporting electrolyte = 7.0 pH buffer (BDH)

Table 4.17

'Onium salt		Concentration in m moles dm^{-3}			
		0.5	1.0	1.5	2.0
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	id(μA)	3.0	6.1	9.0	12.0
$C_6H_5COCH_2N^+(C_2H_5)_3Br^-$	id(μA)	3.1	6.1	9.2	12.3
$C_6H_5COCH_2S^+(CH_3)_2Br^-$	id(μA)	3.4	6.6	10.1	13.4
$C_6H_5COCH_2S^+(CH_2)_4Br^-_{(cyclic)}$	id(μA)	3.3	6.8	10.2	13.6
p-CH_3O-$C_6H_4COCH_2S^+(CH_3)_2Br^-$	id(μA)	3.0	6.1	9.0	12.0

It can be seen by inspection that within experimental error, the diffusion current (id) is proportional to the concentration. This is consistent with a diffusion controlled process.

Figure (4.1) shows the dependence of wave height on concentration for dimethylphenacylsulphonium bromide.

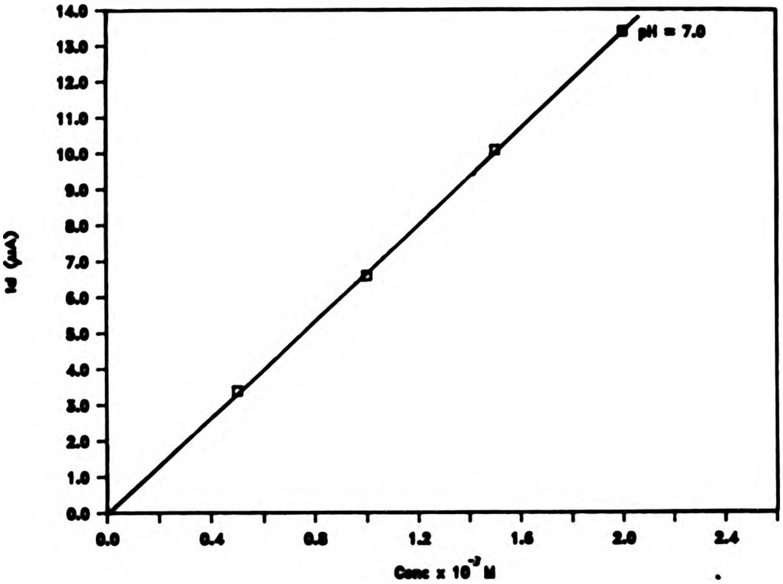


Fig. 4.1

(ii) <u>Effect of mercury column height on diffusion current</u>

Solutions of 'onium salts containing 0.01% gelatine were degassed with nitrogen and the polarogram recorded at different heights (h) of mercury column.

<u>Results</u>. (See Table 4.18).

Concentration of 'onium salt solution = 1×10^{-3} M

Supporting electrolyte = 7.0 pH buffer

Table 4.18

'Onium salt	h(cm)	40	45	50	55	60
$C_6H_5COCH_2S^+(CH_3)_2Br^-$	$h^{1/2}$	6.33	6.71	7.07	7.41	7.75
	id(μA)	5.60	5.80	6.10	6.28	6.55
	id/ $h^{1/2}$	0.86	0.87	0.86	0.86	0.86
	h(cm)	40	45	50	55	60
$C_6H_5COCH_2S^+(CH_2)_4Br^-$	$h^{1/2}$	6.33	6.71	7.07	7.41	7.75
	id(μA)	5.50	5.80	6.10	6.40	6.64
	id/ $h^{1/2}$	0.87	0.87	0.87	0.86	0.85
	h(cm)	40	45	50	55	60
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	$h^{1/2}$	6.33	6.71	7.07	7.41	7.75
	id(μA)	5.50	5.75	5.90	6.18	6.50
	id/ $h^{1/2}$	0.87	0.86	0.84	0.84	0.84
	h(cm)	40	45	50	55	60
$C_6H_5COCH_2N^+(C_2H_5)_3Br^-$	$h^{1/2}$	6.33	6.71	7.07	7.41	7.75
	id(μA)	5.45	5.70	5.95	6.15	6.50
	id/ $h^{1/2}$	0.86	0.85	0.84	0.83	0.84

The constant values of id/$h^{1/2}$ for a given salt solution is consistent with the reduction processes being diffusion controlled.

Figure (4.2) shows the dependence of wave heights on the height of mercury reservoir for dimethylphenacylsulphonium bromide.

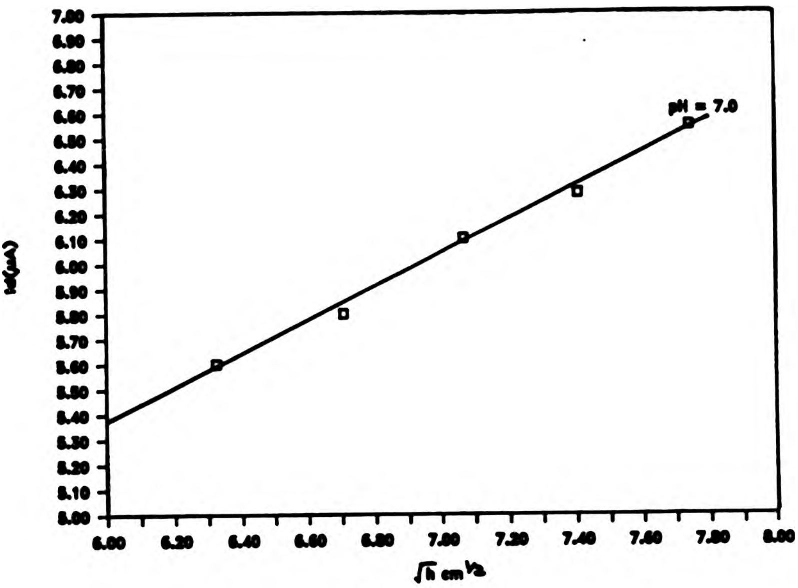


Fig. 4.2

4.3.2. Polarography of 'onium salts

Solutions of the 'onium salts were made in buffers containing gelatine and degassed in a Kalousek cell with nitrogen for five minutes.

The polarograms were recorded manually for more accurate determination of the half-wave potential, $E_{½}$. The result of the cleavage of the $C-S^{+}$ or $C-N^{+}$ bond of the 'onium salt.

The polarogram for dimethylphenacylsulphonium bromide was obtained by varying the applied voltage manually and recording the current on a scalamp galvanometer. The resulting polarogram is given in Figure (4.3).

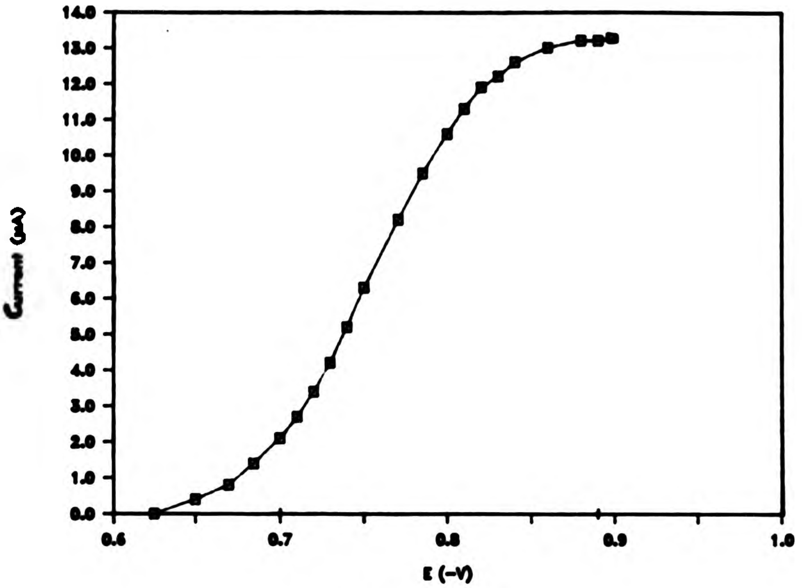


Fig. 4.3

The data in this experiment was subjected to logarithmic analysis to obtain an accurate value of $E_{1/2}$.

Logarithmic analysis for dimethylphenacylsulphonium bromide

Concentration of salt = 10^{-3}M
Supporting electrolyte = 7.0 pH buffer (BDH)
Drop time = 4.0 sec
Height of mercury head = 60.0cm
Mass of mercury flow = 1.6mg sec^{-1}
Limiting current (id) = 13.0µA
Galvanometer sensitivity = 1.0

Table 4.19

Applied voltage E(-V)	Current i(µA)	id-i	log (id-i)/i
0.625	0.00		
0.650	0.40	12.60	1.4983
0.670	0.80	12.20	1.1818
0.685	1.40	11.60	0.9180
0.700	2.10	10.90	0.7152
0.710	2.70	10.30	0.5815
0.720	3.40	9.60	0.4707
0.730	4.20	8.80	0.3212
0.740	5.20	7.80	0.1761
0.750	6.30	6.70	0.0265
0.770	8.20	4.80	-0.2326
0.785	9.50	3.50	-0.4336
0.800	10.60	2.40	-0.6451
0.810	11.30	1.70	-0.8218
0.820	11.90	1.10	-1.0343
0.830	12.20	0.80	-1.1833
0.840	12.60	0.40	-2.8069
0.860	13.00	0.00	0.0000

A plot of E versus log (id-i)/i is shown in Figure (4.4) from which the value of $E_{½}$ and αn was obtained.

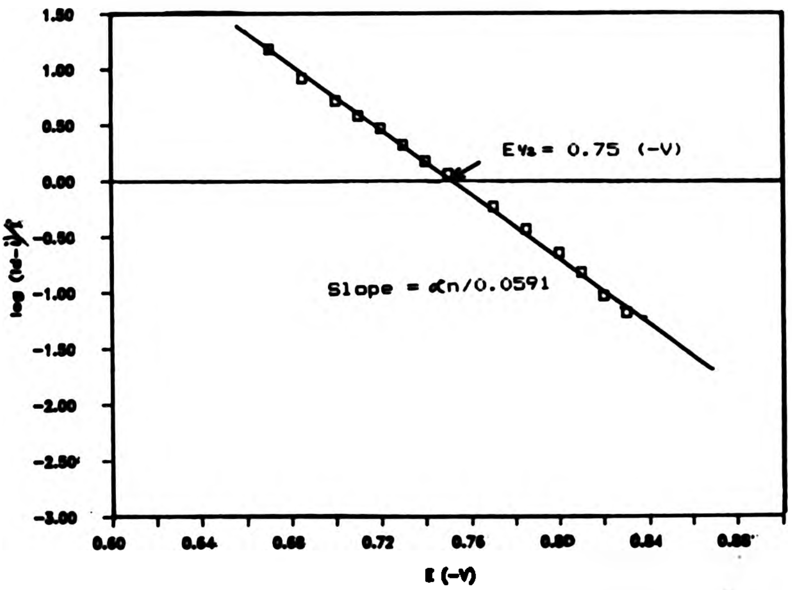


Fig. 4.4

Effect of ligands on E½ values

A number of dialkylphenacylsulphonium salts were investigated, using the manual method for obtaining the polarogram. These are shown in table (4.20) and discussed on page 182.

Table 4.20

Compound	$E_{1/2}$(-V)	αn
$C_6H_5COCH_2S^+(CH_3)_2Br^-$	0.75	0.81
$C_6H_5COCH_2S^+(C_2H_5)_2Br^-$	0.72	0.79
$C_6H_5COCH_2S^+(C_3H_7)_2Br^-$	0.71	0.75
$C_6H_5COCH_2S^+(C_4H_9)_2Br^-$	0.69	0.77
$C_6H_5COCH_2S^+(CH_2)_4Br^-$	0.70	0.85
$C_6H_5COCH_2S^+(CH_2)_5Br^-$	0.70	0.83

Effect of substituents on $E_{1/2}$ values

A number of p-substituted dimethylphenacylsulphonium salts were investigated under similar conditions as above.

Table 4.21

Compound	$E_{1/2}$(-V)	αn
$CH_3OC_6H_4COCH_2S^+(CH_3)_2Br^-$	0.70	0.87
$BrC_6H_4COCH_2S^+(CH_3)_2Br^-$	0.73	0.87
$ClC_6H_4COCH_2S^+(CH_3)_2Br^-$	0.63	0.86
*NO_2-$C_6H_4COCH_2S^+(CH_3)_2Br^-$	0.39	1.36

* First wave-reduction of the nitro group.

With the exception of the p-nitro compound, all the salts in Tables (4.20) and (4.21) have very similar $E_{1/2}$ values, indicating that the electro-reduction process is the same for each salt.

Test for linear free energy relationship

A Hammett equation plot of $E_{1/2}$ of some p-substituted dimethylphenacylsulphonium salts against σ^- values for the p-substituents is shown in Figure (4.5).

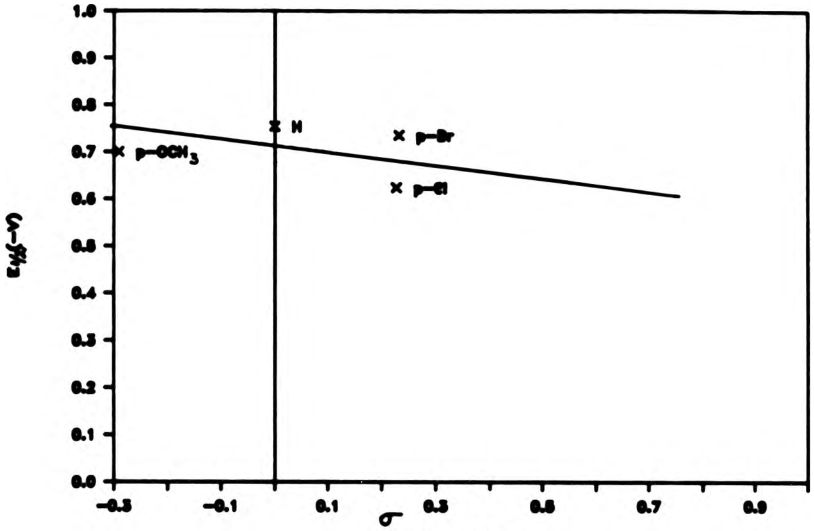


Fig. 4.5

Compound: $p\text{-}XC_6H_4COCH_2S^+(CH_3)_2Br^-$

Table 4.23

Substituent X	$E_{1/2}$(-V)	σ^-
H	0.754	+0.00
OCH$_3$	0.700	-0.29
Cl	0.625	+0.227
Br	0.736	+0.232
NO$_2$	0.385	+0.78

The p-nitro compound was excluded from the plot because it's reduction is quite anomalous. (See discussion, page 183). It can readily be seen that the data does not give a satisfactory fit to the Hammett equation.

The data was analysed using a "B LINREG" programme to give the best straight line based on least mean square treatment.

The solution was given as $y = 0.05x - 0.71$.

The correlation factor of 0.2204 was very low.

4.B.3. Effect of pH on $E_{1/2}$ values of phenacylsulphonium salts

Table (4.24) gives the $E_{1/2}$ values at pH 2.0, 4.0, 7.0, 9.2 for the phenacylsulphonium salts of concentration 10^{-3}M in buffers (see page 84). Polarograms were recorded automatically and are shown in Figure (4.6) for dimethylphenacylsulphonium bromide as an illustration.

Table 4.24

Compound	pH	$E_{1/2}$(-V)	id(μA)
$C_6H_5COCH_2S^+(CH_3)_2Br^-$	2.0	0.70	5.50
	4.0	0.75	5.50
	7.0	0.85	5.60
	9.2	0.88	4.80
$C_6H_5COCH_2S^+(C_2H_5)_2Br^-$	2.0	0.74	5.40
	4.0	0.78	5.50
	7.0	0.81	5.60
	9.2	0.94	5.20
$C_6H_5COCH_2S^+(CH_2)_4Br^-$	2.0	0.68	5.50
	4.0	0.72	5.60
	7.0	0.74	5.60
	9.2	0.82	5.40
$C_6H_5COCH_2S^+(CH_2)_5Br^-$	2.0	0.70	5.30
	4.0	0.74	5.30
	7.0	0.76	5.30
	9.2	0.86	5.20

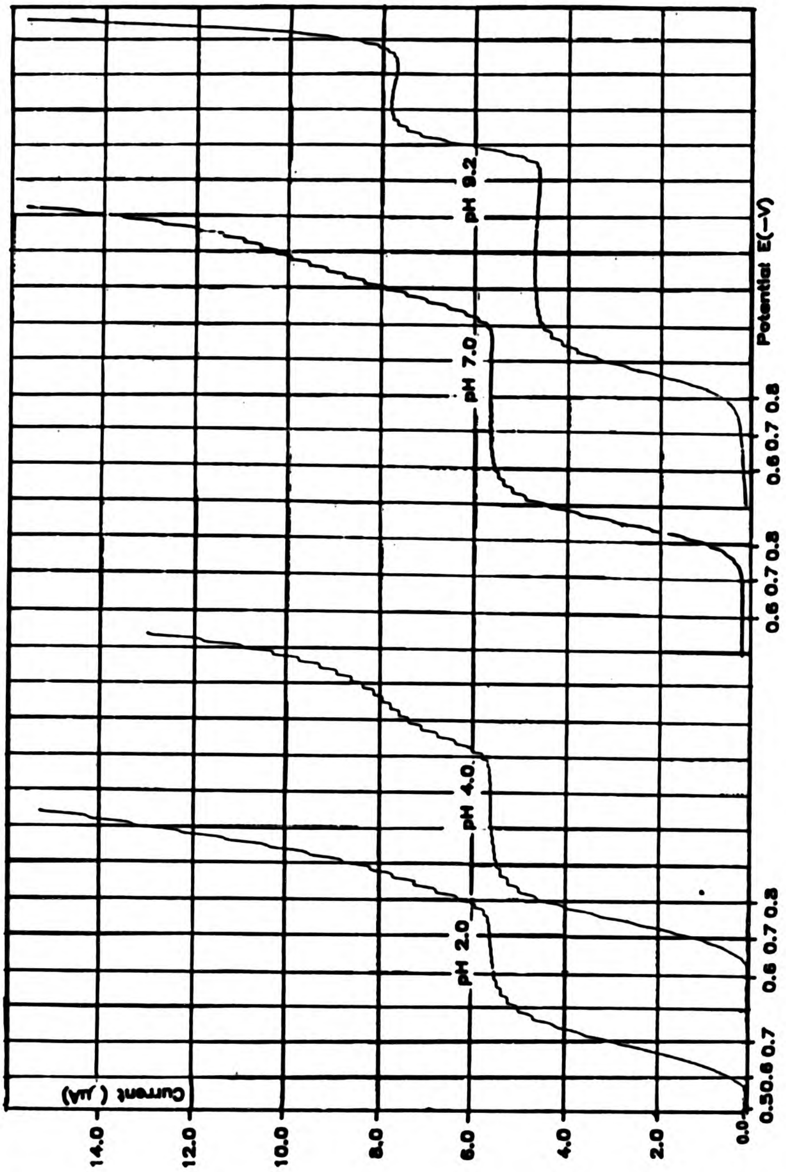


Fig. 4.6 Polarograms for dimethylphenacylsulphonium bromide at different pH values.

The reduction wave of the acetophenone product is not completely observable (not well defined) below pH 8.0 due to the discharge of the supporting electrolyte. This is a general feature of the polarography of phenacylsulphonium compounds.

Effect of pH on $E_{1/2}$ values of p-substituted phenacylsulphonium compounds.

Table (4.25) shows the $E_{1/2}$ values for p-substituted phenacylsulphonium compounds of concentration 10^{-3}M in buffers, which are given on page 84.

Table 4.25

Compound	pH	$E_{1/2}$(-V)	id(μA)
$BrC_6H_4COCH_2S^+(CH_3)_2Br^-$	2.0	0.61	4.60
	4.0	0.62	4.50
	7.0	0.73	4.10
	9.2	0.78	4.00
$ClC_6H_4COCH_2S^+(CH_3)_2Br^-$	2.0	0.57	4.70
	4.0	0.58	4.80
	7.0	0.63	4.60
	9.2	0.65	4.20
$CH_3OC_6H_4COCH_2S^+(CH_3)_2Br^-$	2.0	0.70	4.90
	4.0	0.72	4.90
	7.0	0.77	4.70
	9.2	0.94	4.40
$O_2NC_6H_4COCH_2S^+(CH_3)_2Br^-$	2.0	0.25	5.20
	4.0	0.30	5.00
	7.0	0.45	4.90
	9.2	0.55	4.60

4.3.4. Polarography of phenacylammonium salts

These quaternary salts have the general formula:

$$C_6H_5COCH_2N^+R_3Br^-$$

These gave polarograms similar to those for sulphonium salts, the main difference being the higher negative potentials required for the reduction corresponding to the first wave. From the logarithmic analysis of the polarograms obtained manually, accurate values of $E_{1/2}$ and αn were determined. See Table 4.26.

Concentration = 10^{-3}M

Height of mercury head = 60cm

Rate of flow of Hg = 1.6mg sec^{-1}

Drop time = 4.0 sec

pH = 7.0

Table 4.26

Compound	$E_{1/2}$(-V)	αn
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	0.99	0.85
$C_6H_5COCH_2N^+(C_2H_5)_3Br^-$	0.95	0.80

Polarograms of one of these compounds are shown as an example in Figure (4.6).

The effect of pH on E½ for quaternary phenacylammonium compounds

Similar studies of the effects of pH on the E½ values were carried out for several quaternary phenacylammonium salts.

Concentration = 10^{-3}M

Gelatine = 0.01%

E½ values for the first wave only at different pH values.

Table 4.27

Compound	pH	E½(-V)	id(μA)
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	2.0	0.76	5.50
	4.0	0.88	5.60
	7.0	1.10	5.40
	9.2	1.08	5.20
	13.0	1.08	5.60
$C_6H_5COCH_2N^+(C_2H_5)_3Br^-$	2.0	0.83	4.90
	4.0	0.93	4.60
	7.0	1.08	4.60
	9.2	1.06	4.70
	13.0	1.07	4.40

Buffers used for the above pH values

pH 2.0	Aldrich (tartaric acid, phosphoric acid, potassium hydrogen phthalate)
4.0	Ethanoic acid/sodium ethanoate
7.0	BDH (phosphate buffer)
9.2	Ammonia/ammonium ethanoate
13.0	Sodium hydroxide (0.1M)

Polarograms of trimethylphenacylammonium bromide are shown as an example in figure (4.7)

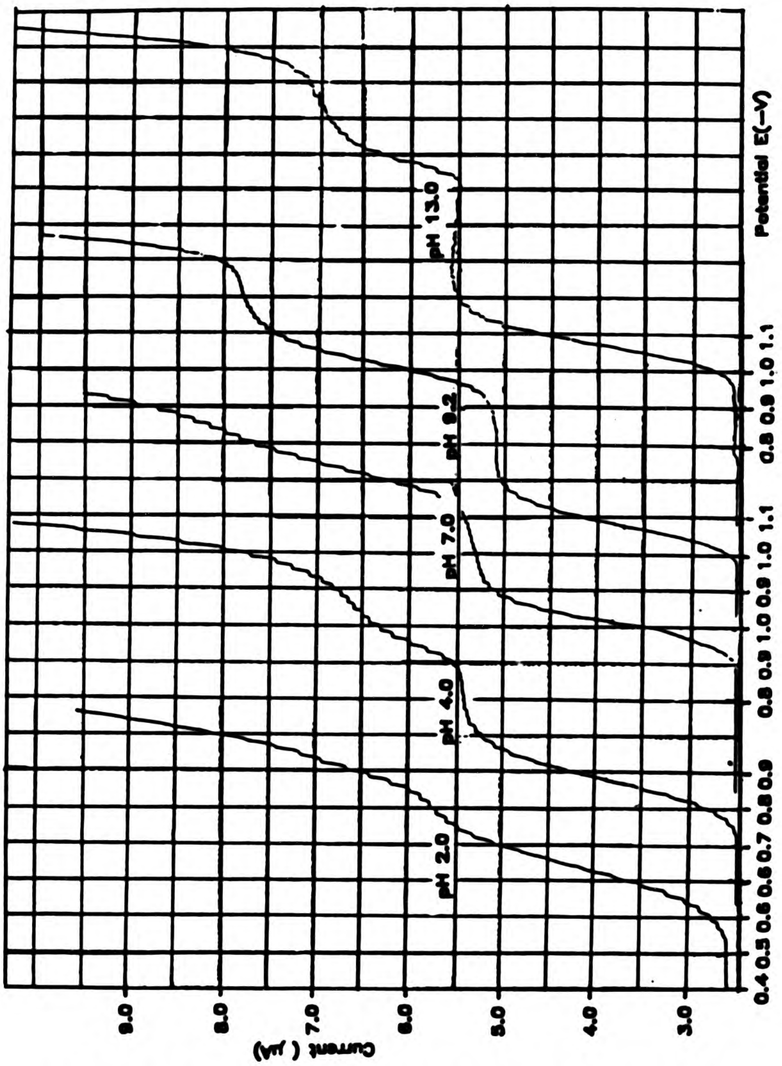


Fig. 4.7 Polarograms for trimethylphenacylammonium bromide at different pH values.

The effect of pH on $E_{1/2}$ for the two compounds in table (4.27) is shown in figure (4.8).

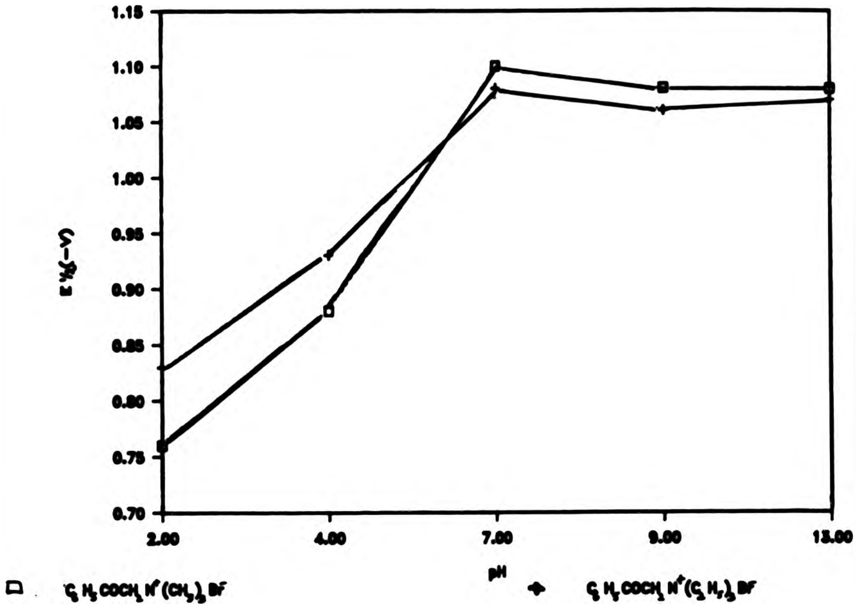


Fig. 4.8

4.8.5. Evaluation of K_e° for a slow electrode (irreversible) process using Koutecky's method

The rate constant for the reduction process was determined by the use of the equation given below.

$$\log K_e^\circ = \frac{\alpha n}{0.0591} \Delta E_{\frac{1}{2}} - \log 0.886 - \log[(t''/D)^{1/2} - (t'/D)^{1/2}]$$

at 25°C

The solutions consisted of:

Dimethylphenacylsulphonium bromide = 1×10^{-3}M
Buffer solution (BDH) = pH 7.0
Gelatine = 0.01%
Temperature = 25°C

Polarograms were recorded manually at two different drop times and these are shown in Figs. (4.9a,4.9b).
The value of α,(the transfer coefficient) and the half-wave potential, $E_{1/2}$, were obtained independently by the logarithmic analysis of each individual polarogram.
The diffusion coefficients, D, were calculated from the Ilkovic equation:

$$i_d = 607\, n D^{1/2} m^{2/3} t^{1/6} C$$

Values for the half-wave potential, $E_{1/2}$, transfer coefficient,capillary constants, and the rate constant K_e° are given in table (4.28).

Table 4.28 Polarographic parameters for dimethylphenacylsulphonium bromide at two different drop times.

	Drop time (s)	
	t_1'	t_1''
	2.25	8.5
Height of Hg head h (cm)	86.0	20.0
Mass of Hg (mg)	8.02	6.8
$E^{1/2}$	0.860	0.822
α	0.564	0.564
id (μA)	7.85	3.8
$D^{1/2}$	1.541×10^{-3}	1.541×10^{-3}
(2.303RT)/F	0.0591	0.0591
$\Delta E^{1/2}$	0.038	0.038
log Ke°	-2.5534	
Ke°	2.796×10^{-3}	

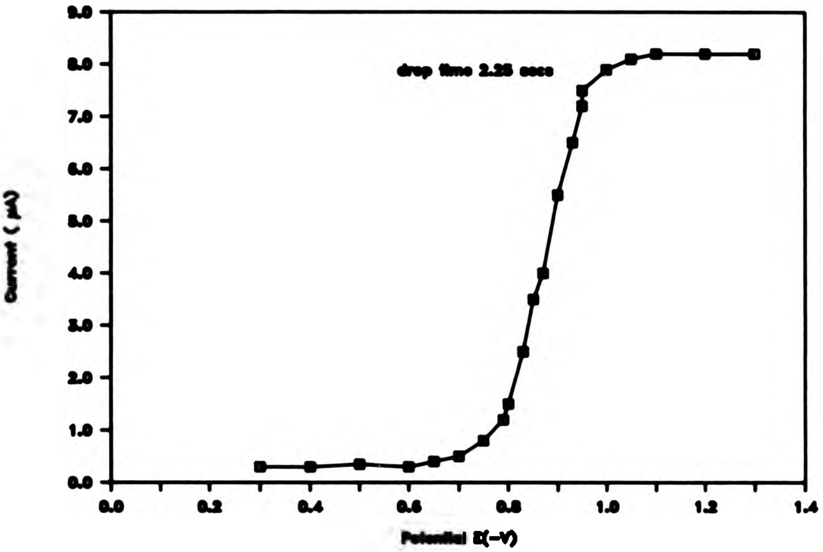


Fig. 4.9a

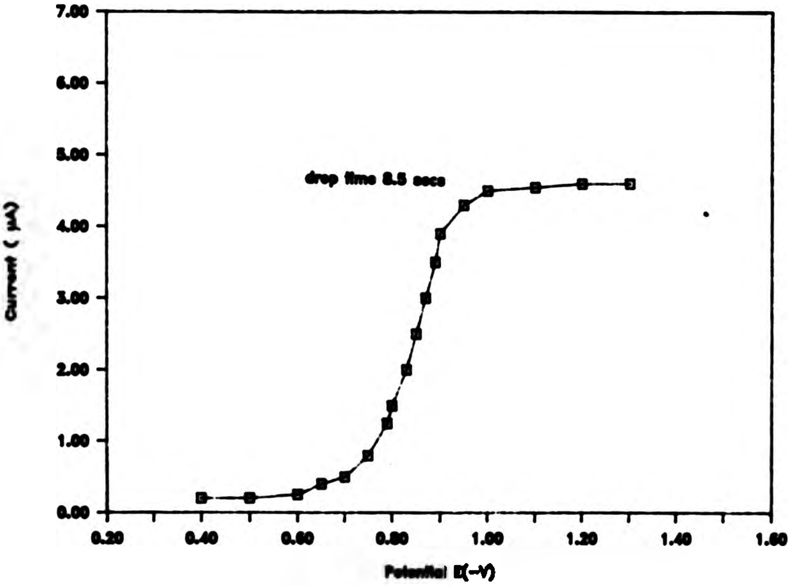


Fig. 4.9b

A similar treatment was carried out for trimethylphenacylammonium bromide. Polarograms are shown in figures (4.10a) and (4.10b).

Results

Concentration of salt = 10^{-3}M

Buffer solution (BDH) = pH 7.0

Temperature = 25°C (298K)

Table 4.29 Polarographic parameters for trimethylphenacylammonium bromide at two different drop times.

	Drop time (s)	
	t_1'	t_1''
	2.3	8.7
Height of Hg head h (cm)	86.5	20.0
Mass of Hg (m_g)	8.23	7.0
$E_{1/2}$	1.12	1.097
α	0.837	0.809
id (μA)	7.3	4.0
$D^{1/2}$	1.28×10^{-3}	1.28×10^{-3}
(2.303RT)/F	0.0591	0.0591
$\Delta E_{1/2}$	0.023	0.023
log Ke°	-2.6943	
Ke°	2.0216×10^{-3}	

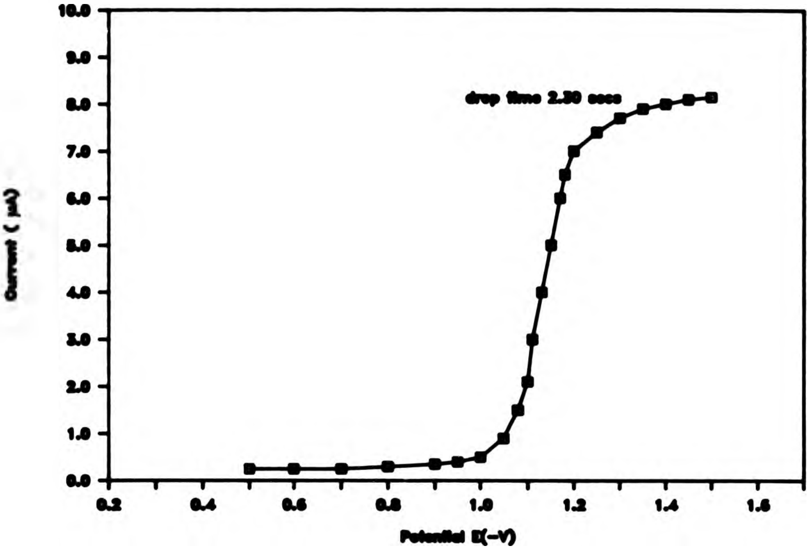


Fig. 4.10a

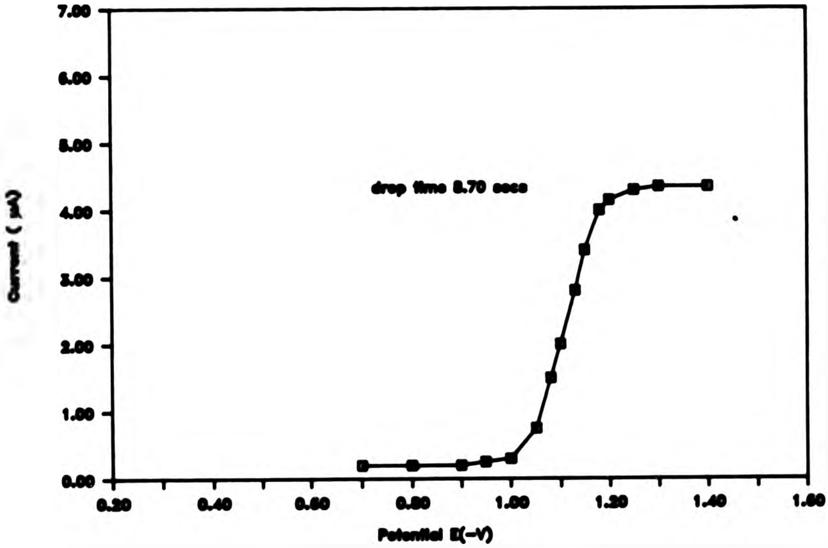


Fig. 4.10b

4.B.6. Polarographic parameters for the determination of activation energy for dimethylphenacylsulphonium bromide and trimethylphenacylammonium bromide

The activation energies for the reduction processes were determined by the use of the following equation.

$$\log i/(id-i) = \log A' - (Q - \tfrac{1}{2}Q_D)/2.303RT$$

All factors involved in the above equation have the same significance as before. (Equation 2.14; page 39)
Solutions of the 'onium salts (10^{-3}M) were made up in 0.1 molar potassium chloride containing gelatine (0.01%).

Polarograms were recorded manually at different temperatures and are shown in Fig. (4.11). The values of α, the transfer coefficient and $E_{1/2}$ were obtained independently by logarithmic analysis for each individual polarogram. In each case the number of electrons (n = 2) was determined by coulometry.
The diffusion coefficients, D, were calculated at various temperatures from the Ilkovic equation.

$$id = 607nD^{1/2}m^{2/3}t^{1/6}c$$

In this treatment, the factor 607 was assumed to be constant over the temperature range, but m and t had to be determined separately.

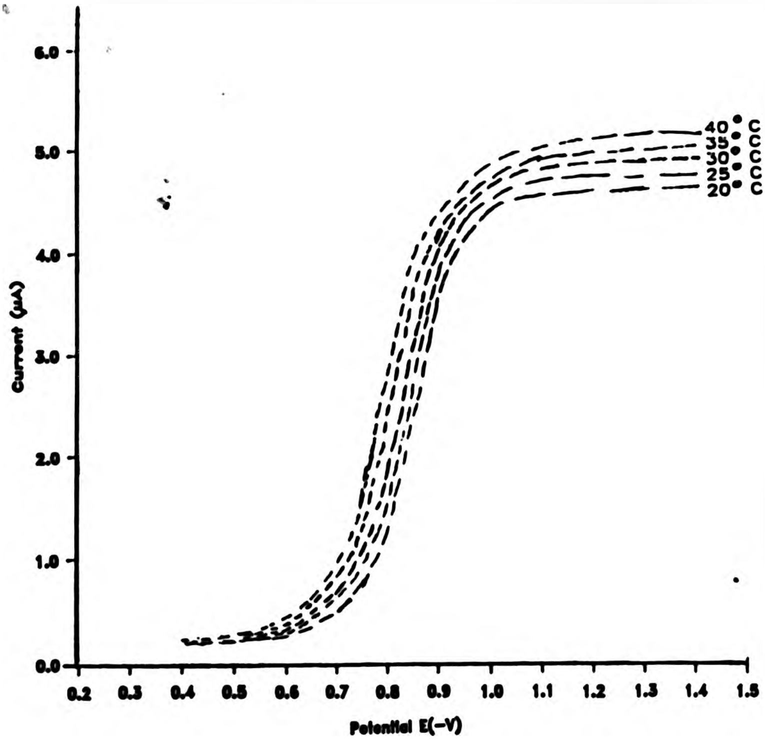


Fig. 4.11 Polarograms for dimethylphenacylsulphonium bromide at various temperatures.

Values for the half-wave potentials, $E_{1/2}$, transfer coefficient and capillary constants are collected in table (4.30).

(a) Dimethylphenacylsulphonium bromide (S^+ salt)

Table 4.30 Polarographic parameters for dimethylphenacylsulphonium bromide at various temperatures.

	Temperature K				
	293	298	303	308	313
$1/T \times 10^{-3}$	3.413	3.356	3.300	3.247	3.195
m(mg.s^{-1})	7.72	7.10	6.66	6.56	6.44
t (s)	3.80	3.45	3.00	2.80	2.60
$t^{1/2}$	1.949	1.857	1.732	1.673	1.612
$D^{1/2} \times 10^{-3}$ ($cm^2.s^{-1}$)	0.7175	0.7918	0.8719	0.8947	0.9640
id (μA)	4.30	4.40	4.50	4.70	4.80
log id	0.633	0.643	0.653	0.672	0.680
n	2	2	2	2	2
(2.303RT)/F	0.0581	0.05913	0.06012	0.06111	0.0621
α	0.798	0.805	0.812	0.818	0.824
$E_{1/2}$ (-V)	0.850	0.840	0.845	0.825	0.815

A similar treatment was carried out for trimethylphenacylammonium bromide. Polarograms shown in Fig. (4.12) were recorded manually at different temperatures.

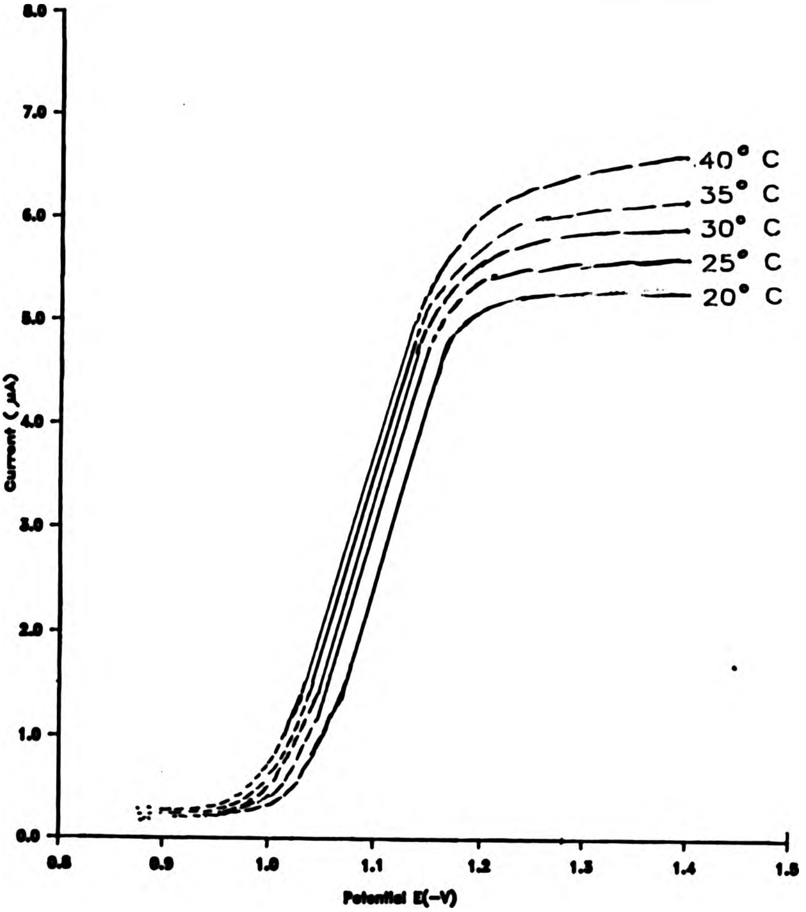


Fig. 4.12 Polarograms for trimethylphenacylammonium bromide at various temperatures.

Values for half-wave potentials, $E_{1/2}$, transfer coefficient and capillary constants are shown in table (4.31).

(b) Trimethylphenacylammonium bromide

Table 4.31 Polarographic parameters for the trimethylphenacylammonium bromide at different temperatures.

	Temperature K				
	293	298	303	308	313
$1/T \times 10^{-3}$	3.413	3.356	3.300	3.247	3.195
$m (mg.s^{-1})$	6.00	5.90	5.86	5.75	5.67
t (s)	3.00	2.80	2.66	2.60	2.50
$D^{1/2} \times 10^{-3}$ $(cm^2.s^{-1})$	1.0386	1.1262	1.1993	1.3350	1.4342
id (μA)	5.00	5.30	5.75	6.10	6.45
log id	0.6973	0.7243	0.7600	0.785	0.8096
n	2	2	2	2	2
$(2.303RT)/F$	0.0581	0.0591	0.06012	0.0611	0.0621
α	0.683	0.695	0.710	0.714	0.737
$E_{1/2}$(-V)	1.110	1.100	1.095	1.087	1.086

Determination of activation energies for the reduction of dimethylphenacylsulphonium and trimethylphenacylammonium bromide at the dropping mercury electrode

(a) Dimethylphenacylsulphonium bromide

Polarograms were plotted manually and the values of the currents at various potentials on the rising part of the waves were directly recorded. Log i/(id-i) values for these polarograms were calculated at various potentials and temperatures. Plots of log i/(id-i) as a function of 1/T at various potentials are shown in figure (4.13). From the slope of the plots, the activation energy was calculated at a particular potential.

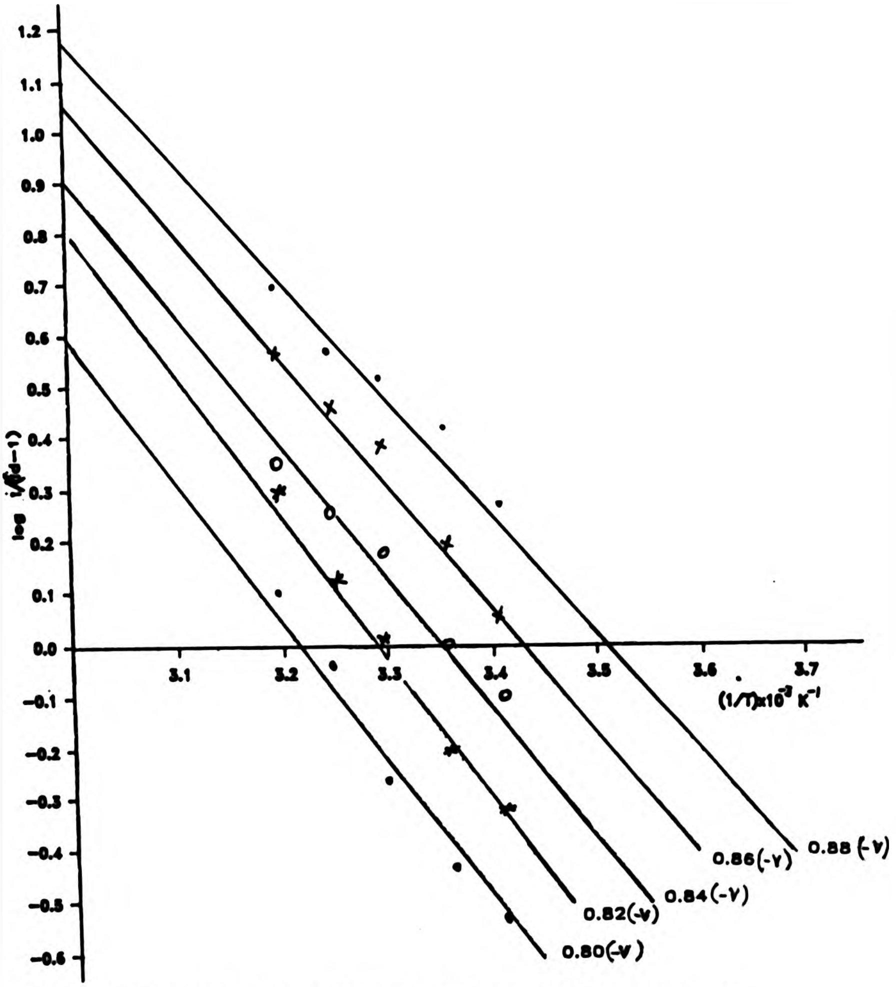


Fig. 4.13 Plot of polarographic function for dimethyl-phenacyl sulphonium bromide.

The activation energies at different potentials are tabulated in table (4.32).

Table 4.32 Activation energies at various potentials for dimethylphenacylsulphonium bromide.

Potential E(-V)	Activation energy Q (KJ $mole^{-1}$)
0.80	55.8
0.82	54.5
0.84	53.5
0.86	51.1
0.88	48.8

The activation energy for the diffusion process, Q_D, was obtained from the plot of log id versus 1/T which is shown in figure (4.14).

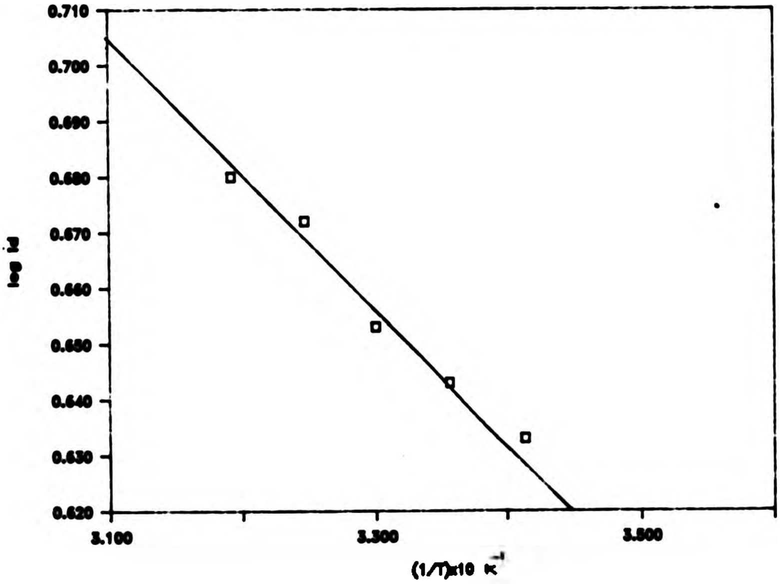


Fig. 4.14

The activation energy for the diffusion process, Q_D, was 9.58 KJ mole^{-1}.

Fig. (4.15) shows the plot of activation energy (Q) against potential extrapolated to a common potential (E = -1.0V).

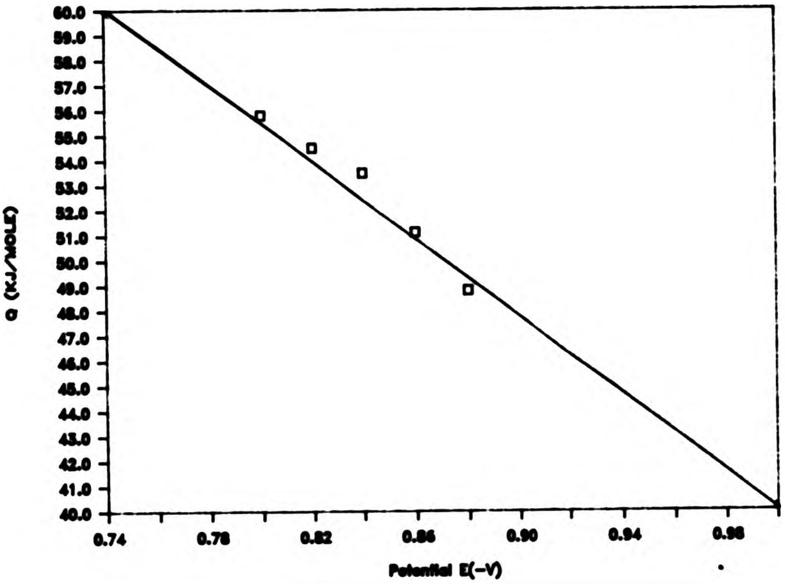


Fig. 4.15

(b) <u>Trimethylphenacylammonium bromide</u>

Similar studies were made with this compound and the same concentration, supporting electrolyte and maximum suppressor were used as before. Polarograms were plotted manually and plots of log i/(id-i) as a function of 1/T are shown in Fig. (4.16).

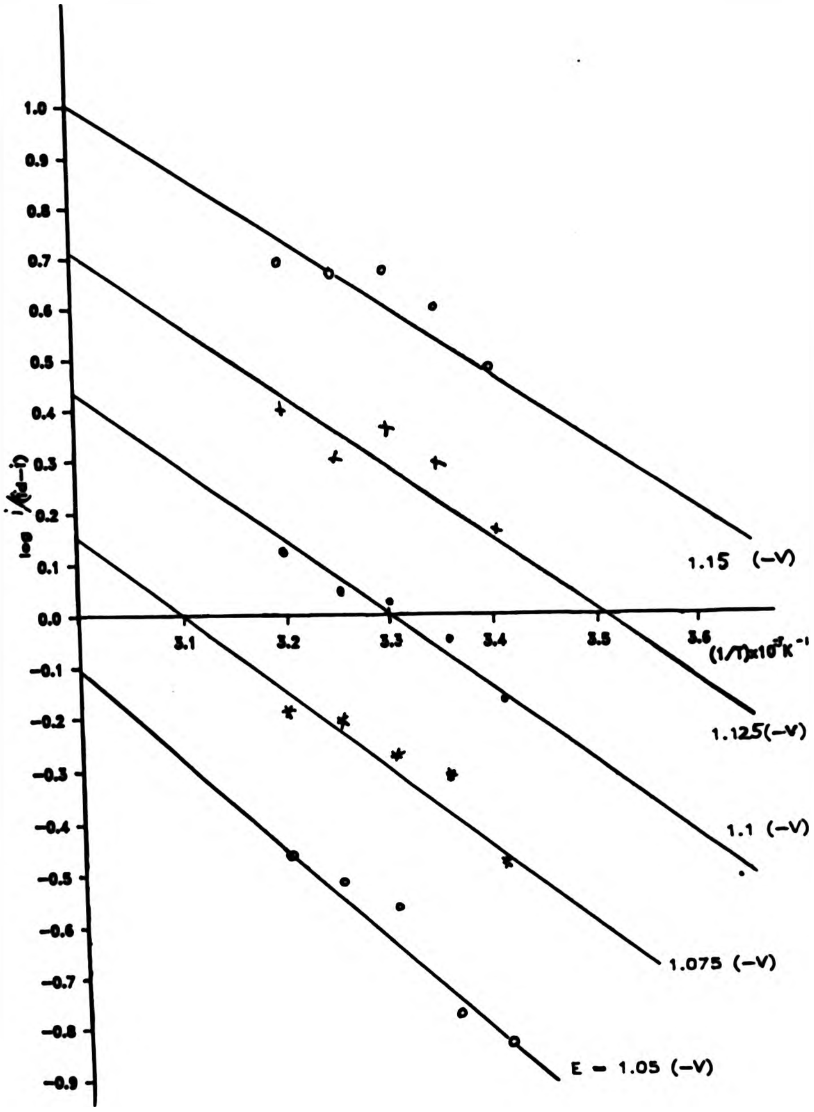


Fig. 4.16 Plot of polarographic function for trimethyl-phenacylammonium bromide.

From the slope of the plot log i/(id-i) versus 1/T, the activation energy, Q, was obtained at various potentials shown in Table (4.33).

Table 4.33 Activation energies at various potentials for trimethylphenacylammonium bromide.

Potential E(-V)	Activation energy Q (KJ mole^{-1})
1.05	44.5
1.075	42.2
1.10	38.7
1.125	36.8
1.15	34.7

The activation energy of the diffusion process, Q_D, was obtained from the plot of log id versus 1/T (Fig. (4.17)). The value was found to be 20.0 KJ mole^{-1}.

Extrapolation of activation energy to a common potential (E = -1.0V) from current data are shown in Fig. (4.18).

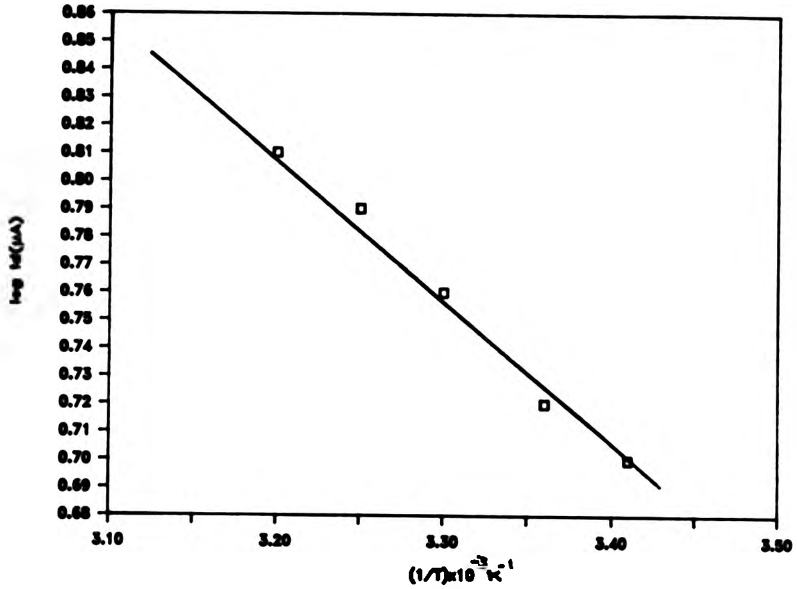


Fig. 4.17

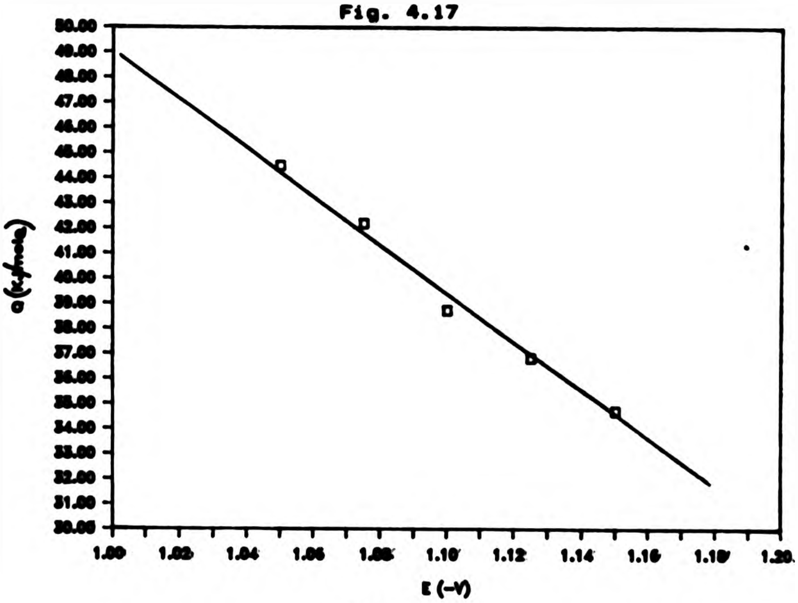


Fig. 4.18

4.B.7. Phenacyl oxime 'onium salts

a) Polarography

Test to establish that the reduction processes in polarography are diffusion controlled

1) Diffusion as function of depolariser concentration

Buffered solutions of different concentrations (0.5 to 2 X 10^{-3}M) of (2-phenyl-2-oximinoethyl)dimethylsulphonium bromide containing gelatine solution (0.01%) were placed in a Kalousek cell and degassed for five minutes. The height of the mercury column was fixed and polarograms recorded. The polarograms consist of two waves, the first wave (lower negative potential) is due to the reduction of the C-X group.

Results

Height of mercury column = 60 cm.

Rate of mercury flow = 1.55 mg/sec.

Drop time = 3.8 sec.

Supporting electrolyte = 7.0 pH buffer (BDH)

Table 4.34

Concentration (10^{-3}M)	Diffusion current id(μA)
0.5	2.50
1.0	4.95
1.5	7.50
2.0	10.00

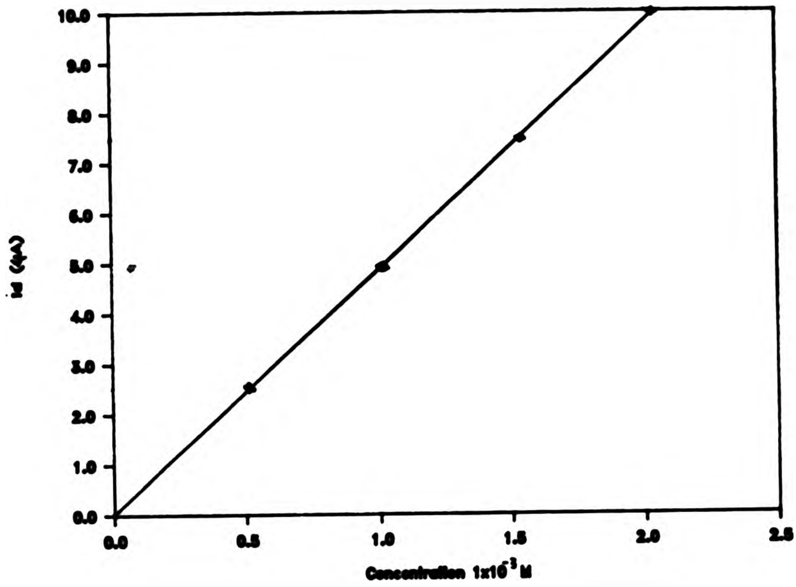


Fig. 4.19 Shows the dependence of wave height on concentration for (2-phenyl-2-oximinoethyl)-dimethylsulphonium bromide.

The strict proportionality is a criterion for showing that the process is diffusion controlled.

2) <u>Effect of mercury column height on diffusion current</u>

Polarograms of a 10^{-3}M solution of (2-phenyl-2-oximinoethyl)-dimethylsulphonium bromide containing (0.01%) gelatine solution in buffer solution (pH 7.0, BDH buffer) were recorded at different heights (h) of mercury column.

Table 4.35

Height of mercury column		Diffusion current	
h(cm)	$h^{\frac{1}{2}}$	id(μA)	id/$h^{\frac{1}{2}}$
40	6.32	4.04	0.640
45	6.70	4.32	0.645
50	7.07	4.58	0.648
55	7.42	4.79	0.646
60	7.75	5.0	0.645

The term id/$h^{1/2}$ is constant. This shows that the reduction process is diffusion controlled.

The $E_{1/2}$ value of (2-phenyl-2-oximinoethyl)dimethylsulphonium bromide in phosphate buffer pH.7 solution were determined at various concentrations, ranging from 0.5 to 2.0 X 10^{-3}M.

Table 4.36

Concentration X 10^{-3}M	$E_{1/2}$(-V)
0.5	0.95
1.0	0.96
1.5	0.95
2.0	0.95

The concentration invariance of E½ shows that the process is diffusion controlled.

Polarography of (2-phenyl-2-oximinoethyl)dialkylsulphonium salts

Solution of the (2-phenyl-2-oximinoethyl)dialkylsulphonium salts made in buffers containing gelatine (0.01%) and placed in a Kalousek cell and degassed with nitrogen for five minutes. The polarograms were recorded automatically on a PO4 polariter for various ligands and the E½ values evaluated are given in table (4.37).

Results:

Concentration of salt = 10^{-3}M

Supporting electrolyte = 7.0 pH buffer (BDH)

Table 4.37

Compound	E½(-V) (first wave)
$C_6H_5CNOHCH_2S^+(CH_3)_2Br^-$	0.95
$C_6H_5CNOHCH_2S^+(C_2H_5)_2Br^-$	0.93
$C_6H_5CNOHCH_2S^+(C_3H_7)_2Br^-$	0.86
$C_6H_5CNOHCH_2S^+(C_4H_9)_2Br^-$	0.74
$C_6H_5CNOHCH_2S^+(CH_2)_4Br^-$	0.84
$C_6H_5CNOHCH_2S^+(CH_2)_5Br^-$	0.80

Effect of pH on E½ values of (2-phenyl-2-oximinoethyl) 'onium salts

Solutions of (2-phenyl-2-oximinoethyl) 'onium salts using different ligands were made up in buffers with varying pH range and polarograms obtained in the usual way.

Results

Concentration of salt = $10^{-3}M$

Maximum suppressor (gelatine) = 0.01%

Results are shown in Table (4.38) at pH values of 2.0, 4.0, 7.0 and 9.2.

The first wave refers to the reduction of 'onium salt to give acetophenone oxime and the sulphide. The second wave concerns the reduction of the resulting acetophenone oxime.

Table 4.38

Compound	pH		2.0	4.0	7.0	9.2
$C_6H_5CNOHCH_2S^+(CH_3)_2Br^-$	$E_{1/2}$(-V)	1st wave	0.62	0.82	0.95	-
		2nd wave	1.00	1.14	1.36	1.45
	id(μA)	1st wave	4.2	4.0	4.0	-
		2nd wave	9.0	9.8	1.6	11.1
	pH		2.0	4.0	7.0	9.2
$C_6H_5CNOHCH_2S^+(C_2H_5)_2Br^-$	$E_{1/2}$(-V)	1st wave	0.76	0.79	0.93	-
		2nd wave	1.08	1.16	1.30	1.46
	id(μA)	1st wave	4.1	4.3	4.0	-
		2nd wave	8.6	8.8	1.2	11.8
	pH		2.0	4.0	7.0	9.2
$C_6H_5CNOHCH_2S^+(C_3H_7)_2Br^-$	$E_{1/2}$(-V)	1st wave	0.74	0.81	0.86	-
		2nd wave	1.02	1.06	-	1.45
	id(μA)	1st wave	4.0	3.9	3.0	-
		2nd wave	9.0	8.4	-	9.9

Table 4.38 (continued).

Compound	pH		2.0	4.0	7.0	9.2
$C_6H_5CNOHCH_2S^+(C_4H_9)_2Br^-$	$E_{1/2}$(-V)	1st wave	0.73	0.78	0.74	-
		2nd wave	1.0	1.1	-	1.43
	id(μA)	1st wave	4.5	4.05	3.7	-
		2nd wave	9.0	9.6	-	9.0

	pH		2.0	4.0	7.0	9.2
$C_6H_5CNOHCH_2S^+(CH_2)_4Br^-$	$E_{1/2}$(-V)	1st wave	0.70	0.71	0.84	-
		2nd wave	1.02	1.08	-	1.44
	id(μA)	1st wave	3.0	4.0	3.7	-
		2nd wave	9.0	9.2	-	9.2

	pH		2.0	4.0	7.0	9.2
$C_6H_5CNOHCH_2S^+(CH_2)_5Br^-$	$E_{1/2}$(-V)	1st wave	0.67	0.68	0.8	-
		2nd wave	0.98	1.06	-	1.49
	id(μA)	1st wave	4.0	3.9	3.9	-
		2nd wave	8.4	8.1	-	9.3

Polarograms for $C_6H_5CNOHCH_2S^+(C_3H_7)_2Br^-$ are shown in Figure (4.20) at different pH values. The profile of the waves for other phenacylsulphonium oximes in this study are similar. The buffers used in the above table and for all subsequent investigations of the effect of pH on $E_{1/2}$ were:

pH 2.0 Aldrich

pH 4.0 Ethanoic acid / sodium ethanoate

pH 7.0 BDH (Phosphate buffer)

pH 9.2 Ammonia/ammonium ethanoate

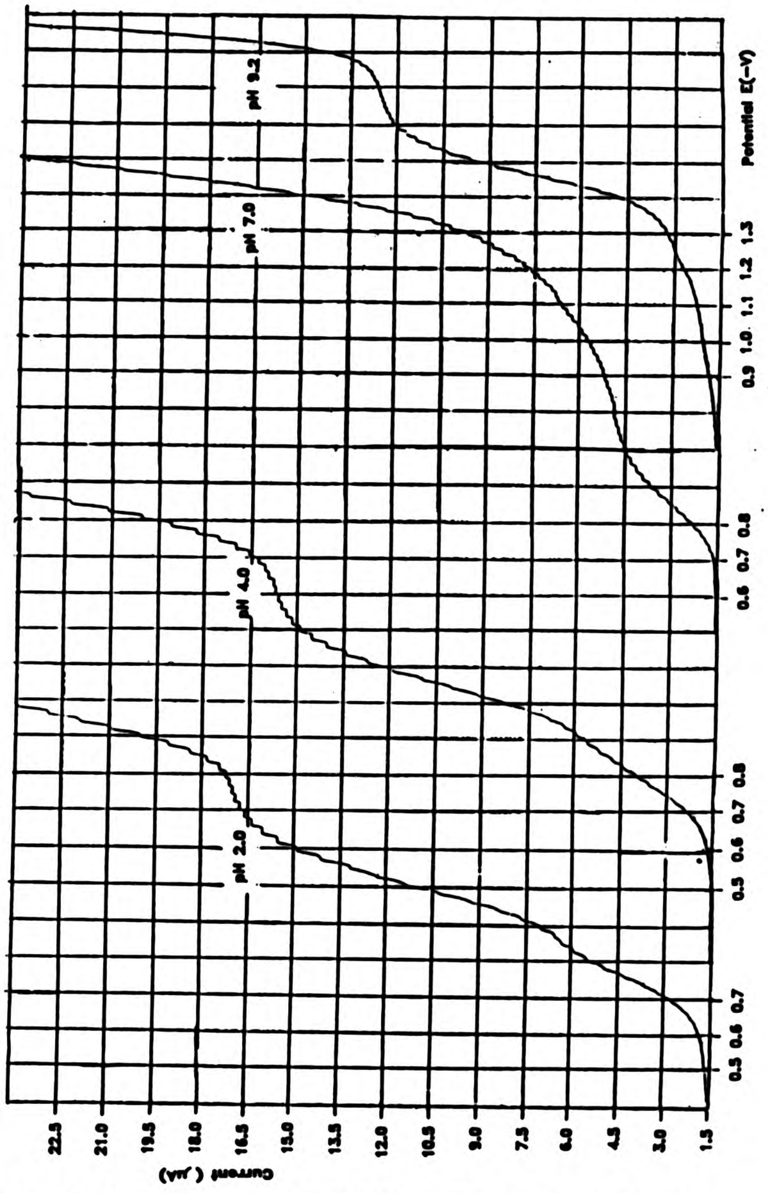


Fig. 4.20 Polarograms for $C_6H_5CNOHCH_2S^+(C_3H_7)_2Br^-$ at different pH values.

Polarography of acetophenone oxime

The effect of pH on $E_{1/2}$ and id values for acetophenone oxime were investigated at several pH values and polarograms obtained in the usual way.

Concentration of acetophenone oxime = 10^{-3}M

(Dissolved in 2.5 cm^3 of ethanol and made up to 50 cm^3 with water containing 0.01% gelatine).

Height of Hg column = 60 cm.

Drop time = 4.0 s.

Table 4.39

pH	$E_{1/2}$(-V)	id(μA)
2.0	0.92	12.8
4.0	1.03	12.8
5.0	1.14	12.8
6.0	1.23	12.6
7.0	1.35	2.12
9.2	1.68	9.6

(The buffers for pH 5 and 6 were ethanoic acid/sodium ethanoate.)

The polarograms are shown in Fig. (4.21).

These results indicate that there is a change in the process of reduction on going from pH4 to higher pH's. This must be consequent on formation of the conjugate base at high pH values. These results are discussed more fully in Chapter 5.

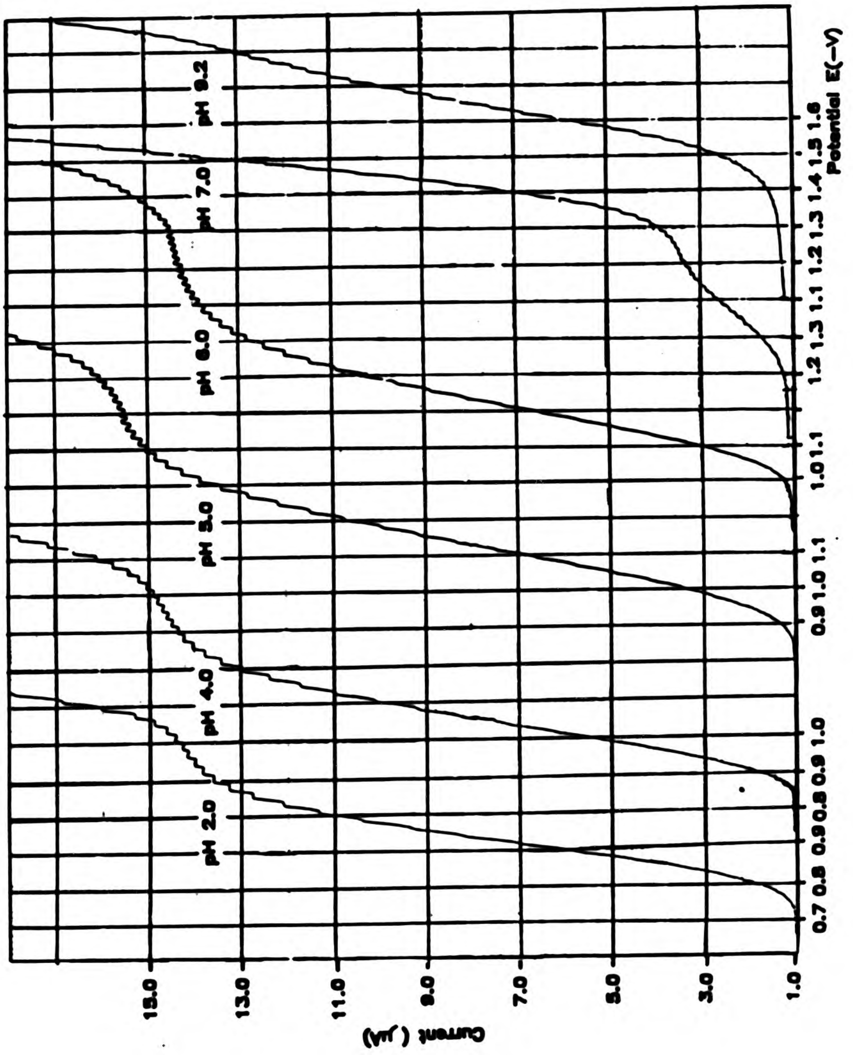


Fig. 4.21 Polarograms for acetophenone oxime at different pH values

Polarography of phenacyl bromide oxime

To better assess the ammonium and sulphonium groups as pseudohalides, the polarography of phenacyl bromide oxime was investigated. This compound is sparingly soluble in water and aqueous alcohol was used as solvent.

Polarography of $C_6H_5CNOHCH_2Br$

The effect of pH on $E_{1/2}$ and id values for the 1st wave at several pH values was investigated and polarograms obtained in the usual manner are shown in figure (4.22). The compound was dissolved in $2.5cm^3$ of ethanol and made up to $50cm^3$ with water.

Concentration = $10^{-3}M$

Height of Hg column = 60cm

Drop time = 4.0 s

Supporting electrolyte = appropriate buffer solution.

Results

Table 4.40

pH	$E_{1/2}$	id (μA)
2.0	0.58	4.2
	1.02	10.5
4.0	0.65	4.2
	1.05	10.8
7.0	-	-
9.2	1.28	-
	1.70	-

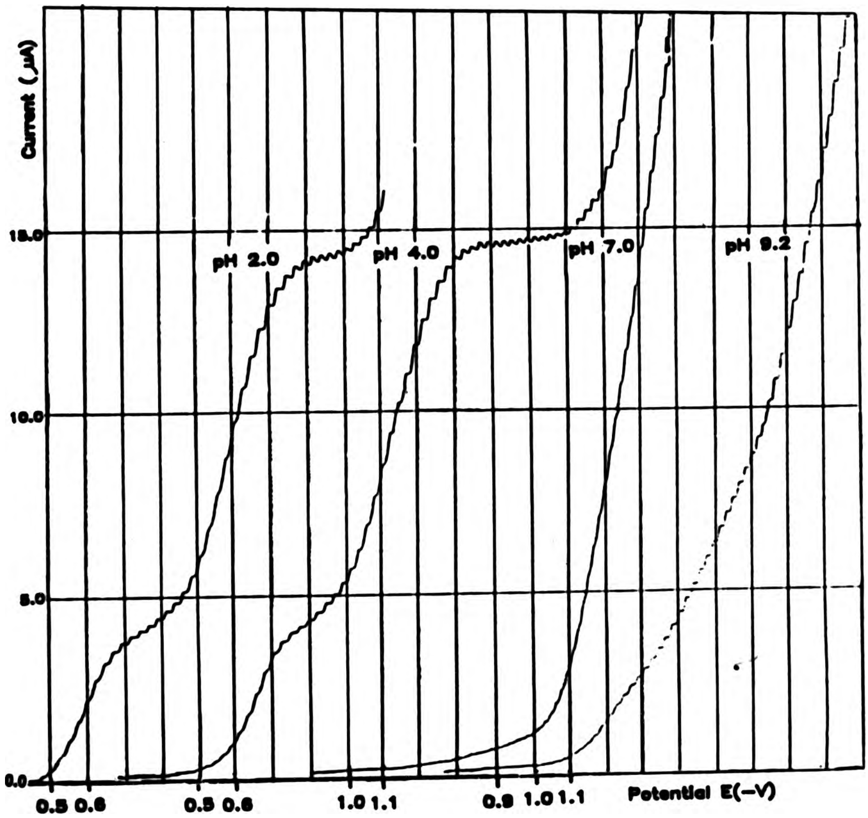


Fig. 4.22 Polaragrams for phenacyl bromide oxime at different pH values.

Polarography of (2-phenyl-2-O-methyloximinoethyl)tetramethylenesulphonium bromide

The effect of pH on $E_{1/2}$, id values and profile of the wave for the above salt was investigated at pH 2.0, 4.0, 7.0 and 9.2 and polarograms obtained in the usual way are shown in figure (4.23).

Results

Compound = $C_6H_5CNOCH_3CH_2S^+(CH_2)_4Br^-$
Concentration of salt = 10^{-3}M
Gelatine solution = 0.01%
Height of Hg column = 60cm
Drop time = 4.0s

Table 4.41

pH	$E_{1/2}$(-V)	id(μA)
2.0	0.63	3.6
	0.92	11.1
4.0	0.68	3.6
	0.96	9.0
7.0	0.77	5.1
9.2	0.68	4.8

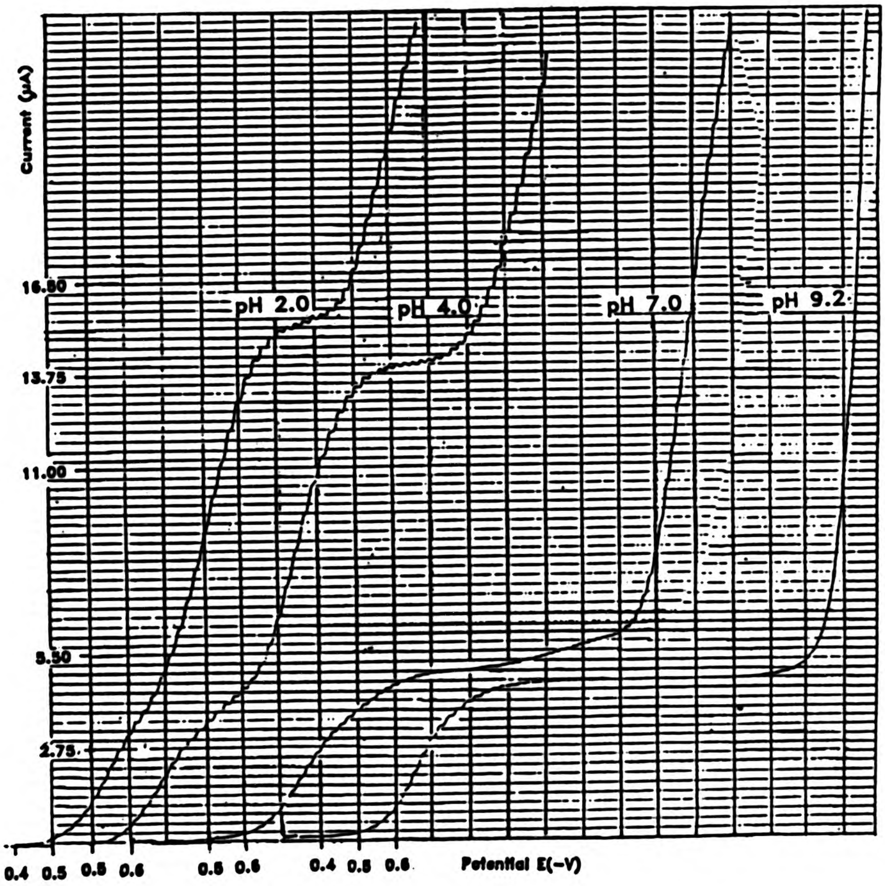


Fig. 4.23 Polarograms of (2-phenyl-2-O-methyloximinoethyl)-tetramethylenesulphonium bromide

Polarography of (2-phenyl-2-oximinoethyl)ammonium salts

Polarograms were obtained using similar conditions and methods as for (2-phenyl-2-oximinoethyl)sulphonium salts.

Results

Concentration of salt = 10^{-3}M

Maximum suppressor = gelatine (0.01%)

Supporting electrolyte = 7.0pH buffer (BDH)

Table 4.42

Compound	$E_{1/2}$(-V) (first wave)
$C_6H_5CNOHCH_2N^+(CH_3)_3Br^-$	1.38
$C_6H_5CNOHCH_2N^+(C_2H_5)_3Br^-$	1.30

Effect of pH on $E_{1/2}$ values for (2-phenyl-2-oximinoethyl)-ammonium compounds

Solutions of phenacyloxime ammonium salts were made up in buffers and polarograms (figure 4.24) obtained in the usual way.

Results

Concentration of salt = 10^{-3}M

Maximum suppressor = gelatine (0.01%)

Results are shown in table (4.43) at pH values of 2.0, 4.0, 7.0, 9.2.

Table 4.43

Compound		pH 2.0	4.0	7.0	9.2
$C_6H_5CNOHCH_2N^+(CH_3)_3Br^-$	$E_{1/2}$(-V) 1st wave	0.97	1.10	1.32	1.2
	id(μA)	10.8	12.0	4.0	6.6
$C_6H_5CNOHCH_2N^+(C_2H_5)_3Br^-$	$E_{1/2}$(-V) 1st wave	0.95	1.00	1.30	1.08
	id(μA)	16.5	12.0	4.5	6.0

(Second wave may be obscured due to discharge of supporting electrolyte.)

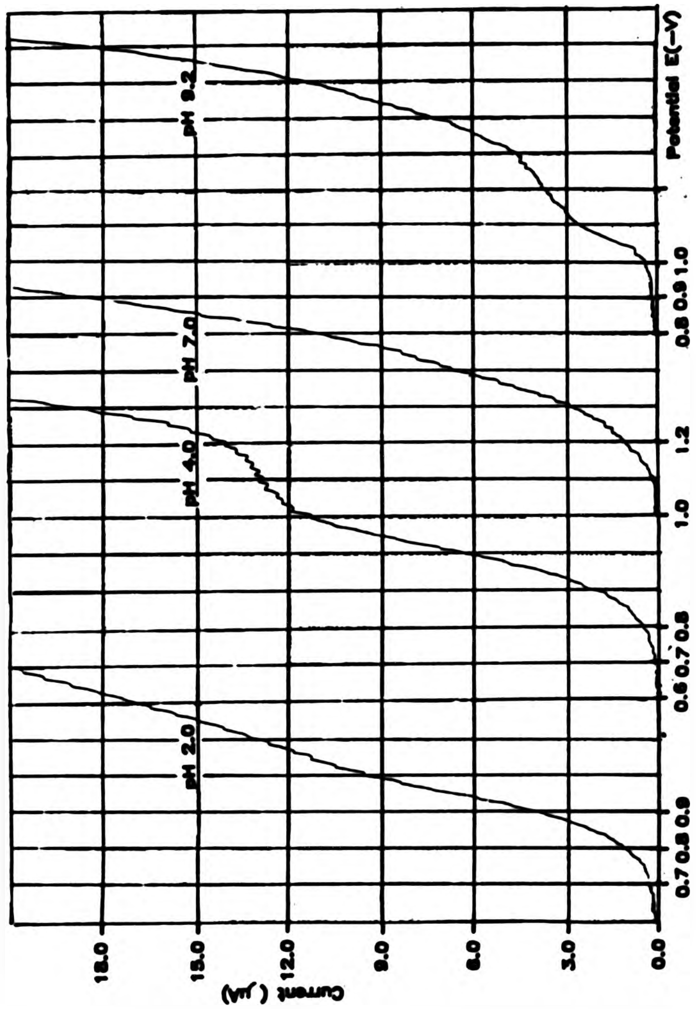


Fig. 4.24 Polarograms for (2-phenyl-2-oximinoethyl)-triethylammonium bromide.

4.C.1. Coulometry of phenacyl 'onium salts

Determination of the value of n by coulometry

As stated earlier, the polarographic analysis of an irreversible reduction process gives αn rather than n. However, it is possible to determine n by coulometry at a fixed potential.

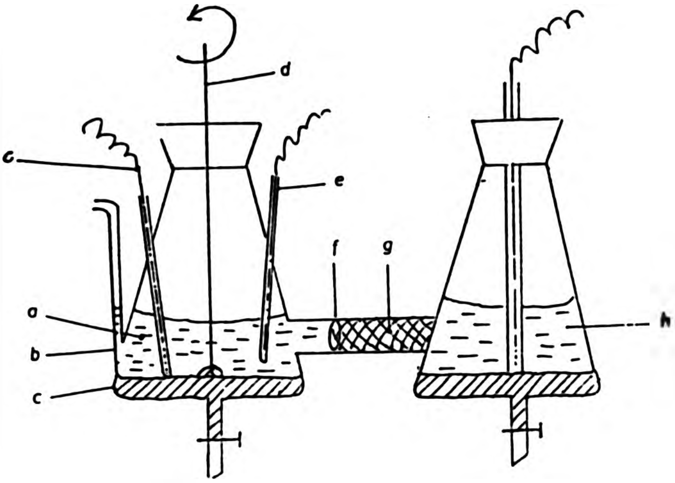
Method and apparatus

The method proposed by Kolthoff and Lingane(4.8) consisted of a cell having a stirred mercury cathode, placed in series with a coulometer. In the present studies, electrolyses were carried out at constant potentials pre-determined from polarograms and corresponded to some point on the current plateau. The electrolysis was terminated after the current had fallen to a constant small value, termed the residual current.

The electrolysis cell (see Fig. 4.25) consisted of two 100 cm^3 conical flasks connected by a bridge containing saturated potassium chloride in agar gel. The right-hand flask contained mercurous sulphate and saturated potassium sulphate, which acted as the anode or auxilliary electrode. $10cm^3$ of mercury was placed into the left-hand flask which was the cathode (the working electrode) followed by $50cm^3$ of molar potassium chloride solution containing 'onium salt of concentration 10^{-2}M.

The reference electrode, a saturated calomel electrode, was positioned close to the working mercury electrode. The three electrodes were connected to a potentiostat and a fixed potential was set between the working and the reference electrode at values previously determined.

A diagram of the cell used for the coulometry and macroscopic reductions is shown below:



a - depolariser

b - gas inlet tube (N_2)

c - working cathode

d - mechanical stirrer

e - reference electrode

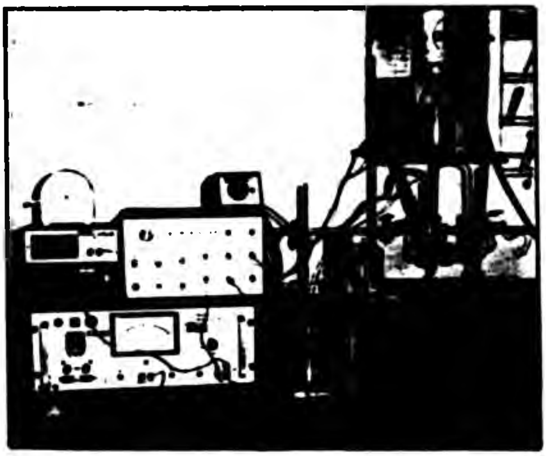
f - fine glass frit

g - agar/KCl salt bridge

h - auxiliary electrode

Electrolysis cell for coulometric and macroscopic reductions

Fig. 4.25



The main electrolysis current flowed between the working and the auxiliary electrode and a milliammeter in the circuit indicated the decrease in current as the substrate was consumed. Also in series with the circuit was an electronic integrator, which registered the total number of coulombs.

Prior to electrolysis, the solution was degassed with nitrogen to remove any oxygen. The mercury pool electrode was vigorously stirred throughout the electrolysis,

(a) to avoid any concentration gradients developing,

(b) to effectively increase the surface area of the mercury exposed, and

(c) to remove products covering the electrode surface.

After a period of time, the current reached a low but almost constant value. This value was multiplied by the time of electrolysis to give the number of coulombs due to this residual current which was subtracted from the total number of coulombs to obtain the 'true' value for electrolysis of substrate.

The following examples illustrate the method:

(a) Salt: Trimethylphenacylammonium bromide

Controlled potential = -1.1V

Total coulombs used in the reduction = 100.50

Residual current = 1.02mA

Time of reduction = 45mins

Coulombs consumed by the residual current

= (45.0 X 60 X 1.02)/1000 = 2.75

Actual number of coulombs used for reduction process

= 100.50 - 2.75 = 97.75

Theoretical number of coulombs for 1 electron reduction

= 96,500 X 5 X 10^{-4} = 48.25

Therefore number of electrons (n)

= 97.75/48.25 = 2.02

(b) <u>Salt: Dimethylphenacylsulphonium bromide</u>

Controlled potential = -0.82V

Observed number of coulombs used in the reduction = 105.6

Residual current = 1.8mA

Time of reduction = 43mins

Coulombs consumed by the residual current

= (43.0 X 60 X 1.8)/1000 = 4.64

Actual number of coulombs used for reduction process

= 105.6 - 4.64 = 100.96

Theoretical number of coulombs for 1 electron reduction

= 96,500 X 5 X 10^{-4} = 48.25

Therefore number of electrons (n)

= 100.96/48.25 = 2.09

The results of a series of salts are shown in table 4.44, where the amount of 'onium salt = 5 X 10^{-4} moles.

Table 4.44

Compound	Controlled Potential (-V)	Corrected No. of Coulombs	No. of Electrons (n)
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	1.1	97.95	2.03
$C_6H_5COCH_2S^+(CH_3)_2Br^-$	0.8	100.96	2.09
$C_6H_5COCH_2S^+(C_2H_5)_2Br^-$	0.8	96.60	2.00
$C_6H_5COCH_2S^+(CH_2)_4Br^-$	0.8	100.9	2.07
$C_6H_5COCH_2S^+(CH_2)_5Br^-$	0.8	96.00	1.98
*$CH_3OC_6H_4COCH_2S^+(CH_3)_2Br^-$	0.83	86.5	1.80

* Due to its low solubility in water, this was determined in aqueous alcohol. The low value of n may be due to this.

Effect of concentration changes on phenacyl sulphonium and ammonium salts subjected to controlled potential electrolysis

In trying to correlate the polarography with the coulometry, the assumption is made that the essential process in each technique is the same. It is more likely that the processes will be the same if the substrate concentrations are similar. Coulometric studies were made over a range of concentrations including the polarographic concentration, to ascertain whether the reduction process was concentration dependent.

The results for a series of compounds follow.

Effects of concentration changes on phenacyl sulphonium and ammonium salts

(i) **Reduction of dimethylphenacylsulphonium bromide**

50cm^3 of a solution of the salt in M potassium chloride was placed in the electrolysis cell and degassed with nitrogen for 10 mins. to electrolysis.

Controlled potential =-0.82V

Table 4.45

Conc. M	Time of Electro- lysis (mins)	Initial Current (mA)	Final Current (mA)	Observed No. of Coulombs	Corrected No. of Coulombs	No. of Electrons (n)
5×10^{-4}	19	14	0.5	5.2	4.7	1.95
1×10^{-3}	22	25	1.0	9.7	9.6	1.98
1×10^{-2}	43	140	1.8	105.6	100.96	2.09

(ii) Reduction of $C_6H_5COCH_2S^+(CH_2)_4Br^-$

Method as previously described.

Supporting electrolyte = 1M Potassium chloride

Controlled potential = -0.85V

These results are shown in table 4.46.

Table 4.46

Conc. M	Time of Electro- lysis (mins)	Initial Current (mA)	Final Current (mA)	Observed No. of Coulombs	Corrected No. of Coulombs	No. of Electrons (n)
5×10^{-4}	15	22	0.1	5.9	5.6	2.03
1×10^{-3}	12	46	2.2	11.3	8.6	1.97
1×10^{-2}	60	200	3.4	128.0	102.6	2.07

(iii) Reduction of $C_6H_5COCH_2S^+(CH_2)_5Br^-$

Controlled potential = −0.90V

Table 4.47

Conc. M	Time of Electro- lysis (mins)	Initial Current (mA)	Final Current (mA)	Observed No. of Coulombs	Corrected No. of Coulombs	No. of Electrons (n)
5×10^{-4}	15	12	0.2	4.8	4.5	1.89
1×10^{-3}	25	40	0.9	9.9	8.31	1.82
1×10^{-2}	60	140	1.1	99.6	92.1	1.98

(iv) Reduction of $C_6H_5COCH_2N^+(CH_3)_3Br^-$

Method as previously described.

Supporting electrolyte = 1M Potassium chloride

Controlled potential = -1.2V

Table 4.48

Conc. M	Time of Electrolysis (mins)	Initial Current (mA)	Final Current (mA)	Observed No. of Coulombs	Corrected No. of Coulombs	No. of Electrons (n)
5×10^{-4}	19	14	0.5	5.5	4.6	1.92
1×10^{-3}	20	25	0.8	10.9	9.3	1.93
1×10^{-2}	55	150	0.83	98.7	95.9	1.98

These results show that the reduction of the salts is essentially a two electron process and independent of concentration over the hundredfold range investigated. (The slightly higher values for the most concentrated solutions are probably due to the residual current correction being relatively smaller than for the more dilute solutions).

4.C.2. Determination of the apparent energy (ε) for the phenacylsulphonium and ammonium salts from coulometric currents

The general procedure was as follows:

An aliquot of the 'onium salt was placed in the electrolysis cell in a thermostat bath, degassed with nitrogen and, after thermal equilibration, was electrolysed at a fixed potential. The solution and the mercury pool cathode were stirred during electrolysis. Current and coulomb values were recorded at half minute intervals over 6 minutes.

e.g. Dimethylphenacylsulphonium bromide

Concentration - 10^{-2}M in KCl (1M)
Temperature - 298K
Applied potential - -0.8V

Table 4.49

Time (mins)	Coulombs	Current i (amps)	lni
0	-	0.038	
0.5	0.5	0.017	-4.07
1.0	1.0	0.016	-4.14
1.5	1.5	0.015	-4.20
2.0	2.0	0.014	-4.27
2.5	2.5	0.015	-4.20
3.0	3.0	0.014	-4.27
3.5	3.5	0.013	-4.43
4.0	4.0	0.013	-4.43
4.5	4.5	0.0125	-4.42
5.0	4.75	0.012	-4.42
5.5	5.0	0.012	-4.42
6.0	5.5	0.011	-4.51

From the graph of lni versus t, the value of $\ln i_o$ was determined by extrapolation.

The experiment was repeated using fresh aliquots of salt solution at the same potential but at different temperatures.

Table (4.50) shows the values of $\ln i_o$ at different temperatures and at a fixed potential (-0.8V).

Table 4.50

Temperature T (K)	1/Temperature 1/T 10^{-3} (K^{-1})	lni_o
276.5	3.62	-4.43
286.5	3.49	-4.10
298.0	3.36	-3.81
307	3.26	-3.60
317	3.16	-3.40

The graph of lni_o versus 1/T at -0.8V (Fig. 4.26) gave a straight line of slope ξ/R from which ξ was evaluated.

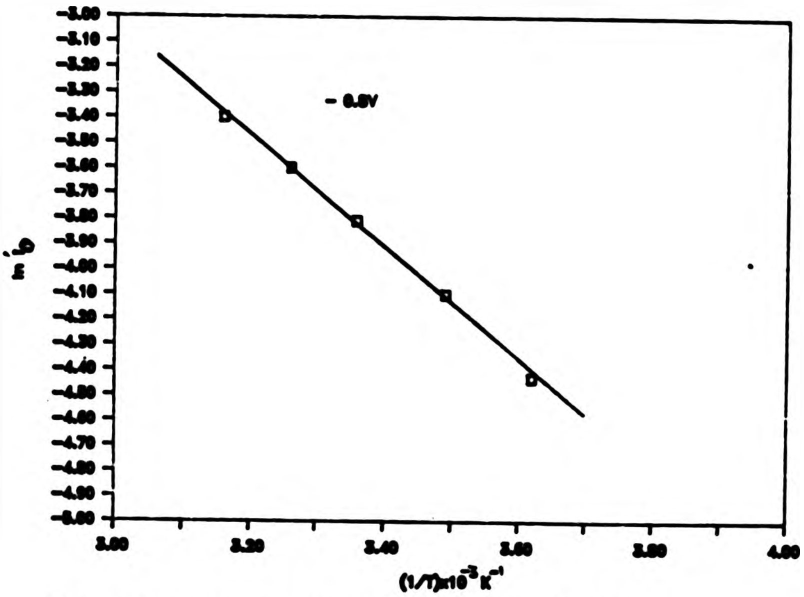


Fig. 4.26. Plot of log lni_o vs 1/T X 10^{-3} for $C_6H_5COCH_2S^+(CH_3)_2Br^-$ at a potential of 0.8(-V).

Similar experiments were carried out at different potentials, the results of which are shown in table (4.51).

Table 4.51

Applied potential E(-V)	ξ(KJmole^{-1})
0.8	48.44
1.0	46.53
1.2	40.29

A similar treatment was carried out for trimethylphenacylammonium bromide. See Table 4.52.

Concentration = 10^{-3}M in KCl (1M)

Temperature = 298K

Applied voltage = -0.8V

Table 4.52

Time t (mins)	Current i (μA)	Coulombs	lni
0.5	0.057	1.0	-2.86
1.0	0.055	3.0	-2.90
1.5	0.054	5.0	-2.92
2.0	0.056	6.0	-2.88
2.5	0.051	7.0	-2.98
3.0	0.050	8.0	-3.00
3.5	0.050	9.0	-3.00
4.0	0.049	10.0	-3.02
4.5	0.048	10.5	-3.04
5.0	0.048	11.0	-3.04

From the graph of lni against t, the value of ln$_o$ was determined by extrapolation to t=0.

The experiment was repeated using fresh aliquots of salt solution at the same potential but at different temperatures.

Table (4.53) shows the values of lni$_o$ at different temperatures and at a fixed potential (-0.8V).

Table 4.53

Temperature T(K)	1/T X 10^{-3}	lni_o
278.5	3.59	-3.16
288.0	3.47	-3.00
298.0	3.36	-2.86
308.5	3.24	-2.70
318.0	3.14	-2.60

The graph of lni_o against 1/T (Fig. 4.27) gave a straight line of slope ξ/R from which the value of ξ was evaluated. Similar experiments were carried out at different potentials and the results are shown in table (4.54).

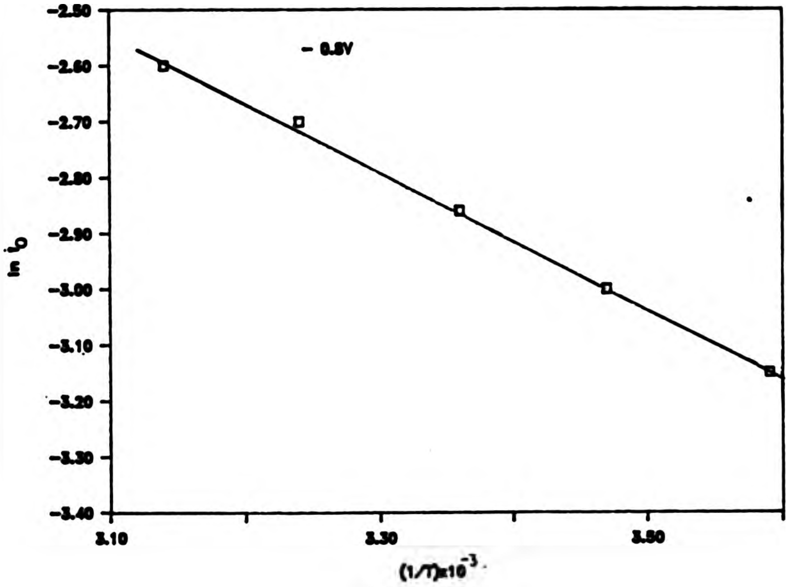


Fig. 4.27.

Table 4.54

Applied potential (-V)	E_a (KJ mole^{-1})
0.8	45.5
1.0	40.6
1.2	38.3

Comparision of tables 4.51 and 4.54 indicates that the activation energy for the reduction of the sulphonium salt is greater than that of the ammonium salt and is contrary to the energies obtained by the polarographic method. These results are discussed on page 208.

4.C.3. Coulometry of phenacyl oxime 'onium salts

The determination of the value of n by coulometry for the phenacyl oxime 'onium salts and their derivatives was carried out by the method described earlier for the phenacyl salts.

The following examples illustrate the method.

(a) (2-phenyl-2-oximinoethyl)dimethylsulphonium bromide

Concentration of salt = 5×10^{-4} moles in 50 cm^3 molar KCl

Applied potential = -1.2V

Observed number of coulombs = 103.0

Residual current = 3.0 mA

Time of reduction = 50.0 mins

Coulombs consumed by residual current = $(50 \times 0.003 \times 60)$

= 9.0

Actual number of coulombs used for reduction process = (103.0 - 9.0)

= 94.0

Theoretical number of coulombs for one-electron reduction = $(5 \times 10^{-4} \times 96{,}500)$

= 48.25

Therefore, number of electrons (n) = (94/48.25)

= 1.95

The results for several oxime salts with different ligands are shown in table (4.55).

Table 4.55

Oxime salt	Controlled potential (-V)	Corrected no. of coulombs	No. of electrons (n)
$C_6H_5CNOHCH_2S^+(CH_3)_2Br^-$	1.2	90.23	1.87
$C_6H_5CNOHCH_2S^+(C_2H_5)_2Br^-$	1.2	91.70	1.90
$C_6H_5CNOHCH_2S^+(C_3H_7)_2Br^-$	1.1	90.23	1.87
$C_6H_5CNOHCH_2S^+(C_4H_9)_2Br^-$	1.1	91.20	1.89
$C_6H_5CNOHCH_2S^+(CH_2)_4Br^-$	1.2	89.75	1.86
$C_6H_5CNOHCH_2S^+(CH_2)_5Br^-$	1.2	92.64	1.92

(b) (2-phenyl-2-oximinoethyl)trimethylammonium bromide

Concentration of salt = 5 X 10^{-4} moles in 50 cm^3 molar KCl
Applied potential = -1.4V
Observed number of coulombs = 123.0
Residual current = 8.0 mA
Time of reduction = 45.0 mins
Coulombs consumed by residual current = (0.008 X 45 X 60) = 21.6
Actual number of coulombs used for reduction process = (123.0 - 21.6) = 101.4
Theoretical number of coulombs for one-electron reduction = (1X10X(50/1000)X96,500) = 48.25
Therefore, number of electrons (n) = (101.4/48.25) = 2.10

The results for ammonium oxime salts are shown in table (4.56).

Table 4.56

Oxime salt	Applied potential (-V)	Corrected no. of coulombs	No. of electrons (n)
$C_6H_5CNOHCH_2N^+(CH_3)_3Br^-$	1.40	101.33	2.10
$C_6H_5CNOHCH_2N^+(C_2H_5)_3Br^-$	1.50	95.05	1.97

The effect of concentration on the electrolysis of phenacyl oxime 'onium salts

Coulometric studies were made for different concentrations of the substrate to ascertain whether the value of n varied with concentration.

(2-phenyl-2-oximinoethyl)dimethylsulphonium bromide

Formula : $C_6H_5CNOHCH_2S^+(CH_3)_2Br^-$

Supporting electrolyte = potassium chloride (1 Molar solution)

Applied potential = -1.2V

Table 4.57

Concentration (M)	Time of electrolyses (mins)	Initial current (mA)	Final current	Total number of coulombs	Corrected number of coulombs	Number of electrons (n)
5 X 10^{-4}	7.0	38	2.0	5.60	4.8	2.00
1 X 10^{-3}	15.0	54	2.5	11.75	9.5	1.98
1 X 10^{-2}	50.0	384	3.0	111.00	94.0	1.95

<u>Reduction of (2-phenyl-2-oximinoethyl)trimethylammonium bromide</u>

Formula : $C_6H_5CNOHCH_2N^+(CH_3)_3Br^-$

Supporting electrolyte = potassium chloride (1 Molar solution)

Controlled potential = -1.4V

Table 4.58

Concentration (M)	Time of electrolyses (mins)	Initial current (mA)	Final current (mA)	Total number of coulombs	Corrected number of coulombs	Number of electrons (n)
5 X 10^{-4}	10.0	21	3.0	6.50	4.7	1.96
1 X 10^{-3}	15.0	40	2.0	10.50	8.7	2.05
1 X 10^{-2}	45.0	250	8.0	123.0	101.4	2.10

These results show that the reduction of the oxime salts is essentially a two-electron process and independent of concentration.

4.D.1. Preparative electrolyses and estimation of products for phenacyl 'onium salts

In order to identify products, larger amounts of substrate were subjected to electrolysis.

The same apparatus was used to carry out these macroscopic reductions as was used for coulometric studies, but with larger amounts of the substrate (10^{-1}M). At the end of the electrolysis, the reduction products were extracted by ether and analysed by glc.

The following examples illustrate the method.

Reduction of phenacyltrimethylammonium bromide

Phenancyltrimethylammonium bromide (1.3g) was dissolved in molar potassium chloride (50cm^3) and the solution was degassed with nitrogen for 10 minutes. The solution was then electrolysed under nitrogen at -1.2V, which corresponded to a potential on the first wave plateau.

Table 4.59

Initial Current (mA)	Final Current (mA)	Time of Electrolysis (mins)	Corrected No.of Coulombs	No. of Electrons (n)
540	0.5	140	915	1.88

Theoretical number of coulombs for 1-electron reduction

$= (1.3/258) \times 96{,}500 = 486.2$

during electrolysis, the current was recorded at fixed time intervals and a current-time graph was plotted, which is shown in Fig. (4.28).

The time and current values are given in the table below:

Table 4.60

Time (mins)	Current (mA)	Time (mins)	Current (mA)	Time (mins)	Current (mA)
0	500	12	375	60	70
1	540	15	298	70	42
2	556	20	225	80	30
3	575	25	195	95	21
4	530	35	150	100	18.7
5	510	40	115	125	3.3
6	505	45	97	130	2.3
7	490	50	87	138	0.5
8	480	55	72	153	0.5

The results show that apart from an initial small increase in current, the current fell off almost exponentially with time. This indicated that the process was essentially due to the reduction of the substrate only. The increase may be accounted for by an initial sharp rise in temperature due to the high current which cannot be avoided even when the cell is put in a thermostatic bath.

The temperature rise did not affect the coulometry.

The electrolysate from the experiment was worked up and analysed for products. The procedure and results are on pages 152 and 154.

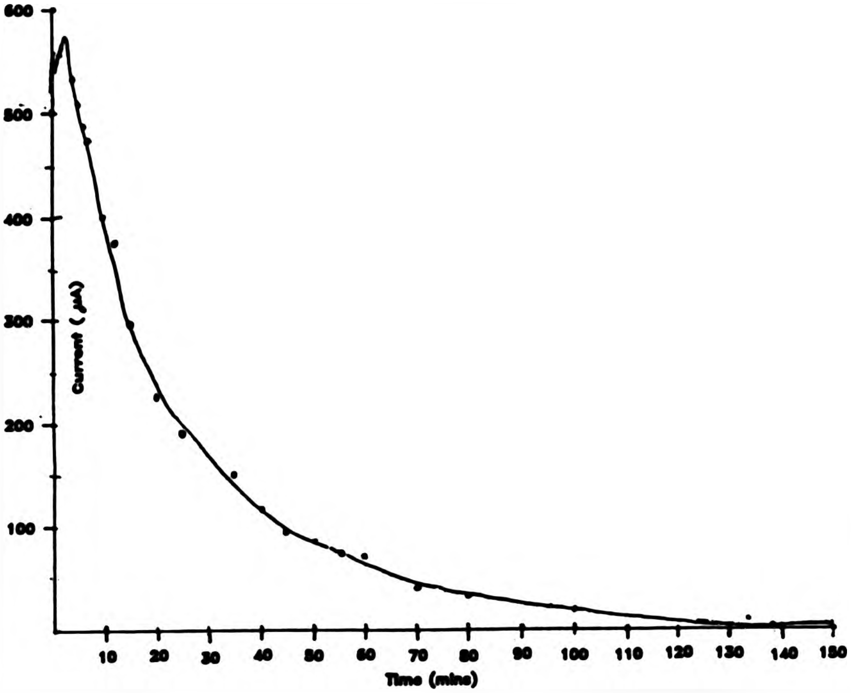


Fig. 4.28.

Investigation of the effect of temperature on reduction

To ascertain whether the reduction process was temperature dependent, the 'onium salts were electrolysed at several temperatures.

Using the apparatus already described, reduction of known amounts of salts were determined at various temperatures, maintained by placing the apparatus in a thermostat and allowing thermal equilibrium to be reached. The following examples illustrate the method:

(i) Reduction of dimethylphenacylsulphonium bromide

The sulphonium salt solution ($50cm^3$) was degassed with nitrogen prior to electrolysis and a very slow flow of nitrogen maintained to exclude oxygen during electrolysis.

Mass of salt = 1.31g

Salt concentration = 10^{-1}M

Supporting electrolyte = molar Potassium chloride

Controlled potential = -0.98V

Theoretical number of coulombs = (1.31/261) X 96,500
= 482.5

Table 4.61

Temperature (°C)	Time of Electrolysis (mins)	No. of Coulombs	No. of Electrons	Coulometric Yield* (%)	Yield of Acetophenone (%)
0	160	849	1.76	88.0	85.0
10	110	860	1.78	89.0	86.0
25	94	839.5	1.74	87.3	85.0
35	80	820	1.70	85.0	83.0
60	67	868	1.80	90.0	88.0

* Based on a 2e reduction process.

(ii) Reduction of trimethylphenacylammonium bromide

Method same as previously described.

Concentration = 10^{-3}M

Supporting electrolyte = molar potassium chloride

Working potential = −1.2V

Table 4.62

Temperature (°C)	Time of Electrolysis (mins)	No. of Coulombs (%)	No. of Electrons	Coulometric Yield* (%)	Yield of Acetophenone (%)
0	180	907	1.88	94.0	93.5
10	120	875	1.82	91.0	90.0
25	90	946	1.87	93.5	92.0
30	40	890	1.84	92.0	91.0
35	42	931	1.93	96.5	93.0
45	35	942	1.95	97.5	95.0
60	29	932	1.93	96.5	92.0

* Based on a 2e reduction process.

The above results indicate that temperature had very little effect, if any, on the number of electrons consumed and the amount of product formed. There seemed to be no general trend, except that the rate of electrolysis, as shown by the time for electrolysis, was faster at higher temperatures.

Effect of applied potential on reduction process

Electrolyses were carried out for phenacylsulphonium and ammonium salts at different applied working potentials at constant temperature, initially at the polarographic plateau value (figures 4.29 and 4.30) and then at lower potentials than the polarographic plateau. In the latter cases, the rates of electrolysis were considerably lower and, accordingly, electrolysis would have been much longer. Therefore, the following reductions were not carried to completion. It should be noted that no correction can be made for residual currents in these experiments.

(i) Dimethylphenacylsulphonium bromide

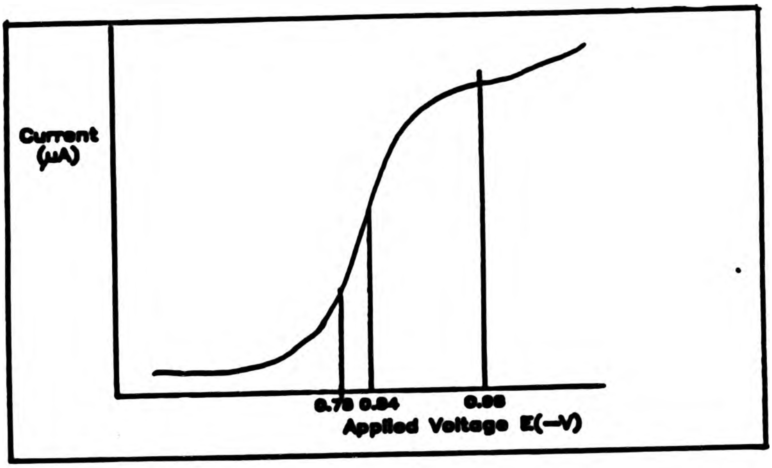


Fig. 4.29. Dimethylphenacylsulphonium bromide

Concentration = 10^{-1} Molar

Supporting electrolyte = Molar KCl

Temperature = 25°C

Table 4.63

Applied Voltage (-V)	No. of Coulombs	Coulometric Yield (%)	Acetophenone Yield (%)
0.98	756	78.3	76.0
0.84	740	76.5	75.0
0.78	125	12.0	11.5

(ii) <u>Trimethylphenacylammonium bromide</u>

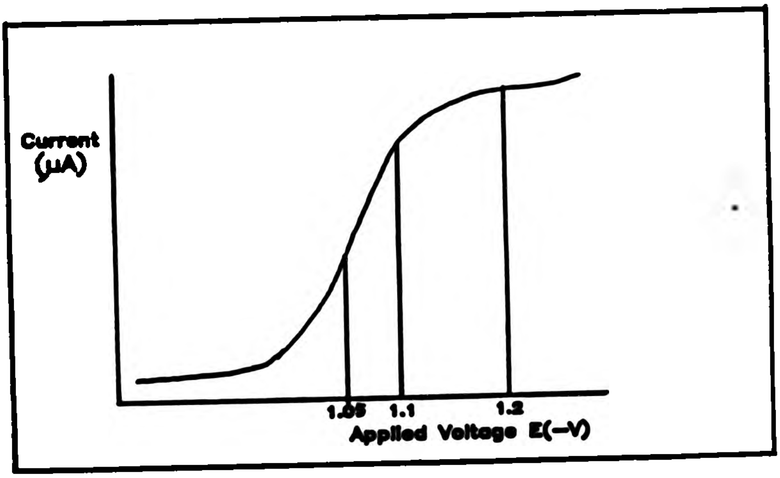


Fig. 4.30. Trimethylphenacylammonium bromide

Table 4.64

Applied Voltage (-V)	No. of Couloombs	Coulometric Yield (%)	Acetophenone Yield (%)
1.2	910	93.5	92.0
1.1	842	80.0	79.0
1.05	241	28.0	26.0

The close correspondence of the yield of acetophenone determined by glc. analysis and coulometry show clearly that the reduction process is independent of the applied potential.

Analysis of the products of electrolysis

At no time during the reduction was any solid precipitate observed indicating that no organo-metallic compounds of the type $RCOCH_2HgBr$ or $(RCOCH_2)_2Hg$ were formed.

After electrolysis, the contents of the working cell were treated by the method described on page 152 and the products analysed by glc., first qualitatively then quantitatively. The only product detected other than the sulphide or tertiary amine, was acetophenone and this was identified by comparison with an authentic sample. A quantitative analysis by glc. required a marker and a calibration graph shown in figure (4.31). 6-methylheptanol was found to be a suitable marker (internal standard). Solutions containing a fixed amount of marker and varying amounts of acetophenone were prepared and samples injected into the glc. apparatus. The areas under the peaks were obtained by an integrator connected to the apparatus.

When analysing an extract of electrolysate, the ratio of the acetophenone and marker peaks was ascertained from the integration, and the concentration of acetophenone was determined by reference to the calibration graph.
The reproducibility of the chromatographs was limited to 2%. This was ascertained after repeated injections in all the glc. analyses reported; the average value of a number of injections was taken.

Results:

Table 4.65

Amount of Acetophenone (g)	Amount of Marker (cm³)	Area of Acetophenone Signal A (arbitrary units)	Area of Marker Signal B (arbitrary units)	Ratio A/B
0.1	0.2	10076	20079	0.502
0.2	0.2	20095	20065	1.01
0.3	0.2	32981	32981	1.53
0.4	0.2	40552	20718	1.96
0.5	0.2	49854	19642	2.54
0.6	0.2	62513	21171	2.96
0.7	0.2	81500	23125	3.52

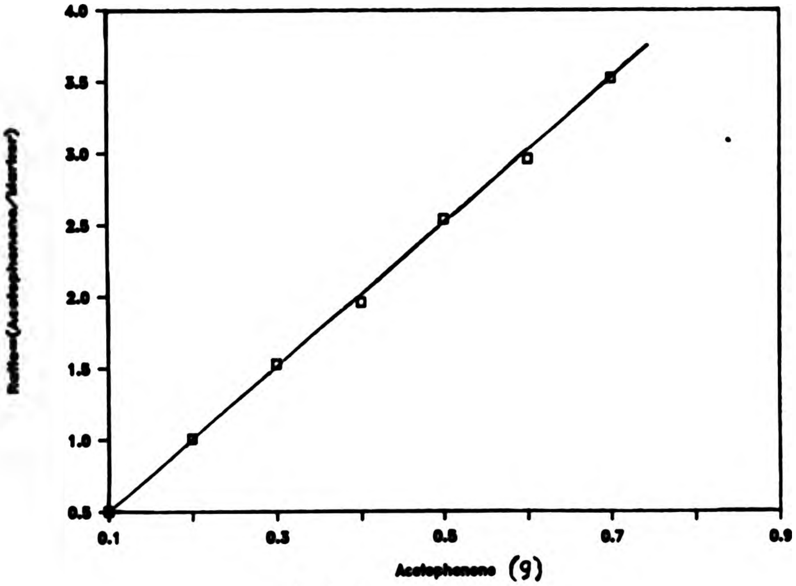


Fig. 4.31.

Complementary methods of analysis

a) Polarography

After electrolysis the electrolysate was examined by polarography to determine the amount of unreacted substrate present.

The following example shows the method.

A solution of 10^{-1}M dimethylphenacylsulphonium bromide in molar potassium chloride ($50cm^3$) was electrolysed and the electrolysate was extracted with ether (see page 152) and diluted to 500 cm^3 with molar potassium chloride. The polarogram of this solution showed a wave corresponding to the sulphonium salt with a diffusion count id = 7.0 μA.

The polarogram of a standard 10^{-3}M of the sulphonium salt in molar potassium chloride showed a diffusion current (id) = 3.5 μA.

$\therefore$ concentration of unreacted sulphonium salt in the

$$\text{electrolysate} = (7.0/3.5) \times 10^{-3}M$$
$$= 2 \times 10^{-2}M$$

Initial concentration of the sulphonium salt

$$= 10^{-3}M$$

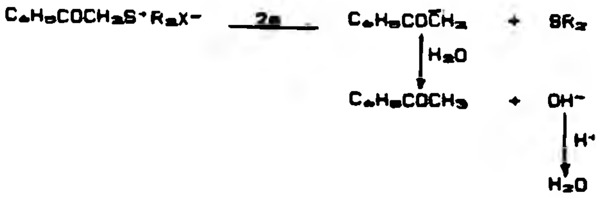
$\therefore$ % unreacted sulphonium salt in electrolysate

$$= (2 \times 10^{-2}/10^{-1}) \times 100$$
$$= 20.0$$

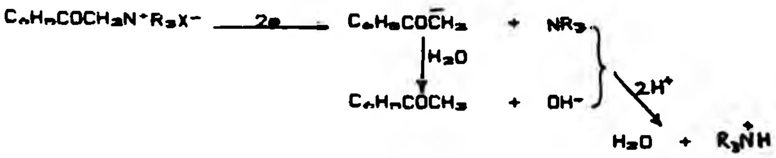
b) <u>Titrimetry</u>

Estimation of the acetophenone was also made from the coulometry and acid titration of the electrolysate. The rationale of these methods was based of the following two electron reduction schemes.

(i) Sulphonium salts



(ii) Ammonium salts



These schemes predict equivalence between the coulometry and the titration. One mole of substrate requires 2 X 96,500 coulombs for reduction, and would generate 1 mole of hydroxide ion. The acid titre for the ammonium salt reduction is twice that for the sulphonium salt because the amine liberated also reacts with the acid.

The following results show how remarkably well these two values correlate and also agree with the completely independent method of glc. analysis.

A) Dimethylphenacylsulphonium bromide

Dimethylphenacylsulphonium bromide (1.305g) was dissolved in 1M KCl solution (50cm^3) and electrolysed at -0.98V at 25°C.

After 53 mins the electrolysis was stopped and the coulomb count noted and the solution titrated with 2M HCl. Electrolysis was then continued and a second coulomb count and titration carried out. The electrolysate was then treated as described on page 152.

Results.

Table 4.66

Time (mins)	Coulombs passed	HCl titre (cm^3)
53	495	1.3
100	756	2.0

1) Coulometry

Number of coulombs required to reduce 1 mole dimethylphenacylsulphonium bromide to acetophenone

= 2 X 96,500

Therefore, number of coulombs required for (1.305/261) moles of this salt = 2 X 96,500 X (1.305/261) = 965

Number of coulombs passed after 53 mins = 495

Therefore, amount of substrate consumed after 53 mins

= (495/965) X 100 = 51.3%

Number of coulombs passed after 100 mins = 756

Therefore, amount of substrate consumed

= (756/965) = 78.3%

2) Titrimetry

1 mole hydrochloric acid is required to neutralise 1 mole of hydroxide generated from 1 mole of dimethyphenacylsulphonium bromide.

Titre of 2 M HCl at 53 minutes

$= 1.3\text{cm}^3$

$= 1.3 \times 2 \times 10^{-3}\text{M HCl}$

$\equiv 1.3 \times 2 \times 10^{-3} \times 261\text{g}$ sulphonium salt

$= 0.679\text{g}$

Therefore, amount of substrate consumed

$= (0.679/1.305) \times 100 = 52.0\%$

Titre of 2 M HCl at 100 minutes

$= 2.0\text{cm}^3$

$\equiv 4 \times 10^{-3} \times 261\text{g}$ sulphonium salt

$= 1.044\text{g}$

Therefore, amount of substrate consumed

$= (1.044/1.305) \times 100 = 80.0\%$

These values show the good agreement between the coulometry and acid titre calculations.

Glc. analysis of the electrolysate.

After electrolysis, the contents of the working cell were transferred to a separating funnel and the mercury removed. The cell was rinsed with ether and water and the washings added to the mixture. The aqueous solution was extracted with ether. 6-Methylheptanol (0.2g in ether) was added as a marker to the ether extract which was then diluted to 25cm^3 with ether. This solution was analysed by glc. using $1 \mu l$ injections.

The area of the peaks obtained were given by a digital integrator.

The ratio of the areas of acetophenone and marker peaks = 2.46

From the calibration graph, this corresponded to 0.486g acetophenone.

The theoretical amount of acetophenone from 1.305g dimethylphenacylsulphonium bromide

= (1.305/261) X 120 = 0.600g

% yield of acetophenone = (0.486/0.6000) X 100 = 80.1

Summary of results

1. Coulometry - % reaction = 78.3
2. Titration - % reacted substrate = 80.0
3. Polarography - % reacted substrate = 80.0
4. Glc. - % product = 80.1

B) Trimethylphenacylammonium bromide

A solution of this salt (1.30g) was electrolysed at -1.4V at 25°C and the products analysed under the conditions given in (A).

Results.

1) Coulometry

The number of coulombs passed = 781.0

The theoretical number of coulombs for complete 2-electron reduction = (1.30 X 96,500 X 2)/258 = 972

Therefore, amount of substrate reacted

= (781/972) X 100 = 80.3%

2) Titration

2 moles of hydrochloric acid are required to neutralise 1 mole of hydroxide ion generated + 1 mole amine formed.

Titre of 1 M HCl to neutralise electrolysate

= 8.0 cm^3

≡ 4 X 10^{-3} X 258g reacted substrate = 1.032g

Therefore, amount of substrate reacted

= (1.032/1.300) X 100 = 79.4%

3) Polarography

The polarogram of standard 10^{-3}M $C_6H_5COCH_2N^+(CH_3)_3Br^-$ in buffer at pH7 gave an id of 3.5μA.

The aqueous solution containing 1.3g of substrate in 50cm^3 was diluted after electrolysis to 500cm^3 with M KCl solution and gave a polarogram with an id = 7.2μA

Then 3.5μA = 10^{-3}M standard solution of substrate and 7.2μA = 2.06 X 10^{-3}M electrolysate solution after 10 fold dilution.

∴ concentration of unreacted ammonium salt in electrolysate = 10 X 2.06 X 10^{-3}M = 2.06 X 10^{-2}M

Initial concentration of ammonium salt = 10^{-3}M

∴ % unreacted ammonium salt in electrolysate

= (2.06 x $10^{-2}/10^{-1}$) x 100

= 20.6

% reacted ammonium salt = 79.4

4) Chromatography

Marker (0.2cm^3 in ether) was added to the ether extract and the whole made up to 25cm^3 with more ether. 1μl was injected into the glc. column as previously described. Using the chromatogram results and the calibration graph, the amount of acetophenone formed = 0.489g

Theoretical amount of acetophenone for 100% reduction

= 0.605g

Therefore % yield of acetophenone = 0.489/0.605 X 100

= 80.9%

Summary of results

1. Coulometry - % reaction = 80.3
2. Titration - % reacted substrate = 79.4
3. Polarography - % reacted substrate = 79.4
4. Glc. - % product = 80.9

4.D.2. Preparative electrolyses and estimation of products for phenacyl oxime 'onium salts

Reductions on this scale allowed the products to be identified qualitatively and quantitatively.

The same apparatus and method was used as already described for the phenacyl 'onium salts.

The following examples illustrate the method.

Reduction of (2-phenyl-2-oximinoethyl)tetramethylene-sulphonium bromide

An aqueous solution of this salt containing 0.5g in 50cm^3 molar potassium chloride was degassed with nitrogen for ten minutes and electrolysed at a temperature of 25°C at a fixed potential of −1.2V which corresponds to the polarographic reduction plateau. The electrolysis, which was carried out under an atmosphere of nitrogen, was continued until a steady residual current was obtained.

Table 4.67

Time of electro-lysis (min.)	Initial current (mA)	Final current (mA)	Corrected number of coulombs	Number of electrons (n)
120	470	2.0	263.6	1.65

Theoretical number of coulombs for 1 electron

$$= (0.5/302) \times 96{,}500 = 159.77$$

During the electrolysis, the current was recorded and a current-time graph plotted. It is shown in Fig. (4.32).

The time and current values are given below:

Table 4.68

Time (mins)	Current (mA)	Time (mins)	Current (mA)	Time (mins)	Current (mA)
0	470	6.0	122	45	17
0.5	510	7.0	95	50	16
1.0	540	10	68	60	16
2.0	456	15	36	70	12
2.5	420	20	51	80	10
3.0	361	25	38	95	6
4.0	302	30	32	100	6
4.5	240	35	26	110	4
5.0	147	40	20	120	2

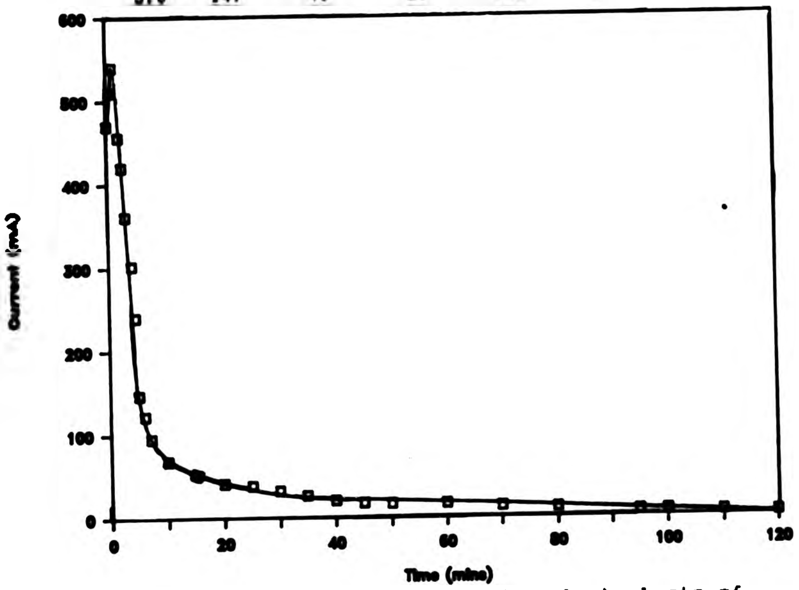


Fig. 4.32 Graph of current vs time for electrolysis of $C_6H_5CNOHS^+(CH_2)_4Br^-$ at 1.2V (25°C)

At the end of the electrolysis the electrolysate in the cathode compartment was transferred to a separating funnel and extracted with ether, 6-methylheptanol (0.1cm^3 in ether) was added as marker to the ether solution which was made up to 25cm^3 with more ether. This solution was analysed by glc, using a capillary column (SE 30) at 150°C.

Reduction of (2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide at different temperatures.

The above salt (0.5g) was dissolved in molar KCl solution (50cm^3) and placed in the cell which was allowed to come to thermal equilibrium in a thermostat before commencing electrolysis. After electrolysis, the solution was worked up for glc analysis as described earlier.

Salt concentration = 3.32×10^{-2} M

Supporting electrolyte = potassium chloride (1 Molar solution)

Controlled potential = −1.2V

Theoretical number of coulombs for 1 electron transfer

= ((0.5/302) X 96,500)

= 159.76

See Table 4.69.

Table 4.69

Temperature	Time of Electrolysis	Corrected number of coulombs	Number of electrons	Coulometric yield	Yield of Acetophenone oxime	Yield of Acetophenone
°C	(minutes)		(n)	(%)	(%)	(%)
10	140	280	1.75	87.5	82	4.0
25	120	274	1.72	86.0	78	5.5
35	95	270	1.69	84.5	78	5.0
45	82	275	1.72	86.0	79	4.0
60	65	274	1.71	85.5	79	3.5

Reduction of (2-phenyl-2-oximinoethyl)trimethylammonium bromide

The same apparatus, method of electrolysis, workup procedure and glc analysis under similar conditions as for the phenacylsulphonium oxime salt.

An aqueous solution of the salt, containing 0.5g in 50cm^3 molar potassium chloride was degassed with nitrogen for ten minutes and electrolysed at a temperature of 25°C at a fixed potential of -1.4V which corresponded to the polarographic reduction plateau.

The electrolysis was carried out under an atmosphere of nitrogen until a steady residual current was obtained.

Table 4.70

Time of electrolysis (min.)	Initial current (mA)	Final current (mA)	Corrected number of coulombs	Number of electrons (n)
100	430	8.0	314.5	1.79

Theoretical number of coulombs for 1-electron reduction

= (0.5/273) X 96,500 = 176.74

During the electrolysis, the current values at fixed intervals were recorded and a current-time graph plotted. It is shown in Fig. (4.33).

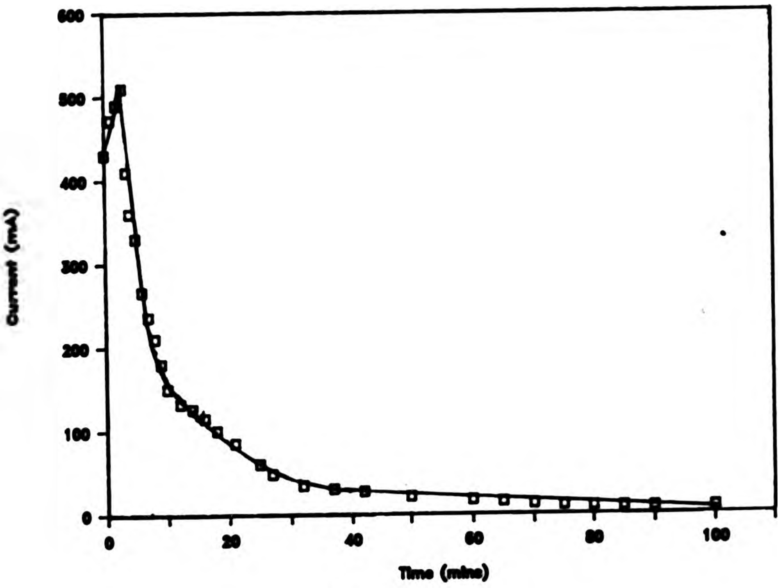


Fig. 4.33.

The time and current values are given in the table below:

Table 4.71

Time (mins)	Current (mA)	Time (mins)	Current (mA)	Time (mins)	Current (mA)
0	430	10	150	42	27
1.0	472	12	132	50	21
2.0	490	14	126	60	17
3.0	510	15	120	65	15
3.5	410	16	115	70	12
4.0	360	18	100	75	10
5.0	330	21	85	80	9
6.0	266	25	60	85	8.5
7.0	236	27	48	90	8
8.0	210	32	34	100	8
9.0	180	37	30		

The purpose of this experiment was to ascertain if there were any anomalous time-current discontinuities indicating significant chemical reactions other than those connected with the reduction. No such changes are shown (see figure 4.33). There was a small initial rise in current followed by an exponential decrease. The initial current increase is due to an initial rise in temperature which quickly falls to that of the surrounding temperature.

Reduction of (2-phenyl-2-oximinoethyl)trimethylammonium bromide at different temperatures

Method as previously described.

Salt concentration = 3.32×10^{-3} M

Supporting electrolyte = potassium chloride (1 Molar solution)

Controlled potential = −1.2V

Theoretical number of coulombs for 1 electron transfer

= ((0.5/302) X 96,500)

= 159.76

Table 4.72

Temperature °C	Time of Electrolysis (minutes)	Corrected number of coulombs	Number of electrons (n)	Coulometric yield (%)	Yield of Acetophenone oxime (%)	Yield of Acetophenone (%)
15	120	309.3	1.75	87.5	81.0	4.5
25	100	314.5	1.78	89.0	80.6	6.1
35	75	311.1	1.76	88.0	80.0	6.0
45	60	314.0	1.78	89.0	80.0	6.5
65	50	312.8	1.77	88.5	82.0	5.0

These results, in common with all the 'onium salts studied in this investigation, show that while the electrolysis rate increased markedly with temperature, the yield and distribution of products was little changed.

The effect of varying the applied working potential

Using the same apparatus as previously described, electrolysis of a known amount of salt was carried out at different potentials on the rising part of the wave to ascertain whether a change in potential would lead to the formation of mercury compounds as reported for benzyl compounds.(1,12)

The following examples illustrate the method.

(2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide

Salt concentration = 1.66 X 10^{-3} moles in $50cm^3$ molar potassium chloride

Temperature = 25°C

Supporting electrolyte = Molar potassium chloride

Table 4.73

Applied voltage	Number of coulombs	Coulometric yield (%)	Acetophenone oxime (%)	Acetophenone (%)
1.2	274	85.70	78.0	5.5
1.1	120.6	37.50	33.0	3.0
1.0	67.5	20.96	19.5	1.6

(2-phenyl-2-oximinoethyl)trimethylammonium bromide

Table 4.74

Applied voltage	Number of coulombs	Coulometric yield (%)	Acetophenone oxime (%)	Acetophenone (%)
1.4	313.0	89.0	78.6	7.1
1.25	124.0	35.0	30.0	3.0
1.0	78.0	22.0	19.0	2.0

There was no evidence for the formation of any insoluble mercury compounds.

Analysis of products

During or at the end of the electrolysis, no solid was formed indicating that no organo-metallic compounds of the type R-CNOHCH$_2$HgBr or (R-CNOHCH$_2$)$_2$Hg was formed.
After electrolysis, the electrolysate was treated by the same method as previously described (see page 152). The products were analysed qualitatively by tlc and glc and compared with authentic samples.

The quantitative analysis of products were analysed by glc using a marker (6-methylheptanol) and a standard calibration graph.
The following examples illustrate the method.

(2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide

(2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide (0.5g) was dissolved in molar potassium chloride solution (50cm^3) and electrolysed at an applied potential -1.2V at 25°C.

Table 4.75

Time of electrolysis (mins)	Initial current (mA)	Final current (mA)	Corrected number of coulombs	Number of electrons (n)
120	470	2.0	263.6	1.65

After 120 minutes, the electrolysis was stopped and the electrolysate was worked up by the same method as described on page 152. The aqueous extract was titrated with molar hydrochloric acid using screened methyl orange as indicator.

Titre value = 1.6cm^3

Results

1) Coulometry

Theoretical number of coulombs required to reduce 0.5g of compound = 96,500 X ((0.5 X 2)/302) = 319.54

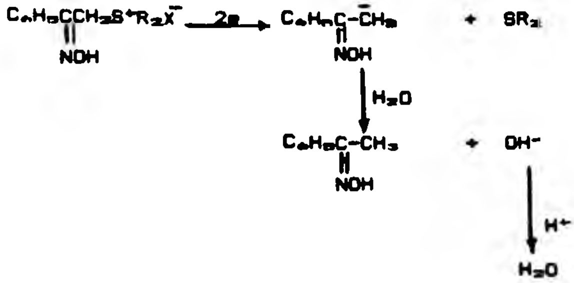
From experiment, the number of coulombs = 263.6

Therefore, the fraction of substrate reduced

= 263.6/319.54 = 0.8249 or 82.5%

2) Titrimetry

Estimation of the acetophenone oxime as the primary product and small amount of acetophenone was also made from the coulometry and acid titration of the electrolysate. The basis of this method is discussed for the phenacylsulphonium salts on page 152. The method should also be applicable to the phenacyl oxime sulphonium salts as shown in the scheme below.



Initial mass of phenacyl oxime sulphonium salt

= 0.5g = 1.66 X 10^{-3} mole.

Electrolysate titre of M HCl

= 1.6cm^3 = 1.6 X 10^{-3} mole.

$\therefore$ % reacted salt = (1.6/1.66) X 100 = 96.4

The high values from titrimetry of this salt and the corresponding ammonium salt is very difficult to account for.

3) Polarography

The aqueous electrolysate after extraction with ether, was diluted to 100cm^3 with distilled water.

Diffusion current of the solution = 8.3μA

Diffusion current of standard 10^{-3} M solution of the salt = 3.1μA.

Therefore, concentration of diluted electrolysate

$= (8.35/3.18) \times 10^{-3} = 2.63 \times 10^{-3}$ M

Therefore, electrolysate contained

$2.63 \times 10^{-3} \times 302 \times 10^{-1}$ = 0.0794g of unreduced salt.

Initial amount of salt = 0.5g

Therefore, % unreacted salt = (0.0794/0.5000) X 100

= 15.8

Therefore, % reacted salt = 84.2

4) <u>Glc analysis of electrolysate</u>

After electrolysis, the contents of the working cell were transferred to a separating funnel and the mercury removed. The cell was rinsed with ether and water and the washings added to the mixture. The electrolysate was extracted with ether, 6-methylheptanol was added as a marker and the ether extract made up to the volume mark 25cm^3 with ether and analysed by glc under similar conditions. as described on page 152.

The ratio of the areas of acetophenone oxime and marker peaks = 1.9

This corresponds to 0.19g of acetophenone oxime from the calibration graph.

Theoretical yield corresponding to 100% reduction to aceto- phenone oxime = 0.247g

% yield of acetophenone oxime = (0.19/0.247)X100

= 76.9

The ratio of the areas of acetophenone and marker peaks = 0.55

This corresponds to 0.011g of acetophenone.

Theoretical yield corresponding to 100% reduction to acetophenone = 0.219g

% yield of acetophenone = (0.011/0.219) X 100 = 5.0

<u>Summary of Results</u>

1.	Coulometry	% reacted salt	=	82.5
2.	Titrimetry	% reacted salt	=	96.4
3.	Polarography	% reacted salt	=	84.2
4.	GLc.	% product	=	81.9

<u>(2-phenyl-2-oximinoethyl)trimethylammonium bromide</u>

The above compound (0.5g) was dissolved in molar potassium chloride solution (50cm^3) and electrolysed at an applied potential of -1.4V at 25°C.

Table 4.76

Time of electro-lysis (mins)	Initial current (mA)	Final current (mA)	Corrected number of coulombs	Number of electrons (n)
100	430	8.0	314.5	1.79

After 100 minutes, the electrolysis was stopped and the electrolysate treated as described on page 152. After extraction with ether, the aqueous electrolysate was neutralised with molar hydrochloric acid, using screened methyl orange as indicator.

Titre = $3.64 cm^3$

Results

1) Coulometry

Theoretical number of coulombs required to reduce 0.5g of compound by 2-electron transfer process

= 96,500 X ((0.5 X 2)/273) = 353.48

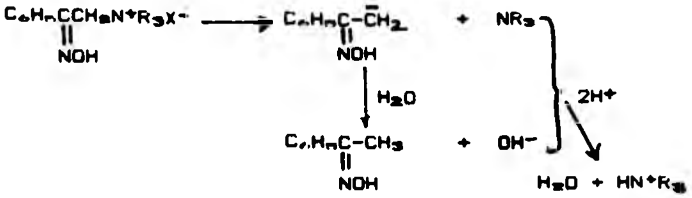
From experiment, the number of coulombs = 314.5

Therefore, the fraction of substrate reduced

= 314.5/353.48 = 0.889 or 88.9%

2) Titrimetry

The basis of this method for sulphonium salts is given on page 152. A similar scheme applies for the reduction of ammonium salts, but because the tertiary amine produced is also basic, the two-electron reduction leads to a mixture requiring two equivalents of acid for neutralisation. The scheme is shown below.



2 moles of hydrochloric acid is required to neutralise the products from reduction of 1 mole of salt.

Therefore, 3.64cm^3 of M HCl = 1.82/1000 M salt

= (1.82/1000) X 273 = 0.497g

Initial mass of salt = 0.500g

Therefore, % reaction = (0.499/0.500) X 100 = 99.3%

3) Polarography

After ether extraction the electrolysate was diluted to 100cm^3 with distilled water and a polarogram recorded.

Diffusion current of diluted electrolysate = 8.45 μA.

The polarogram of standard 10^{-3} M solution of the compound showed a diffusion current = 3.3 μA.

∴ concentration of compound in diluted electrolysate

= (8.45/3.3) X 10^{-3}M = 2.56 X 10^{-3}M

∴ amount of unreduced compound in electrolysate

= 0.256 X 10^{-3} moles

Initial amount of compound = 0.5/273 moles

= 1.832 X 10^{-3} moles

∴ % unreduced compound = (0.256/1.832) X 100 = 14

4. Glc analysis

A known amount of marker was added to the ether extract which was then made up to 25cm^3 with ether. The solution was analysed by glc as previously described.

The ratio of the areas of acetophenone oxime and marker peaks = 2.03

This corresponds to 0.2g of acetophenone oxime from the calibration graph.

Theoretical yield corresponding to 100% reduction to acetophenone oxime = 0.247

% yield of acetophenone oxime = (0.2 /0.247)X100= 80.1

The ratio of the areas of acetophenone and marker peaks = 0.75

This corresponds to 0.0146g

Theoretical yield corresponding to 100% reduction to acetophenone = 0.219g

% yield of acetophenone = (0.0146/0.219) X 100 = 6.6

Total product yield (acetophenone + acetophenone oxime) = 86.7%

Summary of Results

1. Coulometry % reacted salt = 88.9
2. Titrimetry % reacted salt = 99.3
3. Polarography % reacted salt = 86
4. GLc. % product = 86.7

To test whether the 'onium salts underwent chemical reaction other than those due to electrolysis under the experimental conditions employed, a number of experiments were carried out.

(a) The possibility that the acetophenone oxime may have arisen due to the hydrolysis of the phenacyl oxime salt was investigated as follows.

A solution of 0.5g in 50cm^3 of molar potassium chloride was put into the electrolytic cell containing

$10cm^3$ mercury and continuously stirred for 120 minutes and worked up according to the general procedure. The ether extract, when analysed by glc under similar conditions, showed no peaks other than the large solvent peak.

(b) An experiment similar to the above was repeated, as above, except for the absence of potassium chloride and the salt was recovered from the aqueous solution using a rotary evaporator to remove the water.

Salt recovered = 0.486g = 97.2%

This result, and the absence of peaks in the ether extract, confirms the absence of hydrolysis of the phenacyl oxime- sulphonium salt.

(c) The possibility that the acetophenone oxime may have arisen due to the hydrolysis of the phenacyl oxime salt in the presence of hydroxyl ions was investigated.

A solution of (2-phenyl-2-oximinoethyl)tetramethylene-sulphonium salt (0.5g) containing $16.6cm^3$ of 0.1M sodium hydroxide, was made up to the volume mark ($50cm^3$) with molar potassium chloride solution and subjected to the same treatment as described above. The ether extract showed no peaks when analysed by glc. The solution was titrated with 0.1M hydrochloric acid using screened methyl orange as an indicator which required $16.5cm^3$ to neutralise. This is consistent with ylid undergoing no further reaction under these alkaline conditions other than the final protonation.

(d) It is conceivable that the acetophenone may have arisen due to hydrolysis of acetophenone oxime which is formed during the electrolysis of the salt at a fixed potential. This was investigated as follows.

A solution of acetophenone oxime (0.25g) in ethanol ($5cm^3$) containing $18.5cm^3$ of 0.1M sodium hydroxide was made up to $50cm^3$ solution with potassium chloride solution and worked up according to the general procedure. The glc of the ether extract gave a peak which had a retention time corresponding to that of an authentic sample of acetophenone oxime. A quantitative estimation of acetophenone oxime, using 6-methylheptanol as a marker, showed 97% of acetophenone oxime in the ether solution. This shows that very little, if any, of the acetophenone could have arisen from hydrolysis of the acetophenone oxime formed during the electrolysis.

The isolation and identification of acetophenone oxime

A solution of (2-phenyl-2-oximino)trimethylammonium bromide (0.5g) was electrolysed at -1.4V and 25°C.

Coulometric yield = 86.5% (based on 2-electron reduction)

After electrolysis the aqueous solution was extracted with ether and the ether removed by a rotary evaporator.

Mass of solid residue = 0.203g

Theoretical yield corresponding to 100% reduction to acetophene oxime = 0.247g

Assuming all the non-volatile product to be acetophenone oxime, the % yield = (0.203/0.24) X 100 = 82.2

The residue was recrystallised from petrol-ether giving white needles, melting point of 49-50°C (lit. value 48-50°C).

The infra-red spectrum and NMR spectra were identical with those of an authentic sample of acetophenone oxime.

These results are also in accord with the two-electron reduction of the salt to give acetophenone oxime.

Reduction of (2-phenyl-2-O-methyloximinoethyl)-tetramethylenesulphonium bromide

The above compound (0.5g) was dissolved in molar potassium chloride solution (50cm^3) and electrolysed at an applied potential of -1.2V and a temperature of 25°C. The electrolysate was worked up and analysed according to the general procedure.

Table 4.77

Initial current (mA)	Final current (mA)	Time of electrolysis (mins)	Theoretical number of coulombs	Corrected number of coulombs	Number of electrons (n)
620	1.5	40	305.4	304.0	1.99

Results

1) Coulometry

Theoretical number of coulombs required to reduce 0.5g of compound for a 2-electron transfer process

= (0.5/316 X 2 X 96,500) = 305.4

From experiment, the corrected number of coulombs

= 304.0

Therefore, fraction of substrate reduced

= 304.0/305.4 = 0.995 or 99.5%

2) Titrimetry

Titre of M HCl = 1.6 cm^3

∴ amount of salt reacted = 1.6 X 10^{-3} mole

∴ fraction of salt reacted = 1.6/1.58 = 1.01 or 101%

3) Polarography

The aqueous electrolysate, after extraction with ether, was diluted to $100cm^3$ with distilled water.

Diffusion current of this solution = nil.

This showed that the entire salt had been consumed.

4) Glc analysis

Theoretical yield corresponding to 100% reduction to 2-phenyl-2-O-methyloximinoethane = 0.236g

(0.5/316 X 149)

Experimental yield = 0.232g

% yield of 2-phenyl-2-O-methyloximinoethane

= (0.232/0.236) X 100 = 98.4

Summary of Results

1. Coulometry % reacted salt = 99.5
2. Titrimetry % reacted salt = 101
3. Polarography % reacted salt = 100
4. GLc. % product = 98.4

These results show that the O-methyloximino salt is more completely reduced than the corresponding oxime. This may be because a small amount of the oxime may be converted to the non-reducible conjugate base by alkali formed during the reaction.

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Chapter 5

Discussion

The polarography of dialkylphenacyl 'onium salts

The polarograms of almost all the phenacyl sulphonium salts studied, irrespective of ring substitution of the ligands, show two reduction waves. The first wave is due to the reductive cleavage of the C-S bond and the second to the reduction of the aryl methyl ketone to give the corresponding alcohol or pinacol. It is the first wave which is of most interest in this study because we are concerned with the mechanism of this process and the factors which influence it. The second step is related to the reduction of a product derived from the first step and is of minor interest. The second wave is clearly observable in alkaline solution but becomes less well defined in neutral and acid solution, where the general discharge wave of the buffer solution begins to overlap this wave. By contrast the first wave is well defined in neutral and acid solutions, but becomes smaller and somewhat less defined in alkaline solution; this is discussed later in the section on pH studies.

The first wave of almost all the salts has essentially the same diffusion currents, suggesting that the same reaction process is occurring with each salt. All the values for the first wave correspond to an overall two-electron transfer, consistent with the reduction of the C-S bond to give the corresponding ketone which was identified in preparative scale reductions.

$$C_6H_5COCH_2\overset{+}{S}R_2 \xrightarrow{2e+H^+} C_6H_5COCH_3$$

The mechanism of this reaction is discussed later.

These results are similar to those of Saveant(5.1) and Zuman et alia(5.2) on the diethylphenacylsulphonium and methylbutylphenacylsulphonium salts, although in our studies the $E_{1/2}$ values are more negative than those reported by these workers.

Table 5.1

		$E_{1/2}$(-V)
(a)	$C_6H_5COCH_2\overset{+}{S}(CH_3)_2\ Br^-$	0.75
(b)	$C_6H_5COCH_2\overset{+}{S}(C_2H_5)_2\ Br^-$	0.63
(c)	$C_6H_5COCH_2\overset{+}{S}(CH_3)C_4H_9ClO_4^-$	0.58

(a) Present study (b) J.M. Saveant (c) P. Zuman and S. Tang

<u>The effect of substituents on the ease of reduction</u>

A number of p-substituted phenacyl sulphonium salts were examined and their $E_{1/2}$ values are shown in the table below.

Table 5.2

	$E_{1/2}$(-V)
$C_6H_5COCH_2\overset{+}{S}(CH_3)_2\ Br^-$	0.75
$Br{-}C_6H_4COCH_2\overset{+}{S}(CH_3)_2\ Br^-$	0.73
$Cl{-}C_6H_4COCH_2\overset{+}{S}(CH_3)_2\ Br^-$	0.63
$CH_3O{-}C_6H_4COCH_2\overset{+}{S}(CH_3)_2\ Br^-$	0.70
$O_2N{-}C_6H_4COCH_2\overset{+}{S}(CH_3)_2\ Br^-$	0.39

The half wave potentials show that the para-substituents cause a decrease in the $E_{1/2}$ values relative to the parent (unsubstituted) compound. This is not unexpected when the substituent is electronegative, but is surprising in the case of the p-methoxy substituted salt: the well known electron releasing properties of this substituent should reduce the electron deficiency at the carbonyl group and the reaction site, and make reduction more difficult and lead to a more negative $E_{1/2}$value. This unexpected result suggests that the above explanation is unsatisfactory. A similar situation was observed in the reduction of benzyldialkylsulphonium salts, where the p-methyl group caused a lowering of the $E_{1/2}$value(8.3). In that case it was suggested that the results could be accommodated by an initial one-electron transfer step to give a radical, followed rapidly by the transfer of a second electron. Then the initial rate controlling step leads to a radical, and since almost all substituents stabilise radicals, any substituent will lower the reduction potential. In the case of the benzylsulphonium salts, notwithstanding the smooth two-electron one step polarograms, other evidence was found to support the initial one-electron transfer step: reductions at potentials less than the polarographic plateau values gave a product mixture containing dibenzylmercury compounds. The formation of the organomercury compounds is difficult to account for except in terms of radical intermediates. However, in the present work on phenacyl salts there is no such evidence for the formation of radical intermediates:

attempts to prepare diphenacylmercury by electrolysis at low potentials were unsuccessful.

Although the effect of the substituents is small, the data was tested for a Hammett linear free energy relationship. A plot of $E_{1/2}$ values against σ showed appreciable scatter about the best straight line and the slope was very small (see page 77). The data was also subjected to a "retrogressive analysis" for the best straight line, using a computer programme (B Lin Reg) and gave the following relationship:

$$y = 0.05x - 0.71$$

where,

$y = E_{1/2}$ and $x = \sigma$, the Hammett substituent value.

The correlation factor of 0.224 is very unsatisfactory and indicates that the data is not suitable for treatment as a linear relationship.

The small value of the slope would be expected if the carbonyl group exerts the main influence on the ease of reduction and the effect of the ring substituents would be small. These results suggest it would be unwise to conclude that the low value of $E_{1/2}$ for the p-methoxy compound was evidence for the formation of a radical intermediate.

Although the p-nitro substituted salt is included in the table, it was not used in estimating the best straight line because both the polarographic and macroreduction studies show that this compound's behaviour is anomalous: the initial reduction occurs at the nitro group rather than at the C-S site. This is discussed in detail below.

Streitwieser and Perrin(5.4) also found an unsatisfactory Hammett relationship for the polarographic reduction of benzyl chlorides, and suggested that the poor correlation of halfwave potentials with values was due to "the special requirement of a transition state which strikes a balance between radical and anion character". Parmar reached a similar conclusion from work on benzylsulphonium salts(1.11).

Elving and Leone(5.5) investigated the polarography of the phenacyl halides and showed that the p-chloro and p-bromo substituents had almost no effect on the half wave potential.

Table 5.3

	$E_{1/2}$(-V)
$C_6H_5COCH_2Br$	0.16
p-$ClC_6H_4COCH_2Br$	0.17
p-$BrC_6H_4COCH_2Br$	0.17

The main conclusion from the above discussion is that the carbonyl group exerts such an overwhelming influence on the ease of reduction of the C-X group that para ring substituents have a negligible effect.

The reduction of dimethyl-p-nitrophenacylsulphonium bromide

As stated earlier, the p-nitro salt cannot be included in the series with the other substituents because its polarogram is very different from the two wave polarograms of the other salts. A practical problem with this compound was that its very low solubility in water necessitated an aqueous alcohol solution and the presence of alcohol may have altered the course of reduction.

The polarogram at pH7 shown in figure (5.1) has at least three waves, the first and second being well defined. From the wave height the diffusion current of the first wave ($E_{1/2}$=-0.48 V) corresponds to about four electrons per molecule instead of the two-electron waves of the other compounds. The second wave ($E_{1/2}$=-0.98 V) corresponds to two electrons. The third wave ($E_{1/2}$=-1.66 V) is rather ill-defined and corresponds to about two electrons. It is tempting at this stage to suggest that the first wave is a four-electron reduction of the nitro group to the hydroxylamine group.

$$RNO_2 \xrightarrow{4e + 4H^+} RNHOH + H_2O$$

The second wave might be due to the reduction of the hydroxylamine to the amine

$$RNHOH \xrightarrow{2e + 2H^+} RNH_2 + H_2O$$

or the reduction of the sulphonium salt

$$\begin{tikzcd}
R\text{-}\overset{+}{S}(CH_3)_2 \arrow[r, "2e"] & R^- \arrow[d, "H^+"] & + \; S(CH_3)_2 \\
& RH &
\end{tikzcd}$$

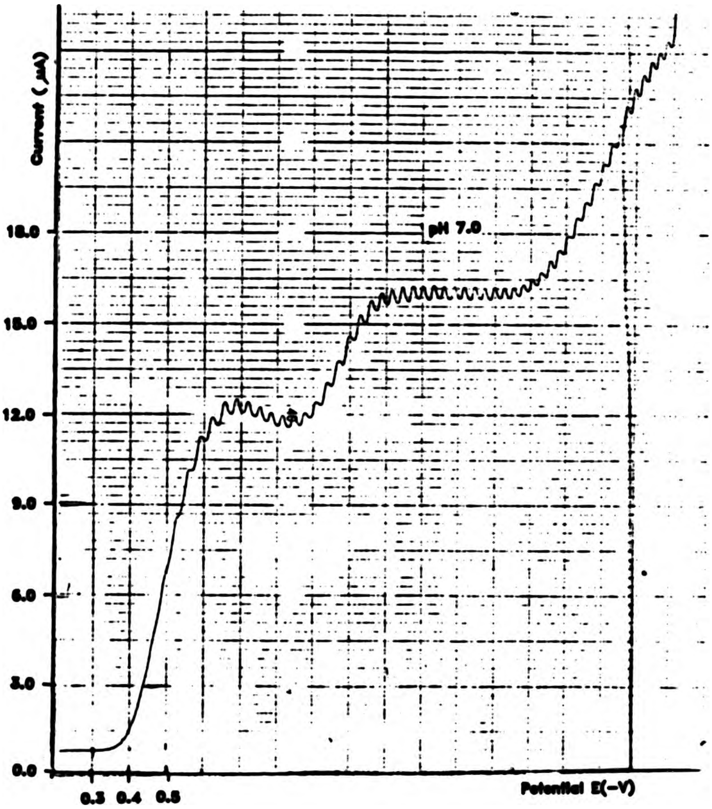


Fig. 5.1 Polarogram of dimethyl-p-nitrophenacylsulphonium bromide.

The reduction of the carbonyl group must be one of the possible reductions for the third wave.

In order to obtain further information on this compound, reductions at controlled potentials were carried out and the coulomb count determined and the solution was also titrated with standardised acid. Reduction of the solution at the plateau of the first wave (−0.75V) gave a coulomb value corresponding to 4.4 electrons and a titration of the resulting solution with acid gave a titre corresponding to 4 H^+ equivalents. This clearly confirms our assignment of four electrons to the first wave. Reduction of a solution at the plateau of the second wave (−1.1V) gave a coulomb value corresponding to 6.2 electrons and an acid titre corresponding to 7 H^+ equivalents. This confirms the second wave assignment as two electrons. The results are therefore consistent with the reaction scheme formulated above, viz., reduction of the nitro group to the hydroxylamine group which is further reduced to the amine at a more negative potential. This could also account for the seventh H^+ equivalent in the titre because the amine product would consume one molar equivalent of acid in salt formation.

$$\begin{tikzcd}
O_2NC_6H_4COCH_2\overset{+}{S}(CH_3)_2 \arrow[r, "6e+6H^+"] & H_2NC_6H_4COCH_2S^+(CH_3)_2 \arrow[d, "H^+"] \\
 & H_3\overset{+}{N}C_6H_4COCH_2S^+(CH_3)_2
\end{tikzcd}$$

This scheme can also account for the absence of any product in the ether extract of the electrolysate, because the product would be "locked" in the aqueous solution as a salt. There are, however, a number of questions left unresolved by this scheme, the most important being why should the C-S bond survive at a potential of -1.1V ? The explanation that the p-amino group will deactivate the carbonyl group by mesomeric interaction is weakened by the fact that the other p-substituents, including the methoxy group, have little effect on the $E_{1/2}$ value. The solution also darkened in colour during the electrolysis and a small amount of substance came out of solution. We were unable to identify this product. However, irrespective of the problems thrown up by these latter observations, the anomaly of the p-nitrophenacyl salt reduction is firmly established.

The effect of ligand R groups

The polarography of a number of phenacyldialkylsulphonium salts with different ligands was investigated. All gave essentially the same two wave polarogram described earlier, the difference being in the $E_{1/2}$ values of the first wave. These are given in table (5.4) on the next page.

The table shows that the salt with the methyl ligands required a higher reduction potential than those with other alkyl ligands, i.e. the other ligands facilitate the reduction process more than the methyl group. A similar effect was observed in the reduction of benzylsulphonium salts, and these values are also given in the table.

Table 5.4

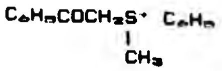
R_2	$C_6H_5\underset{\underset{O}{\Vert}}{C}CH_2S^+R_2Br^-$ $E_{1/2}$(-V)	$C_6H_5CH_2S^+R_2Br^-$ $E_{1/2}$(-V)
$(CH_3)_2$	0.75	1.28
$(C_2H_5)_2$	0.72	1.30
$(C_3H_7)_2$	0.71	1.20
$(C_4H_9)_2$	0.69	1.08
$(CH_2)_4$ (R_2-cyclic)	0.70	1.07
$(CH_2)_5$ (R_2-cyclic)	0.70	1.22

There is no obvious explanation for this in terms of polar or steric effects. However, a consideration of solvation leads to a possible explanation whereby the compound with the small methyl ligands is the most heavily solvated. Larger ligands will tend to exclude solvent molecules due to their size and also their inherent hydrophobic property. Since a two-electron reduction involves a reversal of charge there will be a very considerable change in the orientation of solvating molecules and solvation energy, which should affect the activation energy for the reduction. Because the dimethylphenacylsulphonium salt should be the most heavily solvated, it should be the most difficult to reduce, and this could account for the results. A similar argument concerning the solvation of ligands was used to account for the unexpected increase in acidity with increasing size of ligands in the bis-sulphonium salts, $RRS^+CH_2S^+RR(BF_4^-)_2$.(5.6)

Another possible explanation is concerned with steric effects and entropy. The alkyl ligands will almost certainly be more restricted in their motion in the sulphonium cation than in the transition state leading to the formation of sulphide. This restriction must be greater for the larger ligands and hence there should be a greater increase in entropy on formation of the transition state for the larger ligands than for methyl. However, it might be thought that this effect should be more marked for the open chain diethyl compound than the cyclic five and six membered ring systems, but the $E_{1/2}$ values do not support this. A further point of interest is that the salt with the five membered ring ligand, $C_6H_5COCH_2\overset{+}{S}(CH_2)_4$ Br− is only slightly easier to reduce than the salts with methyl and ethyl ligands. This is in sharp contrast to the behaviour of the analogous benzylsulphonium salts where the high reactivity of the benzyltetramethylenesulphonium salt is of preparative value.

Saveant reported on the phenacylsulphonium salts A and B(5.7) .

(A) $C_6H_5COCH_2S^+(C_7H_5)_2$ Br− $E_{1/2}$= −0.63V

(B) 

$C_6H_5COCH_2\overset{+}{\underset{CH_3}{S}}C_6H_5$ Br− $E_{1/2}$= −0.58V

and interpreted the lower $E_{1/2}$ value of B to be due to interaction of the S^+ atom with the π-electrons of the phenyl group. It was because of complications of this kind that aryl ligands were excluded from this study.

The Effect of pH

In common with Zuman's results on methylbutylphenacylsulphonium perchlorate, the $E_{1/2}$ values of the sulphonium salts studied were only slightly dependent on pH in acid solution (pH 2-6), but showed a significant increase in negative value in alkaline solutions.

Table (5.5) shows the variation of $E_{1/2}$ versus pH for buffered solutions of 10^{-3}M dimethylphenacylsulphonium bromide.

Table 5.5

pH	2.0	3.0	4.0	5.0	7.01	7.78
$E_{1/2}$(-V)	0.760	0.761	0.762	0.763	0.765	0.775
pH	8.36	9.24	10.20	11.25	12.0	13.0
$E_{1/2}$(-V)	0.78	0.80	0.83	0.88	0.94	0.98

The intersection of $E_{1/2}$ versus pH plot, shown in figure (5.2) gives the approximate pK_a (8.6) of the substrate. A value of 8.4 was determined from the pH versus titre graph of the reaction of the sulphonium salt with standard sodium hydroxide solution. A similar value of 8.4 was obtained by Aksnes and Songstad(5.8). Zuman and Tang(5.2) obtained pK_a values of 7.7 and 7.8 for methylbutylphenacylsulphonium perchlorate. Saveant obtained similar results using diethylphenacylsulphonium bromide.(5.7)

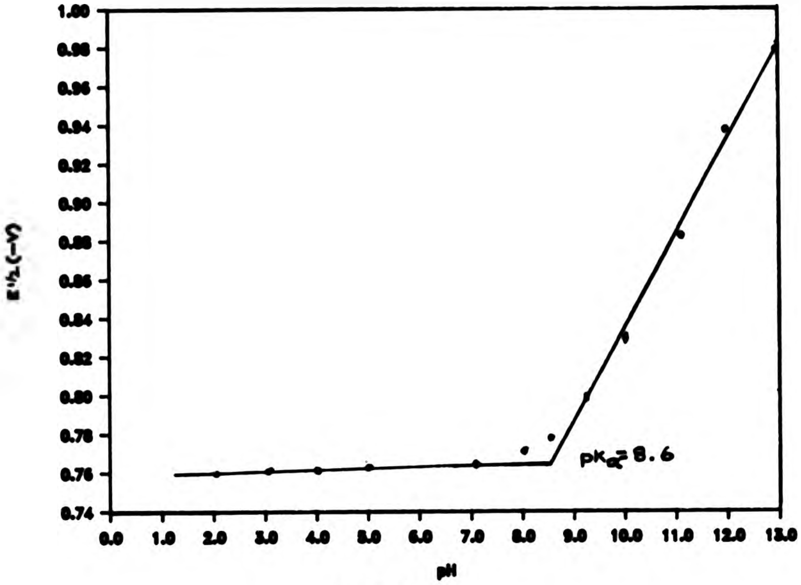
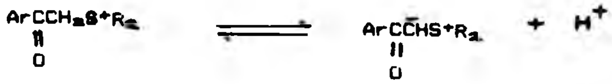


Fig. 5.2

Tables showing the $E_{½}$ values at pH 2.0, 4.0, 7.0 and 9.2 for a number of different phenacylsulphonium salts are shown in the experimental section (page 79). These are insufficient for the detailed analysis discussed above for dimethylphenacylsulphonium bromide but suggest rather similar behaviour.

As the earlier workers showed, the results can be accounted for in terms of deprotonation of the sulphonium salt in alkaline solution. The latter reaction gives the relatively unreducible ylid and accounts for the decrease in the diffusion current values (id) as the solution becomes more alkaline.



$$\underset{\substack{\|\\ O}}{ArC}CH_2S^+R_2 \rightleftharpoons \underset{\substack{\|\\ O}}{ArC}\bar{C}HS^+R_2 + H^+$$

Phenacyltrialkylammonium salts

The phenacyltrialkylammonium salts also give similar two-wave polarograms, the first wave corresponding to a two-electron transfer and C-N bond breaking, and the second to reduction of the acetophenone. There are two main differences from the sulphonium salts:

1) The $E_{1/2}$ values of the phenacylammonium salts are more negative than those of the corresponding sulphonium salts, e.g.

Table 5.6

	$E_{1/2}$(-V)
$C_6H_5COCH_2S^+(CH_3)_2\ Br^-$	0.75
$C_6H_5COCH_2N^+(CH_3)_3\ Br^-$	0.99

This difference must be related, at least in part, to the difference in bond strengths of the C-N^+ and the C-S^+ bonds. Values for these are not known, but the values for amines and sulphides probably "parallel" this difference (see table 1.2 page 18).

This matter is discussed in more detail in the section on rate constants and activation energies.

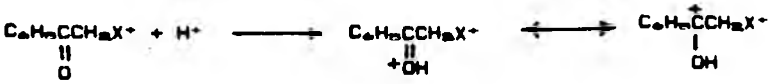
2) The pH dependence of $E_{1/2}$ is quite different to that of the sulphonium salts. Unlike the latter salts the $E_{1/2}$ values of the ammonium salts are independent of the pH over the range 7-13. This difference relates to the difference in acidities of the two salts: The quaternary phenacylammonium salts are very weak acids (pK_a=13)(8.7)

and little, if any, deprotonated under conditions where the sulphonium salt is converted into its conjugate base (ylid). The difference between nitrogen and sulphur in stabilising negative charges is well known e.g. base catalysed H/D exchange.(5.7)

Table 5.7 Base catalysed H/D exchange in D_2O

	$H^{\#}$(kJ/mol)	$S^{\#}$(kJ/°/mol)
$(CH_3)_3S^+I^-$	94	-4.2 ± 0.4
$(CH_3)_4N^+I^-$	139±3	-62.7 ± 0.4

In the pH range 3-7 there is a marked difference between Saveant's results(5.1) and those of Zuman and Horak(5.10) on the $E_{1/2}$/pH dependence of quaternary phenacylammonium salts. Saveant reports that in this region the $E_{1/2}$ value is unchanged, whereas Zuman's results show a linear dependence on pH below 7, the $E_{1/2}$ value becoming less negative with increasing acidity. We did not investigate this discrepancy, but such results as we have support Zuman's work. The difference in behaviour indicates that in this pH range the phenacylammonium salts are more basic than the sulphonium salts. This is not easy to explain on structural grounds, since the basic site in both salts must be the carbonyl group.



$$C_6H_5\underset{\underset{O}{\|}}{C}CH_2X^+ + H^+ \longrightarrow C_6H_5\underset{\underset{^+OH}{\|}}{C}CH_2X^+ \longleftrightarrow C_6H_5\underset{\underset{OH}{|}}{\overset{+}{C}}CH_2X^+$$

The following tentative explanation is proposed. The sulphonium salt is more acidic than the ammonium salt and therefore may be expected to be less basic than the ammonium salt. Also protonation of the carbonyl group will inevitably increase the acidity of the $CH_2S^+R_2$ group and again lead to lower basicity than that of the ammonium salt.

Comparison with the phenacyl halides

The changes in $E_{1/2}$ with pH of the sulphonium salts are contrary to those exhibited by the phenacyl halides. The results of Elving and Leone show that these compounds have $E_{1/2}$ values which are pH dependent in acid solution but independent of pH in alkaline solution.(8.8, 8.11)

Although they recognised that protonation of the carbonyl group would assist the reduction, they preferred a mechanism in which the acid was hydrogen bonded to the outgoing halide ion. The opposite behaviour of the phenacyl- sulphonium salts finds ready explanation in

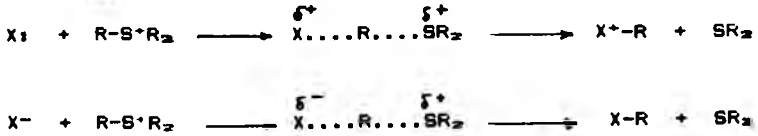
1) the difficulty in protonation or hydrogen bonding at the site of the positive charge,

2) the positively charged sulphonium group would make protonation of the carbonyl group difficult (see discussion of basicity of ammonium and sulphonium salts earlier in this section).

As stated earlier, the phenacylammonium salts, like the phenacyl halides, show $E_{1/2}$ /pH dependence in acid solution but in this case the protonation or hydrogen bonding must be on the carbonyl group.

In alkaline solution the acidic phenacylsulphonium salt is converted into the ylid, thus accounting for the

$E_{1/2}$/pH dependence, whereas the phenacyl halides are non-acidic and have $E_{1/2}$ values which are independent of pH. One problem with the phenacyl halides is their chemical lability, leading to nucleophilic substitution with water or anions. This gave rise to complex polarograms, particularly with phenacyl bromide. Sulphonium and ammonium salts in aqueous solution are much more stable to such substitution: e.g. solutions of dimethylphenacylsulphonium bromide in Britton-Robinson buffers (pH 3.36 and 9.24) after standing for five days gave polarograms that had id values approximately two thirds the values for the fresh solutions. This stability to nucleophilic substitution is almost certainly due to the unfavourable dispersal or destruction of charge necessary for the formation of the transition states.(5.12)



$$X: + R\text{-}S^{+}R_2 \longrightarrow \overset{\delta+}{X}\ldots R\ldots\overset{\delta+}{SR_2} \longrightarrow X^{+}\text{-}R + SR_2$$

$$X^{-} + R\text{-}S^{+}R_2 \longrightarrow \overset{\delta-}{X}\ldots R\ldots\overset{\delta+}{SR_2} \longrightarrow X\text{-}R + SR_2$$

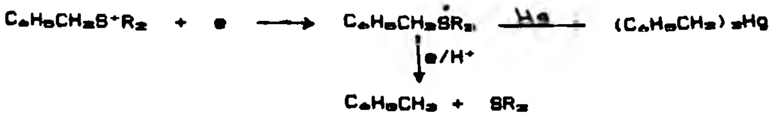
Transition state

This part of the investigation demonstrates clearly the differences in $E_{1/2}$/pH dependence of sulphonium and ammonium salts, and suggests reaction mechanisms which are consistent with these observations and account for the contrasting behaviour of the related phenacyl halides.

Coulometry and Preparative Scale Reductions

The purpose of the coulometric studies and "macroscopic" reductions (i.e. preparative scale processes) was not only to complement the polarographic investigation with quantitative current measurements and to unambiguously identify the products, but also to correlate the electrolytic reduction with other methods of reduction. As indicated in the experimental section, the combined use of polarography, coulometry and quantitative product analysis both checks and reinforces the findings from each method, and any mechanism which is consistent with all three is thereby more reliable.

As stated earlier, the polarography of the phenacyl salts indicated a two-electron reduction for the first wave, and this was verified by reduction at potentials corresponding to the plateau of the first wave and measuring the coulombs necessary to reduce a known amount of substrate. These results are similar to those obtained by Saveant and by Zuman's group. However in the present investigation coulometry was also used to probe further for any evidence of an initial one-electron transfer process. This was particularly important because of the previous studies by Settineri et alia and by Parmar. These workers showed that although aqueous solutions of benzyldialkylsulphonium salts gave polarograms corresponding to a two-electron reduction, by electrolysing solutions at lower potentials than those corresponding to the polarographic plateau diffusion currents, products were obtained corresponding to a one-electron reduction process.



$$\begin{tikzcd} C_6H_5CH_2S^+R_2 + e \arrow[r] & C_6H_5CH_2\dot{S}R_2 \arrow[r, "Hg"] \arrow[d, "e/H^+"] & (C_6H_5CH_2)_2Hg \\ & C_6H_5CH_3 + SR_2 & \end{tikzcd}$$

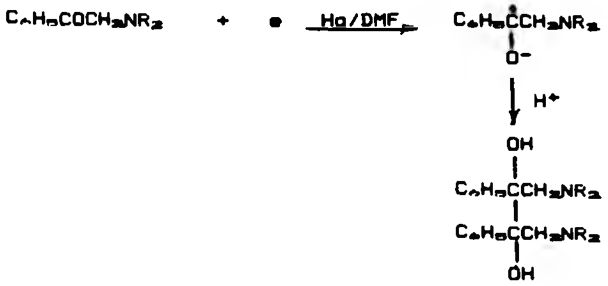
Parmar also showed that in cases where a mixture of one-electron and two-electron reduction products was obtained the coulometry values were between those corresponding to one- and two-electron reduction. Both of these workers also found that increase in temperature promoted the formation of the one-electron reduction product, dibenzyl mercury.

Contrary to the behaviour of the benzylsulphonium salts the electrolysis of dimethylphenacylsulphonium bromide and trimethylphenacylammonium bromide at potentials below that corresponding to their first wave plateau gave rise to the two-electron reduction product, acetophenone; no dibenzoylethane or diphenacyl mercury was detected. The coulometry value was consistent with the quantitative amount of acetophenone and thus confirms the two-electron reduction. The only effect of reducing the applied voltage was to increase the time necessary for electrolysis.

Temperature studies also failed to show any evidence for a one-electron reduction process. Electrolysis over a range of 0-60°C gave only acetophenone as product and coulometry values closely concordant with the amount of acetophenone (see table 4.61 on page 142). The slightly smaller values for the acetophenone at the higher temperatures are almost certainly due to some loss of this compound at these temperatures. The only effect of increasing the temperature was to decrease the time necessary for electrolysis, i.e. increase the reaction rate. This observation correlates with the increase in the polarographic diffusion current with increasing temperature; this is discussed in the section on rates of reaction. These results are in sharp contrast with those on the electrolysis of benzyldialkylsulphonium salts, where increasing the temperature favoured the formation of the one electron reduction product, dibenzylmercury.(8.3,8.4)

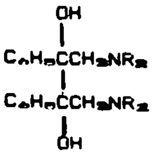
Reaction mechanisms

The failure to detect a one-electron process, either from polarography, coulometry or product analysis suggests that either a one-electron reduction intermediate is not formed, or if it is, it is reduced so rapidly that its existence under the experimental conditions of aqueous solution becomes hypothetical, i.e. the process becomes practically indistinguishable from a two-electron transfer. It is most important to refer to the experimental conditions because under other conditions the reaction mechanism may be different. Reference has already been made in the introduction to the occurrence of one-electron reductions of benzylsulphonium and benzylammonium salts in aprotic solvents, but the reduction of a series of phenacyl sulphides, amines and ethers by Andrieux and Saveant is more relevant to the present study.(8.13) These workers showed that in dimethylformamide and in acetonitrile,phenacylamines gave polarograms indicating a one-electron first wave reduction, which was confirmed by coulometric studies and product analysis of preparative scale reductions, in which the main products were the aminopinacols.

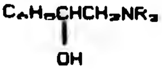


$$C_6H_5COCH_2NR_2 + e \xrightarrow{Hg/DMF} C_6H_5\underset{O^-}{\dot{C}}CH_2NR_2 \xrightarrow{H^+} \begin{array}{c} OH \\ | \\ C_6H_5CCH_2NR_2 \\ | \\ C_6H_5CCH_2NR_2 \\ | \\ OH \end{array}$$

By carrying out the reductions in the cavity of an e.s.r. spectrometer, they were able to record the spectra of the radical anion intermediate. They also showed that by varying the potential and the acidity of the solution they were able to control the one- and two-electron reductions to give the three reduction products



$$\begin{array}{c} OH \\ | \\ C_6H_5CCH_2NR_2 \\ | \\ C_6H_5CCH_2NR_2 \\ | \\ OH \end{array}$$



$$C_6H_5\underset{OH}{CH}CH_2NR_2$$

$C_6H_5COCH_3$

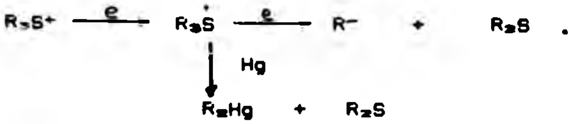
However, in aqueous solution only two-electron reduction with cleavage of the C-N bond was observed.

$$C_6H_5COCH_2NR_2 \xrightarrow{2e/2H^+} C_6H_5COCH_3 + HNR_2$$

Methyl phenacyl ether reduced similarly to the phenacylamines in dimethylformamide and the pinacol ether mixture was isolated. However the corresponding phenyl phenacyl ether, $C_6H_5COCH_2OC_6H_5$, gave only the two-electron reduction product of C-O bond fission. Similarly, phenacyl fluoride showed only two-electron reduction with C-F bond breakage. It was pointed out that where the bond breaking involved a poor leaving group (NR_2, OR, SR) one-electron reduction was observed but when a good leaving group was present (OC_6H_5, SC_6H_5, F) only two-electron reduction occurred.

Before discussing schemes to account for the differences between one- and two-electron reductions of the benzyl and phenacyl sulphonium salts and the neutral phenacyl compounds, $C_6H_5COCH_2X$, it is necessary to consider the possible sites for electron transfer in the molecular species.

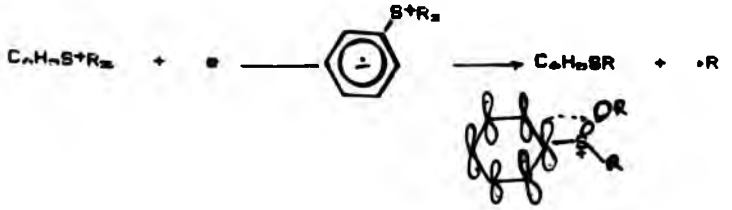
Because the sulphur atom in a sulphonium salt bears a positive charge and this atom has vacant d-orbitals, one scheme would be electron transfer from the electrode to the sulphur atom.



Neither in this nor in previous studies has any evidence been produced for the existence of the anion R_3S^- so it is reasonable to assume that transfer of the second electron to the radical is concerted with the cleavage of the $C-S^+$ bond. This process has great similarity to an SN2 displacement, and in the case of simultaneous two-electron transfer would be directly analogous, the only difference being that the displacement is on the sulphur atom and not on carbon. However there are well attested examples of nucleophilic substitution of sulphonium salts in which it has been established that the substitution is at the carbon atom, and this is also the expected site for bimolecular substitution.(8.14)

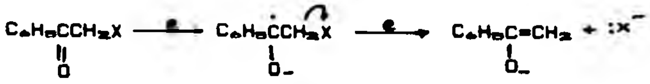
$$C_6H_5CH(CH_3)\,S^+(CH_3)_2 + Br^- \longrightarrow C_6H_5CH(CH_3)Br + S(CH_3)_2$$

Therefore it is unlikely that two-electron transfer occurs at the sulphur atom. The electrons are presumably transferred to the LUMO, and if we exclude the sulphur atom d-orbitals for the above reasons, this may be the complementary anti-bonding orbital to the C-S$^+$ bonding orbital. Because the anti-bonding orbital is more anti-bonding than the bonding orbital is bonding, filling the anti-bonding orbital must result in cleavage of the C-S$^+$ bond. If there are other unfilled low energy orbitals present these may also accept electrons. Beak and Sullivan(8.18) reduced dialkylphenylsulphonium salts with potassium in graphite in tetrahydrofuran, and because of the failure of trialkylsulphonium salts to undergo reduction they suggested the reaction went via electron transfer to the LUMO of the phenyl group to give a ligand radical anion sulphonium cation which then decomposed to a sulphide and a radical.



Overlap between the π ring orbital and the σ^* orbital of the bond being broken should facilitate the bond breaking.

In the case of the phenacyl compounds the most likely site for electron acceptance is the carbonyl group. The most compelling evidence for this is the formation of the aminopinacols from phenacylamines. Also the valence shell limitation of the nitrogen atom in the amines and ammonium salts precludes addition of electrons to the nitrogen atom. The same mechanism must hold for the phenacyl sulphur compounds, although here there is no sulphur valence shell limitation. The addition of the second electron, either with or subsequent to the addition of the first, is accompanied by C-X bond breakage.

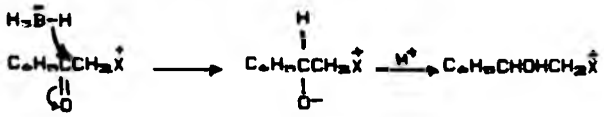


$$\underset{\underset{O}{\|}}{C_6H_5CCH_2X} \xrightarrow{e} \underset{\underset{O^-}{|}}{C_6H_5\dot{C}CH_2X} \xrightarrow{e} \underset{\underset{O^-}{|}}{C_6H_5C{=}CH_2} + :X^-$$

(A)

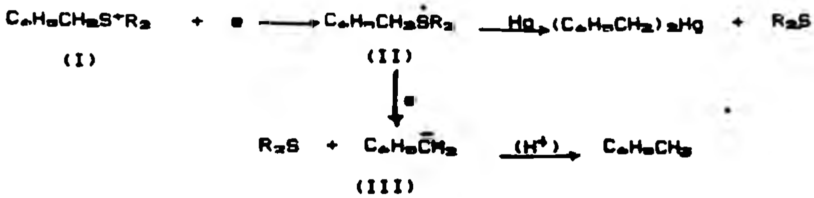
In acid solution neutralisation of the radical ion (A) by a proton donor would give the radical which could couple to form the pinacol or accept a second electron to give a species which can eliminate the X group if this is a good leaving group or accept a proton to give the secondary alcohol.

The addition of two electrons to the carbonyl group, together with an atom to localise the electron pair between this atom and the carbon does not result in C-X bond breakage. An example of this is the reduction of phenacylammonium and sulphonium salts to the β-hydroxy 'onium salts using sodium borohydride.(5,14)



Electron transfers are necessarily accompanied by changes in charge which will have a large effect on the solvation energies of the species involved, particularly with highly polar solvents. The fact that water strongly favours the two-electron reductive cleavage in phenacyl systems even where there is a poor leaving group indicates that solvation plays an important part in these reactions. A consideration of the solvation changes suggests an explanation for the differences between the benzylsulphonium and phenacylsulphonium salts and the related phenacyl compounds.

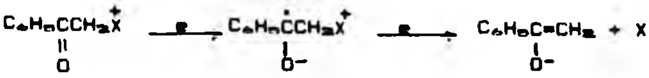
Benzylsulphonium salts



The reactant sulphonium ion (I) will be highly solvated whereas the radical intermediate (II) should be much less solvated. Because of the absence of solvation, this radical should be able to get physically closer to the mercury cathode and there react to form either organomercury compounds or accept an electron to form the anion (III). The addition of a second electron to give the carbanion (III) should again result in much solvation. Therefore in highly polar solvents, such as water, this step may compete favourably with the alternative reaction of the radical intermediate to form the organomercury compound, particularly at high cathode potentials.

The effect of temperature can also be accounted for by solvation effects because the polarity of water, as expressed by its dielectric constant, decreases with increasing temperature and thus reduces solvation, whereas increase in temperature should increase the rate of formation of the mercury compound. Both of these effects can account for the experimental observation that increase in temperature favours one-electron reduction.

Phenacyl 'onium salts



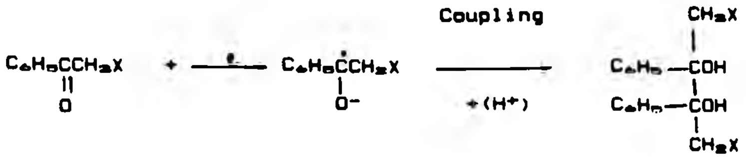
$$C_6H_5C(=O)CH_2\overset{+}{X} \xrightarrow{e} C_6H_5\dot{C}(O^-)CH_2\overset{+}{X} \xrightarrow{e} C_6H_5C(O^-)=CH_2 + X$$

(IV)

The proposed one-electron intermediate (IV) should be more highly solvated than the reactant species, and its formation should be strongly favoured by polar solvents. The continued presence of the positively charged 'onium group should facilitate the transfer of the second electron particularly as this would be concerted with the formation of a double bond and cleavage of the C-X bond. The bond breaking would be favoured by the highly electronegative X^+ groups, which are known to be good leaving groups in nucleophilic substitution and heterolytic elimination reactions. The ease of the addition of the second electron should greatly reduce the lifetime of the one-electron intermediate, and hence the opportunity for reactions such as coupling or reaction with mercury.

It can also be seen that, unlike the benzylsulphonium salt case, addition of the first electron to give (IV) does not result in any significant loss of solvation molecules, and hence cannot assist the approach of the radical ion to the mercury surface.

Phenacyl amines and alkyl ethers



$$C_6H_5\underset{\underset{O}{\|}}{C}CH_2X + e \longrightarrow C_6H_5\underset{\underset{O^-}{|}}{\dot{C}}CH_2X \xrightarrow[+(H^+)]{\text{Coupling}} \begin{array}{l} \quad\quad\;\; CH_2X \\ \quad\quad\quad\;\, | \\ C_6H_5-COH \\ \quad\quad\quad\;\, | \\ C_6H_5-COH \\ \quad\quad\quad\;\, | \\ \quad\quad\;\; CH_2X \end{array}$$

As in the case of the phenacyl 'onium salts the one-electron addition intermediate should be more solvated than the uncharged reactants. However, the addition of the second electron would be more difficult than with the 'onium salts because of the absence of charge on the X group and the fact that the $R_2\bar{N}$ and $R\bar{O}$ groups are known to be poor leaving groups. Therefore reactions of the radical intermediate such as coupling should be more likely with these compounds than with the 'onium salts. The fact that in water even the phenacyl amines undergo two-electron reduction with bond breakage rather than give one-electron reduction products may be ascribed to very highly polar properties of water which can solvate the amino group by hydrogen bonding and assist it as a leaving group.

Comparison with other reductions of phenacyl 'onium salts

At the inception of this work it was envisaged that the electrochemical reductions could be usefully compared with previous studies on chemical reductions of phenacyl 'onium salts in this laboratory. Reference has already been made to one such study, where reduction of the salts with sodium borohydride caused reduction only at the carbonyl group to give the β-hydroxy 'onium salt.(5.16) However, the other studies were under conditions too different from the electrochemical conditions to permit detailed comparison. Walcott's reductions were in sodium/liquid ammonia/ethanol and with amalgamated zinc in strongly acid solution.(5.17) He invariably used an excess of reductant which was present at the outset of the reaction. This is very different from the electrochemical method, where, in effect, the substrate is always in excess and the addition of the "reductant" is controlled by the size of the cathode and the applied potential. Some of Walcott's results are shown in tables 5.8 and 5.9.

Table 5.8

Reductant: Zinc amalgam/aq HCl (3 molar equivalents per molar equivalent of 'onium salt).

	Products (%)				
	$C_6H_5C_2H_5$	$C_6H_5CHCH_2$	$C_6H_5COCH_3$	$C_6H_5CHOHCH_3$	unreacted 'onium salt
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	22	23	19	0.8	26
$C_6H_5COCH_2S^+(CH_3)_2Br^-$	53	9	12	0.4	7

Table 5.9

Reductant: Sodium/liquid ammonia/ethanol. (2 molar equivalents per molar equivalent of 'onium salt).

	Products(%)			
	$C_6H_5C_2H_5$	$C_6H_5COCH_3$	$C_6H_5CHOHCH_3$	$(C_6H_5COCH_2)_2$*
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	13	9	21	10

* This was a mixture of dibenzoylethane (mainly), 1,4-dihydroxy-1,4-diphenylbutane and 1,4-diphenylbutane.

The present purpose is not to discuss these results in detail but to draw attention to a few salient points.

1. The proliferation of products resulting from uncontrolled reduction of initial products. This contrasts with the simpler controlled electrochemical reduction product mixture.
2. The higher reactivity of the sulphonium salt compared with the ammonium salt. The present study shows similar behaviour.
3. Some dibenzoylethane (and further reduction products) was always obtained in the sodium/ammonia reduction of the phenacylammonium salt. This is in sharp contrast with our present work and the results of Zuman and Saveant. The latter worker's account of one-electron reduction of phenacylamines also makes no report of dibenzoylethane. Walcott showed that the only reasonable source of dibenzoylethane was benzoyl

radicals. There is no obvious explanation for these differences and because of the very different experimental conditions it is not advisable to speculate further.

Rates of reaction and activation energies for phenacylsulphonium and phenacylammonium salts

a) Rate of reaction

Rate constants for dimethylphenacylsulphonium and trimethylphenacylammonium salts were determined polarographically using Koutecky's method which relates the reaction rate to the $E_{1/2}$ value for different drop times, obtained by varying the height of the mercury column using the equation:

$$\log Ke^{\circ} = \alpha n/0.0591 \Delta E_{1/2} - \log 0.886 - \log[(t_1''/D)^{1/2} - (t_1'/D)^{1/2}]$$

The results for the two salts at 25°C were.

	Ke° (cm.s^{-1})
$C_6H_5COCH_2S^+(CH_3)_2Br^-$	2.80×10^{-3}
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	2.02×10^{-3}

These results show that, although the overall process of reduction is irreversible, the 'degree . of irreversibility' is greater for the ammonium salt than the sulphonium salt. This may be due to a steric effect. The ammonium salt has 4 ligands tetrahedrally arranged about the nitrogen and this group must have a larger volume than the analogous tricoordinated sulphonium group. This steric effect should make the approach of the charged atom to the electrode more difficult for electron transfer either to the charged atom or, more likely, to the adjacent carbonyl group.

b) Activation energies

The activation energies for reduction of the two salts were determined by two methods. In the first method the value of the parameter was evaluated from the change of position of the normal polarographic current versus potential wave at different temperatures (page 93). Using the equation

$$\log (i/id-i) = \log A' - \frac{Q - \frac{1}{2}Q_D}{2.303RT}$$

where,

Q = activation energy

Q_D = activation energy of diffusion

A′ is the apparent frequency factor

the following values for Q were obtained.

	Q(kJ mole^{-1})
$C_6H_5COCH_2S^+(CH_3)_2Br^-$	40
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	47

This difference may be related to the differing C-X$^+$ bond energies in the two salts. This is more likely to affect the activation energy than the pre-exponential factor and these results are consistent with the known difference between C-N and C-S bond strengths (table 1.2, page 18).

The pre-exponential factor was calculated from the Arrhenius equation for the two compounds from the following equation

$$Ke = Ae^{-Q/RT}$$

or in terms of log to base ten

$$\log Ke = \log A - Q/2.303RT$$

	log A	A
$C_6H_5COCH_2S^+(CH_3)_2Br^-$	5.54	3.49×10^5
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	4.56	2.86×10^4

These results are consistent with the experimental finding that the sulphonium salt reacts faster than the ammonium salt. Thus both the pre-exponential factors and the activation energies are more favourable for the reduction of the sulphonium salt than for the ammonium salt.

A second method of determining the activation energy was by measuring the current of a stirred electrode solution system at different temperatures and treating the current as a measure of the rate of reaction.

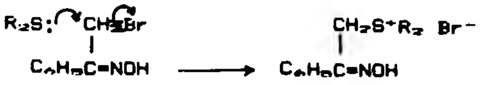
The following results were obtained

	ξ(kJ mole^{-1})
$C_6H_5COCH_2S^+(CH_3)_2Br^-$	46.5
$C_6H_5COCH_2N^+(CH_3)_3Br^-$	40.6

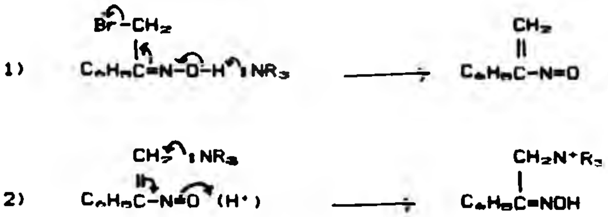
It can be seen that they are at variance with those obtained from the polarographic method. This may be due to the following reasons. The practical work was quite difficult. It was found that unless the surface of the mercury electrode was stirred as well as the bulk of the electrolyte, the currents rapidly fell to a low value, indicating that adsorbed products on the surface of mercury pool were having a considerable effect on the current and hence the rate of reaction. Stirring the mercury pool electrode on the surface was impossible to control with any degree of accuracy and reproducibility. This led to considerable fluctuation in the current over a wide range and it was difficult to estimate the mean value over short periods. The reproducibility of the experiments was also poor. The rate of transport of electrolyte to the surface must be a factor, which is not included in the theory. It is surprising that the results are of the right order of magnitude considering these difficulties.

Phenacyl oxime 'onium salts

These compounds were prepared by reaction of 2-bromoacetophenone oxime with a sulphide or tertiary amine. The reaction with sulphides is probably an SN2 reaction.



However, the reaction with amines may be either a bimolecular substitution or go via a 1,4 elimination process to give the nitrosoalkene, followed by a 1,4 addition reaction to give the overall substitution product.(9,10)



This two step mechanism was not investigated in this work.

The purpose of studying these compounds was to see how the C=N group compared with the C=O group in the activation of α-substituted 'onium salts. Because of the difference in valency between nitrogen and oxygen, the nitrogen atom of the imino group must have a substituent. Ideally it would have been better to have had an imine group, but simple imines are readily hydrolysed. Therefore we chose the oximino group: oximes are readily prepared and stable in solution under the conditions of our study. Because the oxime group is a weak acid and is deprotonated in alkaline solution, an O-methyloximino 'onium salt was also examined.

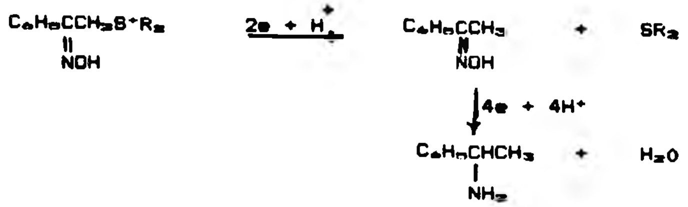
The presence of a substituent on the nitrogen atom gives rise also to stereoisomerism when, as in our compounds, the two substituents on the adjacent carbon atom are not identical. In the present study we had to accept this complication, and no attempt was made to isolate the stereoisomers or determine the stereochemistry of the salts.

POLAROGRAPHY

The polarograms of these salts have less well defined waves than the phenacyl 'onium salts.

Phenacyloxime sulphonium salts

Under acid conditions the first wave of the (2-phenyl-2-oximinoethyl)dialkylsulphonium salts corresponds to a two-electron transfer and the second, which is almost twice the height of the first, to a four-electron reduction. This suggests a two-stage reduction scheme similar to the phenacyl 'onium salts.



$$C_6H_5\underset{\underset{NOH}{\|}}{C}CH_2S^+R_2 \xrightarrow{2e + H^+} C_6H_5\underset{\underset{NOH}{\|}}{C}CH_3 + SR_2$$

$$C_6H_5\underset{\underset{NOH}{\|}}{C}CH_3 \xrightarrow{4e + 4H^+} C_6H_5\underset{\underset{NH_2}{|}}{C}HCH_3 + H_2O$$

The first wave corresponds to the reduction of the C-X$^+$ bond. The second wave relates to the reduction of acetophenone oxime and apart from identification, it does not further concern us. However, the polarography of acetophenone oxime was determined for comparison with the salts (page 111).

The evidence for the first reduction step derives from a number of facts (see below).

(a) The polarograms of the (2-phenyl-2-oximinoethyl) salts with different ligands differ in the $E\frac{1}{2}$ values of the first wave but the second wave characteristics are almost identical. This would be expected for the above reaction scheme.

(b) Coulometric determination for reduction at potentials corresponding to that of plateau of the first polarographic wave gave values corresponding to 2 electrons (this is discussed further on page 216).

(c) Potentiostatic controlled reduction of (2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide at the first wave plateau value, followed by work-up of the electrolysate gave acetophenone oxime and tetrahydrothiophene as the main products and quantitative glc analysis showed these to be present in almost equimolar amounts.

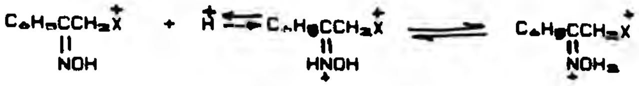
(d) (2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide at pH4 has a $E_{1/2}$ value (-0.71V) for the first wave which is significantly lower than that for the reduction of the oxime group of acetophenone oxime ($E_{1/2}$ = -1.03V) and is very similar to that of the phenacyltetramethylenesulphonium bromide ($E_{1/2}$ = -0.72V) and that of 2-bromoacetophenone oxime ($E_{1/2}$ = -0.65V). This suggests that essentially the same kind of process is occurring in all three compounds.

Effect of Ligands

Table 4.37 (page 106) shows the variation of $E_{1/2}$ values for (2-phenyl-2-oximinoethyl)dialkylsulphonium salts with different ligands. These results are similar to those of the phenacylsulphonium salts i.e. the ease of reduction generally increases with the size of the ligands. The same explanation of differential solvation of the ions is suggested. There is a larger spread in values (0.21V) of the phenacyloximino salts compared with that of the phenacyl salts (0.1V). This is also consistent with the suggestion that the ligand effects on $E_{1/2}$ are due mainly to differential solvation because the oximino compounds should be more solvated than the carbonyl compounds.

Effect of pH

Table 4.38 on (page 107) shows the $E_{1/2}$ and id values for both of the reduction waves for a series of (2-phenyl-2- oximinoethyl)dialkylsulphonium salts over a range of pH (2 - 9.2). The id values of the two waves show clearly that the same processes are occurring in each salt and that the $E_{1/2}$ values of both waves are pH dependent. The increasing ease of reduction with increasing acidity of the media suggests that the protonated form is more readily reduced, as expected.



$$C_6H_5\underset{\underset{NOH}{\|}}{C}CH_2\overset{+}{X} + \overset{+}{H} \rightleftharpoons C_6H_5\underset{\underset{H\underset{+}{N}OH}{\|}}{C}CH_2\overset{+}{X} \rightleftharpoons C_6H_5\underset{\underset{\underset{+}{N}OH_2}{\|}}{C}CH_2\overset{+}{X}$$

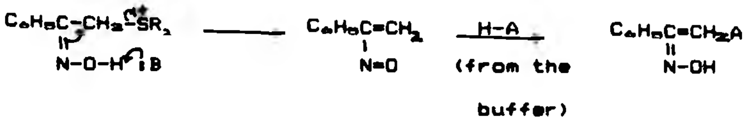
The id values at pH 7 are much lower than at more acid pH. This would be expected if only the conjugate acid of the oxime reduces: under less acid conditions its concentration is smaller.

At pH 9.2 there is only one wave, with a very negative $E_{1/2}$ value which suggests that the first wave has disappeared.

The reduction at pH 9.2 was investigated by complementary coulometric and product analysis studies. If the reduction at this pH was due to the reduction of the oxime group rather than the carbon-sulphur bond then the product would still contain the sulphonium group and not be ether extractable. However, it was found that analysis of the ether extract from a potentiostatically controlled reduction at this pH showed tetrahydrothiophene as the main product: no acetophenone or acetophenone oxime was detected. A further discrepancy between the polarographic and larger scale reductions is that the former, from its wave height corresponds to approximately four electrons whereas the coulometry of the large scale reduction corresponded to two electrons. We are unable to explain this difference. Further examination showed that the tetrahydrothiophene arose from a chemical reaction with the buffer and not through electrolysis.

Therefore the polarogram at pH 9.2 must be due to a reaction product and not the oxime salt. Further confirmation for this comes from polarography at pH 9.2 of the O-methylether of the oxime salt which shows a well defined two-electron wave ($E_{1/2} = -0.68$ V).

The following reaction scheme, which has been established for the corresponding oxime halides, could account for the chemical decomposition of the oxime salt.(8,10)



The O-methyloxime salts cannot undergo this reaction.

The polarography of the O-methylether derivative of (2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide salt was examined to see how much the proton of the oxime group affected the reduction process. It was expected to be more significantly involved at high pH conditions rather than lower pH. This was borne out in practice; at pH 2 and 4 the polarograms of the oxime salt and its O-methylether are almost identical except for slightly lower values of $E_{1/2}$ of the O-methyl compound. At pH 7 the first wave of the O-methyl compound is well defined and the second wave has disappeared, indicating no reduction of the oxime group. The same is true at pH 9.2 and differs completely from the polarogram of the oxime salt at this pH, which we have suggested is due to an artefact from the oxime salt. The value of this comparison in interpreting the oxime salt polarogram has already been referred to in the previous section.

Coulometry and preparative scale reduction

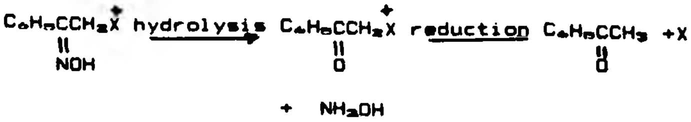
These studies to complement the polarography were carried out under potentiostatic control.

As stated earlier (page 212) reductions of the oxime salts at the plateau of the first polarographic wave gave coulometry values (1.86 - 1.92) corresponding close to the two electrons required for reduction to acetophenone oxime. These values are shown in table 4.55. The table also shows the invariance of this reduction to the ligands on the sulphur atom. Table 4.56 on (page 136) shows coulometry values for the reduction of the analogous quaternary ammonium salts, and they correspond to almost exactly 2 electrons (1.97 - 2.1).

Preparative scale reductions of the sulphonium and the ammonium salts at their first wave plateau values, followed by work up of the electrolysate allowed isolation and identification of acetophenone oxime as the main product. Glc analyses of ether extracts of electrolysates showed that in addition to acetophenone oxime and the sulphide or amine, there was always a small amount (4-7%) of acetophenone present (see tables on pages 160, 165).

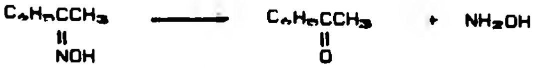
Two routes by which the acetophenone might arise are:

(a) Hydrolysis of the oxime salt to the phenacyl salt which then undergoes reduction



$$\underset{\|}{\overset{}{C_6H_5C}}\!\overset{+}{CH_2X}\ (=NOH)\ \xrightarrow{\text{hydrolysis}}\ C_6H_5C(=O)CH_2\overset{+}{X}\ +\ NH_2OH\ \xrightarrow{\text{reduction}}\ C_6H_5C(=O)CH_3\ +X$$

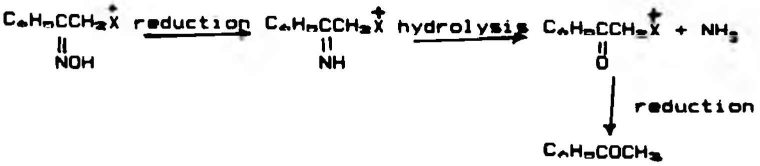
(b) Hydrolysis of the acetophenone oxime product



$$C_6H_5C(=NOH)CH_3 \longrightarrow C_6H_5C(=O)CH_3 + NH_2OH$$

Both these routes were tested and shown to be negative.

A third possibility is the reduction of the oxime salt to the imine salt followed by hydrolysis to the phenacyl salt and its reduction.



$$C_6H_5C(=NOH)CH_2\overset{+}{X} \xrightarrow{\text{reduction}} C_6H_5C(=NH)CH_2\overset{+}{X} \xrightarrow{\text{hydrolysis}} C_6H_5C(=O)CH_2\overset{+}{X} + NH_3 \xrightarrow{\text{reduction}} C_6H_5COCH_3$$

The formation of a ketone due to hydrolysis of the ketimine formed has been reported for camphor oxime(8,17). The objection to this mechanism is that a reduction at the oxime group should require a higher potential than that used to cleave the C-X$^+$ bond.

The reduction was shown to be independent of concentration over a range from 10^{-1}M to 10^{-3}M, showing that the process under preparative conditions was essentially the same as under polarographic conditions. The reduction was also found to be independent of temperature over the range 10 - 60°C (page 159). The latter result was of particular importance because of Parmar and Settineri's results with benzylsulphonium salts. There was no evidence for a one-electron reduction process, either from coulometry, product analysis or acid titre. The only difference observed was the rate of reduction: the higher the temperature the faster the reduction. In this respect the oximino 'onium salts resemble the phenacyl 'onium salts.

The phenacyloxime ammonium salts

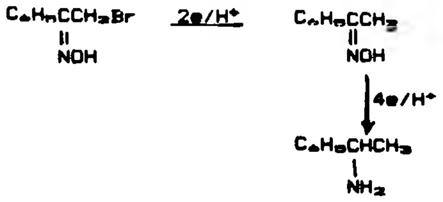
The polarography of the (2-phenyl-2-oximinoethyl) ammonium salts is much more difficult to interpret than that of the sulphonium salts. At pH4 the trimethyl salt shows a single wave with the diffusion current corresponding to a 6 electron reduction process. This could be accounted for if the reduction of the C-N^+ bond and the reduction of the oxime group to the amine overlapped appreciably. At pH7 the only wave observed corresponds to a two-electron transfer, consistent with the reduction of the C-N^+ group in the absence of reduction of the oxime group. The polarogram at pH9.2 shows a well defined wave, clearly separated from the general discharge wave and corresponding to . a four-electron reduction. Since the wave is so different in appearance to the waves at other pH values, and also occurs at a lower $E^{1/2}$ value than the wave at pH7, it strongly suggests that this wave is due to the reduction of a product resulting from the chemical reaction of the 'onium salt with the buffer. A similar observation was made in the case of the sulphonium salts and the product may arise from a similar elimination addition reaction proposed earlier (page 210, 215).

The polarogram at pH2 shows a very ill defined wave ($E_{1/2}$ = 0.97V) which is merged with the general discharge due to the buffer. This otherwise anomalous polarogram can now be rationalised: the reduction of the C-N and oxime groups are now almost completely merged into one overlapping general wave.

The polarography of the corresponding triethylammonium salt shows some differences from the trimethyl compound but can also be interpreted along the same lines. The large single reduction wave at pH2 is more sharply separated from the general discharge wave than with the trimethylammonium compound. It also has a higher diffusion current than the corresponding waves at pH4. This is due to the higher concentration of the conjugate acid at the lower pH, and since the neutral oxime is electroinactive, this should result in a larger diffusion current. The wave at pH7 is poorly defined and it is difficult to assign $E_{1/2}$ and id values. The wave at pH 9.2 is rather better defined but again has a lower $E_{1/2}$ value than the trimethylammonium salt. This would argue that the reduction wave at pH9.2 is not due to reduction product with the buffer. However these waves are not sufficiently well defined to warrant firm deductions and it must be concluded that further work in this area is necessary. One matter, not mentioned so far, is the problem of stereoisomerism of the salts. In principle each stereoisomer should have its own electro-chemical characteristics. In so far as they may differ under experimental conditions, the polarograms and coulometry of any mixture of these isomers should be more complex than with pure isomers. This might account for some of these ill defined polarograms.

Phenacyl bromide oxime

As stated earlier in the introduction, the 'onium salts may be regarded as pseudohalides and for comparison the polarography of the phenacyl bromide oxime was examined. Because of its insolubility in water, 5% ethanol-water solution was used, but the difference should not seriously affect the comparison. Polarograms are shown on page 113. Under acid conditions (pH2 and 4) the polarograms show two well defined waves. The wave height of the second wave is twice that of the first and very similar to that of acetophenone oxime under the same conditions. These results parallel those of the oximino sulphonium salts and suggest a similar two-step reduction process.



$$\underset{\text{NOH}}{\overset{\|}{C_6H_5CCH_2Br}} \xrightarrow{2e/H^+} \underset{\text{NOH}}{\overset{\|}{C_6H_5CCH_3}} \xrightarrow{4e/H^+} \underset{NH_2}{C_6H_5CHCH_3}$$

At pH7 both waves are absent from the polarogram which shows only the general discharge wave. At pH9.2 there is an ill defined wave ($E_{1/2}$ -1.3V) but this merges with the general discharge wave at higher potentials. Obviously some species is being reduced at this pH and again there is the possibility that it might arise from the elimination-addition mechanism suggested earlier (page 208).

The absence of reduction waves at pH7 is not easy to explain, but examination of the effect of pH on the polarography of acetophenone oxime gives at least partial explanation. In acid solutions (pH2, 4) acetophenone oxime exhibits well defined waves corresponding to four-electron reduction to the amine, the electroactive species being the protonated oxime. On going from pH4 to pH7 there is a very marked drop in the diffusion current to about 1/6th the value at pH4 and a sharp rise in $E_{1/2}$ value. This behaviour is consistent with a low concentration of protonated oxime at this pH. The α-bromoxime will be less basic than acetophenone oxime and at pH7 the concentration of the conjugate acid may be small. This can account for the lack of reduction of the oxime group, but the absence of the C-Br reduction wave is not explained.

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Chapter 6

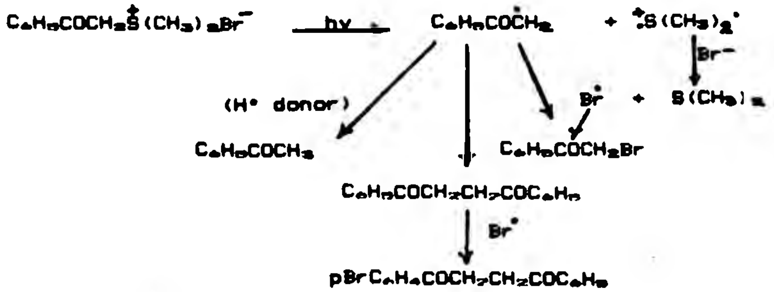
Photochemistry

Introduction

The earliest reports on the photolysis of sulphonium salts were in 1969(6.1, 6.2). One of these groups, from this laboratory, was concerned mainly with the photolysis of phenacyl-type salts in aqueous solution.

$$C_6H_5COCH_2S^+(CH_3)_2Br^- \xrightarrow{h\nu} C_6H_5COCH_3 + (C_6H_5COCH_2)_2 + C_6H_5COCH_2Br$$
$$+ pBrC_6H_4COCH_2CH_2COC_6H_5 + \text{polymer}$$
$$+ (CH_3)_2S$$

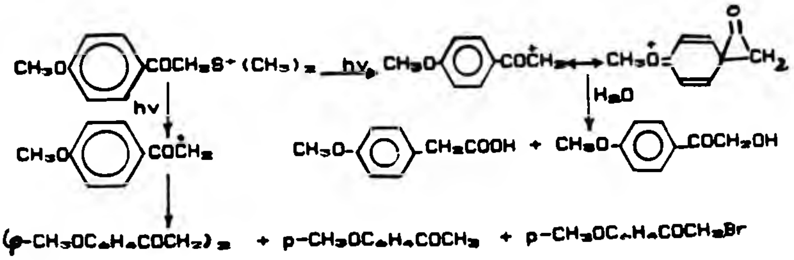
All of these products derive from C-S bond cleavage processes. Altering the anion varied the proportions of the main products, dibenzoylethane and polymer, and they concluded that only a mechanism with initial homolysis to give the phenacyl radical could account for their results.(6.2)



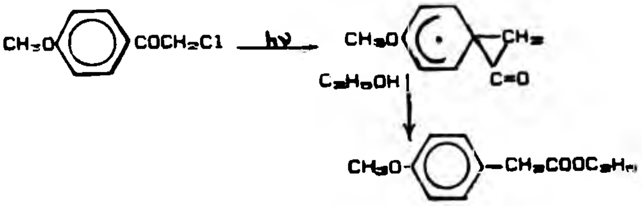
Although photolysis of phenacyl bromide gave all the above products, it was shown that little, if any, of the products formed in the photolysis of the sulphonium salt arose through prior formation of phenacyl bromide. The high yield of p-bromophenacyl bromide (61%) from the photolysis of p-bromophenacyldimethylsulphonium bromide, suggested that some of the p-bromophenacyl bromide may have arisen from an SN2 reaction between the photoexcited cation and a bromide ion

$$Br^- + (p\text{-}BrC_6H_4COCH_2S(CH_3)_2)^{+*} \longrightarrow p\text{-}BrC_6H_4COCH_2Br + S(CH_3)_2$$

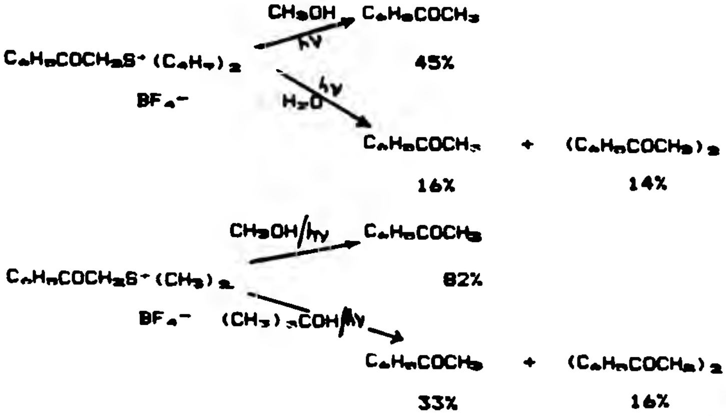
The p-methoxy substituted salt gave a product mixture which included two minor products which may have been formed from an initial heterolysis of the C-S bond.



The proposed heterolysis should be facilitated by strong electron releasing groups from the para position as shown. Anderson and Reese(6.4) proposed a similar cyclopropane structure for a possible intermediate in the photolytic rearrangement of p-methoxyphenacyl chloride, but formulated it as a radical.

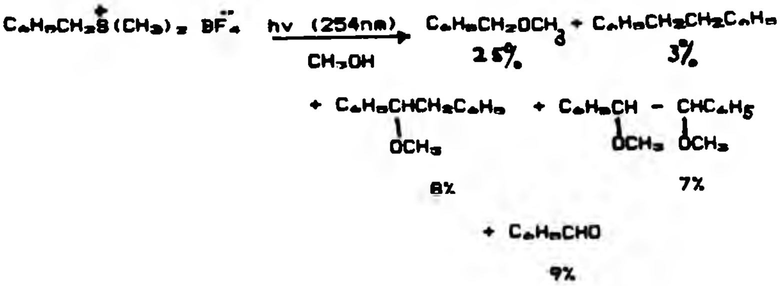


Maycock and Berchtold(6,9) studied the photolysis of a number of dialkylphenacylsulphonium fluoroborates in methanol solution with rather similar results, obtaining the corresponding aryl methyl ketone as the main product. The dimer product, dibenzoylethane,was obtained in only two instances, when water and when tertiary butanol was the solvent, i.e. when a good hydrogen atom donor was absent.



All the reactions could be best accounted for by initial homolysis of the C-S bond. Both groups of workers referred to the uncertainty of the electronic excited state involved, but were of the opinion that, for phenacyl compounds, it was most likely the n-π^* state.

Maycock and Berchtold also investigated the photolysis of sulphonium salts with benzyl or benzyl type ligands and isolated compounds which suggested that most of the product arose from heterolytic C-S$^+$ bond breaking with only minor products from homolytic cleavage.



$$C_6H_5CH_2\overset{+}{S}(CH_3)_2\ BF_4^- \xrightarrow[CH_3OH]{h\nu\ (254nm)} \underset{25\%}{C_6H_5CH_2OCH_3} + \underset{3\%}{C_6H_5CH_2CH_2C_6H_5}$$

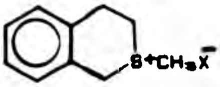
$$+ \underset{8\%}{C_6H_5\underset{OCH_3}{CH}CH_2C_6H_5} + \underset{7\%}{C_6H_5\underset{OCH_3}{CH} - \underset{OCH_3}{CH}C_6H_5}$$

$$+ \underset{9\%}{C_6H_5CHO}$$

The benzaldehyde and methoxydibenzyls were thought to arise from secondary reactions of benzylmethylether and photolysis in tertiary butanol gave a much simpler product mixture.

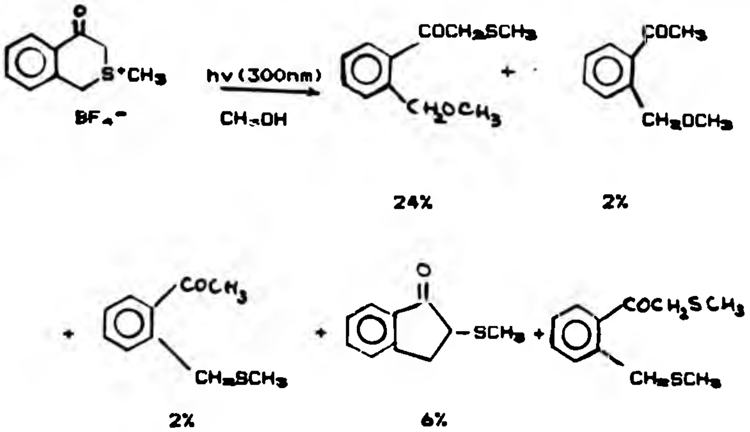
They suggested that the main product was formed by solvolysis of the photoexcited species, without elaborating on whether it was an SN1 or SN2 type process. The following compounds were photolysed with the same kind of result, mainly the formation of benzyloxy compounds and only minor amounts of radical derived products.

$(C_6H_5CH_2)_2S^+CH_3\bar{X}$ $m\text{-}CH_3OC_6H_4CCH_2S^+(CH_3)_2\bar{X}$



X = BF_4^-

They drew attention to the marked difference between C-S^+ bond breaking in the benzyl and phenacyl salts and reported an interesting salt which has both benzyl and phenacyl structural features.



Again, heterolysis of the benzyl C-S⁺ bond appears to predominate, although the spectral conditions ($\lambda = 300$nm) would be expected, at first sight, to favour the cleavage of the phenacyl C-S⁺ bond. However, the carbonyl group is conjugated with the benzyl group and excitation energy of the carbonyl group may be readily transferred to the benzyl group. These workers did not state that photolysis of the benzylsulphonium salts was impossible at wavelengths ≥300nm, but this is implied in the experimental report. This absence of photolysis at 300nm is in line with a single experiment reported by Laird and Williams on the photolysis of benzyldimethylsulphonium bromide in aqueous solution which required acetone as a sensitizer.(6.3)

$$C_6H_5CH_2S^+(CH_3)_2Br^- \xrightarrow[H_2O/(CH_3)_2CO]{h\nu} \underset{56\%}{C_6H_5CH_2OH} + \underset{34\%}{C_6H_5CH_2CH_2C_6H_5}$$

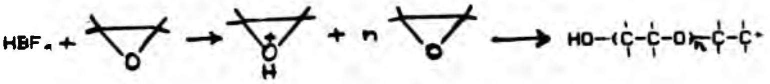
$$+ \underset{1\%}{C_6H_5CH_2Br}$$

These results also indicate heterolytic and homolytic processes, the former predominating. These workers pointed out that the absence of heterolytic bond breaking in the phenacyl salts, in the absence of strong electron releasing substituents, may be due to the inability of the phenacyl cation to adequately delocalise the charge.

In connection with their studies on polymerisation Crivello et alia re-examined the photolysis of a number of 'onium salts including sulphonium and tellurium salts, many having complex anions, e.g. BF_4^- , AsF_6^- , etc. By nmr monitoring of the photolysis of dialkylphenacylsulphonium salts in hexadeuteroacetone and in tetradeuteromethanol they obtained evidence for hydrogen exchange with the solvent and concluded that the primary photolysis step was reversible formation of the ylid and the conjugate acid of the counter ion.(6.8)

$$C_6H_5COCH_2S^+(CH_3)_2\ BF_4^- \rightleftharpoons C_6H_5COCH{=}S(CH_3)_2 \quad + \quad HBF_4$$

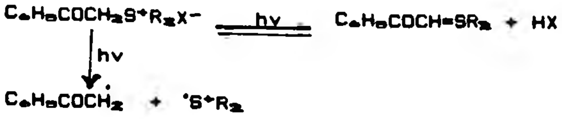
In the presence of oxirane monomer this lead to the formation of the polymeric ether, the process being termed a photoinitiated cationic polymerisation (see next page).



Although this mechanism is quite satisfactory to explain their polymersation studies, it fails completely to explain the formation of products found by the earlier workers, particularly the "dimer", dibenzoylethane.

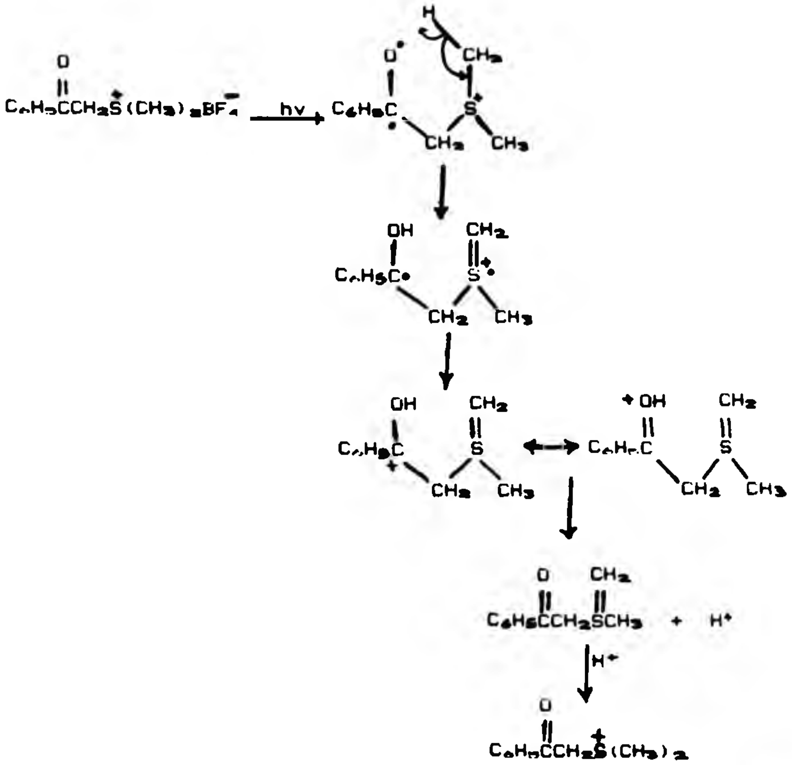
Crivello and Lee simply state that "a slower photolytic reaction involves homolysis of the phenacyl-sulphur bond".

The results of all three groups can be rationalised by a scheme in which the reversible proton transfer to give the ylid and the homolysis C-S bond breaking process are regarded as concurrent reactions, the extent and importance of each being dependent on the experimental conditions.



$$\begin{tikzcd} C_6H_5COCH_2S^+R_2X^- \arrow[r, shift left, "h\nu"] \arrow[d, "h\nu"] & C_6H_5COCH{=}SR_2 + HX \arrow[l, shift left] \\ C_6H_5CO\dot{C}H_2 + {}^{\bullet}S^+R_2 & \end{tikzcd}$$

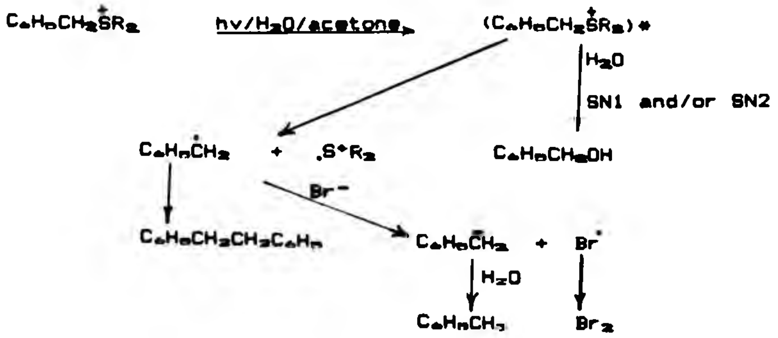
Crivello and Lee(6,9) also showed that suitable polycylic aromatic hydrocarbons e.g. anthracene, could act as sensitizers to excite dialkylphenacylsulphonium salts to act as initiators in oxirane polymerisations. These workers also investigated the photolysis of dialkylphenacylsulphonium salts in hexadeuterodimethyl sulphoxide and observed that H/D exchange was more rapid at the methyl positions than the methylene position. They proposed a modified Norrish II type reaction to account for this.(6,10)



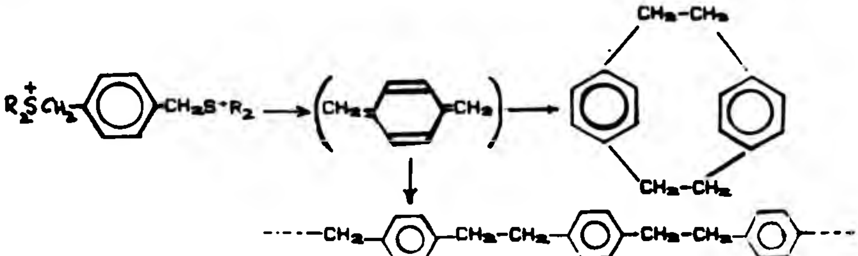
The photolysis of benzyldialkylsulphonium salts in aqueous solution was studied more fully by Parmar.(6,11) He confirmed the results of the earlier experiment by Laird and Williams and investigated the effect of ring subsitutuents and ligands on the course of photolysis and showed that the salt with the bidentate tetramethylene ligand was considerably more photoactive than the salt with two methyl or ethyl ligands. The product mixture again indicated concurrent heterolysis and homolysis processes with the former being more favoured.

$$C_6H_5CH_2\overset{+}{S}(CH_2)_4\overset{-}{Br} \xrightarrow{h\nu/H_2O/acetone} C_6H_5CH_2OH + C_6H_5CH_2CH_2C_6H_5 + C_6H_5CH_3 + p\text{-}BrC_6H_4CH_3 + C_6H_5CH_3 + S(C_4H_8)$$

The benzyl alcohol derived from heterolysis of the C-S⁺ bond while the bibenzyl and toluene came from homolytic bond cleavage.



Ring substituents influenced the ease of these reactions, eg. the p-chloro and p-methyl salts gave large amounts of the corresponding substituted bibenzyls, showing that these substituents favoured homolysis rather than heterolysis of the C-S⁺ bond. Parmar also investigated the photolysis of p-xylylenebis(dialkylsulphonium bromide) salts and showed that the para-isomer, in which the two substituents are conjugated, underwent simultaneous cleavage of both bonds to give the dimeric product, the cyclophane, and the linear polymer, poly-p-xylylene.



The ortho isomer was almost inert to photolysis under the same conditions, probably due to unfavourable steric hindrance. The meta isomer underwent homolysis at only one of the sulphonium centres.

A Japanese group reported that the photolysis of benzhydryldiethylsulphonium tetrafluoroborate gave products derived from the benzhydryl cation.(6.13)

$$(C_6H_5)_2CHS^+(C_2H_5)_2\ BF_4^- \xrightarrow[CH_3OH]{h\nu} \underset{90\%}{(C_6H_5)_2CHOCH_3}$$

The photolysis of triarylsulphonium salts was examined by Knapczyk and McEwan.(6.1) A complex mixture of products was obtained which was strongly dependent on the counter ion eg.

			X=Cl (%)	X=I (%)
$(C_6H_5)_3S^+\ X^-$	$\xrightarrow[CH_3OH]{h\nu}$	C_6H_6	10	10
	+	C_6H_5X	0.5	47
	+	$C_6H_5OCH_3$	11	6
	+	$(C_6H_5)_2$	2	1
	+	$(C_6H_5)_2S$	30	43
	+	HX	49	4

Two concurrent primary processes were suggested to account for these products. The first is a charge transfer type process.

$$(a)\ (C_6H_5)_3S^+\,X^- \xrightarrow{h\nu} \dot{X} + (C_6H_5)_3\dot{S} \longrightarrow (C_6H_5)_2S + C_6\dot{H}_5$$

$$\begin{tikzcd}
(b)\ (C_6H_5)_3\overset{+}{S} \arrow[r, "h\nu"] & C_6\dot{H}_5 + (C_6H_5)_2\overset{\cdot+}{S} \arrow[d, "CH_3OH"] \\
 & C_6H_5\dot{S} + C_6H_5OCH_3 + H^+
\end{tikzcd}$$

It is also conceivable that at least some of the aryl halide and anisole may have come from heterolysis of the excited sulphonium cation, $[(C_6H_5)_3\overset{+}{S}]^*$.

$$\begin{tikzcd}
\left[(C_6H_5)_3\overset{+}{S}\right]^* \arrow[r] & (C_6H_5)_2S + C_6H_5^+ \arrow[r, "Cl^-"] \arrow[d, "CH_3OH"] & C_6H_5Cl \\
 & C_6H_5OCH_3 + H^+ &
\end{tikzcd}$$

Crivello and Lam(6.6) also examined the photolysis of triarylsulphonium salts having complex counter ions. They agreed with a mechanism proposed by Knapczyk and McEwan(6.1) and formulated it as follows

$$Ar_3S^+\,X^- \xrightarrow{h\nu} (Ar_2\dot{S}, \dot{Ar})X^- \longrightarrow Ar_2S^{\cdot+} + \dot{Ar} + X^-$$

$$Ar_2S^{\cdot+} + R{-}H \longrightarrow Ar_2S^+H + R^{\cdot}$$

$$Ar_2S^+H \longrightarrow Ar_2S + H^+$$

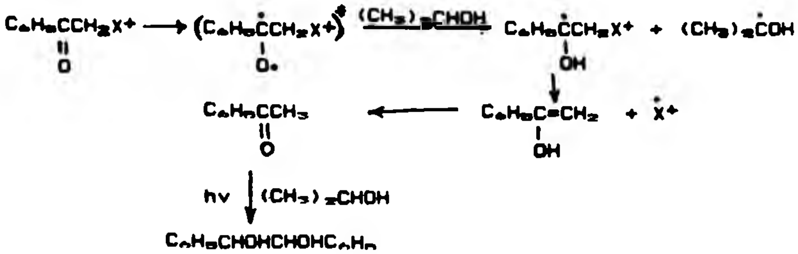
They proposed that the formation of the strong acid Ar_2S^+H was responsible for the cationic polymerisation of oxirane monomer when triarylsulphonium salts were used as photoinitiators (see page 230). It was also shown that perylene could be as a photosensitiser of the triarylsulphonium salts in the polymerisation studies.(6.13) These workers also showed that dialkyl(4-hydroxyphenyl)sulphonium salts could photocatalyse cationic polymerisation of oxirane monomers.(6.14)

However, this investigation of aryl sulphonium salts is probably less relevant to our study because the sulphur atom is directly conjugated with the aromatic electron system, whereas in our case, the sulphur atom is separated from a π-electron system by a methylene group.

The photolysis of sulphonium ylides and sulphimines has been reviewed by Coyle(6.10) but these compounds are outside the scope of this study. Recently dialkylphenacylsulphonium salts have been used in the design of photoresists.(6.7) In the plastics industry advantage is taken not only of the photolability of these salts but also their high thermal stability.

Photolysis of quaternary ammonium salts

The failure of phenacyltrialkylammonium salts to undergo photolysis in aqueous solution(4.5) was attributed to the higher bond strength of C-N compared with C-S(1.37) (see page 18). However, in aqueous 2-propanol, both the phenacylammonium and phenacylsulphonium salts underwent photolysis to give acetophenone and its pinacol reduction products. No dibenzoylethane or polymer products were found. This difference must be due to the availability of a good hydrogen atom donor, 2-propanol and the reaction was formulated as shown.



$$C_6H_5\underset{\displaystyle O}{\overset{\|}{C}}CH_2X^+ \longrightarrow \left(C_6H_5\underset{\displaystyle O\cdot}{\overset{|}{\dot{C}}}CH_2X^+\right)^* \xrightarrow{(CH_3)_2CHOH} C_6H_5\underset{\displaystyle OH}{\overset{|}{\dot{C}}}CH_2X^+ + (CH_3)_2\dot{C}OH$$

$$C_6H_5\underset{\displaystyle OH}{\overset{|}{C}}{=}CH_2 + \dot{X}^+ \longrightarrow C_6H_5\underset{\displaystyle O}{\overset{\|}{C}}CH_3 \xrightarrow[(CH_3)_2CHOH]{h\nu} C_6H_5CHOHCHOHC_6H_5$$

mixture of stereoisomers

Both Parmar(6.11) and McKenna et alia(6.16) showed that photolysis of benzyltrialkylammonium salts gave products similar to those from sulphonium salts, indicating concurrent heterolytic and homolytic reactions.

$$C_6H_5CH_2N^+(CH_3)_3X \xrightarrow[\substack{ROH \\ (R=H,alkyl)}]{h\nu} C_6H_5CH_2OR + C_6H_5CH_3 + C_6H_5CH_2CH_2C_6H_5$$

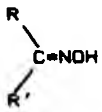
Parmar also showed that the ammonium salts were more reactive than the sulphonium salts.

Since the oxime ammonium salts used in the present investigation did not undergo photolysis, further review of ammonium compounds is not relevant.

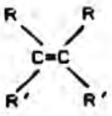
<u>Oximes</u>

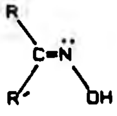
Because the present study uses compounds containing an oxime group, the following is a summary of the photolysis of oximes.

Oximes have the general formula

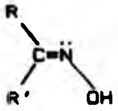


and are isoelectronic with the alkene system in which the two double bonded carbons have ligands which are coplanar and perpendicular to the π-bond. The oxime group has the same general stereochemistry: the hydroxyl group and lone pair of electrons on the nitrogen atom represent two ligands.

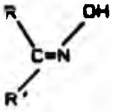




Thus, if the ligands R, R' are different, there are two possible stereoisomers.



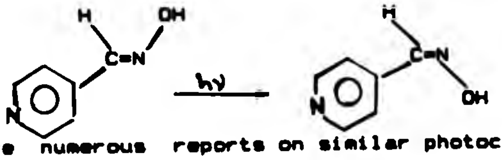
(A)



(B)

Like the corresponding alkene geometrical isomers, the two oxime stereoisomers differ in energy and the energy barrier is usually sufficiently high to permit the independent existence of each isomer. The interconversion of these isomers may be accomplished by a number of methods, one of which, pertinent to this study, is by irradiation with u.v. light. One of the earliest investigations was of ortho-, meta- and para-nitrobenzaldoximes.(6.17, 6.18) A more recent example is the photoisomerisation of the thermally stable syn-isonicotinealdehyde oxime to the pharmacologically active anti- isomer.(6.19)

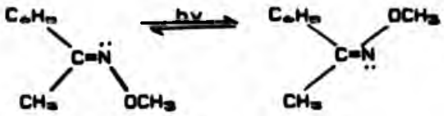
eg.



There are numerous reports on similar photochemical isomerisations of oxime ethers, usually the O-methyl and O-benzyl ethers.(6.18, 6.20, 6.21)

As in the photochemical isomerisation of alkenes, the process tends to give the predominantly less stable isomer, and is often a good method of preparing this isomer.

Padwa and Albrecht(6.22,6.23) pointed out that the great configurational stability of oxime ethers at room temperature, in contrast to the imines, made them ideal compounds to study carbon nitrogen double bond photoisomerisation. The presence of the alkoxy group greatly reduces the rate of thermal interconversion ($k < 10^{-13}$ at 60°C). These workers therefore made a detailed study of photostereoisomerisation of the syn (Z) and anti (E) O-methyl ethers of acetophenone oxime.



anti (E) syn (Z)

Irradiation of solutions of either isomer led to the same photostationary state with

$$[syn]/[anti] = 2.2$$

This value is very close to that calculated from quantum yields and extinction coefficients of each of the stereoisomers.

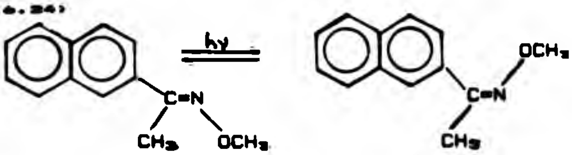
$$[syn]/[anti] = (\epsilon_{anti}[\Phi\ anti \rightarrow syn])/(\epsilon_{syn}[\Phi\ syn \rightarrow anti])$$
$$= 2.4$$

The thermal equilibrium mixture is

$$[syn]/[anti] = 0.02$$

This is an excellent example of the general observation that irradiation favours the formation of the less stable isomer. Since the isomerisation could not be quenched with high concentration of piperylene, which is known to be a good triplet quencher, they concluded that the direct irradiation isomerisation involved the directly excited singlet states. They also examined the photoisomerisation brought about by using a variety of sensitisers. In these cases, the experimental and calculated values for the photostationary states did not agree and this was attributed to different rate constants for the quenching of the sensitiser triplets by the two oxime ethers. The fact that the sum of the triplet sensitised yields $\Phi_{S\rightarrow A}$ + $\Phi_{A\rightarrow S}$ was less than unity indicated that radiationless decay process(es) other than those involving syn-anti isomerisations were occurring but the authors concluded that the syn-anti isomerisation provided the major route for deactivation of the excited state. No other reaction products were reported.

The same group also studied the related naphthyl oxime ethers.(6,24)



.

They showed that, unlike the acetophenone oximes, the photostationary states of these stereoisomers was concentration dependent. The thermal equilibrium was

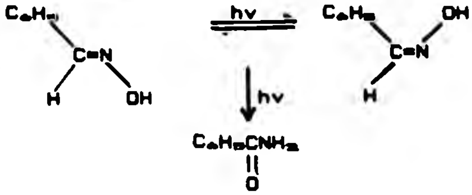
[anti]/[syn] = 24

and irradiation increased the proportion of syn isomer.

[anti]/[syn] = 0.8 - 1.6 (depending on concentration)

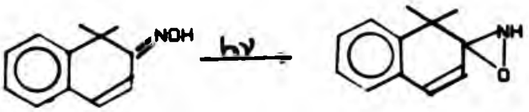
This system was also found to be temperature and solvent dependent. They put forward a reaction scheme involving eximers to account for this result. The higher polarisability of the naphthalene group would be expected to be more favourable to eximer formation than the phenyl group.

The photoexcitation of oximes can also result in other reactions. P. de Mayo's research group found that aryl aldoximes can undergo a photoinduced Beckmann rearrangement in competition with photostereo-isomerisation.(6.25)



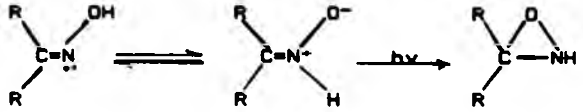
They also showed that the major route for energy degradation was the syn-anti isomerisation. They found that the syn-anti isomerisation could be brought about using sensitisers and because the calculated value for the sensitised photostationary state was not too different from the experimental values they concluded that the syn-anti isomerisation due to direct irradiation also went via a triplet state. In the photostructural isomerisation to the amide, it was suggested that an oxaziridine may be an intermediate and there are cases where these have been isolated.(6.26, 6.27)

eg.



The most likely state leading to oxaziridine formation was assumed to be the $\pi \rightarrow \pi^*$ singlet or triplet, but quenching experiments with piperylene or oxygen showed the reaction to take place from a singlet state.(6,38)

Isotopic labelling with ^{18}O showed the overall oxygen rearrangement to be intramolecular.(6,36) The similarity of this photochemical oxaziridine formation to the one observed with nitrones can be rationalised by assuming that the immediate precursor of the oxaziridine is the prototropic tautomer rather than the oxime itself. This assumption is supported by the fact that the quantum yields for oxaziridine formation in the oxime series are much lower than in the nitrone series.



Both thermal and photochemical pathways may be involved in the ring cleavage of the transient oxaziridine.

In the present work there was no evidence for the occurrence of the Beckmann rearrangement (see discussion).

The present work stems from that of Laird and Williams on phenacyl 'onium salts in this laboratory. Phenacyl oxime 'onium salts were required for the electrolysis studies reported earlier in this thesis and it was opportune to examine the photochemistry of these compounds. This explains why the photochemical part of this research project is smaller than the electrolysis studies.

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CHAPTER 7

Experimental

General procedure for the photochemical experiments of phenacyl 'onium' oxime salts in water

A solution of the salt (1g) in water (200cm^3) was deoxygenated by bubbling nitrogen through for twenty minutes, and then irradiated for five hours with a medium pressure mercury lamp surrounded by a quartz cooling jacket. This apparatus is shown in figure (7.1).

A slow flow of nitrogen was maintained throughout the photolysis to exclude oxygen and assist the stirring of the solution. The reaction vessel was covered with aluminium foil, not only to maximise the use of the light but also as a safety practice.

The work-up procedure

The photolysate was extracted with ether (3x15cm^3) and then by chloroform (3x15cm^3). The combined extracts were dried with anhydrous magnesium sulphate, evaporated to a small volume on a rotary evaporator and transferred to a 25cm^3 volumetric flask. A known amount of marker was added, and the solution was made up to 25cm^3 with anhydrous ether and the mixture was analysed by glc. The marker was a 1% solution of 6-methylheptanol in anhydrous ether. An aliquot of 5cm^3 was added in the above procedure.

The aqueous layer of photolysate after the extractions was diluted to a known volume with 0.1M potassium chloride solution and then analysed by polarography. The polarogram was compared with the polarogram of a standard solution of the oxime 'onium salt to determine the amount of substrate consumed during the photolysis.

The period of five hours irradiation was chosen for the following reasons.

1. By then about half of the substrate had reacted. By terminating the photolysis before complete reaction of the substrate it should be possible to compare the relative ease of various salts. Further irradiation to secure complete reduction also ran the risk of possible over-irradiation of the reaction products and ensuing complications.
2. By limiting the irradiation to five hours, it was often possible to complete the work up and analysis during the same day and hence minimise any further "dark" reactions. In initial experiments the procedure described by Laird and Williams(6.3) in their investigation of phenacyl salts was used in which the lamp cooling jacket was washed hourly with acetone to remove any deposits. The combined washings were evaporated to leave a solid. In the present investigation of phenacyl oxime salts trial experiments showed that the amount of solid was very small (6-10mg) compared with the deposit from phenacylsulphonium salts ($\simeq$110 mg) and therefore this washing procedure was omitted.

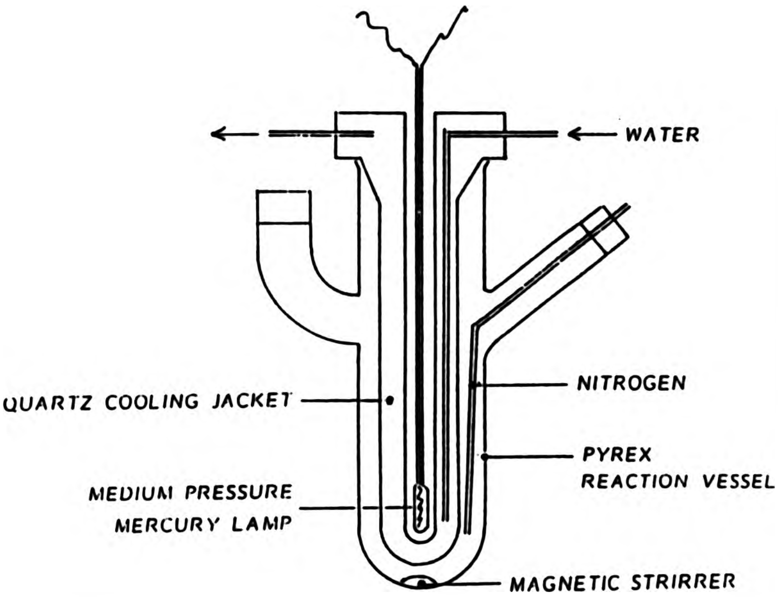
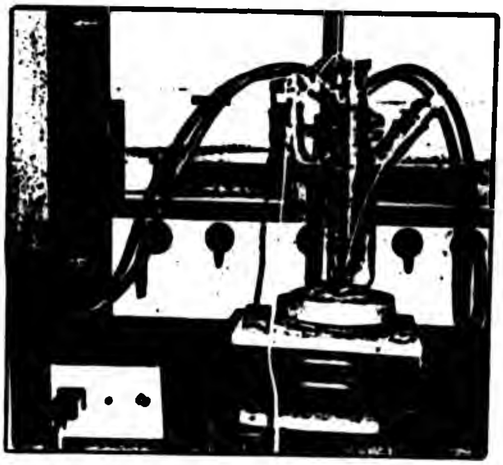


Fig 7.1 Diagram of the U.V irradiation apparatus



Photolysis of (2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide

A solution of the above salt (1.0g) in water (200cm^3) was irradiated for five hours and worked up according to the general procedure. The extracts were analysed by glc using a SE 30 column at 150°C. and hydrogen carrier gas (2cm^3/min). The quantative amounts of products were analysed by glc using a marker (6-methylheptanol) and a standard calibration graph.

The glc chromatogram showed six peaks apart from those of the marker and the solvents. See table 7.1.

Table 7.1

Peak number	Compound	Retention time(mins)	Amount (mg)
1	Benzaldehyde	0.45	10.0
2	Benzonitrile	0.55	trace
3	Acetophenone	0.80	126.0
4	Z-Acetophenone oxime	1.8	13.0
5	E-Acetophenone oxime	2.2	61.0
6	Tetrahydrothiophene	0.25	131.0

Peaks 1,2,3,5 and 6 were identified as benzaldehyde, benzonitrile, acetophenone, acetophenone oxime and tetrahydrothiophene by their retention times compared with those of known samples and by glc/ms analysis (see pages 252 to 255). Peak 4 was assigned to Z-acetophenone oxime, on the basis of glc/ms analysis which gave a molecular ion peak at m/e=135 and a fragmentation pattern almost identical with that of E-acetophenone oxime.$^{(6,20)}$ The extract was also examined by tlc, using SiO_2 fluorescein plates and eluant petroleum ether (40°-60°)/ diethylether (3:2). Two "spots" were observed under UV light with Rf values of 0.75 and 0.60. These had identical retention times compared with authentic samples of acetophenone (0.75) and acetophenone oxime (0.60). There was also a very small amount of substance which did not migrate in the eluant.

After extracting with ether and trichloromethane the aqueous photolysate was diluted to 1000cm^3 with 0.1M potassium chloride. The polarogram had $E_{1/2}$= -0.76V and diffusion current id = 5.4 µA.

The polarogram of 10^{-3}M solution of (2-phenyl-2-oximino-ethyl)tetramethylenesulphonium bromide had $E_{1/2}$= -0.78V and diffusion current id = 3.25 µA.

Therefore the amount of 'onium salt in photolysate

= 5.4/3.25 x 10^{-3} moles = 1.66 X 10^{-3} moles

Molecular weight of 'onium salt = 302g/mole

Initial mass of 'onium salt = 1.0g

= 1/302 = 3.31 X 10^{-3} moles

% unreacted 'onium salt = (1.66/3.31) X 100 = 50.2

Therefore % reacted onium salt = 49.8

"Dark reaction" for (2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide

The possibility of any of the products arising by hydrolysis ("dark reaction") of the initial salt was tested by keeping a solution of the salt (1.00g in 200cm^3 water) in the dark for twelve hours. It was then worked up according to the general procedure. Analysis of the ether extract by glc showed the absence of any products. Examination of the aqueous fraction by polarography showed 98% unreacted salt present. On evaporating the aqueous solution, 0.98g of salt was recovered.

Photolysis of acetophenone oxime

A solution of acetophenone oxime (0.50g dissolved in 10cm^3 methanol) in distilled water (190cm^3) was irradiated for five hours and worked up according to the general procedure. The extract was analysed by glc using a SE 30 column at 150°C and hydrogen carrier gas (2cm^3/min). See table 7.2.

Table 7.2

Peak number	Compound	Retention time (mins)	Relative amount %
1	Acetophenone	0.7	83.9
2	1-phenylethanol	0.7	
3	unknown	0.9	-
4	unknown	1.2	-
5	Z-Acetophenone oxime	1.75	3.2
6	E-Acetophenone oxime	2.1	12.9

The chromatogram showed six product peaks, the first two showing much overlap. This double peak was better resolved on a Silar 5cp column in the glc/mass spectrometer apparatus, although there was still much overlap. However, by careful sampling at the two ends of the combined signal peak, it was possible to get the mass spectrum of each component in the absence of the other. The two components were identified by their spectra as acetophenone and 1-phenylethanol and this was confirmed by mass spectrometry of authentic samples of these compounds.

Peak 6 was identified by glc/mass spectrometry and by glc retention time as the common E-isomer of acetophenone oxime, by comparison with an authentic sample of the compound. Peak 5 gave a mass spectrum almost identical with that of peak 6 and was assigned as the Z-stereoisomer of acetophenone oxime. Peaks 3 and 4 refer to two unidentified products and because they represented less than 7% of the product they were neglected in calculating the relative percentages of the other products. The percentage yields of acetophenone + 1-phenylethanol and the isomeric oximes were obtained using peak height ratios.

The photolysis of 2-phenyl-2-O-methyloximinoethyl)tetramethylenesulphonium bromide

A solution of the above salt (0.5g) in water (200cm^3) was irradiated for five hours and worked up according to the general procedure. The extracts were analysed by glc using SE 30 column at 150°C and hydrogen as a carrier gas

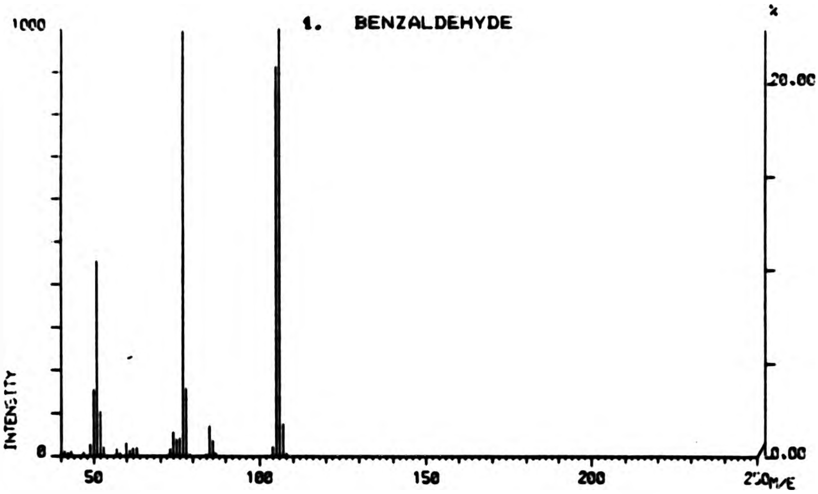
($2cm^3$/ min).

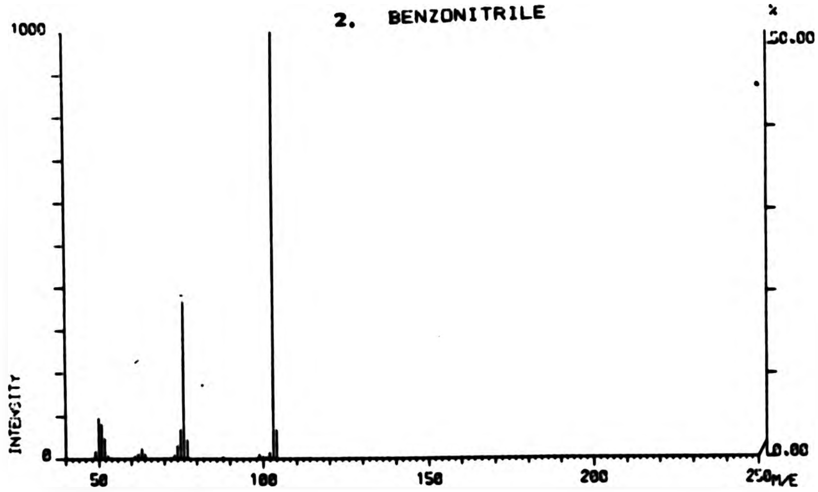
The products were identified from their similarities with the retention times and mass spectra of authentic samples. The relative amounts were estimated from their peak heights. See table 7.3.

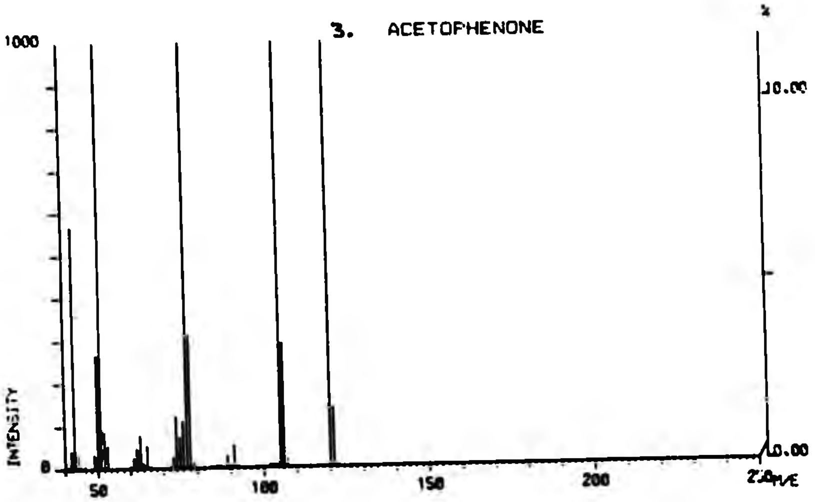
Table 7.3

Peak number	Compound	Retention time (mins)	Relative amount %
1	Tetrahydrothiophene	0.2	-
2	unknown peak (with -shoulder)	0.4	-
3	Acetophenone	0.7	17
4	Z-Acetophenone O-methyloxime	1.0	40
5	E-Acetophenone O-methyloxime	1.4	36

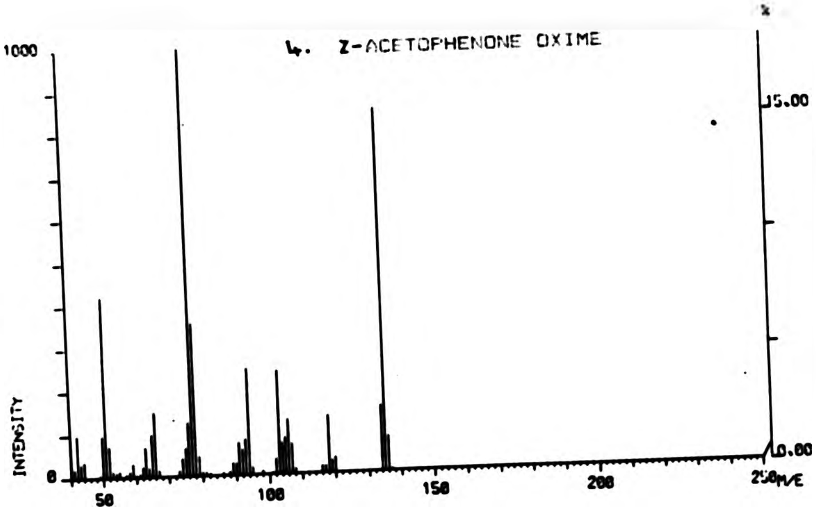
Mass spectra of compounds 1-6 (page 247) from photolysis of (2-phenyl-2-oximinoethyl)tetramethylenesulphonium bromide.





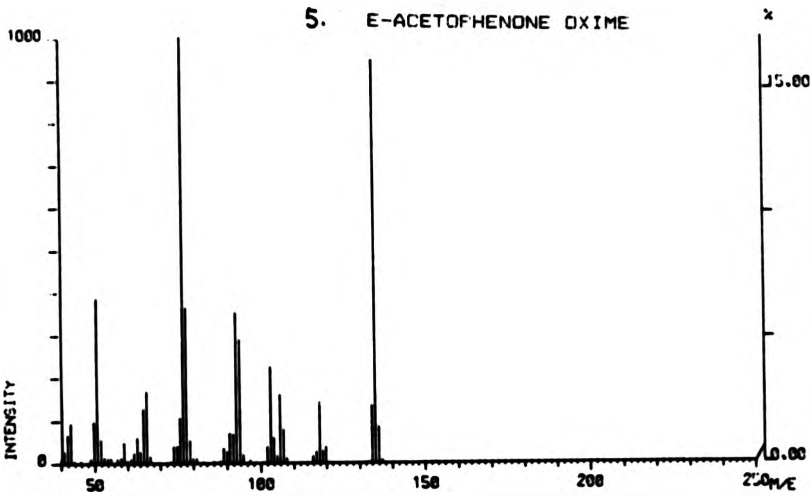


3. ACETOPHENONE

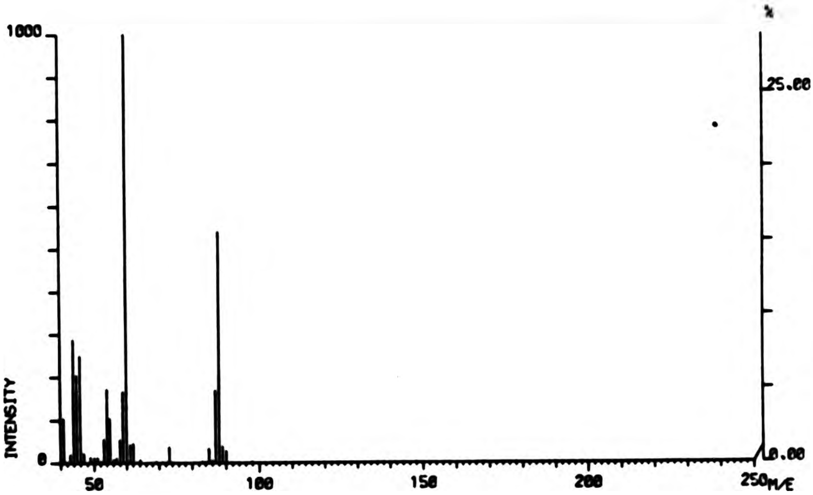


4. Z-ACETOPHENONE OXIME

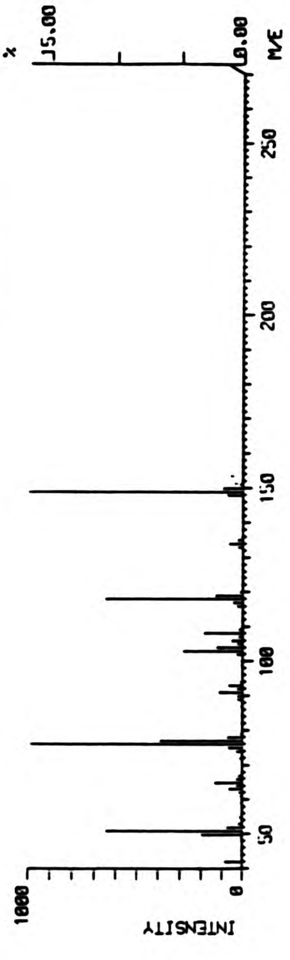
5. E-ACETOPHENONE OXIME



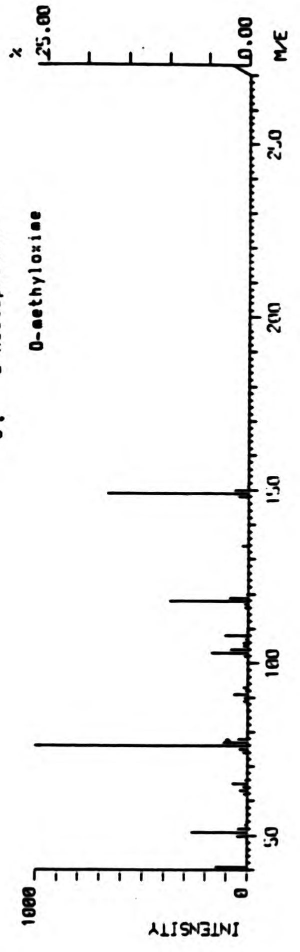
6. TETRAHYDROTHIOPHENE



4. Z-Acetophenone O-methyloxime



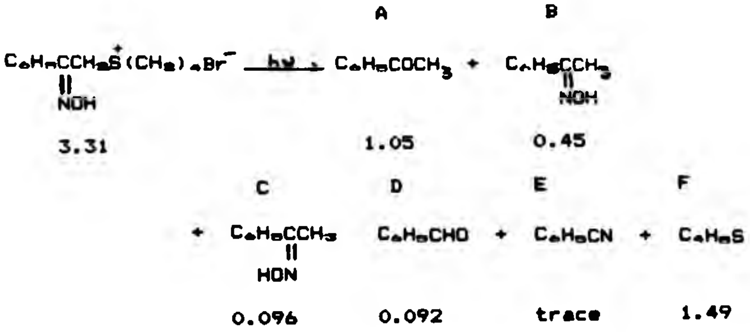
5. E-Acetophenone O-methyloxime



CHAPTER 8

Discussion

Irradiation of a solution of (2-phenyl-2-oximinoethyl) tetramethylenesulphonium bromide gave the products shown (see page 247).



$$C_6H_5\underset{\underset{NOH}{\|}}{C}CH_2\overset{+}{S}(CH_2)_4Br^- \xrightarrow{h\nu} C_6H_5COCH_3 + C_6H_5\underset{\underset{NOH}{\|}}{C}CH_3$$

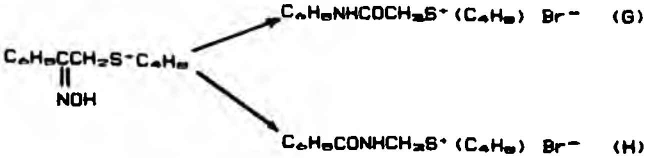
$$+ C_6H_5\underset{\underset{HON}{\|}}{C}CH_3 \quad C_6H_5CHO + C_6H_5CN + C_4H_8S$$

The amount of each substance is expressed in millimoles.

All the products other than tetrahydrothiophene are derived from the phenacyloxime portion of the reactant salt. Assuming that there are no significant amounts of undetected products, the molar sum of these phenyl containing products (A-E; 1.69 millimoles) should correspond to the molar fraction of tetrahydrothiophene (1.49 millimoles), provided no tetrahydrothiophene was lost through other reactions. These values are fairly close and the relatively small difference between these figures may be accounted for if any tetrahydrothiophene is consumed in other reactions (see later section on mechanism) and by an experimental observation that tetrahydrothiophene was not completely extracted from the aqueous solution in the work up procedure, only about 92% being extracted. These results also indicate the amount of salt decomposed by photolysis, because the molar sum of products (A-E) divided by the initial amount of salt should give the fraction of the reactant which was decomposed to give these products.

$$\text{molar sum A-E} = 1.69/3.31 = 0.51$$

i.e. 49% of the initial salt was not converted to the products A-E. This figure can be compared with the estimation of unreacted salt by polarography, based on the diffusion currents before and after photolysis. This gave a value of 50% reacted salt. The surprising closeness of these two values, obtained by entirely independent methods must be somewhat fortuitous since other experiments gave slightly different values and the polarographic and chromatographic analysis methods are only accurate to 2%. However, these results also show that little if any of the salt decomposes to give products other than those detected. This therefore rules out any Beckman rearrangement in the photolysis. The products of such a rearrangement would be (G) and (H).



$$\underset{\text{NOH}}{\overset{}{C_6H_5\underset{\|}{C}CH_2S^+C_4H_8}} \rightarrow C_6H_5NHCOCH_2S^+(C_4H_8)\ Br^- \quad (G)$$

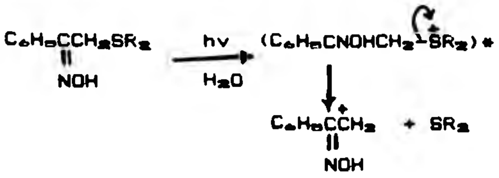
$$\rightarrow C_6H_5CONHCH_2S^+(C_4H_8)\ Br^- \quad (H)$$

(G) and (H) would have been water soluble and not ether extractable and hence not detected.

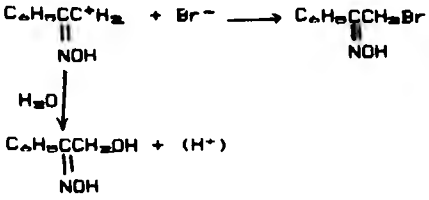
However, they should have been detected in the polarogram of the aqueous photolysate fraction either by the appearance of a new wave(s) or by a decrease in the value of the diffusion current unless they had the same $E_{1/2}$ potential as the oxime salt, which is unlikely.

Possible C-S⁺ bond cleavage processes

1. Heterolysis of C-S⁺ bond to form the carbonium ion



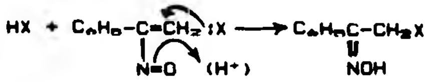
This carbonium ion would be expected to undergo nucleophilic addition by Br^-, H_2O



The two step reaction amounts to SN1 substitution. The carbonium ion should also be an acid and could lose a proton.

(P)

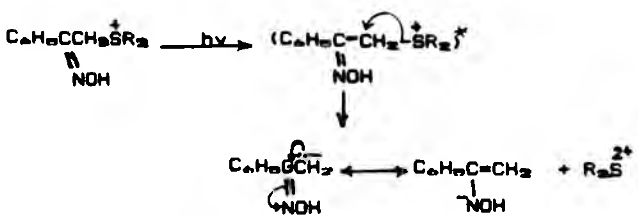
The nitrosoalkene (P) has been suggested as a possible intermediate in one of the electrolysis experiments (see page 215). (P) should undergo facile heterolytic addition of protic substances, e.g. H_2O, HBr to give phenacyl alcohol oxime and phenacyl bromide oxime.



$$HX + C_6H_5\text{-}\underset{N=O}{C}=CH_2\,{:}X \;(H^+) \longrightarrow C_6H_5\underset{NOH}{C}\text{-}CH_2X$$

Since neither of these compounds were detected, this heterolytic cleavage of the $C\text{-}S^+$ bond can be discarded.

2. Heterolysis to give the phenacyl oxime anion



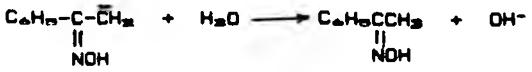
$$C_6H_5\underset{NOH}{C}CH_2\overset{+}{S}R_2 \xrightarrow{h\nu} (C_6H_5\underset{NOH}{C}\text{-}CH_2\text{-}\overset{+}{S}R_2)^*$$

$$\downarrow$$

$$C_6H_5\underset{NOH}{C}\bar{C}H_2 \longleftrightarrow C_6H_5\underset{\bar{N}OH}{C}=CH_2 + R_2\overset{2+}{S}$$

(Q)

The phenacyl oxime anion (Q) should be readily protonated with water to give acetophenone oxime.



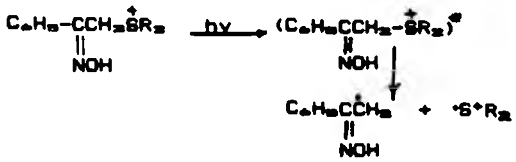
$$C_6H_5\text{-}\underset{NOH}{C}\text{-}\bar{C}H_2 + H_2O \longrightarrow C_6H_5\underset{NOH}{C}CH_3 + OH^-$$

However, this mode of heterolysis is intuitively very unlikely. It implies a higher electronegativity for the phenacyloximino group than the positively charged SR_2 group, and requires the formation of doubly charged sulphur species as a product. This is hardly conceivable, but if such a species were formed it would react very readily with nucleophiles such as water to give sulphoxides.

$$\begin{tikzcd}[column sep=small] R_2S^{\cdot+} + OH_2 \arrow[r] & R_2S^{+}\text{-}OH + H^{+} \arrow[d] \\ & R_2S{=}O + H^{+} \end{tikzcd}$$

No sulphoxide was detected in the reaction products therefore this mode of heterolysis can be disregarded.

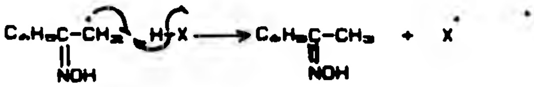
3. <u>Homolysis of C-S⁺ bond</u>



$$C_6H_5\text{-}\underset{\underset{NOH}{\|}}{C}CH_2\overset{+}{S}R_2 \xrightarrow{h\nu} (C_6H_5\underset{\underset{NOH}{\|}}{C}CH_2\text{-}\overset{+}{S}R_2)^{*} \longrightarrow C_6H_5\underset{\underset{NOH}{\|}}{C}\dot{C}H_2 + {}^{\cdot}S^{+}R_2$$

The phenacyloximino radical should dimerise to form dibenzoylethane dioxime and/or to abstract hydrogen from suitable hydrogen donors.

$$2C_6H_5\underset{\underset{NOH}{\|}}{C}\dot{C}H_2 \xrightarrow{\text{coupling}} C_6H_5\underset{\underset{NOH}{\|}}{C}CH_2CH_2\underset{\underset{NOH}{\|}}{C}C_6H_5$$

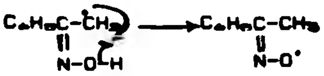


$$C_6H_5\underset{\underset{NOH}{\|}}{C}\text{-}\dot{C}H_2 \;\; H\text{-}X \longrightarrow C_6H_5\underset{\underset{NOH}{\|}}{C}\text{-}CH_3 + X^{\cdot}$$

Each of these reactions however raises difficulties in accounting for the experimental results.

a) No dibenzoylethane dioxime was detected in the products.

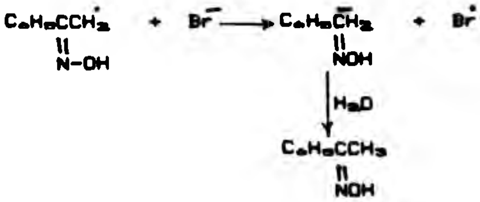
b) There is no obvious hydrogen atom donor. Water is a very poor donor, probably because of the adverse thermochemistry: a relatively strong O-H bond would be broken to form a significantly weaker C-H bond. A possible solution to this is that the isomeric radical B is formed, possibly from a "hot" radical A, immediately following the initial homolysis.



A B

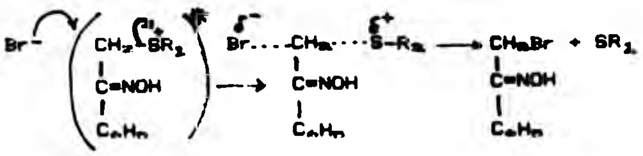
This could account for the absence of dioxime dimer and the formation of acetophenone oxime because the hydrogen transfer with water would be energetically much less unfavourable.

There is also the possibility of the reaction of either radical, A or B with bromide ion to give the anion which would be readily protonated by water e.g.

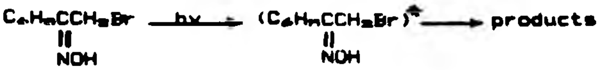


The bromine atom may form bromine and either of these species may oxidise some of the thioether and thus account for some of the loss of yield of this compound.

4. SN2 displacement of S^+R_2 by bromide ion



Another conceivable mechanism is the SN2 displacement of the S^+R_2 group by bromide ion to give α-bromoacetophenone oxime, followed by photolysis of this compound. The first of these reactions would have to involve the photoexcited state of the sulphonium ion, because the dark reaction does not occur under the experimental conditions. The product would be very unlikely to be electronically excited although it might be vibrationally excited.

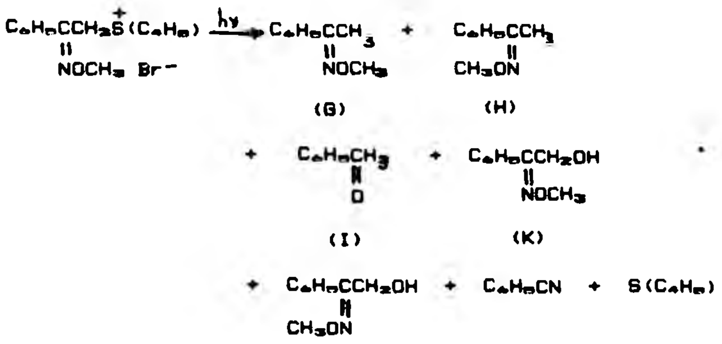


$$\underset{\underset{NOH}{\|}}{C_6H_5CCH_2Br} \xrightarrow{h\nu} (\underset{\underset{NOH}{\|}}{C_6H_5CCH_2Br})^* \longrightarrow \text{products}$$

The second step requires a second photoexcitation and any consideration of a mechanism for the formation of the observed products would run into the same difficulties outlined above for mechanisms 1,2 and 3 for the sulphonium salts. For these reasons and also the fact that no bromo oxime was detected in the product reaction, the mechanism is rejected. The absence of significant amounts of organobromine compounds was also confirmed by silver nitrate titration of the aqueous photolysate after extraction with ether and chloroform; the titre was almost exactly the value expected for the original bromide ion.

Ignoring the formation of acetophenone, which is dealt with in the next section, the results of this investigation are not sufficient to permit the unambiguous assignment of any reaction mechanism to the photolysis. The absence of products expected from heterolytic C-S⁺ bond cleavage argues against this process. Similarly the absence of the expected dimer product dibenzoylethane dioxime casts doubt on the homolytic process, although a suggestion was made of a possible radical rearrangement to give the oxygen radical species (page 260). An experiment using the oxime-O-methyl ether sulphonium salt was investigated, which might be a test of the radical rearrangement hypothesis.

Photolysis of (2-phenyl-2-O-methyloximinoethyl)tetramethylenesulphonium bromide gave the following products.



$$C_6H_5\underset{NOCH_3}{\underset{\|}{C}}CH_2\overset{+}{S}(C_4H_8)\ Br^- \xrightarrow{h\nu} C_6H_5\underset{NOCH_3}{\underset{\|}{C}}CH_3 + C_6H_5\underset{CH_3ON}{\underset{\|}{C}}CH_3$$

(G) (H)

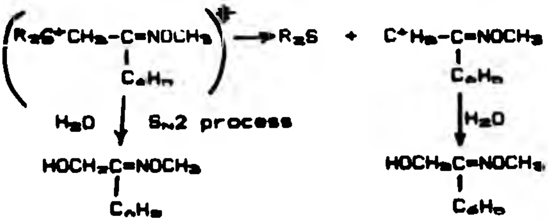
$$+\ C_6H_5\underset{O}{\underset{\|}{C}}CH_3 + C_6H_5\underset{NOCH_3}{\underset{\|}{C}}CH_2OH$$

(I) (K)

$$+\ C_6H_5\underset{CH_3ON}{\underset{\|}{C}}CH_2OH + C_6H_5CN + S(C_4H_8)$$

(L)

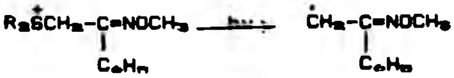
The product mixture was analysed by glc and the known components identified by mass spectrometry. No marker was used in the experiment and analysis is on the basis of peak heights. Despite this lack of precision the results are still of interest. The major products by far were the two geometrical isomers of O-methyl acetophenone oxime (75%), present in the proportion of 1.1:1 in which the less stable stereoisomer predominates. This may be compared with the value 2.4:1 obtained by Padwa and Albrecht in the photoequilibration of these isomers in pentane solution.(6.33) More detailed examination of the product mixture by glc/mass spectra revealed a number of small peaks at somewhat higher retention times then for compounds G and H. Two of these (K&L) had identical mass spectra, with molecular ion peaks m/e = 165. These have been tentatively assigned as the stereoisomeric α-hydroxyacetophenone-O-methyloximes. If this assignation is correct it is the first evidence of possible heterolytic bond breaking, either by an SN1 type process to give the cation (X) or by an SN2 process between the excited molecule and a water molecule.



$$\left(R_2S^{+}CH_2-\underset{C_6H_5}{C}=NOCH_3\right)^{\ddagger} \longrightarrow R_2S + C^{+}H_2-\underset{C_6H_5}{C}=NOCH_3 \quad (X)$$

$$\xrightarrow[H_2O]{S_N2\ \text{process}} HOCH_2\underset{C_6H_5}{C}=NOCH_3 \qquad \xrightarrow{H_2O} HOCH_2\underset{C_6H_5}{C}=NOCH_3$$

It might be thought that homolysis of the C-S⁺ bond to give the radical (Y),

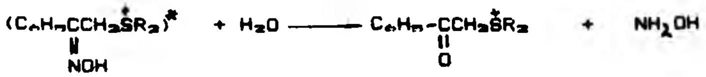


$$R_2\overset{+}{S}CH_2-\underset{C_6H_5}{C}=NOCH_3 \xrightarrow{h\nu} \dot{C}H_2-\underset{C_6H_5}{C}=NOCH_3 \quad (Y)$$

should result in the formation of the dimer, because this could not isomerise to the oxygen radical. However, no evidence for the presence of the di-O-methyl ether of dibenzoylethane dioxime or any related large molecular weight compound was found.

The formation of acetophenone

The foregoing mechanisms were concerned only with the cleavage of the C-S$^+$ bond and not with the formation of the major product, acetophenone. Two schemes, which can be tested, are (a) the formation of the carbonyl group precedes the breakage of the C-S$^+$ bond, (b) the formation of the carbonyl bond comes after the C-S$^+$ bond breaking. The simplest route for (a) should be the decomposition (e.g. hydrolysis) of the oxime salt to give the phenacyl salt which then undergoes photolysis to give acetophenone. The first of these steps must involve the photoexcited oxime salt because no dark reaction occurs under the experimental conditions.

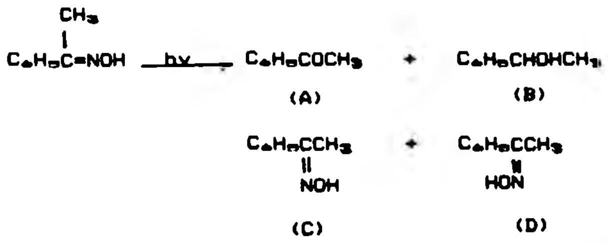


$$(C_6H_5\underset{\overset{\|}{NOH}}{C}CH_2\overset{+}{S}R_2)^{*} + H_2O \longrightarrow C_6H_5-\underset{\overset{\|}{O}}{C}CH_2\overset{+}{S}R_2 + NH_2OH$$

This mechanism can be ruled out for a number of reasons. Interruption of the photolysis after partial decomposition of the oxime salt, and polarographic examination of the aqueous solution after ether extraction gave a polarogram indicating a single species, with $E_{1/2}$ value identical with that of the oxime salt. Polarographic experiments with a mixture of the oxime salt and the corresponding phenacyl salt gave polarograms differentiating both species. Moreover, photolysis of any phenacyl sulphonium salt should give only small amounts of acetophenone and much larger amounts of dibenzoylethane and phenacyl bromide, neither of which was present in the product.(6.3)

The simplest scheme for the formation of acetophenone after the cleavage of the C-S$^+$ bond is by decomposition of acetophenone oxime formed in the first photolysis. This reaction must also be from photoexcited acetophenone oxime because there is no dark reaction under the given conditions. This proposition was tested by irradiating an aqueous solution of acetophenone oxime containing just sufficient alcohol to keep it in solution.

Analysis by glc of the extract of the photolysate showed a mixture of acetophenone, 1-phenylethanol and the two stereoisomeric acetophenone oximes.



$$C_6H_5\overset{\displaystyle CH_3 \atop |}{C}{=}NOH \xrightarrow{h\nu} \underset{(A)}{C_6H_5COCH_3} + \underset{(B)}{C_6H_5CHOHCH_3}$$

$$\underset{(C)}{\underset{\displaystyle NOH}{C_6H_5\overset{}{C}CH_3 \atop \|}} + \underset{(D)}{\underset{\displaystyle HON}{C_6H_5CCH_3 \atop \|}}$$

Acetophenone and 1-phenylethanol formed the bulk of the product. Their retention times were almost identical and it was difficult to estimate their relative amounts, but, as is shown below, this does not detract from the purpose of the experiment. The products were identified by glc retention times and glc/mass spectrometry compared with authentic samples of compounds (A), (B), (C). Compound (D) was identified as the stereoisomer of (C) from its mass spectrum which was almost indistinguishable from that of (C). Examples of the similarity of mass spectrometry of Z/E oxime stereoisomers have been reported in the literature.(8,1) Some minor unidentified products (less than 10% in total) were also detected but these could be neglected in the following appraisal of the experiment.

It is difficult to envisage the formation of the 1-phenylethanol except by reduction of acetophenone. This requires a hydrogen donor and the most likely donor is the methanol present in the solvent. The photoreduction of ketones by alcohols is a well known reaction and is sometimes a preparative method. The reaction may be formulated as shown below.

$$C_6H_5COCH_3 + CH_3OH \xrightarrow{h\nu} C_6H_5CHOHCH_3 + CH_2{=}O$$

In the photolysis of the oxime onium salt-water system there was no alcohol present so the acetophenone formed was not reduced. It should be noted that the reaction mechanism for the formation of acetophenone from acetophenone oxime was not investigated and is not crucial to the purpose of carrying out this experiment.

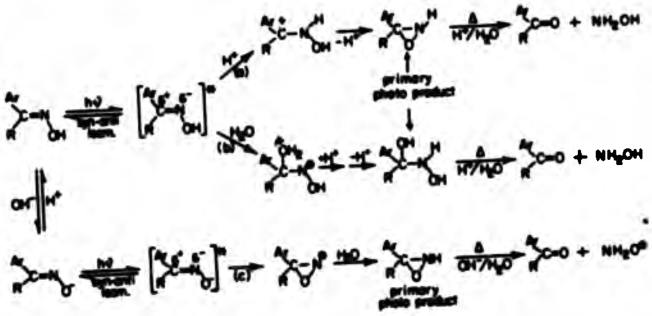
Taking the combined yields of acetophenone and 1-phenylethanol as representative of acetophenone formed from acetophenone oxime, the relative amounts of the acetophenone and the two stereoisomeric acetophenone oximes are as shown.

acetophenone : combined E+Z oximes 5:1

E-oxime : Z-oxime 4:1

The acetophenone : oxime ratio is over twice that observed in the oxime sulphonium salt experiment (2:1). The lower ratio in the oxime salt experiment is to be expected because the acetophenone oxime is a reaction product and its concentration, initially zero, will always be less than in the acetophenone oxime photolysis experiment. More interesting is the ratio of the two oxime stereoisomers, which is very similar (4.0, 4.6) in both experiments. This strongly suggests that in the photolysis of the oxime sulphonium salt the oxime isomer product ratio is due to photoisomerisation of the acetophenone oxime product, rather than being related to any particular initial product ratio from the oxime sulphonium salt precursor. The photolysis of acetophenone oxime experiment does not, by itself, prove that all the acetophenone formed by the photolysis of the oxime sulphonium salt comes from the acetophenone oxime product, but is consistent with it. This therefore supports the results of the polarographic investigation of residual salt described earlier (page 211 and 212) namely that the acetophenone formed in the photolysis of the oxime sulphonium salt comes wholly or mainly from products after the cleavage of the $C-S^+$ bond.

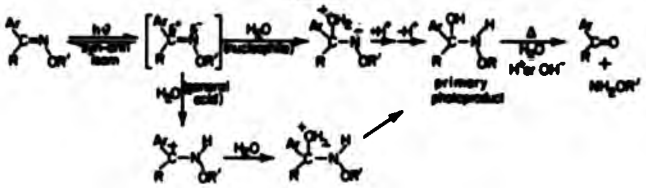
The reaction mechanism for the photolytic conversion of the oxime to ketone was not investigated, because it is a secondary reaction, in so far as it is the reaction of a product of the sulphonium salt. However, it is interesting to compare our results with those of a very recent publication (May 1987) by Haley and Yates,([illegible]) long after the present study was completed. These workers investigated the photolysis of a number of oximes in aqueous solution, including acetophenone oxime. They report that the reaction is a photocatalysed hydrolysis, although there is no mention of the other product of hydrolysis, hydroxylamine, in the experimental account. They also found indirect evidence for the formation of the oxazirane intermediate, but found no evidence for the formation of products other than acetophenone and the two stereoisomeric oximes: no possible Beckman rearrangement products were detected. They established that the process was both acid catalysed and base catalysed. From studies with possible sensitisers and quenchers they concluded that the reaction went via the lowest singlet state. They proposed the following scheme.



They also investigated the photolysis of the O-methyl ether of acetophenone oxime and found that this also gave acetophenone, but was pH independent over a large range (2-12).

The following reaction scheme was put forward.

Scheme V



Our results differ from theirs mainly by the presence of 1-phenylethanol. This is because of the absence of alcohol in their solvent: the presence of a small amount of acetonitrile in their solvent appeared to have no effect on the photolysis. We also found evidence for a small amount of two unidentified products (<10% total). Also like them we found no evidence for Beckmann rearrangement products. Haley and Yates did not report on the relative amounts of the two stereoisomeric oximes in the product.

The absence of reaction when (2-phenyl-2-oximino-ethyl)trimethylammonium bromide was subjected to the same photolysis conditions as the sulphonium salt parallels the behaviour of the corresponding phenacylsulphonium and ammonium salts in aqueous solution.(4,23) In the latter case it was suggested that the difference was due to the different bond strengths of the $C-S^+$ and $C-N^+$ bonds: this suggestion is equally applicable to the oximino salts in the present study.

Summary

The results of the photochemical investigation of the (2-phenyl-2-oximinoethyl)dialkylsulphonium salts in aqueous solution clearly show the easy rupture of the C-S bond, a result similar to that for the phenacylsulphonium salts. However, whereas in the latter case the evidence for the mechanism for bond cleavage as homolysis is conclusive, except perhaps in special cases, it is more difficult to assign a mechanism for the oximinosulphonium salts. Although the homolytic mechanism is the more likely, the results of the present limited study do not give unambiguous evidence for the intervention of free radicals. The evidence for some heterolysis of the O-methyl salt is tentative.

When the project was first envisaged it was thought that correlations between the electrochemical and photochemical processes of the phenacyl 'onium salts and phenacyl oxime 'onium salts might be found. This expectation was not necessarily justified because the electronic states of the substrate in the two processes are very different: electrolysis involves the ground state and photolysis the excited state. In so far as both processes lead to C-S bond cleavage this is one correlation. Although the activating effect of the α-carbonyl group or oximino group on this bond breaking in both processes is important, attention has already been drawn to the importance of solvation and any detailed explanation of correlations between electrolysis and photolysis should include this factor. The present investigation shows that still more work is needed to properly understand these reactions.

References

(8.1) Middleditch B. S. and Desiderio D. M.; Advances in mass spectrometry, 6 173 (1974)

(8.2) Haley M. F. and Yates K.; J. Org. Chem., 52, 1817, 1825 (1987)

TITLE STUDIES ON THE ELECTROCHEMICAL REDUCTION AND THE PHOTOLYSIS OF PHENACYL 'ONIUM SALTS AND RELATED COMPOUNDS

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