THE ELECTROCHEMICAL OXIDATION OF MERCURY (II) - OLEFIN COMPLEXES

by

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ABSTRACT
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It has been known for many years that acidic solutions of mercuric ions absorb olefins rapidly to form σ bonded complexes. The electrochemical oxidation of eleven such complexes (those of ethylene, propene, but-1-ene, but-2-ene, pent-1-ene, pent-2-ene, hex-1-ene, hex-2-ene, oct-1-ene, isobutene and cyclohexene) is reported. The high solubility of these mercury(II) - olefin complexes allows concentrated aqueous solutions of olefins to be made so that the oxidation can be carried out at high current densities. The electrode reaction is the first reported example of an electrochemical oxidation of a complex resulting in the fission of a metal-carbon bond thus regenerating the mercuric ion. The mercuric ion can, therefore, be regarded as a catalyst since the complex may be readily regenerated by bubbling olefin through the solution. The effect of pH (for the propene complex) and of electrode potential (for the propene, but-1-ene and but-2-ene complexes) on the products of the reaction was investigated. The products of the oxidation of the complexes of eleven olefins were determined at one fixed potential.

The principal products which are found are carboxylic acids, together with small amounts of aldehydes and ketones which, it is shown, are probably the first products of the electrode reaction. A mechanism which involves the rearrangement of a carbonium ion has been suggested for the reaction. The carbonium ion can rearrange either by an alkyl or a hydride shift and the ratio of products formed via these two routes has been shown to depend on the size of the migrating group and, for propene, on the anion present. Values of the ratio of alkyl to hydride shift were obtained for several alkyl groups and the relative alkyl to alkyl shift ratios calculated from these are compared with values in the literature.

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INTRODUCTION

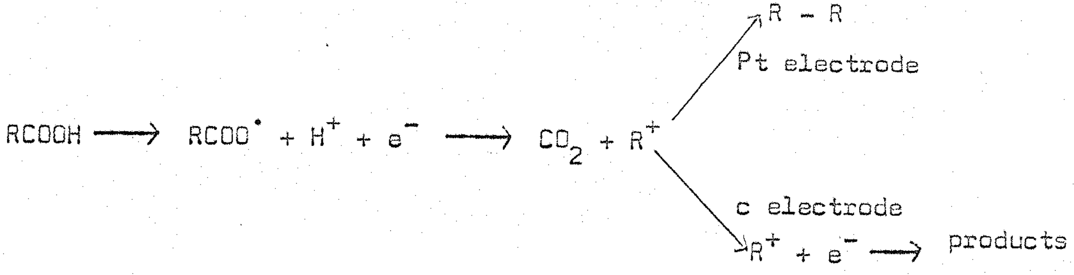
Organic Electrochemistry has existed as a branch of chemistry since the middle of the last century. At the turn of the century much interest was shown in the possibility of synthesising organic compounds by electrochemical methods. This work is summarised in a book by Fichter[1] which is in many respects a depressing volume as few of the electrochemical reactions described there are sufficiently selective for synthetic use. This was partly because the conditions under which the electrolyses were carried out e.g. electrode potential, pH, were not strictly controlled, and partly because the mechanism of the electrode process was not sufficiently understood to allow the choice of suitable operating conditions.

Since the mid 1920's many advances have been made in the study of organic electrode reactions using the technique of polarography-electrolysis at a dropping mercury electrode. Whilst this technique has provided an insight into the mechanism of electrode reactions, very little preparative work was done. This lack of data on products and yields of electrode reactions has contributed to a general lack of interest in organic electrochemistry in the past.

In more recent years the forecast of falling electricity prices has recreated interest in the possibility of large scale industrial electrosynthesis; and thus in organic electrochemistry. Modern developments in electronics has made it possible to build sophisticated electronic control and monitoring equipment. This, coupled with an understanding of reaction intermediates (derived from organic chemistry) and the development of an understanding of electrode kinetics, has caused the expansion of the subject in the past few years so that it is now possible to study quite complex reactions in detail.

Early workers in the field of organic electrochemistry believed that oxidations or reductions were performed by 'active oxygen' or 'active hydrogen' produced at the electrode. In recent years it has been shown that the active species involved are, in fact, the same active species which are involved in ordinary organic reactions e.g. carbanions, carbonium ions and various types of radicals. Several factors have been responsible for the recognition of these species, the principal one being the use of aprotic solvents such as acetonitrile, dimethylformamide and dimethylsulphoxide in which the intermediates have a much longer lifetime than in water. Of the methods used to identify these intermediates perhaps the most important are the various spectroscopic techniques - e.s.r. and u.v., visible and infra-red spectroscopy both of light reflected from the electrode and at transparent electrodes.[2,3,4,5.] Other powerful tools are the various electrochemical methods such as cyclic voltammetry and potential step methods as well as vastly improved analytical techniques which allow the identification of minor as well as major products.

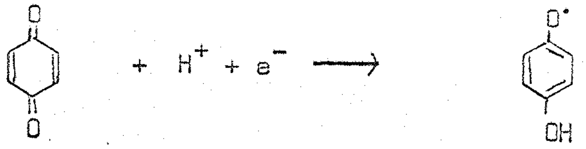
As the intermediates are produced at the electrode and have very short half lives they will remain in the vicinity of the electrode, or attached to it for the whole of their lifetime and thus their reactivity and reactions will be modified by the electrode. An example of this is the Kolbe reaction which gives different products on carbon[6,7,8.] and platinum[9] electrodes



Uncharged radicals are the active intermediates produced in many electrode reactions at both the anode and cathode, some illustrations of which are given below

$$RCOOH \longrightarrow R^{\bullet} + CO_2 + H^+ + e^- \qquad 9$$

$$Al(CH_3)_4^- \longrightarrow \dot{C}H_3 + Al(CH_3)_3 + e^- \qquad 10$$



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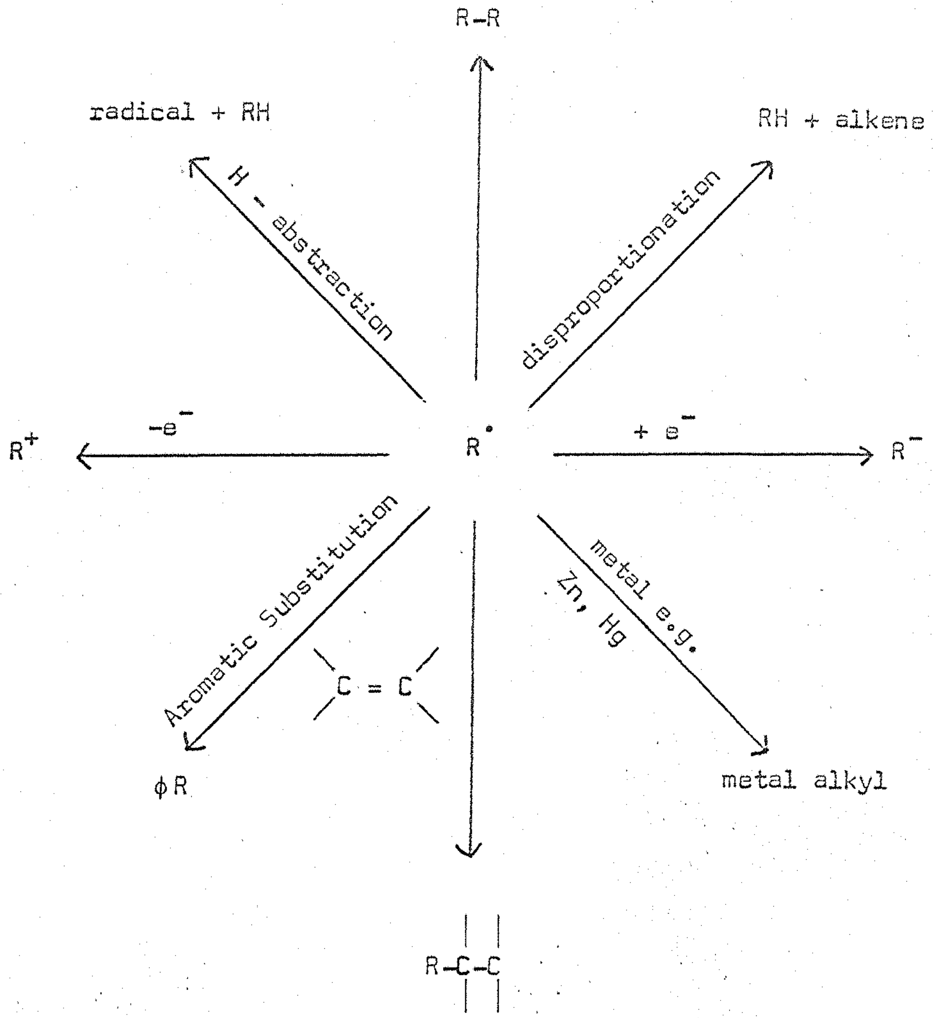
$$^-CH(COOEt)_2 \longrightarrow \dot{C}H(COOEt)_2 + e^- \qquad 12$$

$$\phi_2\ C{=}O + H^+ + e^- \longrightarrow \phi_2\ \dot{C}OH \qquad 13$$

$$\phi_4\ N^+ + e^- \longrightarrow \phi^{\circ} + \phi_3N \qquad 14$$

$$RI + e^- \longrightarrow R^{\bullet} + I^- \qquad 15$$

Most of these radicals are very reactive species and they can react in a number of ways, the principal way being shown in the diagram below



The most common mode of reaction, which is also a characteristic of reactions involving radicals, is dimerisation as is shown in the Kolbé reaction, the reductive dimerisation of acetone to give pinacol[13] and the formation of biphenyl from the reduction of tetraphenylammonium ions[14]. However, under carefully controlled conditions other products can be formed in good yields e.g.

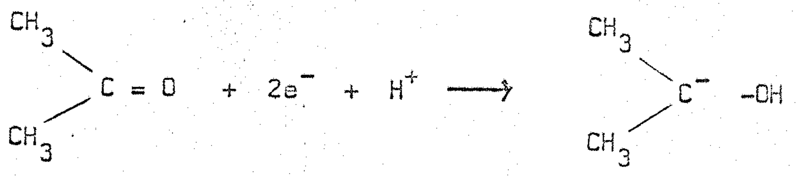
$$4RMgI \xrightarrow[\text{anode}]{Pb} 4e^- + 4Mg^{2+} + 4I^- + PbR_4 \qquad 16$$

$$\mathrm{RCOOH} \longrightarrow e^- + H^+ + CO_2 + R^\bullet \longrightarrow RCH_2CH = CH - \dot{C}H_2 \longrightarrow \mathrm{dimer} \qquad 17$$

although in all cases by products from competing reactions are observed. One of the most important factors controlling the path of reactions with radical intermediates is the concentration of radicals on the electrode surface, which will depend on the electrode potential, as a high surface concentration of radicals will favour dimerisation reactions. Other important factors controlling the path are the concentration of electroactive species - which affects the rate of formation of radicals - and the relative rates of the competing radical processes e.g. dimerisation and reaction with the solvent.

The other principal type of species is the charged intermediate - carbanions and carbonium ions. Carbanions, particularly those of the aromatic hydrocarbons, have been widely studied as aromatic hydrocarbons are easily reduced in aprotic solvents and polarographic techniques can be used to study the reactions. The ion most easily formed is a carbanion radical which, in the absence of proton donors is relatively stable and can be re-oxidised to the parent hydrocarbon;[18] on a longer timescale the carbanion radical will dimerise or disproportionate to a dianion. The dianion can then proton abstract from the solvent giving a dihydroaromatic product. Aliphatic carbanions are also common intermediates which are produced at more negative potentials than the corresponding radicals

$$RCl + 2e^- \longrightarrow R^- + Cl^- \qquad 15$$



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and the final product is usually produced by proton abstraction from the solvent. Thus ethyl chloride gives ethane and acetone gives isopropanol.

Carbon dioxide reacts with carbanions in a general reaction; for example the reduction of benzyl chloride in the presence of carbon dioxide gives phenylacetic acid[20]. Compounds, such as acrylonitrile, which contain an activated alkenic group can be reduced to form a dianion

$$CH_2 = CHCN + 2e^- \longrightarrow C^-H_2 - C^-HCN$$

$$CH_2 = CHCN + \bar{C}H_2 - \bar{C}HCN + 2H^+ \longrightarrow NCCH_2CH_2CH_2CH_2CN$$

which will react with a further molecule of acrylonitrile to give the hydrodimer, adiponitrile.[21] This reaction is the basis of the Baizer process for the production of adiponitrile. There are other examples (e.g. 1,3 butadiene[22] and α,β unsaturated acids[23]) which will reduce in the same way and it is also possible to form crossed hydrodimers[24].

It might be expected that, in an aprotic solvent, aromatic hydrocarbons would oxidise in two one electron steps to give a carbonium ion radical and a carbonium ion. However, cationic species are generally much less stable than the corresponding anionic species and although this simple behaviour is found in a few cases the most common mode of oxidation is an e.c.e. mechanism. In this mechanism an electron transfer is followed by a rapid chemical reaction, and then a further electron transfer. The first electron transfer step has been shown to be reversible using rapid scan cyclic voltammetry.[25] The products of the oxidation which have been reported are many and varied which is, perhaps, not surprising as the cation intermediates are very reactive. An important class of reactions which occur via carbonium ion intermediates is the substitution of aromatic compounds,[26] the general mechanism for which is

$$\phi H \longrightarrow \phi^+ + H^+ + 2e^- \xrightarrow{X^-} \phi X$$

where X is halogen, $-CN$, $-OCH_3$ or $-OCOCH_3$

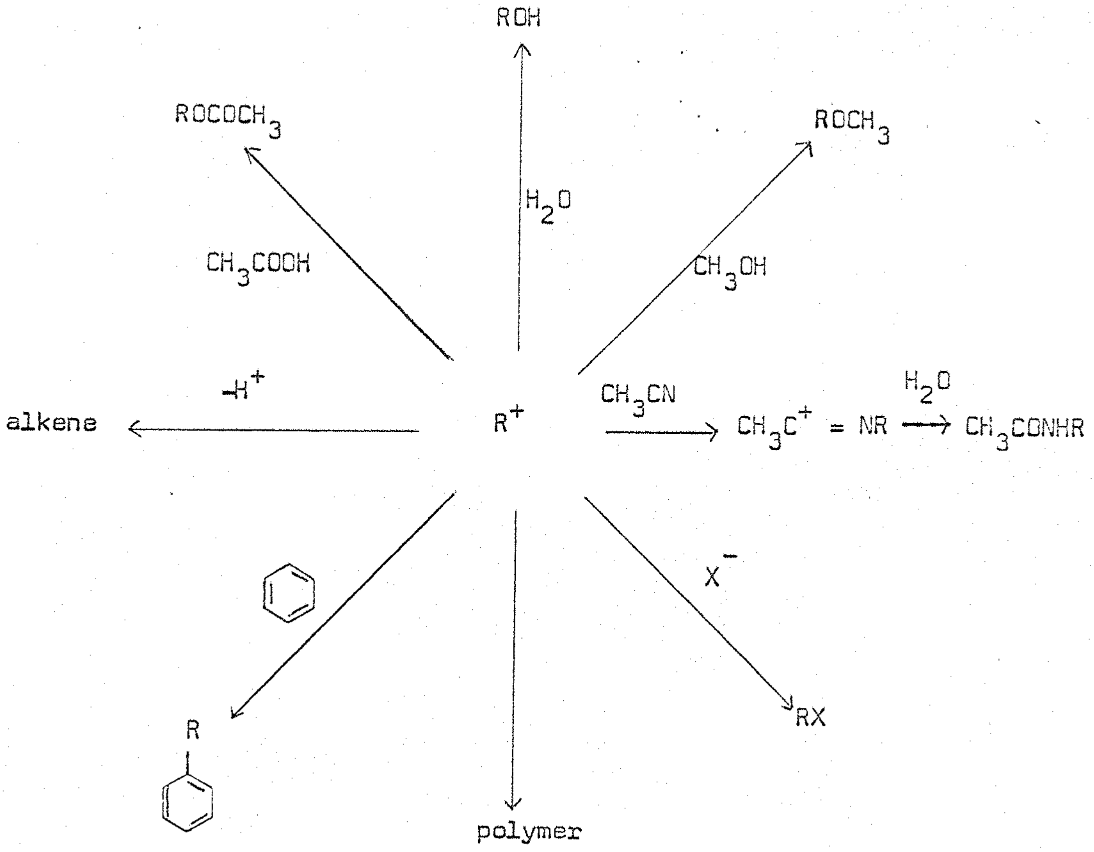
Aliphatic carbonium ions may be prepared by oxidising carboxylic acids,[27] alkyl iodides,[28] hydrocarbons[29] or primary amines[30]

$$RCO_2H \longrightarrow R^+ + CO_2 + 2e^- + H^+$$

$$CH_3I \longrightarrow CH_3^+ + I^+ + 2e^-$$

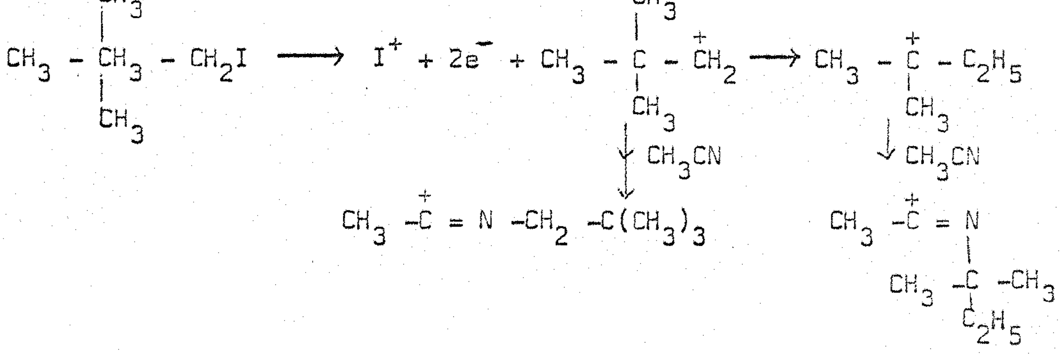
$$CH_2 = CH - CH_2R \longrightarrow CH_2 = CH - \overset{+}{C}HR + H^+ + 2e^-$$

$$RCH_2NH_2 \longrightarrow RCH_2\,N^+H_2 + e^- \longrightarrow R\overset{+}{C}H_2 + \dot{N}H_2$$

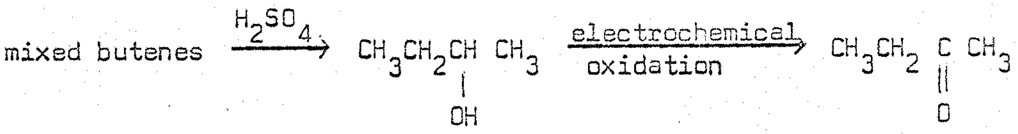


A summary of the probable reactions of aliphatic carbonium ions in common solvents is shown above.

Carbonium ions formed electrochemically show the same skeletal rearrangements as carbonium ions formed chemically. Thus, when neopentyl iodide is oxidised in acetonitrile N-tert-pentyl acetamide can be isolated as well as N-neopentyl acetamide.[28]



It can be seem from the foregoing paragraphs that while there has been much work done on aromatic hydrocarbons and activated aliphatic compounds, very little work has been reported on aliphatic hydrocarbons. Aliphatic hydrocarbons would be very useful starting materials for electro-organic syntheses as they are both plentiful and cheap. Although they may be oxidised to CO_2 in fuel cells they are difficult to partially oxidise to specific compounds. The partial oxidation requires electrodes which are catalytically inactive so that the compound is not dissociatively adsorbed as well as a high electrode potential to effect electron transfer from a compound with a high ionisation potential. The use of organic solvents is also necessary as hydrocarbons are only slightly soluble in aqueous solutions. At the present time there are only two electro-organic synthetic reactions in use with aliphatic hydrocarbons as starting materials, the oxidation of mixed butenes to ethyl methyl ketone;



$$\text{mixed butenes} \xrightarrow{H_2SO_4} CH_3CH_2\underset{\displaystyle OH}{\underset{|}{CH}}\,CH_3 \xrightarrow[\text{oxidation}]{\text{electrochemical}} CH_3CH_2\underset{\displaystyle O}{\underset{\|}{C}}\,CH_3$$

and the preparation of propene oxide from propene

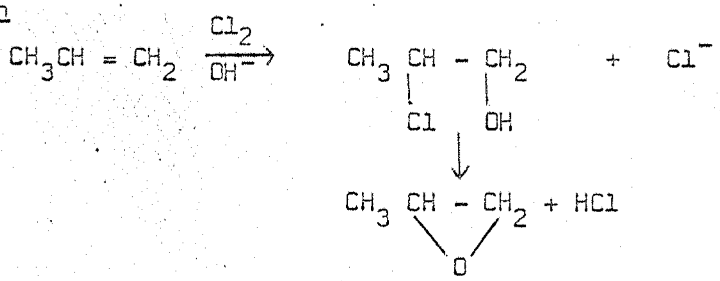
At Cathode

$$H_2O \longrightarrow \tfrac{1}{2}H_2 + OH^-$$

At Anode

$$Cl^- \longrightarrow \tfrac{1}{2}\,Cl_2$$

In Solution



$$CH_3CH=CH_2 \xrightarrow[OH^-]{Cl_2} CH_3\underset{Cl}{CH}-\underset{OH}{CH_2} + Cl^-$$

In order to overcome these two problems of low solubility in aqueous solution and high oxidation potential one may define four possible approaches:

1. Use a very stable non-aqueous solvent which is not oxidised even at the high potentials used e.g. acetonitrile, sulpholane or propylene carbonate. Studies[29,31] have been made of the oxidation of various hydrocarbons in acetonitrile; however the products which can be obtained are governed by the fact that the carbonium ion intermediate reacts rapidly with the solvent.
2. Use of very acidic solvents such as fluosulphonic acid and HF. Hydrocarbons are generally soluble in fluosulphonic acid and with the addition of acetic or propionic acid as a base electrolyte the dissolved hydrocarbons are readily oxidised electrochemically.[31] The products are complex involving reaction with the base electrolyte and their isolation involves destruction of the fluosulphonic acid.
3. Molten Salts. Using low melting point eutectics it has been shown that the chemical oxidation of aliphatic hydrocarbons is possible e.g.

$$Cu^{2+} + CH_4 \xrightarrow{Cl^-} CH_3Cl + Cu^+ + HCl$$

$$Cu^+ + HCl + O_2 \longrightarrow Cu^{2+}$$

and it is therefore possible that an electrochemical oxidation would be feasible.

4. In the case of olefins, their solubility in aqueous solution can be greatly increased by forming complexes with certain transition metal ions such as Pd(II)[32], Tl(III)[33], and Hg(II)[34] and these organometallic compounds could possibly be oxidised electrochemically. Very little is known about the electrochemical reactions of organometallic compounds although recently the reduction of Hg(II)-olefin complexes[35] and the oxidation of the tetraethyl aluminium[36] anion have been studied. Of the three metal ions which readily form complexes the Hg(II) system is perhaps the most interesting as the complexes which it forms are more stable towards thermal decomposition than those of palladium and thallium.

Hg(II)-olefin complexes have been widely studied since their discovery and characterisation by Hofmann and Sand at the beginning of this century. In general, when an olefin reacts with a mercuric salt substitution, oxidation, or addition can occur so that the products are often intractable, insoluble precipitates. Deniges[37] tried to tackle this problem in the late 19th century but it was not until several years later that Hofmann and Sand[38] set down the conditions for the formation of the simple olefin-mercuric salt adduct. They considered that addition of the mercuric salt had taken place across the double bond and they recognised two types of compound

$HOCH_2CH_2HgCl$ I

$O(CH_2CH_2HgCl)$ II

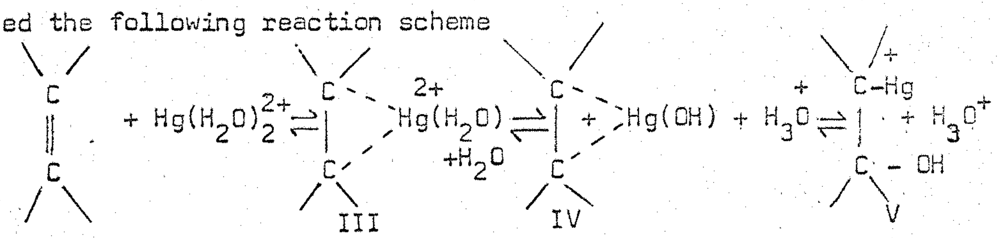
as well as other products resulting from substitution and polymerisation. These compounds represent an enigma as they react as simple co-ordination compounds towards strong ligands such as CN^- evolving ethylene, whereas towards organic reagents they react as substituted alkyl mercury compounds.

In 1914, Schoeller, Schrauth and Essers[39] showed that, in general, the solvent plays an important role in the addition reaction. Thus mercuric salts in an alcohol will react with olefins to produce a compound of the type

$$RO\,CH_2\,CH_2\,HgX$$

and more recently it has beem shown that similar reactions occur in glacial acetic acid[40], piperdine[41], and acetonitrile[42]. These compounds all show similar reactions to those of the complexes prepared by Hofmann and Sand.

Since 1950 much work has been done on the kinetics and mechanism of the reaction between olefins and mercuric ions in aqueous nitric and perchloric acid solutions. Brandt and Plum[43] have shown that the reaction between the di-aquo mercuric ion and olefin is bi-molecular, reversible and slightly faster in perchloric than nitric acid. They proposed the following reaction scheme



They were not able to demonstrate kinetically the presence of ions III and IV but assumed them to be present in small amounts. Ion V, it should be noted, has the same structure as I.

More recently Halpern and Tinker[44] have studied the reaction in perchloric acid for many olefinic compounds. They found the rate law to be

$$\text{Rate} \ \alpha \ \left[Hg^{2+}\right] \left[\text{olefin}\right]$$

over the range of $\left[H^{+}\right]$ between 10^{-1} and 10^{-3} molar. The rate was found to increase with increasing perchlorate ion concentration and was unaffected by hydrogen peroxide and oxygen. They found evidence that there was an intermediate with considerable carbonium ion character but could find no evidence that this was a π complex of the type III or IV although again the existence of this type of complex could not be ruled out, particularly in two limiting cases.

1. The formation of the π complex is the rate determining step. This is not inconsistent with the kinetic data but is very unlikely as most complexing reactions of mercury are almost diffusion controlled - much faster than the observed rate.

2. The formation of the π complex is a pre-equilibrium followed by a rate determining rearrangement involving water. This is much more probable as, although no Michaelis-Menton fall off in the first order dependence an olefin concentration is detected, the upper limits on equilibrium constants is consistent with the values of formation constants observed for Silver I-olefin complexes.

Further evidence for the structures of the complexes existing in aqueous solution comes from the analysis of the products of the thermal decomposition of the complexes. This reaction was first observed by Deniges[45,46] and has recently been studied in detail by Fielding and Roberts[47] in this country, and Metzger and co-workers in France[48,49,50]. The principal products of the reaction result from an oxidation in the allylic position with retention of the double bond. Thus mercury II - propene complex would give principally acrolein with small amounts of acetone and propionaldehyde[47,48]

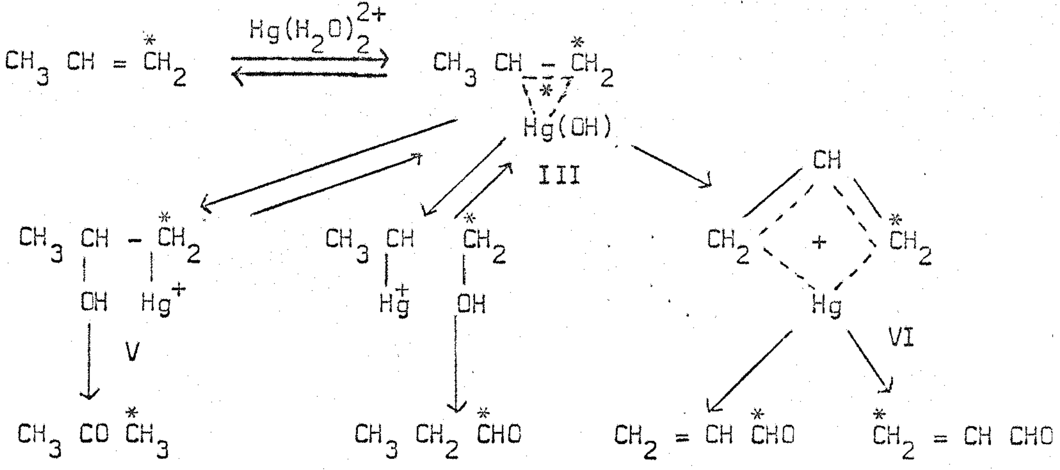
$$(CH_2 = CH - CH_2)\ Hg^{2+} \longrightarrow CH_2 = CH - CHO$$

The reaction is very specific with, under favourable conditions, 85% of the propene being converted to acrolein. Other α-olefins react similarly[47,49] but β olefins seem to oxidise with loss of the double bond e.g. but-2-ene gives mostly methyl ethyl ketone[49].

In order to try to elucidate the mechanism of the reaction Strini and Metzger[48] performed an experiment in which the methylene group of the propene was labelled with C^{13}. They found that propene regenerated from the solution had the label undisturbed and the labels on the other products were distributed as follows

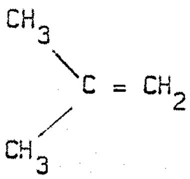
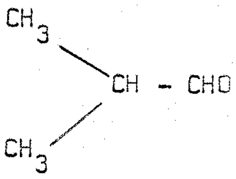
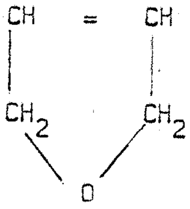
$$CH_3\ CO\ \overset{*}{C}H_3 \qquad CH_3\ CH_2\ \overset{*}{C}HO \qquad \left.\begin{array}{r} CH_2 = CH - \overset{*}{C}HO \\ \text{and } \overset{*}{C}H_2 = CH - CHO \end{array}\right)\ \begin{array}{l}\text{equal}\\ \text{amounts}\end{array}$$

This led them to propose the following mechanism

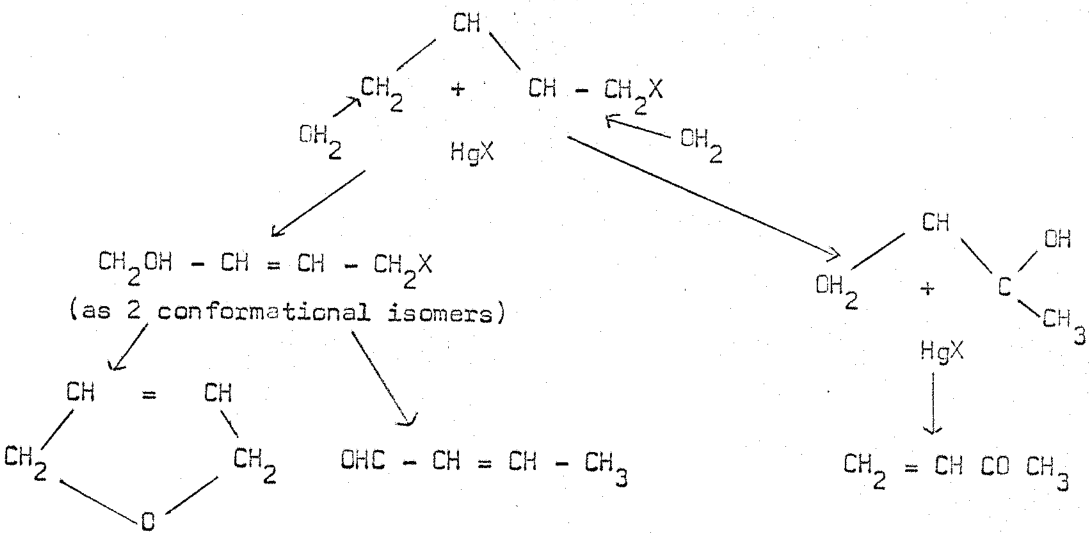


To explain the even distribution of label in the acrolein they had to introduce a symmetric intermediate VI - a π-allyl complex but to explain the other products the π and σ complexes (III and V), as suggested by other workers are adequate. The reaction involving the formation of the π-allyl complex from the π complex (III ⟶ VI) must be assumed to be irreversible and require a high temperature if labelled propene is to be recovered unchanged from a solution of propene in a mercuric salt. The existence, if only in small amounts, of the π complex (III) is however essential to this reaction scheme to provide a "link" between the other reacting species.

The products obtained from the thermal decomposition - mostly unsaturated aldehydes as can be seen from the table - make this reaction potentially interesting commercially.[48,49,50]

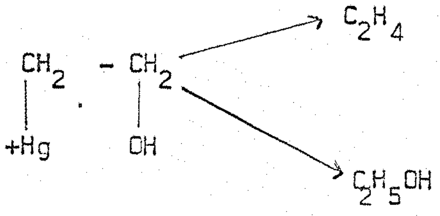
Olefin	Major Product	Minor products all < 10%
$CH_3\ CH = CH_2$	85% $CH_2 = CH\ CHO$	CH_3COCH_3 $CH_3CH_2\ CHO$
$CH_3\ CH_2\ CH = CH_2$	70% $CH_3\ COCH = CH_2$	$CH_3COCH_2CH_3$ $CH_3CO\ CO\ CH_3$ $CH_3CH_2CH_2CHO$ $(CH_3)_3\ COH$
$CH_3CH = CH\ CH_3$	50% $CH_3COCH_2\ CH_3$	$CH_3CO\ CH = CH_2$
	55% $(CH_3)_3\ COH$	
$CH_2 = CH - CH = CH_2$	40% $CH_3\ CO\ CH = CH_2$ 40% 	$CH_3\ CO\ COCH_3$ $CH_3\ CH = CH\ CHO$

Butadiene[50] is an interesting case as only one double bond is attacked and a considerable amount of product appears as an expoxide. These products can, however, all be explained using the mechanism outlined above as resulting from hydrolysis of a complex similar structure to (VI)

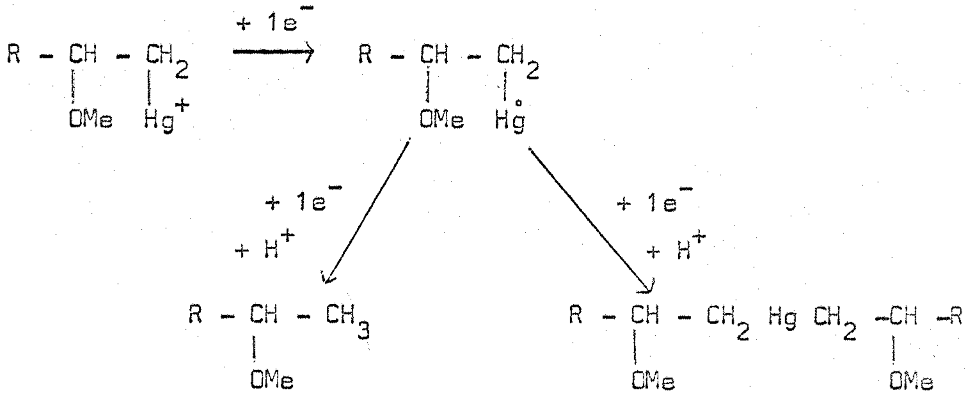


The general reaction which has been outlined above has commercial possibilities if the inorganic product - a sludge of metallic mercury and insoluble Mercury (I) salts - can readily be reoxidised to Mercury (II) in solution i.e. if the mercury can be used as a "catalyst" whose purpose is to dissolve the olefin and direct the course of the reaction. This cannot be done using oxygen and a catalyst as is done with the palladium (0) - palladium (II) complex in the Wacker process (redox potentials are for oxygen in acid solution +0.81v. for $Hg^0 \longrightarrow Hg^{II}$ +0.85v and for $Hg^I \longrightarrow Hg^{II}$ +0.91v) but this system does not appear to have been studied. Another method of reoxidising the mercury sludge which has been investigated is the use of an electrochemical method[51]. However is has been shown that a process based on this method would not be commercially viable.

Thus at the present time the structures[52] and thermal decomposition reactions of mercury olefin complexes have been thoroughly investigated. The electrochemical oxidation of these complexes has not, however, been studied although their electrochemical preparation and reduction has been investigated. It is possible to prepare the complexes by polarising a mercury electrode anodically in aqueous acid in order to produce mercuric ions which will then complex with any olefin which is present[53]. It is possible to reduce mercury-olefin complexes at a mercury cathode to give varying products according to potential and solvent. In aqueous solution at low potential the olefin is regenerated but at higher potentials an alcohol is formed[54]



while in a methanol - water mixture the reaction proceeds via two distinct 1-electron steps to give first of all a radical and then either an ether or a dimer[35].



From this summary of previous work it can be seen that very little work has been reported on the oxidation of aliphatic hydrocarbons and in particular there are no reports of the direct partial electrochemical oxidation in aqueous solution. The realisation of such reactions in aqueous solution is difficult because of the limited solubility of hydrocarbons in water. The particular system chosen was therefore one in which the hydrocarbon was made soluble by complexing with a metal ion. There has been no work reported on the electrochemical oxidation of such complexes and the aim of the work in this thesis was therefore to investigate the products and mechanism of such reactions in aqueous media.

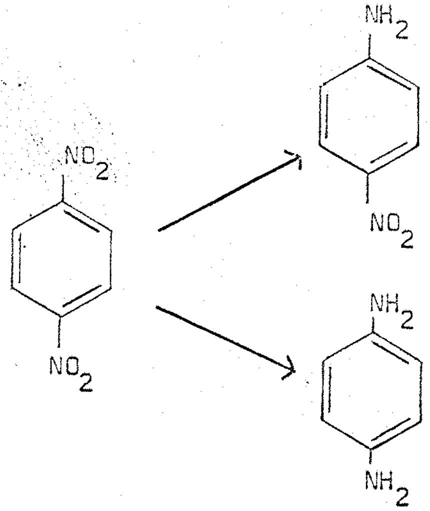
Techniques and Experimental

The potentiostatic Technique

As can be seen from the previous chapter a very large number of organic compounds can be made by electrolysis. The factors which affect an electrochemical reaction are:

1) Electrode potential
2) Solvent
3) Electrolyte
4) pH
5) Mass Transfer
6) Temperature
7) Pressure
8) Electrode material
9) Concentration of electro-active species

The factor which distinguishes an electrode reaction from other types of reaction is that the potential of the electrode, and thus the energy which is introduced into the reactants, may be carefully controlled. This allows electrode reactions to be very selective in the products obtained. Thus p-dinitrobenzene may be reduced either to p-diaminobenzene by using a very low potential, or only partially reduced, at a slightly less negative potential, to p-nitroaniline.[55]



If electrode reactions were controlled only by thermodynamic criteria, i.e. all steps in the reactions were fast, the importance of the electrode potential could readily be understood since it is related to the free energy change in a reaction by the equation

$$\Delta G^{o} = -nFE^{o} \tag{1}$$

where n is the number of electrons transferred in the reaction

F is the Faraday

E^{o} is the standard electrode potential of the reaction.

Since it is possible to perform electrode reactions over a potential range from approximately + 3.5 volts to -2.5 volts, even in aqueous solution if suitable electrolytes (e.g. perchlorates for oxidations and quaternary ammonium salts for reductions) are chosen, a driving force of some 250 KJ mole^{-1} is available. Spontaneous chemical reactions using air as oxidant or hydrogen as reductant are limited (in electrochemical terms) to the potential range between the reduction of oxygen and the oxidation of hydrogen, and this driving force amounts to roughly 40 KJ mole^{-1}. Thus electrochemistry allows larger amounts of energy - comparable to the energies of chemical bonds - to be introduced into molecules at room temperature.

An electrode reaction which is controlled only by thermodynamics is known as a reversible reaction and the current-potential curves are given by the Nernst equation e.g. for the reaction

$$A \rightarrow B + e^-$$

$$E = E^o + \frac{RT}{nF} \ln \frac{C_A}{C_B} \qquad (2)$$

$$\text{i.e.} \quad \eta = E - E^o$$

$$= \frac{RT}{nF} \ln \frac{C_A}{C_B}$$

$$\text{or} \quad C_A = C_B \exp \frac{nF}{RT} \eta \qquad (3)$$

where η is the overpotential

C_A, C_B the concentrations of the species A & B which are taken as a measure of the activities of the species

R - gas constant

T - absolute temperature

E^o, n, F as defined in equation (1)

However, many reactions are, in fact, slow and thus it is not correct to compare this available driving force to the standard free energy change. Instead the rate constants must be estimated. A difference in electrical potential ϕ exists between an electrode surface and the surrounding solution so that in transferring a charge of nF coulombs mole^{-1} an amount of work $\alpha nF\phi$ can be done, where α $(0 < \alpha < 1)$ is the transfer coefficient. Thus the rate of the simple electrode reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + e^-$$

is given by

$$\text{Rate} = nk_1\ C_A \exp \frac{\alpha nF}{RT}\phi\ - nk_{-1}\ C_B \exp \frac{(1 - \alpha)\ nF}{RT}\phi$$

and thus the current is

$$i = i_{\text{forward}} - i_{\text{back}}$$

$$= nF\ k_1\ C_A \exp \frac{\alpha\ nF}{RT}\phi - nF_{k-1}\ C_B \exp \frac{(1-\alpha)nF}{RT}\phi$$

If the overpotential $\eta\ (= \phi\ - E^o)$ is high then $i_{\text{forward}} >> i_{\text{back}}$

$$\text{Thus}\quad i = nF\ k_1\ C_A \exp\frac{\alpha\ nF}{RT}\ (E^o + \eta)$$

and taking logarithms

$$\ln_i = \ln\ (nF\ k_1\ C_A) + \frac{\alpha\ nF}{RT}\ E^o + \frac{\alpha\ nF}{RT}\ \eta$$

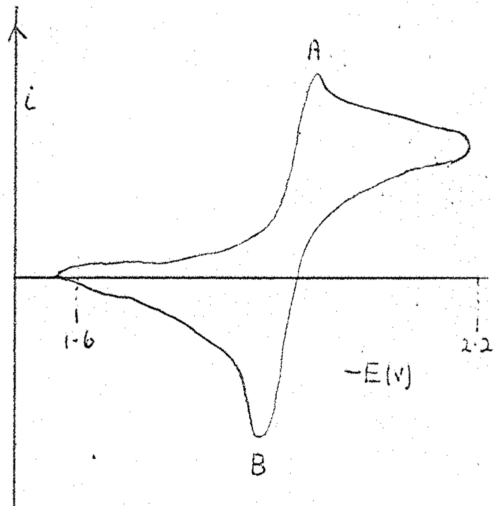
$$= A + B\eta$$

This is known as the Tafel equation.

However, as well as electron transfer, a typical electrode reaction also involves diffusion of the reactive species to the electrode and the product away from the electrode. Thus at high overpotentials, where the electron transfer step is fast, diffusion becomes the slow rate controlling step.

A study of steady-state current-potential curves gives information about the slow step in the reaction. The linear portion of a plot log i against η gives information about the kinetics of the electron transfer i.e. k_1 and α, and the limiting value of the current gives, in the simplest case, information about diffusion. However, a chemical reaction controlling the production of the electroactive species may cause the value of the limiting current to be lowered. A series of plots of log i against η for different concentrations of the electroactive species will give information about the order of the reaction.

It is possible to obtain all of this information, and more, by applying various potential-time profiles to the working electrode. If a triangular profile of high sweep rate (0.1 - 1000 v sec^{-1}) is applied the current-potential curve may be recorded oscillographically. This technique - which is known as cyclic voltammetry - can be used to obtain the same information as is obtained from steady state plots i.e. k_1, α and data about diffusion and preceding chemical reactions. Furthermore the presence of intermediates produced in the forward sweep can be detected on the reverse sweep. An example of this is shown on the right for the reduction of anthracene. On sweeping to negative potentials a peak A is obtained where



Cyclic voltammogram of anthracene in acetonitrile the anthracene is reduced to the radical anion and on sweeping back to more positive potentials another peak B corresponding to the re-oxidation of the radical anion is obtained. If the radical anion, or other intermediate, has reacted to any extent then the number of coulombs in peak B will be considerably less than that passed in peak A and lack of any reverse peak at B would indicate that the intermediate had a very short lifetime.[58] Thus information can be obtained about the rate of reaction of intermediates with the solvent or other species present and, in fact, peaks may sometimes be observed on the cyclic voltammogram which can be identified as corresponding to the reduction or oxidation of the products of these reactions.

Other potential-time profiles which are useful are those in which a single potential step or a combination of potential steps is applied to the electrode. A single potential step will give a current-time transient the initial part of which will give the rate of the electron transfer step, and the whole of the transient the rate of diffusion or of the preceding steps.[59] If a double potential step - first of all producing, and then removing an intermediate - is used the kinetics of a following chemical reaction in which the intermediate is involved may be determined[60].

The Potentiostat

In order to control the potential of an electrode an electronic regulator called a potentiostat is used. This measures - using a high impedance system - the potential of the working electrode with respect to an unpolarised reference electrode and compares this potential with a reference potential. By using an amplifier the difference in these potentials is used to control the current passed between the working and counter electrodes in the cell, thus adjusting the potential of the working electrode to be close to the reference potential. The reference potential may be set at any value manually using a potentiometer or varied as a function of time by using an electronic function generator. The current flowing through the cell is measured by monitoring, using a meter, pen recorder or oscilloscope, the voltage developed across a resistor connected in series with the counter electrode.

Apparatus

All electrolyses and electrochemical measurements were carried out using Chemical Electronics valve or type T70/2A transistorised potentiostats. These are fast response machines with rise times of the order of 1μsec the valve instrument having a maximum output of 1.5 amps at 150 volts and the T70/2A a maximum output of 2 amps at 70 volts. A Chemical Electronics wave form generator type RB1 and a motor driven linear sweep generator (for very slow linear sweeps) from the same company were used to supply the potential-time profiles used. Currents were recorded using Telequipment type D53 or Tektronix type 545A oscilloscopes or a Telsec 700 y - t recorder

The three compartment cell which was used for all measurements (Fig I) has working and secondary electrodes separated by an anion exchange membrane - Permaplex type A20 which is permeable to anions but not to the organic products or mercuric ions. A platinum foil secondary electrode was used and smooth platinum wire or gauze was used to give working electrodes of different surface areas. The reference electrode was separated from the working electrode by a Luggin capillary and tap and was connected to the main cell body with a syringe joint so that its position relative to the working electrode could be easily adjusted. The reference electrode consisted of a silver wire dipping into a 10^{-2} M solution of silver ions in 2M perchloric acid which has a potential of + 700 mV v.s. N.H.E. All potentials in this thesis are quoted against this electrode.

Current-Potential curves

For each olefin current-potential curves were obtained over the range +0.3 to +3.0 volts using a sweep rate of 150 mV min^{-1}, the currents being recorded on a Telsec 700 y - t recorder. These were then replotted in the form log I v.s. potential. Solutions which were 0.01M, 0.03M, 0.1M, 0.3M and 1M in the complex were used and in all cases the solutions were 1M in perchloric acid. Sodium perchlorate was added to keep the total perchlorate ion concentration constant as the current-potential curve for the inert base electrolyte varies with perchlorate ion concentration.

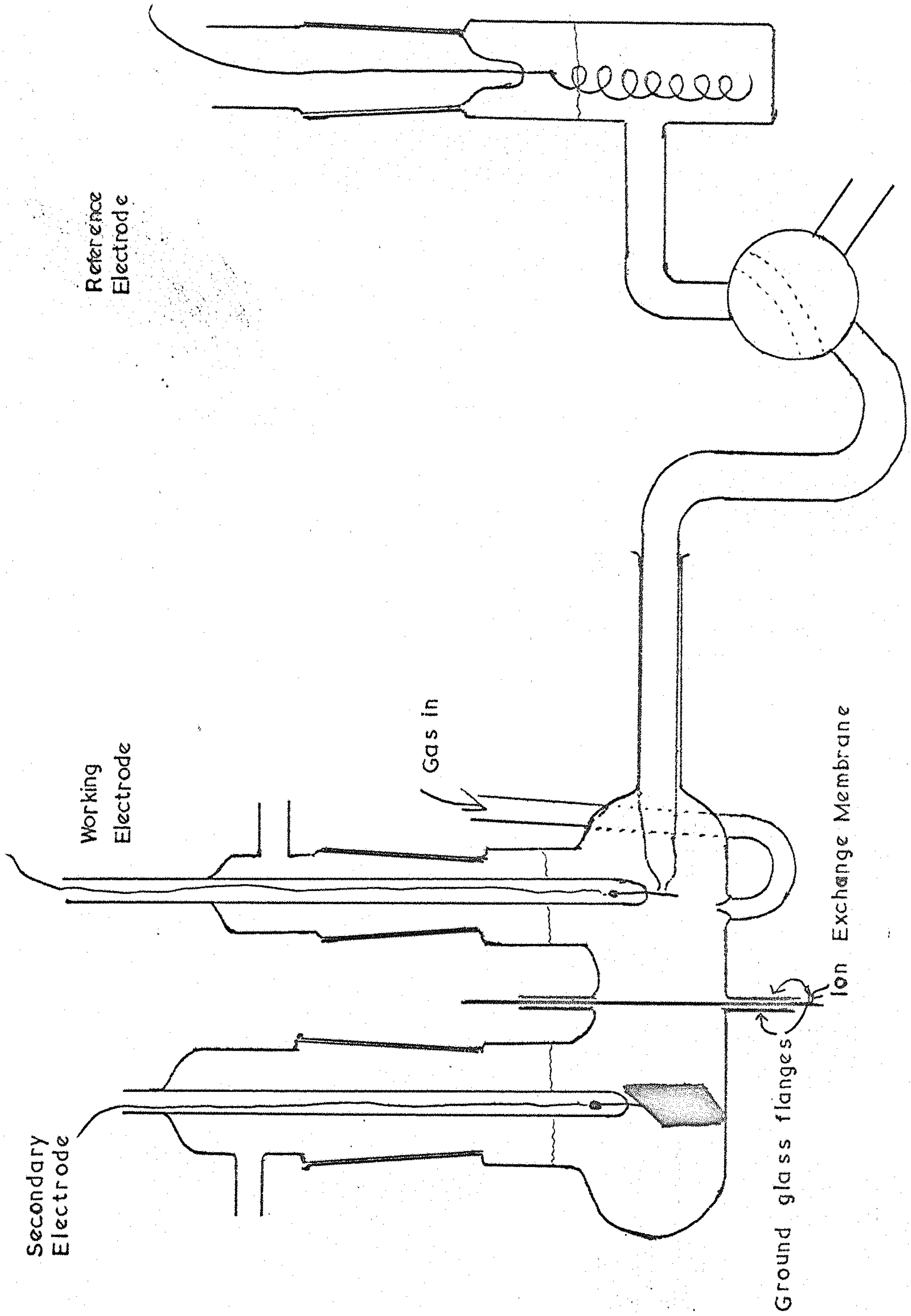

Reference Electrode
Working Electrode
Gas in
Ion Exchange Membrane
Ground glass flanges
Secondary Electrode

Figure I

Controlled Potential Electrolyses

Controlled potential electrolyses were carried out at various potentials using the cell described above. The working electrode compartment was filled with a known volume of a solution of the mercury-olefin complex (1M in complex, 1M in perchloric acid) and a gentle stream of the olefin (or nitrogen saturated with the olefin in the case of liquid olefins) passed through during the course of the electrolysis. This stirred the solution in the working electrode compartment and recomplexed any free mercuric ion which was formed. The size of the working electrode was chosen to keep the current through the cell below 150 - 200 mA as higher currents caused heating of the contents of the cell. Wherever possible electrolyses were carried out until about 1000 coulombs had been passed.

Cleaning of glassware

The cell and all glassware used for the preparation of solutions or analysis of the organic products was cleaned by first of all soaking for ½ hour in a concentrated solution of potassium hydroxide in alcohol. The glassware was then rinsed with triply distilled water, soaked for a short while in a mixture of 50% concentrated nitric acid and 50% concentrated sulphuric acid and then rinsed and allowed to soak in triply distilled water for several hours before drying.

Materials

Water All solutions were prepared with triply distilled water which was prepared as follows: water from a metal still was first of all distilled from very dilute, alightly alkaline potassium permanganate and then from very dilute phosphoric acid in all-glass apparatus. The water was stored in securely stoppered glass flasks until used.

Perchloric acid B.D.H. 72% 'Analar' grade acid was used without further purification. Other acids used were also B.D.H. 'Analar' grade.

Mercuric Perchlorate was prepared by dissolving G.P.R. yellow mercuric oxide in the minimum amount of 30% - 40% perchloric acid (excess acid was always present) and crystallising the mercuric perchlorate after removing excess water on a rotary evaporator. The mercuric perchlorate was difficult to crystallise and as it is very soluble in water no recrystallisations were attempted. It was dried at room temperature in a vacuum oven. This procedure is reported to give the hydrate $Hg(ClO_4)_2\ 4H_2O$.[61] Care had to be taken in handling the solid as it is deliquescent.

Sodium Perchlorate was prepared from 'Analar' Sodium carbonate and perchloric acid. It was recrystallised from water and dried in a vacuum oven at room temperature. The solid obtained was the monohydrate $NaClO_4\ H_2O$.

Olefins gaseous and liquid olefins were all used as supplied without further purification.

Ethylene and Propylene were Matheson C.P. grade supplied by Cambrian Chemicals.

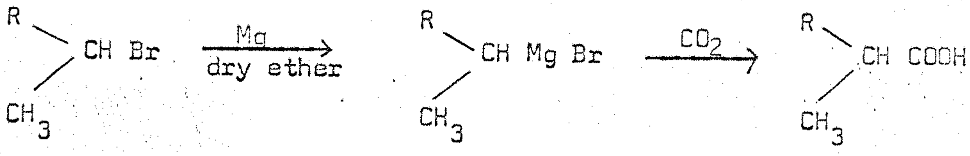
Isobutene, butadiene, 1-octene and cyclohexene were B.D.H. reagent grade.

1-butene and 2-butene were supplied by I.S.R. Ltd.

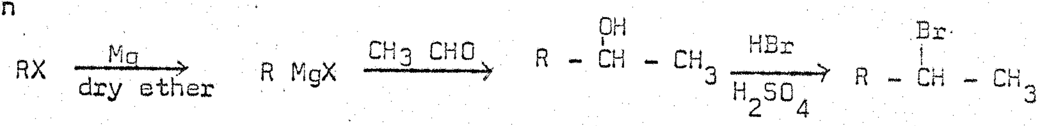
All other olefins were supplied by Koch Light Laboratories Ltd.

The chemicals used as standards in the analysis were supplied by B.D.H. Ltd or Koch Light Laboratories Ltd; or prepared by standard techniques

Substituted acetic acids of the type $R - \overset{\overset{\displaystyle CH_3}{|}}{CH} - COOH$ were prepared from the secondary alkyl bromide via a Grignard reaction



In some cases the secondary alkyl bromide had, itself, to be prepared from a primary alkyl halide and acetaldehyde, again via a Grignard reaction



$$RX \xrightarrow[\text{dry ether}]{Mg} R\,MgX \xrightarrow{CH_3\,CHO} R - \overset{\overset{\displaystyle OH}{|}}{CH} - CH_3 \xrightarrow[H_2SO_4]{HBr} R - \overset{\overset{\displaystyle Br}{|}}{CH} - CH_3$$

Analysis

Both qualitative and quantitative analysis was carried out by vapour phase chromatography on a Pye 104 dual column chromatograph using flame ionisation detectors. Initially qualitative analysis was carried out using I.R., N.M.R. and mass spectrometry following preparative scale vapour phase chormatography. However once the general pattern for the reaction had been established the products were identified by their V.P.C. retention times with certain checks using a V.P.C. – mass spectrometer combination (Pye 104 chromatograph and A.E.I. MS.12 mass spectrometer)

Quantitative analysis involved taking a 0.5 ml sample (increased to 1 ml in some cases where only a small number of coulombs had been passed) of the electrolysis solution and distilling the solution at 35 – 40°C under vacuum, the distillate being collected in a liquid nitrogen cooled receiver. The distillate was then transferred to a 1 ml volumetric flask and made up to the mark. The products were then analysed by vapour phase chromatography, two different column packings being used. Aldehydes and ketones were analysed on a 9 foot column of 25% polypropylene glycol on 60/80 mesh celite at temperatures between 60 and 80°C and acids on a 9 foot column of 10% polyethylene glycol adipate, 1% phosphoric acid on 60/80 mesh celite at temperatures between 80 and 120°C. In each case the analyses was carried out isothermally, the temperature required increasing with the increasing molecular weights of the products, using a carrier gas flow rate of

60 mls/min of nitrogen. Two acids could not be determined this way - adipic acid and formic acid.

Adipic acid was determined by distilling the whole cell solution, extracting the distillate with ether and then esterifying with diazo methane. The methyl ester obtained was then analysed by vapour phase chromatography.

Formic acid was determined, in the cases of ethylene and propylene only, by distilling the whole cell solution. This distillate was then treated with excess sodium carbonate and the solution evaporated to dryness on a rotary evaporator. The solids left - consisting of sodium carbonate and the sodium salts of the organic acid products - were then redissolved in water and reacted with an excess of standard potassium permanganate at a temperature of 100°C for a few minutes. Under these conditions only formic acid is oxidised quantitatively, other organic acids not reacting at all with the permanganate. The manganese dioxide formed was then filtered off and the amount of permanganate left determined, after acidification by a back titration method using oxalic acid. The amount of formic acid present was calculated assuming the oxidation by permanganate to be a 2 electron process.

Electrochemical behaviour of the base electrolytes

Polarisation curves were run for various concentrations of the three acids which were used as base electrolytes to discover any effects - such as the dependance of current on anion concentration - which would have to be allowed for in subsequent experiments involving the mercury-olefin complexes. The three acids studied, corresponding to the anions used in experiments on the complex, were perchloric, nitric and sulphuric acids.

Perchloric acid

Polarisation curves for various concentrations of this acid are shown in Fig.II. They show two distinct 'Tafel' regions, the first from 1.2 to 1.6 volts may be attributed to oxygen evolution, while a second starts at 2.3 volts. In the intervening region (1.6 to 2.3 volts) the current decreases rapidly with increasing perchlorate ion concentration indicating inhibition of oxygen evolution by strong adsorption of perchlorate ions[62]. Beck and Moulton[63] showed that the limiting current in this region was the same on both rotating and stationary electrodes from which they deduced that the limiting current was not the result of a diffusion controlled electrode reaction but was produced by the adsorption of perchlorate ions. Since the potential had to increase to a point where perchlorate ions could be discharged before the current could increase, a limiting current region in the polarisation curve is observed. The principal electrode reaction in the two 'Tafel' regions is the oxidation of water to give oxygen. The

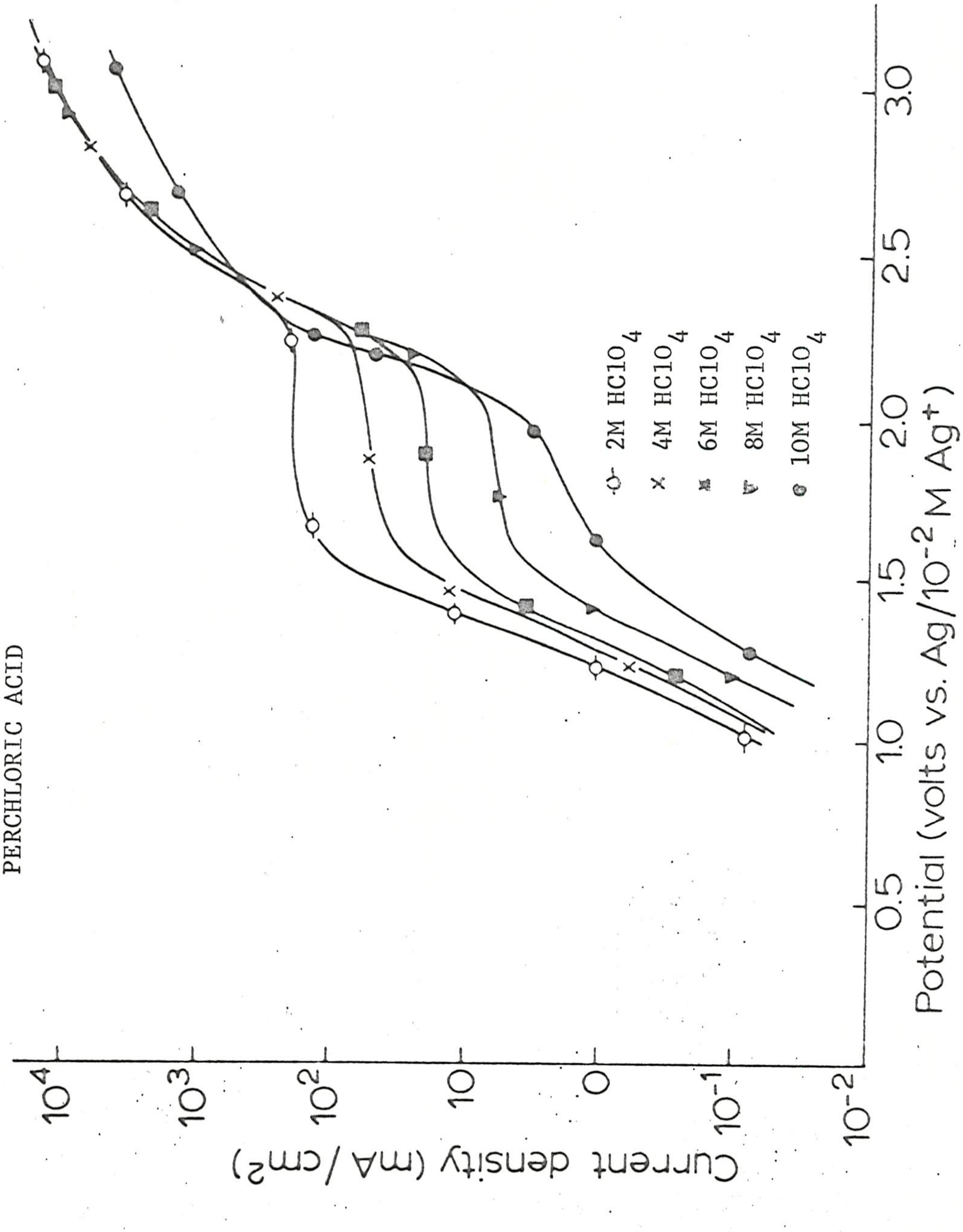

PERCHLORIC ACID
2M HC10$_4$
4M HC10$_4$
6M HC10$_4$
8M HC10$_4$
10M HC10$_4$
Current density (mA / cm^2)
10^{-2}
10^{-1}
0
10
10^2
10^3
10^4
Potential (volts vs. Ag/10^{-2} M Ag$^+$)
0.5
1.0
1.5
2.0
2.5
3.0

Figure II

mechanism of this reaction, however, varies between the two Tafel regions, as has been shown by isotope studies using labelled $HCl^{18}O_4$.[64,65] No ^{18}O enrichment of the oxygen evolved was found in the lower 'Tafel' region (between 1.2 and 1.6 volts) indicating that the mechanism is probably the direct oxidation of water at the electrode. In the upper Tafel region (above 2.3 volts) ^{18}O enrichment of the evolved oxygen was observed indicating that the perchlorate ion takes part in the oxidation of water. At these high potentials chlorine dioxide and chlorate ions are observed in solution and small amounts of ozone are evolved indicating that the reactions occurring in this region are complex. It has been shown[66] that as the temperature of the perchloric acid is lowered greater current yields of ozone are obtained, these being at an optimum value of about 50% when working with a refrigerated anode in a perchloric acid/water eutectic at -50°C.

Thus it is important, because of the large effect of the concentration of perchlorate ions on current to ensure that all polarisation curves are obtained using solutions having a constant perchlorate ion concentration.

Sulphuric acid

As can be seen from Fig III, the polarisation curves for sulphuric acid are very similar to those for perchloric acid. The polarisation curves again show two distinct Tafel regions, one from 1.2 to 1.9 volts which can, as in the case of perchloric acid be attributed to oxygen evolution, and a second commencing at 2.4 volts.

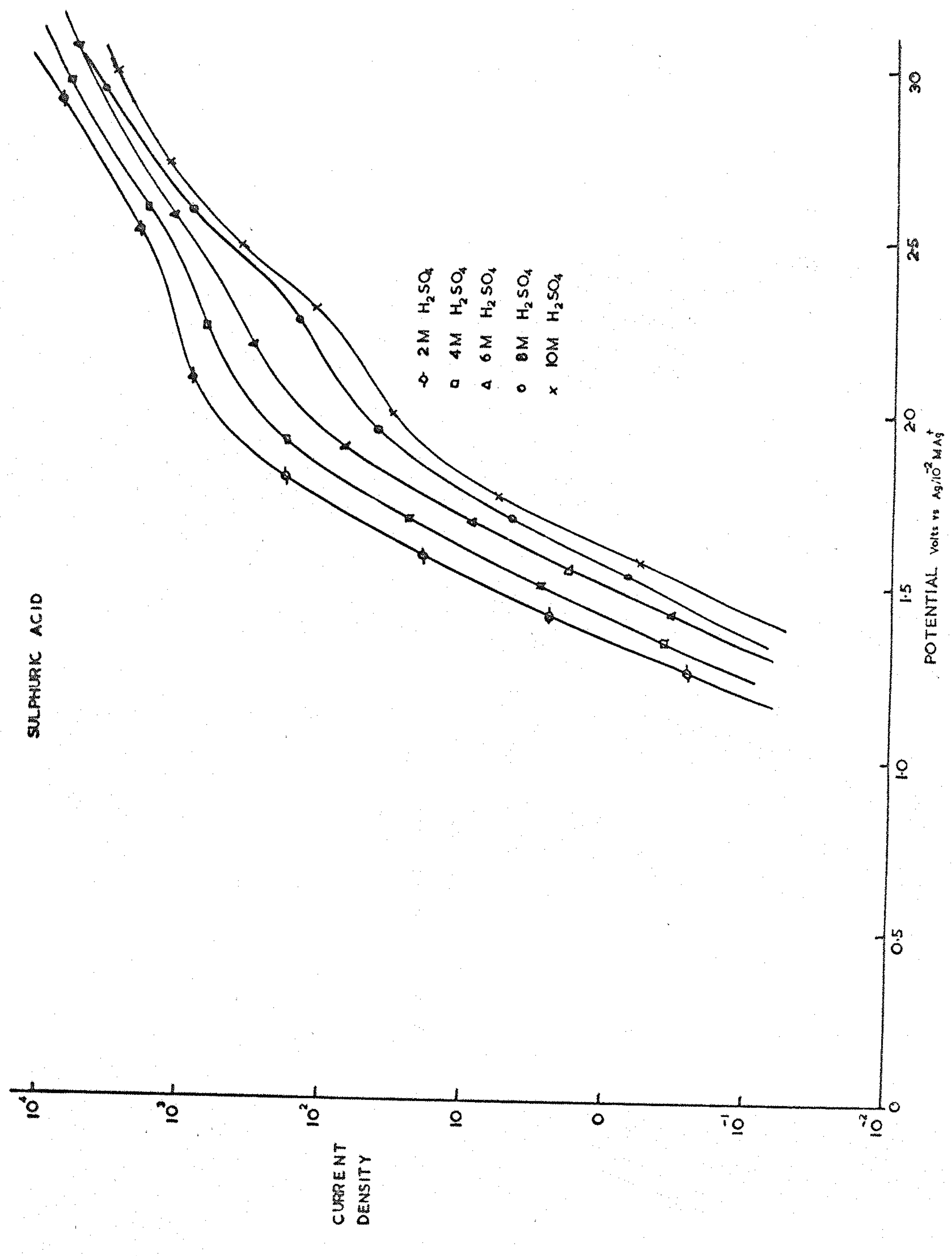

SULPHURIC ACID
CURRENT DENSITY
10^4
10^3
10^2
10
0
10^{-1}
10^{-2}
0
0.5
1.0
1.5
2.0
2.5
3.0
POTENTIAL Volts vs $Ag/10^{-2} M Ag^+$
2 M H_2SO_4
4 M H_2SO_4
6 M H_2SO_4
8 M H_2SO_4
10 M H_2SO_4

Figure III

In the intervening region (1.9 to 2.4 volts) the current decreases with increasing sulphate ion concentration indicating possible adsorption of the sulphate ion. This effect seems, however, to be less marked than is the case with perchlorate. In the second Tafel region above 2.4 volts the reactions occurring are much more complex than is the case in perchloric acid, as the sulphate ion is more readily oxidised than the perchlorate ion. Much of the current in this region is due to oxygen evolution but there is some production of peroxymono - and peroxydi - sulphate[67,68], both of which are themselves powerful oxidising agents. Once again the importance of working in solutions of constant sulphate ion concentration is shown because of the effect of sulphate ion concentration on the current in certain regions.

The silver - silver ion reference electrode which is used in perchlorate and nitrate solutions cannot be used in sulphate as silver sulphate is insoluble. The reference electrode which was used was a mercury-mercurous sulphate electrode in saturated potassium sulphate solution. This electrode has a potential of +680 m.V. vs. the N.H.E. The potentials quoted in the sections on oxidations in solutions containing sulphate ions are corrected to the silver-silver ion scale so as to be directly comparable with the potentials in solutions containing perchlorate and nitrate ions.

Nitric acid

The behaviour of nitric acid, as can be seen from the polarisation curves in Fig.IV, is quite different to that of perchloric and sulphuric acids. Except for the low concentrations of nitric acid

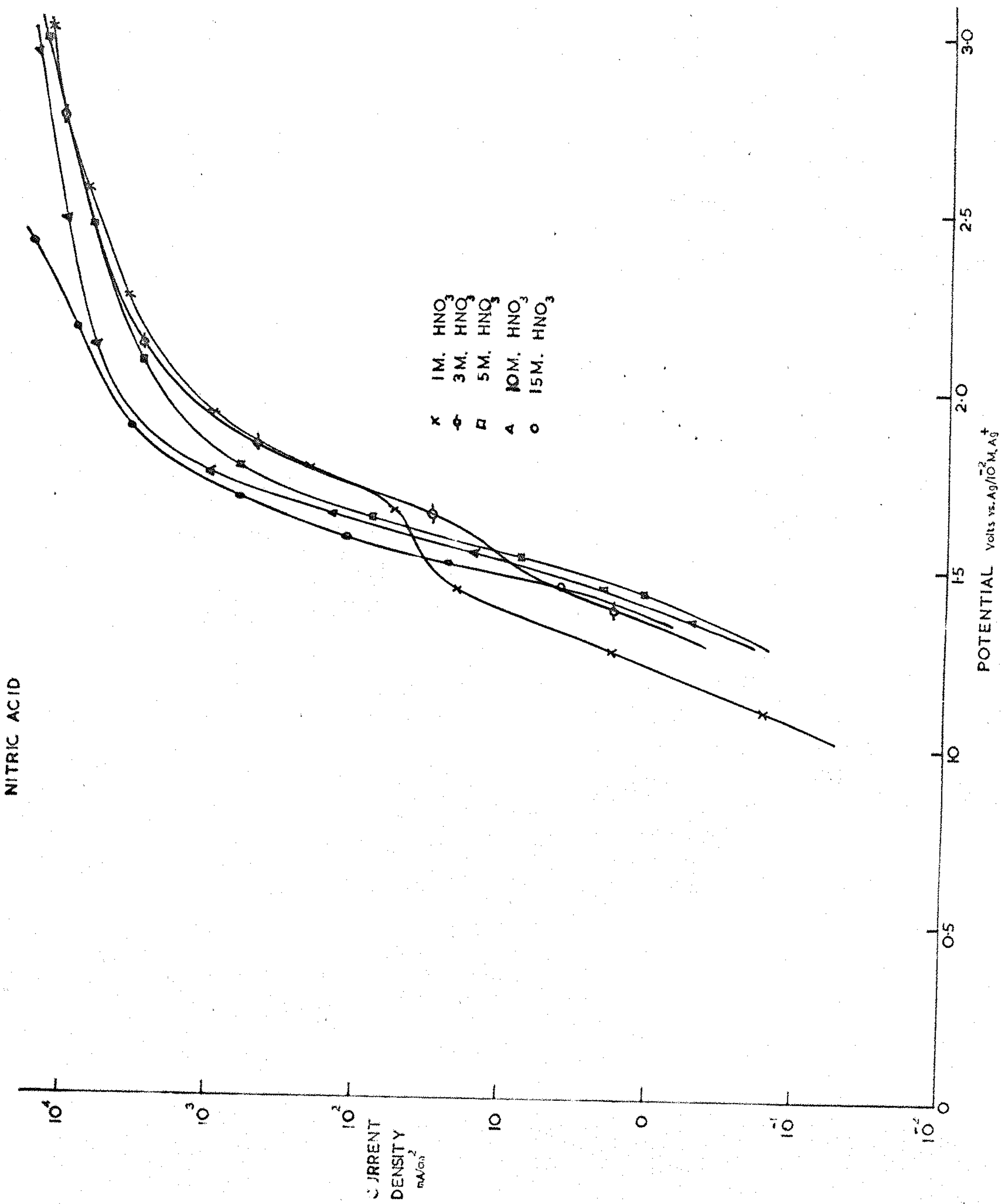

NITRIC ACID
CURRENT DENSITY mA/cm²
10⁴
10³
10²
10
0
10⁻¹
10⁻²
0
0·5
1·0
1·5
2·0
2·5
3·0
POTENTIAL Volts vs. Ag/10⁻² M, Ag⁺
× 1M. HNO₃
⌀ 3M. HNO₃
□ 5M. HNO₃
△ 10M. HNO₃
○ 15M. HNO₃

Figure IV

there is a complete absence of any plateau region, the current increasing rapidly to about 1 Amp/cm^2 at 1.8 volts. The slower rate of increase of current beyond this point is probably due to ohmic potential drop which begins to take effect at these high current densities. The curve for 1M nitric acid shows a marked inflexion at about 1.5 volts and there is a similar, less marked inflexion in the curve for 3M nitric acid. There is no information available in the literature as to the cause of this inflexion. From the shape of the polarisation curves it seems as though there is very little, if any, strong adsorption of the nitrate ion as no marked limiting current regions can be seen. There is no evidence from discolouration of the solution for decomposition of the nitrate ion to oxides of nitrogen. The importance of working in solutions of constant nitrate ion concentrations is shown if effects due to the inflexion at 1.5 volts are to be avoided.

Results and Discussion

In perchlorate solutions

The solubility of mercuric perchlorate in water is very high allowing high concentrations of the mercuric ion to be attained in solutions containing perchloric acid. A solution molar in mercuric perchlorate and molar in perchloric acid was used for much of the preparative work. Such a solution was shown to absorb propene and other olefins rapidly and quantitatively to form a 1 : 1 mercury - olefin complex, so that solutions of these complexes could be made by simply bubbling the olefin, or its vapour in a stream of nitrogen, through the solution containing the mercuric ion.

Polarisation curves

Polarisation curves were run for propene, but-1-ene, but-2-ene and cyclohexene over the concentration range 0.01 M to 1.0 M of the complex, the concentration of the perchlorate ion being kept constant for all runs. The polarisation curves for the mercury (II) - propene complex are shown in Figs. V and VI. There is no evidence, from these plots, for oxidation of the complex at potentials below that required for oxygen evolution. However in the region 1.2 - 2.2 volts the current decreases with increasing concentration of the complex up to a concentration of 0.1M (see Fig.VI). This decrease in current must be due to strong adsorption, possibly of the complex, interfering with the oxidation of water to oxygen. The species adsorbed could be the complex or possibly free olefin produced by dissociation of the complex as strong

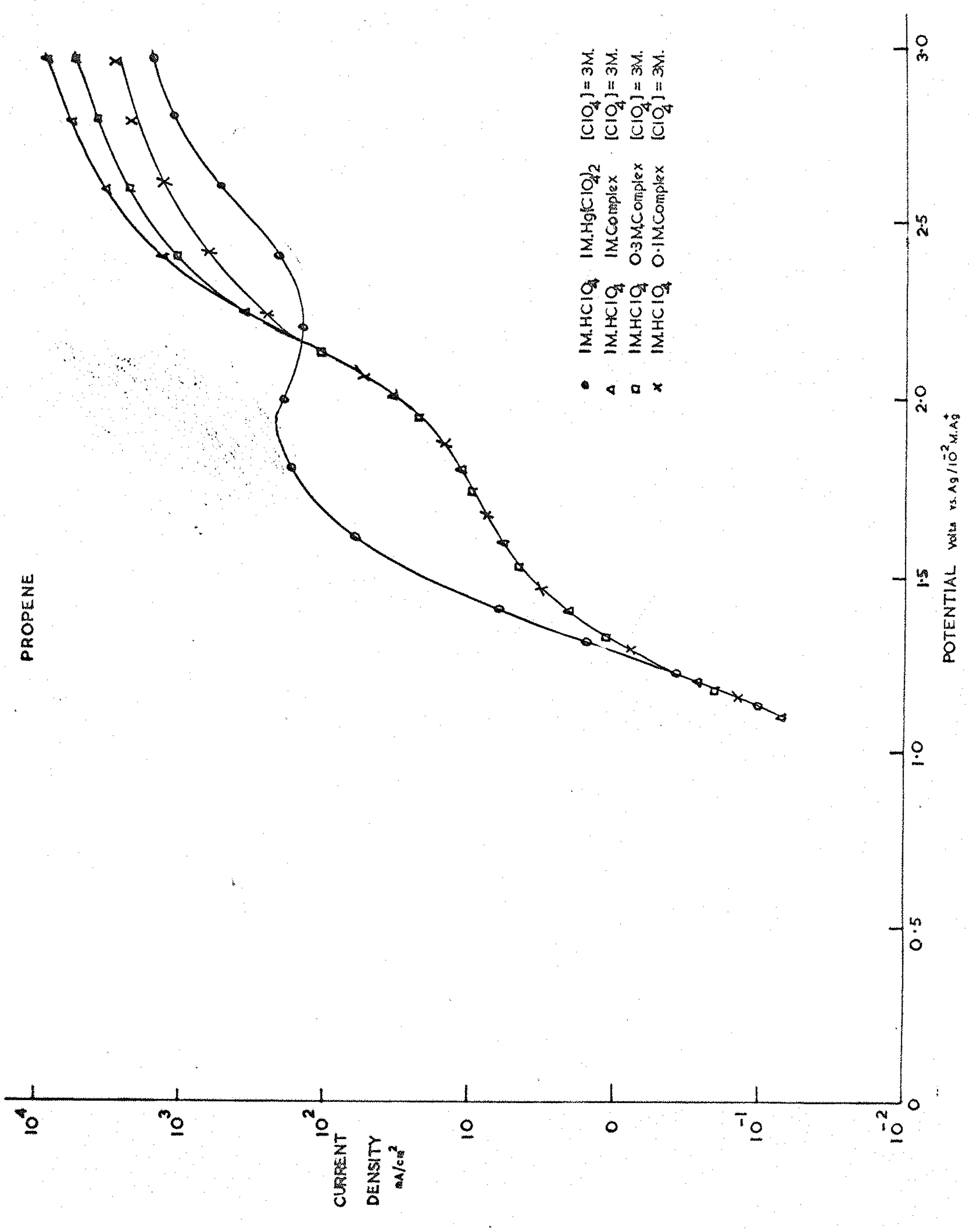

PROPENE
CURRENT DENSITY mA/cm²
10⁴
10³
10²
10
0
10⁻¹
10⁻²
0
0·5
1·0
1·5
2·0
2·5
3·0
POTENTIAL Volts vs. Ag/10⁻²M.Ag⁺
● IM.HClO₄ IM.Hg(ClO₄)₂ [ClO₄⁻] = 3M.
△ IM.HClO₄ IM.Complex [ClO₄⁻] = 3M.
□ IM.HClO₄ 0·3M.Complex [ClO₄⁻] = 3M.
× IM.HClO₄ 0·1M.Complex [ClO₄⁻] = 3M.

Figure V

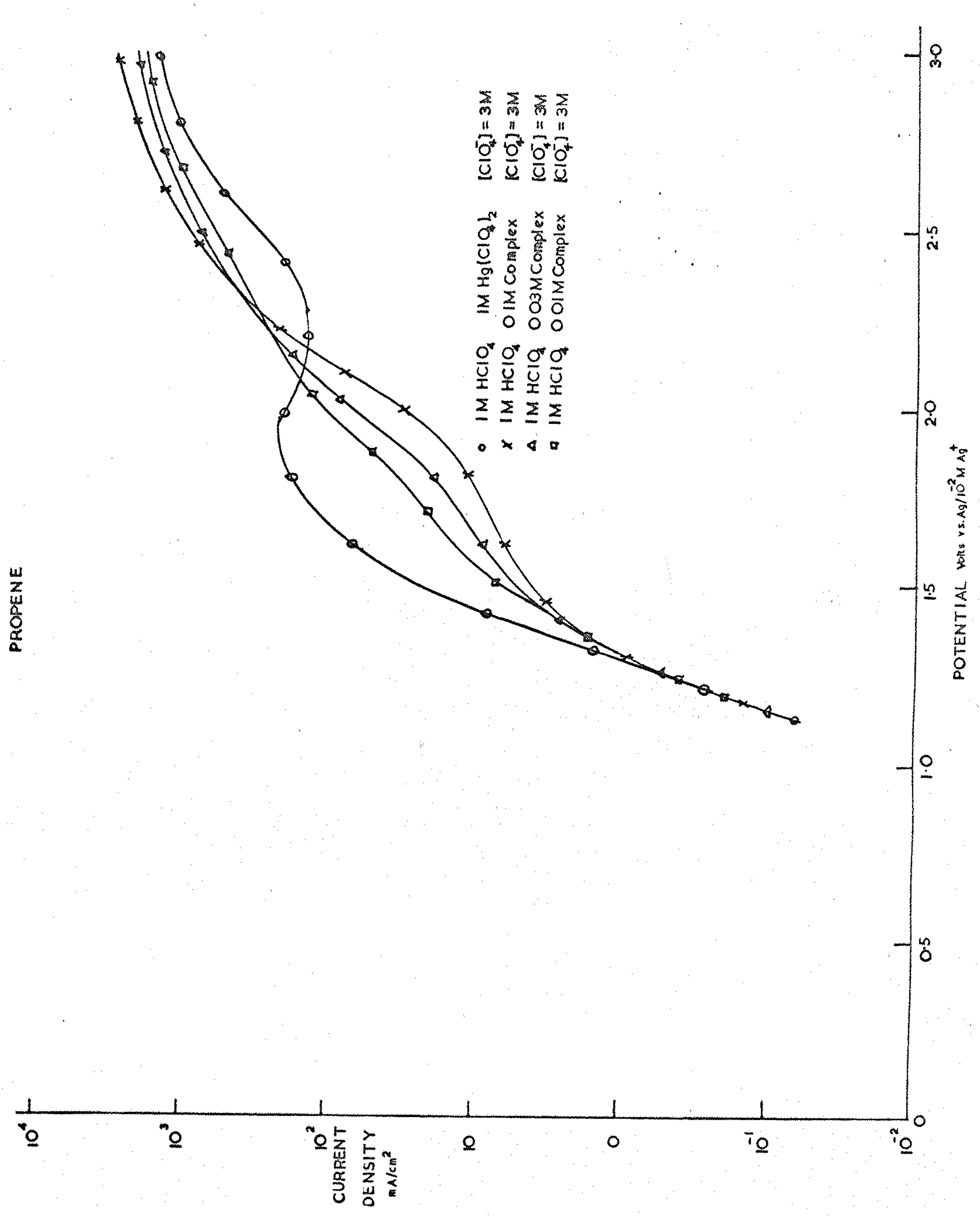

PROPENE
CURRENT DENSITY mA/cm²
10⁴
10³
10²
10
0
10⁻¹
10⁻²
0
0·5
1·0
1·5
2·0
2·5
3·0
POTENTIAL Volts vs. Ag/10⁻² M Ag⁺
o 1M HClO₄ 1M Hg(ClO₄)₂ [ClO₄⁻] = 3M
x 1M HClO₄ 0·1M Complex [ClO₄⁻] = 3M
Δ 1M HClO₄ 0·03M Complex [ClO₄⁻] = 3M
□ 1M HClO₄ 0·01M Complex [ClO₄⁻] = 3M

Figure VI

adsorption of olefins has been shown to occur at high potentials.[69] Higher concentrations of the complex (0.1 - 1.0 M see Fig.V) give currents which are zero order with respect to the concentration of the complex in this range of potentials, indicating maximum coverage of the electrode by adsorbed species. At higher potentials the current shows a first order dependance on complex concentration although the effect is somewhat masked by ohmic potential drop due to the high current densities ($>1 A/cm^2$) in this region. It seems possible, from the magnitude of the current, that the reaction becomes diffusion controlled at these potentials.

Polarisation curves for the but-1-ene (Figs. VII and VIII), but-2-ene (Figs. IX and X) and cyclohexene (Figs XI and XII) complexes all show a remarkable similarity to the polarisation curves for the propene complex except in the region below 1.2 volts. In this region these complexes all show a wave of low current density which is probably due either to the direct oxidation of a small amount of free olefin dissolved in the solution or the oxidation of a hydration product of the olefin. Rough calculations show that the concentration of the species being oxidised is not much greater than millimolar (i.e. about 0.1% of the complex concentration used in the preparative runs.)

For the propene complex the shape of the polarisation curve was found to be independent of pH over the restricted range of -0.5 to + 1.5 as polarisation curves run at pH's of -0.5, +0.5 and +1.5 were co-incident. Higher pH's than +1.5 could not be used because of precipitation of a hydroxy-mercury complex.

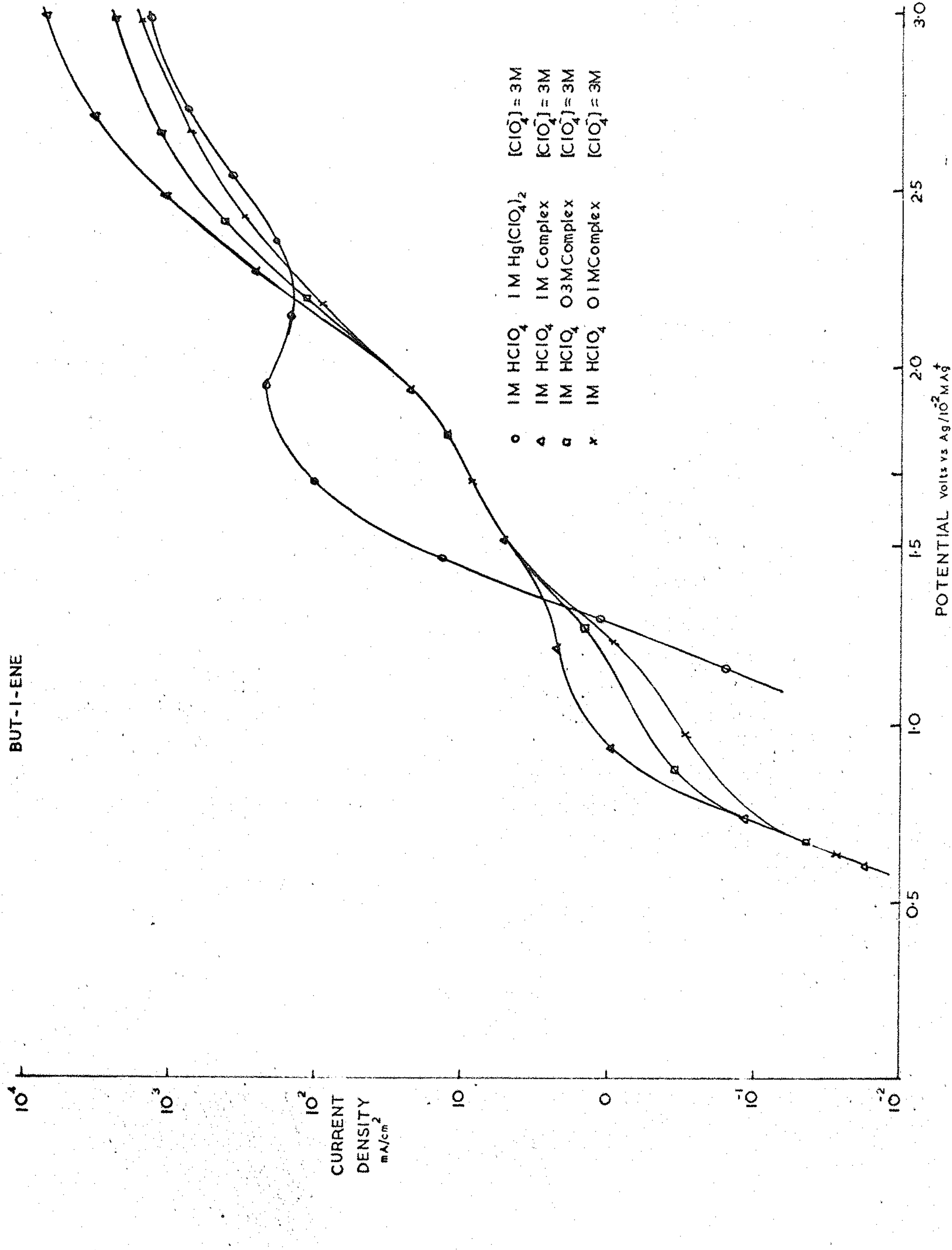

BUT-I-ENE
CURRENT DENSITY mA/cm²
10^4
10^3
10^2
10
0
-1 0
-2 0
POTENTIAL Volts vs Ag/10⁻²M Ag⁺
0·5
1·0
1·5
2·0
2·5
3·0
o IM HClO₄ IM Hg(ClO₄)₂ [ClO₄⁻] = 3M
△ IM HClO₄ IM Complex [ClO₄⁻] = 3M
□ IM HClO₄ O3M Complex [ClO₄⁻] = 3M
x IM HClO₄ O1M Complex [ClO₄⁻] = 3M

Figure VII

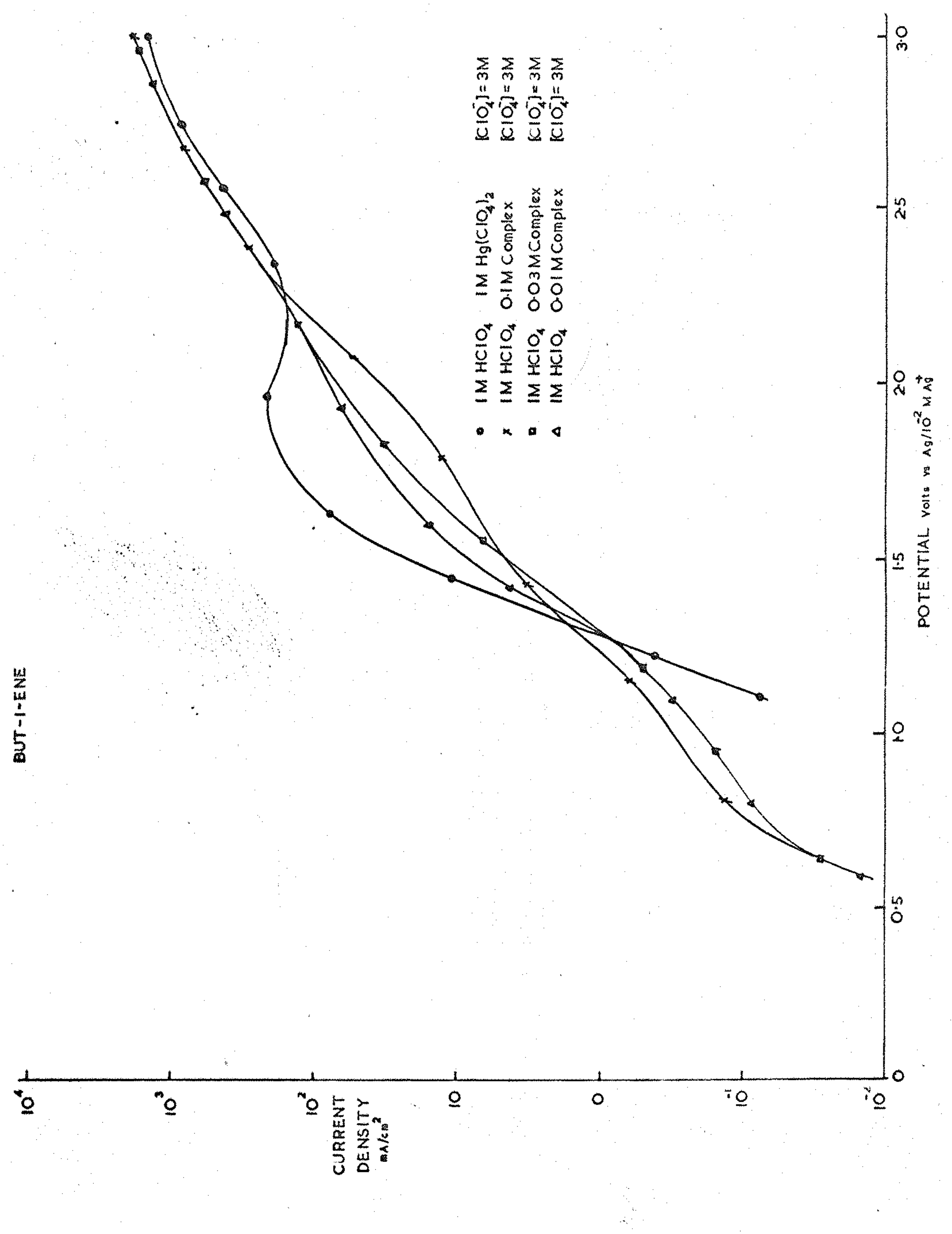

BUT-1-ENE
CURRENT DENSITY mA/cm^2
10^4
10^3
10^2
10
0
10^{-1}
10^{-2}
POTENTIAL Volts vs Ag/10^{-2} M Ag$^+$
0
0·5
1·0
1·5
2·0
2·5
3·0
● 1 M HClO$_4$ 1 M Hg(ClO$_4$)$_2$ [ClO$_4^-$] = 3M
x 1 M HClO$_4$ 0·1 M Complex [ClO$_4^-$] = 3M
▫ 1 M HClO$_4$ 0·03 M Complex [ClO$_4^-$] = 3M
Δ 1 M HClO$_4$ 0·01 M Complex [ClO$_4^-$] = 3M

Figure VIII

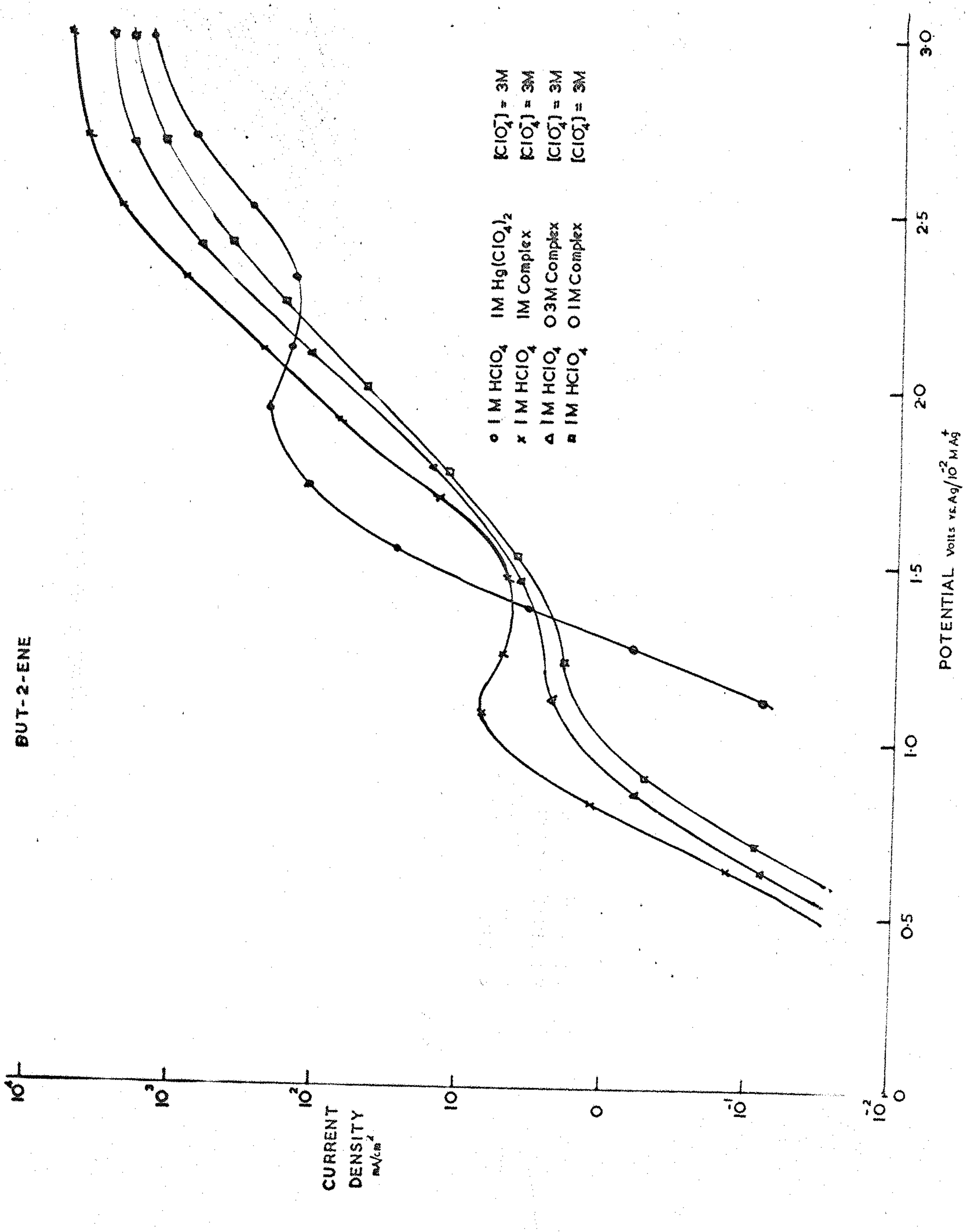

BUT-2-ENE
CURRENT DENSITY mA/cm²
10⁴
10³
10²
10
0
10⁻¹
10⁻²
0
0·5
1·0
1·5
2·0
2·5
3·0
POTENTIAL Volts vs.Ag/10⁻² M Ag⁺
○ I M HClO₄ IM Hg(ClO₄)₂ [ClO₄⁻] = 3M
× I M HClO₄ IM Complex [ClO₄⁻] = 3M
△ I M HClO₄ O 3M Complex [ClO₄⁻] = 3M
□ IM HClO₄ O IM Complex [ClO₄⁻] = 3M

Figure IX

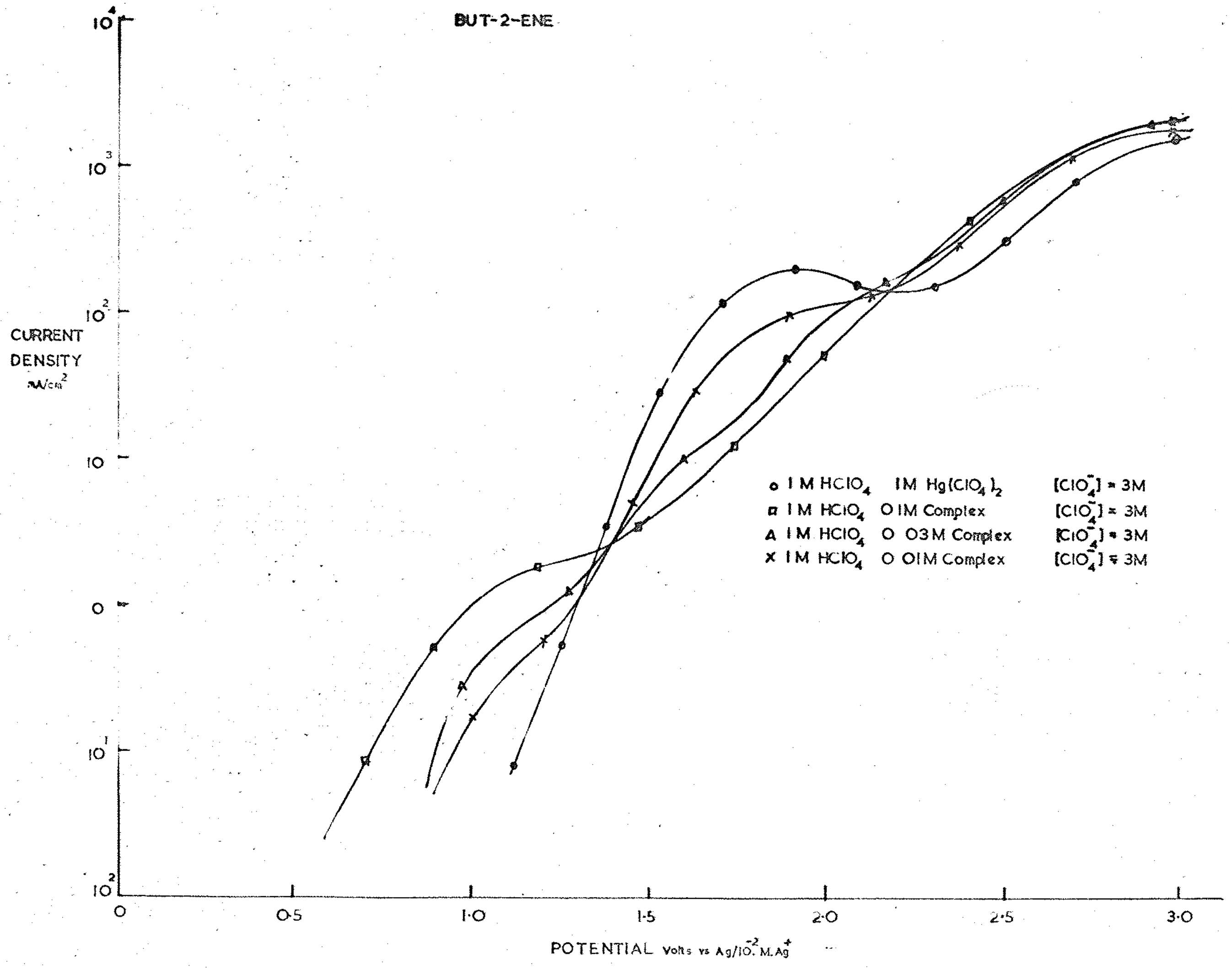

BUT-2-ENE
CURRENT DENSITY μA/cm²
10⁴
10³
10²
10
0
10⁻¹
10⁻²
0
0·5
1·0
1·5
2·0
2·5
3·0
POTENTIAL Volts vs Ag/10⁻²M.Ag⁺
○ 1M HClO₄ 1M Hg(ClO₄)₂ [ClO₄⁻] = 3M
□ 1M HClO₄ 0·1M Complex [ClO₄⁻] = 3M
Δ 1M HClO₄ 0·03M Complex [ClO₄⁻] = 3M
× 1M HClO₄ 0·01M Complex [ClO₄⁻] = 3M

Figure X

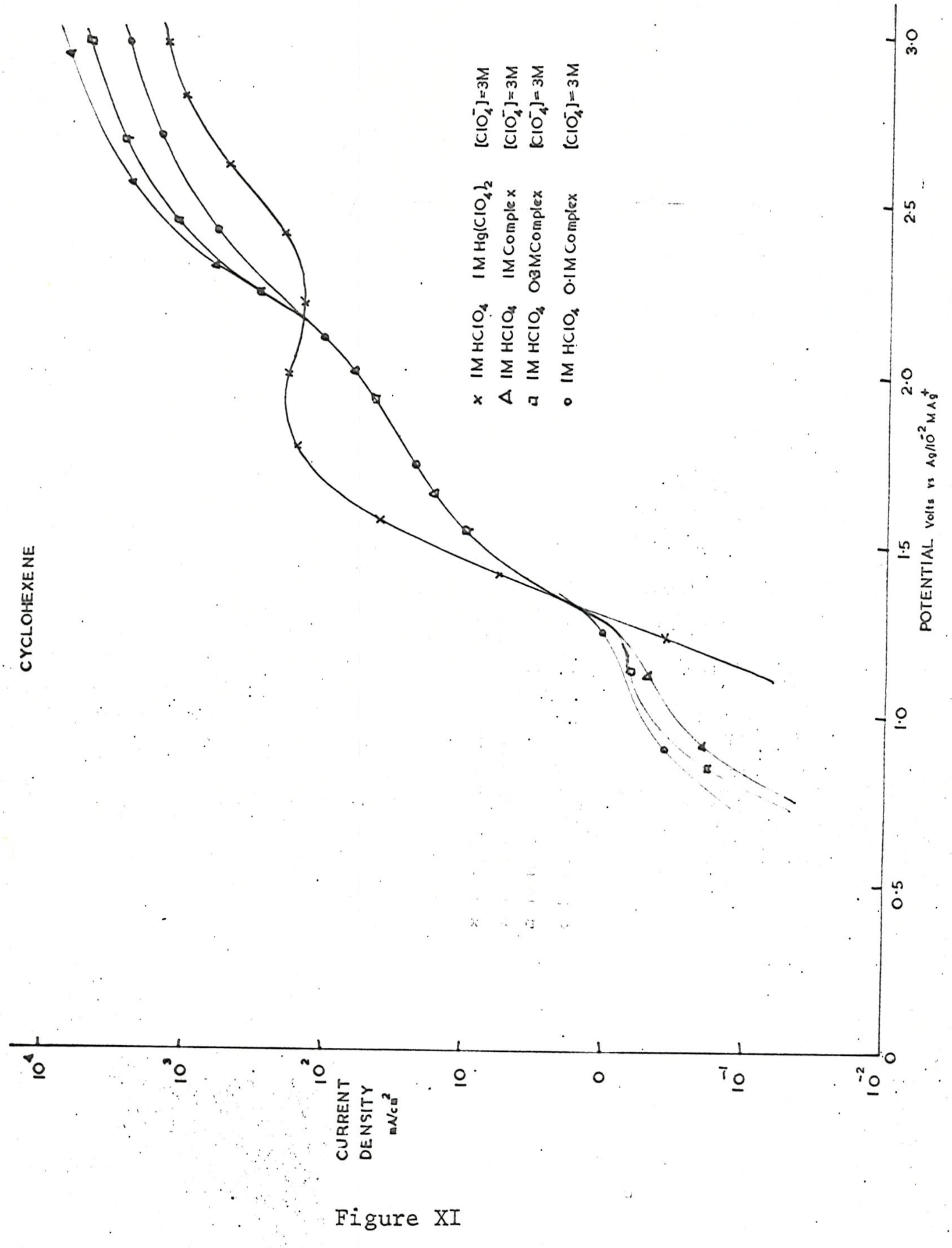

CYCLOHEXENE
CURRENT DENSITY mA/cm²
10^4
10^3
10^2
10
0
10^{-1}
10^{-2}
0
0·5
1·0
1·5
2·0
2·5
3·0
POTENTIAL Volts vs Ag/10^{-2} M Ag$^+$
× 1M HClO$_4$ 1M Hg(ClO$_4$)$_2$ [ClO$_4^-$]=3M
Δ 1M HClO$_4$ 1M Complex [ClO$_4^-$]=3M
□ 1M HClO$_4$ 0·3M Complex [ClO$_4^-$]=3M
○ 1M HClO$_4$ 0·1M Complex [ClO$_4^-$]=3M

Figure XI

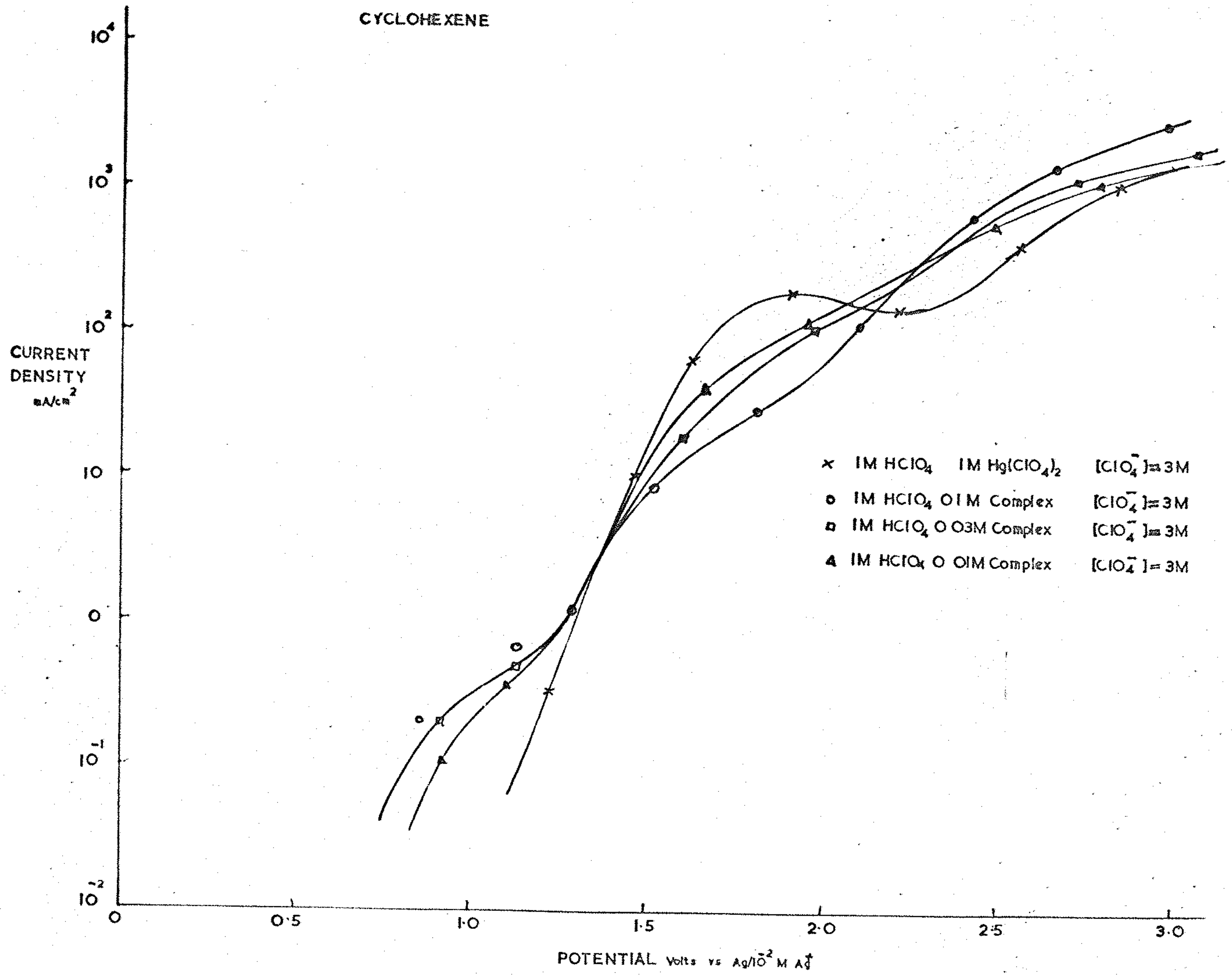

CYCLOHEXENE
CURRENT DENSITY mA/cm^2
10^4
10^3
10^2
10
0
10^{-1}
10^{-2}
0
0·5
1·0
1·5
2·0
2·5
3·0
POTENTIAL Volts vs Ag/10^{-2} M Ag^+
× IM $HClO_4$ IM $Hg(ClO_4)_2$ $[ClO_4^-]$ = 3M
o IM $HClO_4$ O1M Complex $[ClO_4^-]$ = 3M
□ IM $HClO_4$ O O3M Complex $[ClO_4^-]$ = 3M
▲ IM $HClO_4$ O O1M Complex $[ClO_4^-]$ = 3M

Figure XII

The electrode reaction of the propene complex was shown to be completely irreversible using cyclic voltammetry as cyclic voltammograms run at high sweep rate, such as that shown in Fig. XIII., show no peaks on the reverse sweep. Thus any intermediates produced during the anodic reaction have very short half-lives.

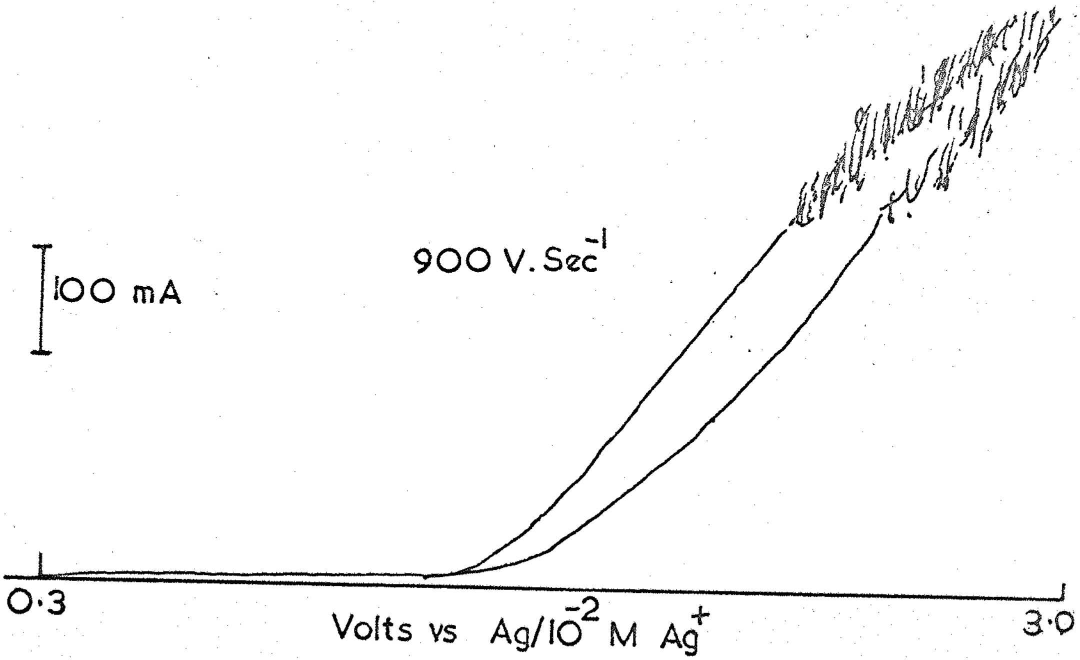
The products of the electrode reaction

From the evidence of the polarisation curves oxidation of the complex is obviously occurring above 2.2 volts as the current here is higher than for the base electrolyte and, although there is no direct indication from the polarisation curves, oxidation probably occurs also at lower potentials.

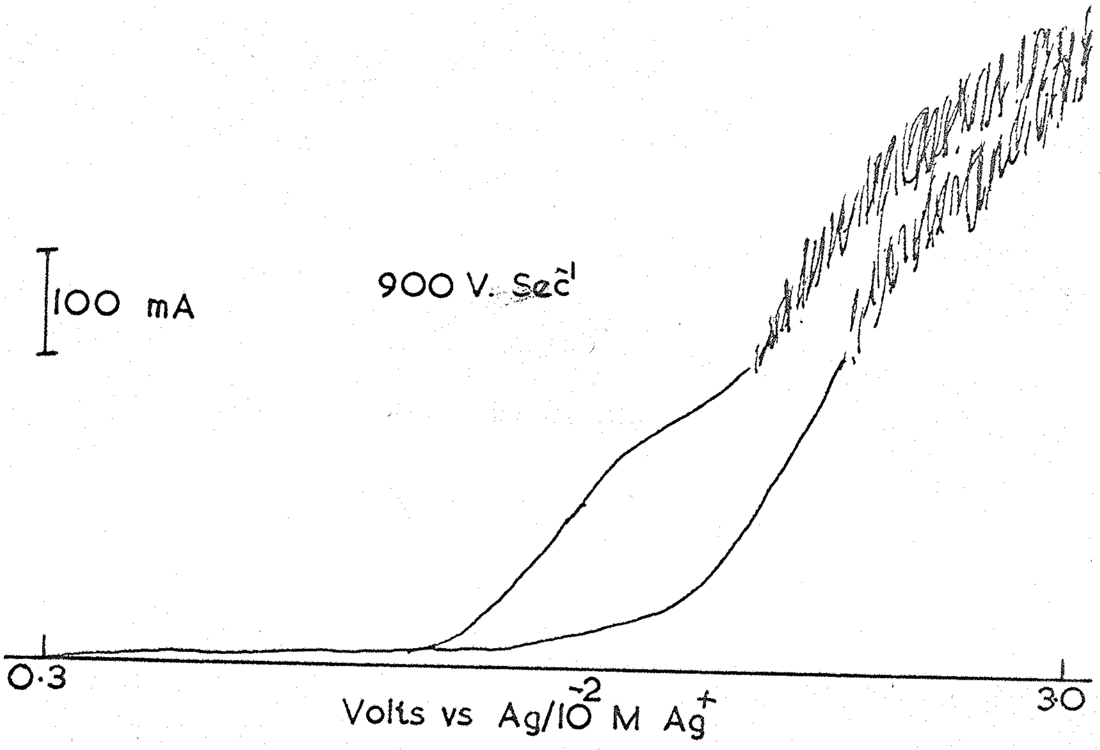
Controlled potential electrolyses were therefore carried out at several potentials for the propene, but-1-ene and but-2-ene complexes and at one fixed potential for the other complexes.

The fixed potential chosen was 2.4 volts as one which gave good total current yields of organic products for the three complexes which had been thoroughly studied.

The results obtained for the propene complex are shown in Table I. Of these products acetone and propionaldehyde were identified solely from their retention times on the vapour phase chromatograph. Acetic and propionic acids were identified by separating small quantities from the mixture of products by preparative vapour phase chromatography and then using spectroscopic techniques, particularly



Base Electrolyte



Complex

Figure XIII

mass spectrometry and n.m.r. spectroscopy.

TABLE I

Variation of current yield of products with potential for propene

Potential (V) / Product	1.80	1.95	2.10	2.25	2.40	2.55	2.70
Acetone	3.4	7.3	10	6.5	5.8	2.4	2.3
Propionaldehyde	-	-	0.9	0.8	0.5	0.2	-
Formic acid	-	-	44	62	64	51	55
Acetic acid	2.7	9.2	52	69	70	56	59
Propionic acid	2.1	4.5	18	24	24	17	16
Total current yield	8.2	21	81	98	100	76	77
Apparent alkyl/ hydrid shift ratio	0.38	0.43	0.45	0.55	0.55	0.53	0.48

N.B. In this table, and all others quoting current yields, the yield of only one of a pair of acids produced together e.g. formic and acetic in this table should be used to calculate the total current yield.

The spectra obtained are shown in Figs. XIV, XV, XVI and XVII. The n.m.r. spectrum of the compound thought to be acetic acid is shown in Fig. XIV. It shows two single peaks one at 7.9 τ which is characteristic of aliphatic hydrogen close to an electron withdrawing group and the other at -1.3 τ - characteristic of an acidic proton. The ratio

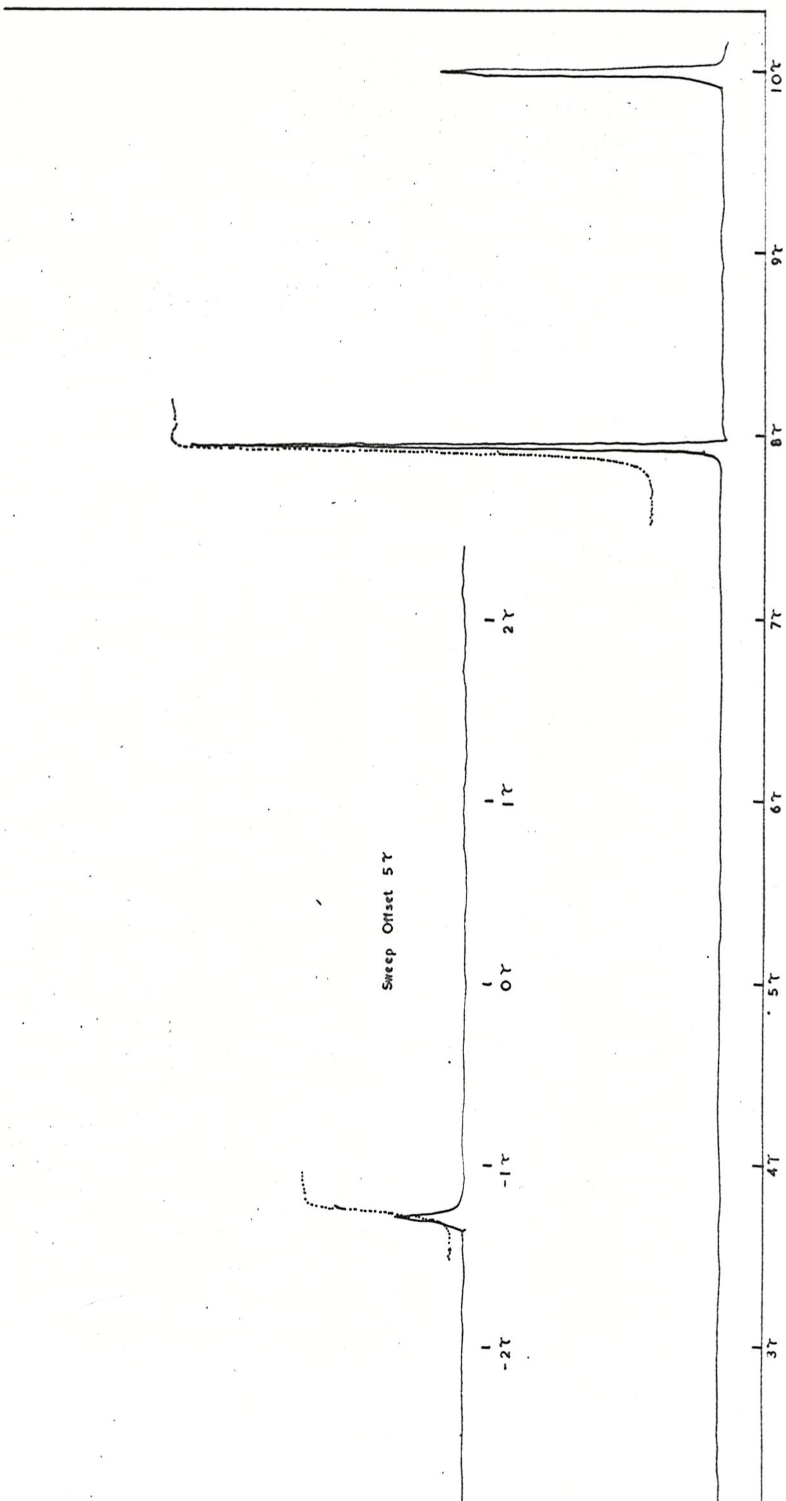


Figure XIV

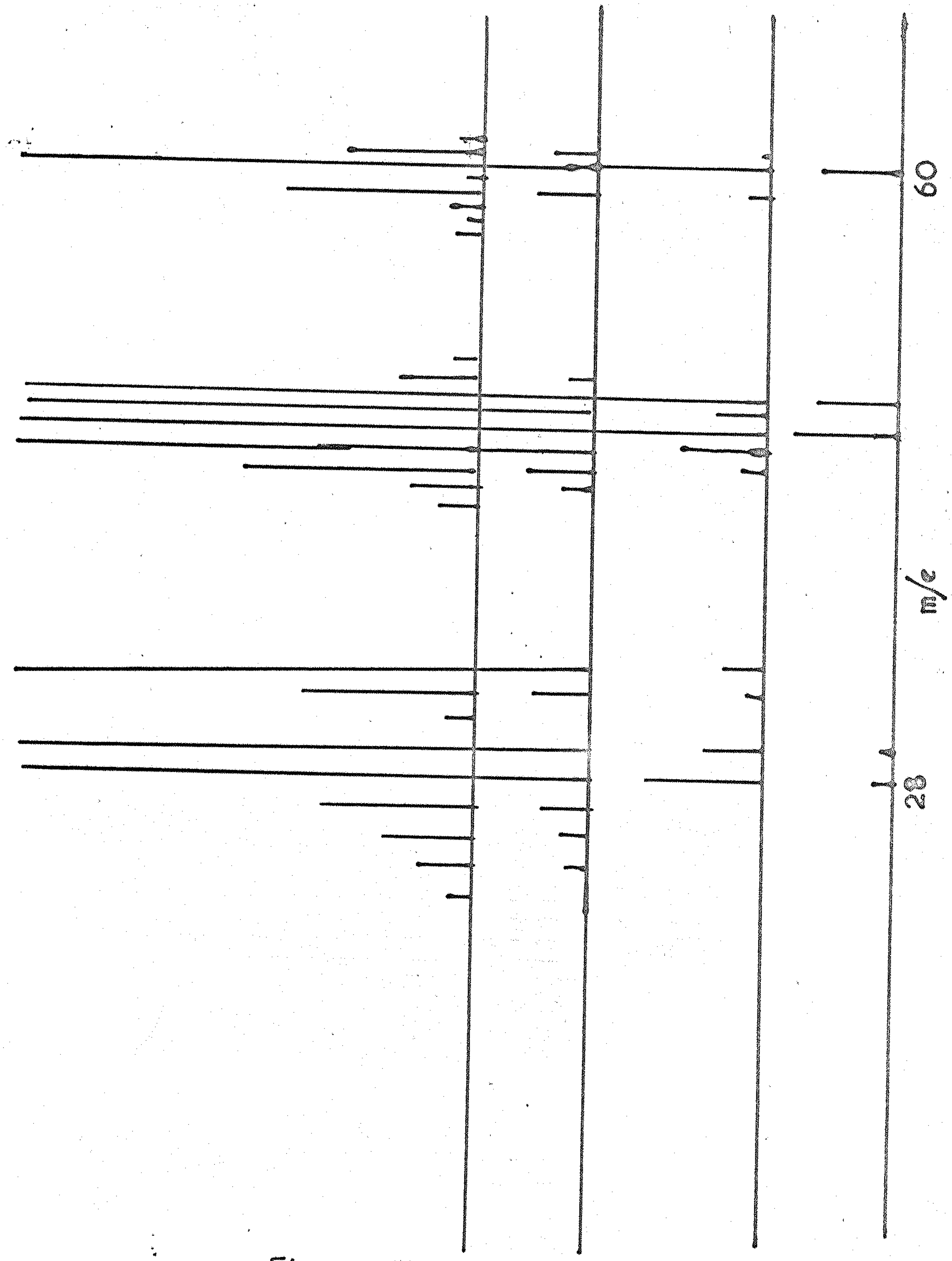


Figure XV

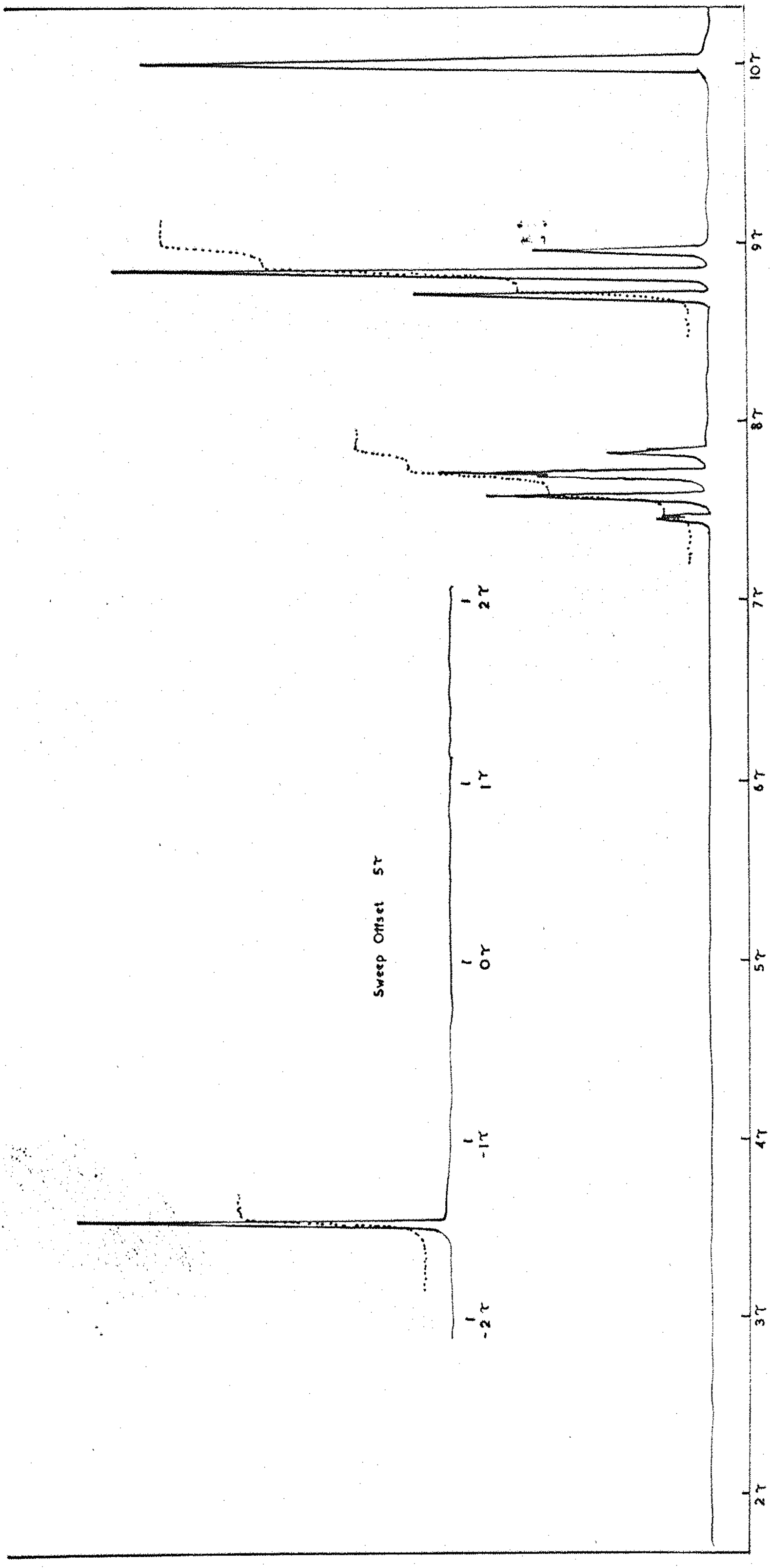


Figure XVI

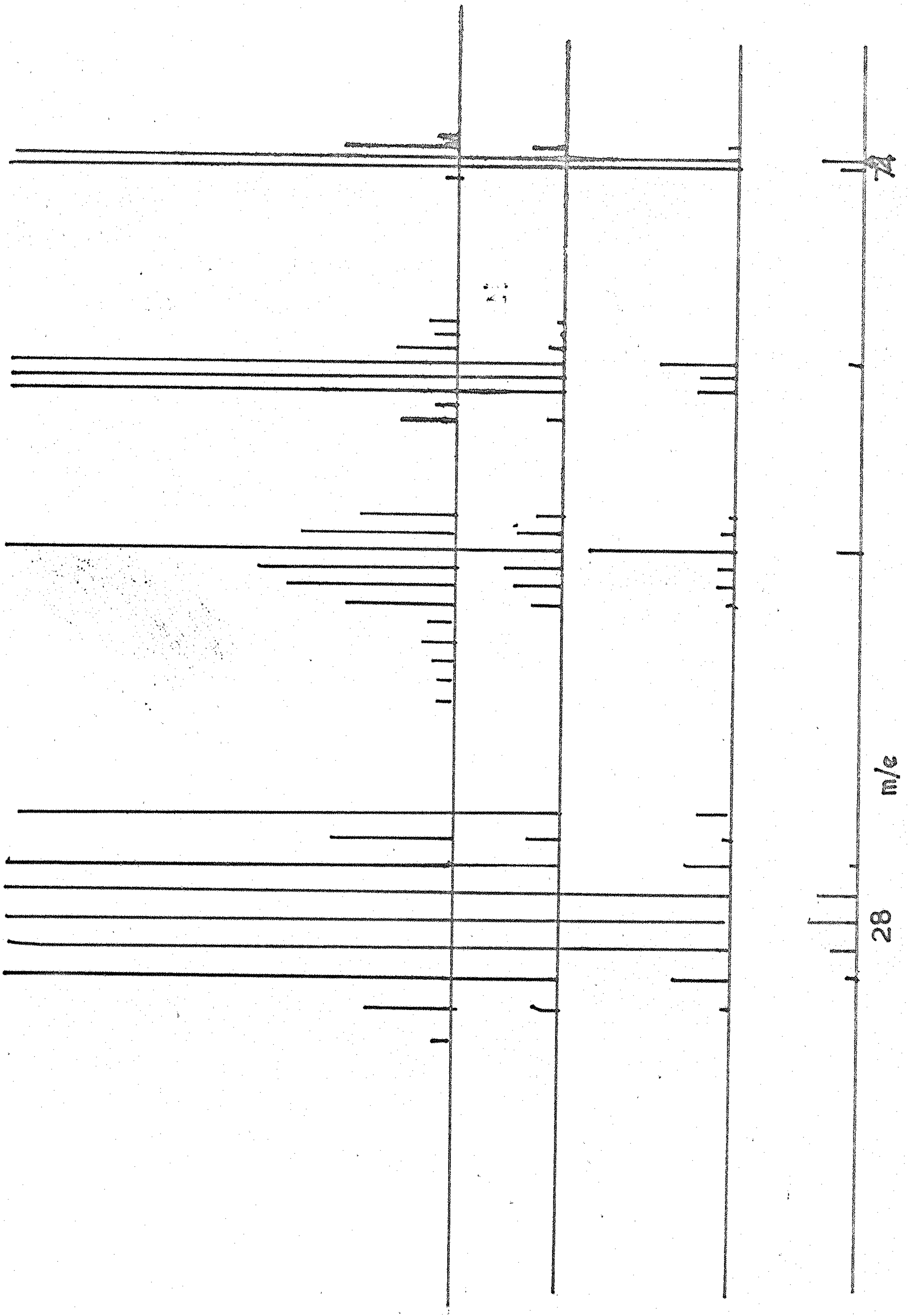


Figure XVII

of the peak areas was 3 : 1 giving three aliphatic protons to each acidic proton. There was no splitting showing that the hydrogens were not attached to adjacent carbon atoms. This indicates that the compound is probably acetic acid. This is confirmed by the mass spectrum (Fig. XV) which has as its six strongest peaks 43, 60, 45, 28, 44, 42. This is in complete agreement with the published spectrum of acetic acid.[70] The other compound gives the n.m.r. spectrum shown in Fig. XVI, which consists of three sets of peaks centered on 8.8 τ 7.6 τ and -1.5 τ in the ratio 3 : 2 : 1. The peak at -1.5 τ is an acidic proton whilst the other two signals are split, the one at 7.6 τ into a quartet (1 : 3 : 3 : 1) indicating splitting by three adjacent hydrogens and the one at 8.8 τ into a triplet (1 : 2 : 1) indicating splitting by two adjacent hydrogens. As the ratio of the total areas of these two signals are 2 : 3 this is obviously the signal from an ethyl group and thus the compound is propionic acid. The mass spectrum (Fig. XVII) which has as its six strongest peaks 28, 29, 74, 27, 45, 73 agrees with the published spectrum for propionic acid.[70] Formic acid, which cannot be detected using a flame ionisation detector on a v.p.c. was identified by a spot test involving the reduction of mercurous chloride[71]. Acetone and propionaldehyde, which could interfere with this test were removed by making the solution alkaline and evaporating to dryness under vacuum. The formate which remained was used directly in the test and the acetate and propionate also present did not interfere. Thus the oxidation of the propene complex produces acetone, propionaldehyde, propionic acid and acetic and formic acids in almost equal amounts. From Table I it can be seen that for some potentials the current yields of organic products is extremely high, and in some cases equal to 100%. This supports the observation that virtually no oxygen evolution from the electrode could be seen at these potentials.

The results in Table I were all obtained using a solution in which the concentration of perchloric acid was molar i.e. the pH was approximately 0. Another run, at 2.4 volts, the results of which are shown in Table II was performed using a solution the pH of which was 1.5. The results show that while the overall yield is lower, suggesting an increase in oxygen evolution, the proportions of the product is similar.

TABLE II

Variation of current yield of products with pH for propene

product / pH	Acetone	Propionaldehyde	Formic acid	Acetic acid	Propionic acid
0	10	0.9	59	52	18
1.5	6.3	1.3	34	36	14

The products from the oxidation of the but-1-ene complex (see Table III follow the same pattern as those from propene although total current yields are somewhat lower. There is the aldehyde - n-butyraldehyde - and its corresponding acid, n-butyric acid together with methyl ethyl ketone and formic, acetic and propionic acids.

TABLE III

Variation of current yield of products with potential for but-1-ene.

Potential (V) / Product	2.10	2.40	2.70
Methyl ethyl ketone	4.5	7	6
n-Butyraldehyde	2	1	1
Formic acid	-	8	-
Acetic acid	30	44	40
Propionic acid	7	8	7
n-Butyric acid	15	33	10
Total current yield	58	93	64
Apparent alkyl/ hydride shift ratio	0.7	0.85	0.33

But-2-ene (see Table IV) gives only one carbonyl compound - methyl ethyl ketone, together with formic, acetic, propionic and a fourth acid. This acid was separated by preparative vapour phase chromatography and its n.m.r. and mass spectra obtained. The n.m.r. spectrum is shown in Fig.XVIII. It shows three signals centred on 8.8 τ (a doublet), 7.5 τ (a multiplet) and -1.7τ (a singlet) in the ratio 6 : 1 : 1. The singlet at $-1.7\ \tau$ is an acidic proton. The doublet at 8.8τ has a τ value which indicates an alkyl group and it is

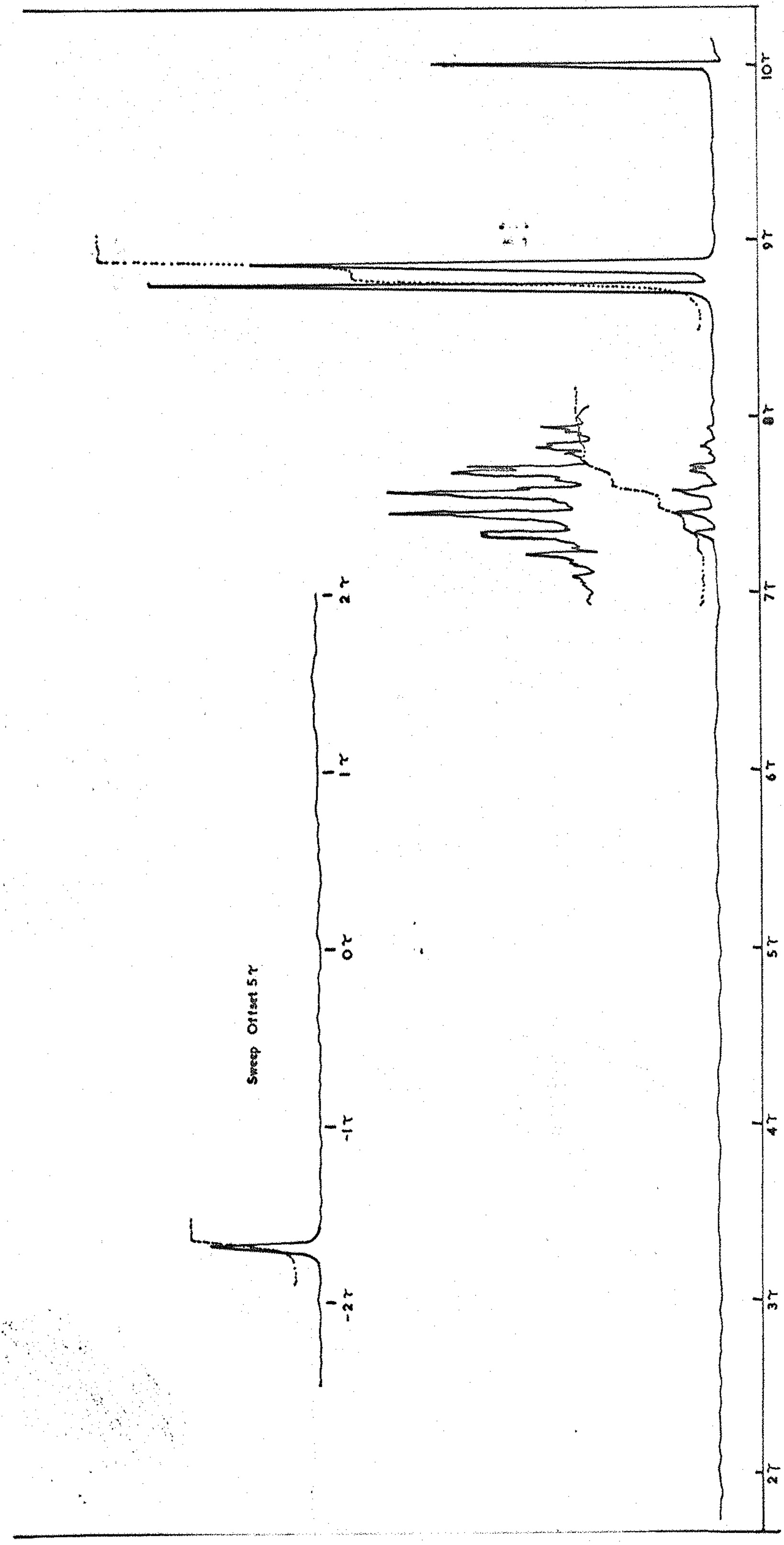


Figure XVIII

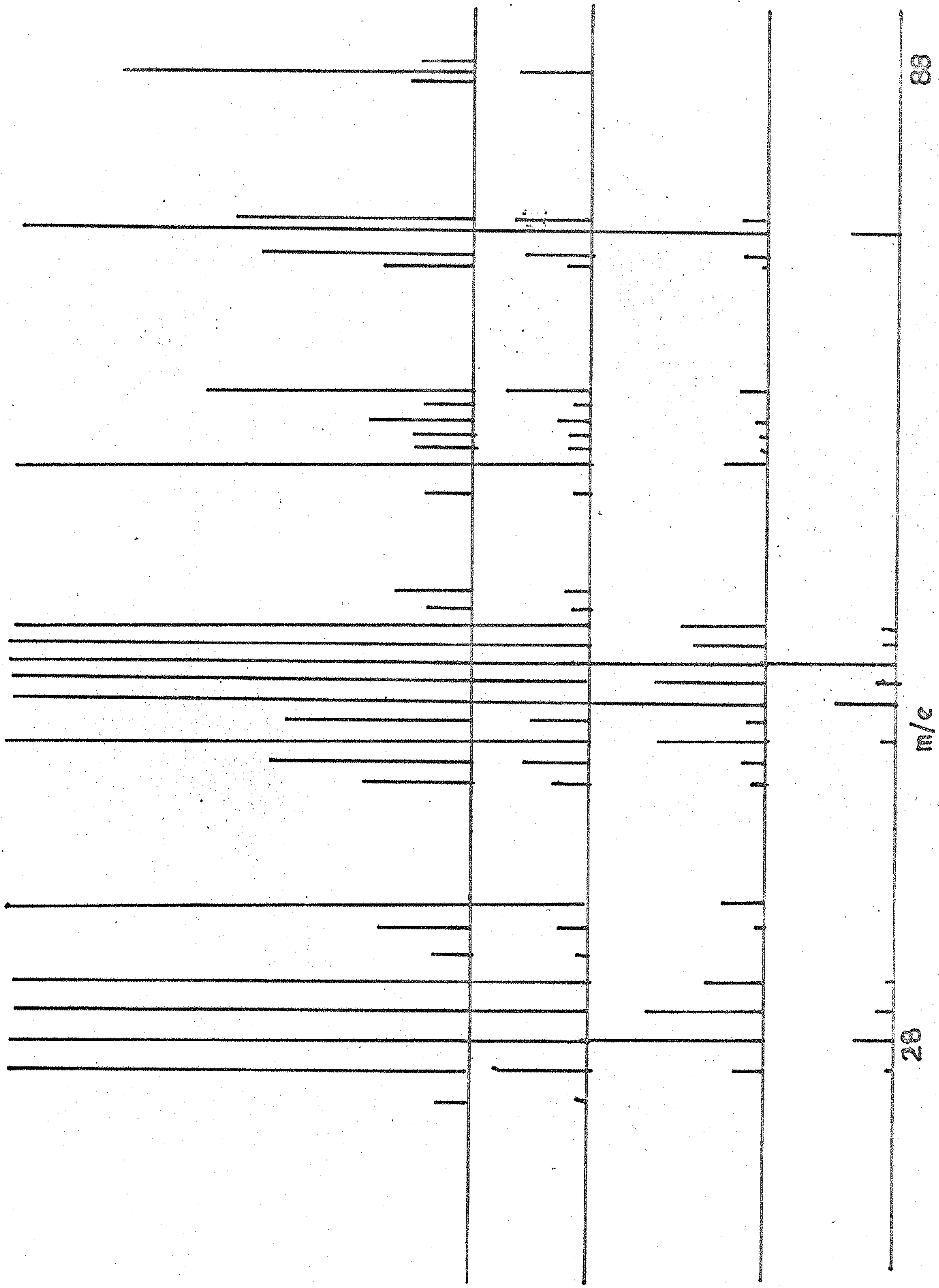


Figure XIX

TABLE V

Products predicted by Mechanism IV expressed as current yields

Olefin	Acid Products	Carbonyl Products	Apparent Alkyl Shift: Hydride Shift	% Current accounted for by Mechanism IV
ethylene	acetic acid 33%	acetaldehyde 10%	-	43%
propene	propionic acid 24%, acetic acid 70%, formic acid 64%	propionaldehyde 1%, acetone 6%	0.55 (CH_3)	100%
1-butene	n-butyric acid 33%, propionic acid 8%, formic acid 8%, acetic acid 44%	n-butyraldehyde 1%, methylethylketone 7%	0.85 (C_2H_5)	93%
2-butene	isobutyric acid 18%, propionic acid 4%, formic acid 8%, acetic acid 73%	methylethyl ketone 5%	0.37 (CH_3)	100%
isobutene	acetic acid 95%, propionic acid 1% formic acid 1%	methylethylketone 1%	-	100%
1-pentene	n-pentanoic acid 18%, n-butyric acid 20%, formic acid 20%, propionic acid 14%, acetic acid > 14%		1.06 (C_3H_7)	52%

TABLE V (Continued)

Olefin	Acid Products	Carbonyl Products	Apparent Alkyl Shift: Hydride Shift	% Current accounted for by Mechanism IV
2-pentene	methylethylacetic acid 17% propionic acid 38%, acetic acid > 38%		0.84 (C_2H_5)	55%
1-hexene	n-hexanoic acid 24%, n-pentanoic acid 22%, formic acid 22%, n-butyric acid 12%, acetic acid > 12%		1.41 (C_4H_9)	58%
2-hexene	methylpropylacetic acid 17% propionic acid 28%, n-butyric acid 24%, acetic acid >24%		0.90 (C_3H_7)	69%
cyclohexene	cyclopentane carboxylic acid 10%, adipic acid < 1%	cyclopentane aldehyde 18% cyclohexanone < 1%	10.0 (–)	31%
1-octene	n-octanoic acid 1% n-heptanoic acid 3% formic acid 3% n-hexanoic acid 2% acetic acid > 2%			6%

either two groups of three protons in slightly different environments or six equivalent protons split by one proton on an adjacent carbon.

TABLE IV

Variation of current yield of products with potential for but-2-ene.

Potential Product	1.80	1.95	2.10	2.25	2.40	2.55	2.70
Methyl ethyl ketone	6	7.5	7	8	5	7	7
Formic acid	-	-	4	5	8	-	
Acetic acid	7	19.5	60	60	73	60	61
Propionic acid	1	2	4	5	4	2	2
iso Butyric acid	4.2	9.5	20	26	18	14	10
Total current yield	18	38.5	95	99	100	90	80
Apparent alkyl/ hydride shift ratio	0.26	0.42	0.45	0.55	0.37	0.32	0.22

The multiplet at 7.5 τ could correspond to an alkyl group attached to an electron withdrawing group, and split by five or more adjacent protons. This suggests that the compound is isobutyric acid. The mass spectrum (Fig. XIX) has a molecular ion peak at 88 corresponding to isobutyric acid and strong peaks at 73 (molecular ion less a methyl group and 43 (the isopropyl group). The six principal peaks of the spectrum are 43, 41 , 27, 73, 39, 45 which corresponds to the published spectrum of isobutyric acid[70]. The variation of the current yields with potential follows a similar pattern to propene and but-1-ene.

The results obtained for the other olefins which were oxidised at 2.4 volts only are shown in Table V. From this table it can be seen that in general α-olefins give rise to only straight chain acids whereas β olefins give rise to one branched chain acids as well as straight chain acids. The results for the other olefins will be discussed later in the light of the proposed mechanism for the reaction. One point which may be noted immediately from this table is the absence of detectable amounts of aldehydes and ketones formed from these higher olefins. This indicates that they are more readily oxidised than aldehydes and ketones of lower molecular weight.

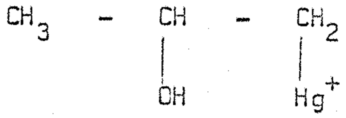
The mechanism of the electrode reaction

In the results for the propene complex (Table I) the acids which are obtained can be explained in terms of further oxidation of acetone and propionaldehyde. This suggests the following reaction sequence

$$\begin{tikzcd}
 & & CH_3\,CH_2\,CHO \arrow[r, "-2e^-"] & CH_3\,CH_2\,COOH \\
Hg\,(CH_2 = CH - CH_3)^{2+} \arrow[r, dash, "-2e^-"] & {} \arrow[ur, "A"] \arrow[dr, "B"'] & & \\
 & & CH_3\,CO\,CH_3 \arrow[r, "-6e^-"] & CH_3\,COOH + HCOOH
\end{tikzcd}$$

where the ratio of the products formed by routes A and B is approximately 1 : 3, and is independant of electrode potential. The presence of much more acetone than propionaldehyde is as expected as acetone will be the more difficult to oxidise as its oxidation involves the breaking of a carbon-carbon bond.

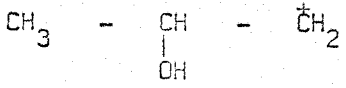
A study of work which has been done on mercury-olefin complexes (see pages 11 to 17) suggests that the mercury-propene complex exists in aqueous acid solution as the ion



$$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - \underset{\displaystyle Hg^+}{\underset{|}{CH_2}}$$

I

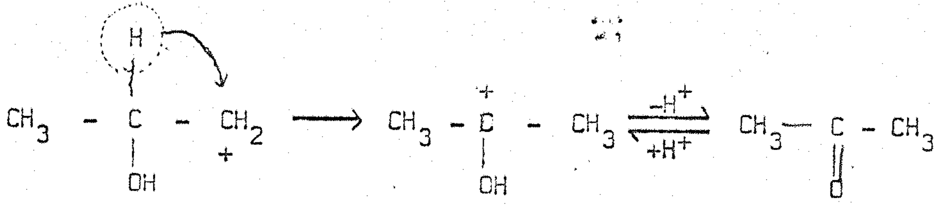
As the ion I is in equilibrium with the free olefin the first electrochemical step in the reaction could be either the oxidation of the ion I on the electrode or the oxidation of the free olefin. If the reaction is the oxidation of free olefin it would be expected that, as has been shown in acetonitrile[29], the oxidation potential would vary with the structure of the olefin, e.g. in acetonitrile there is a difference of 0.75 volts between the oxidation potentials of propene and cyclohexene. No such difference in oxidation potential can be seen from the polarisation curves, which are all very similar. This indicates that it is probably the ion I which is being oxidised and, as no mercury containing organic products are found, it is reasonable to suppose that the first step is the electrochemical cleavage of the mercury-carbon bond to give the carbonium ion II



$$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - \overset{+}{C}H_2$$

II

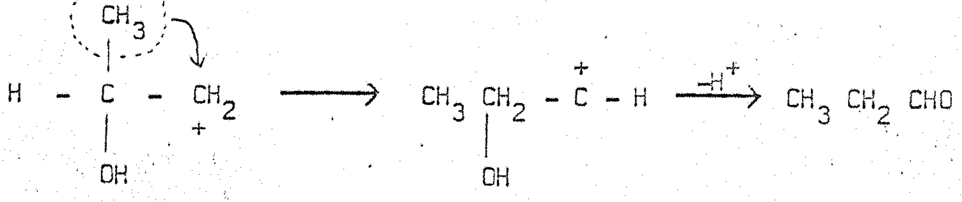
This carbonium ion is produced at the electrode surface and has a very short half-life, rearranging in what could even be a concerted reaction via a hydride shift to give an ion which is a protonated form of acetone.



II

The acetone molecule, which must still be very close to the electrode can then be further oxidised directly on the electrode to give two of the observed acid products, acetic and formic acids, or diffuse into the bulk of the solution.

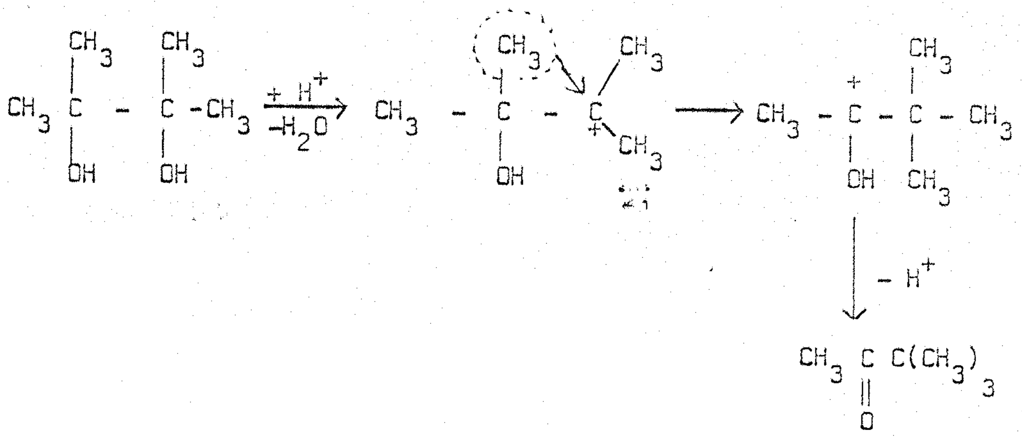
There are three mechanisms which could explain the production of propionaldehyde and propionic acid. The first mechanism involves carbonium ion II which could rearrange via a methyl shift instead of a hydride shift to give a protonated form of propionaldehyde



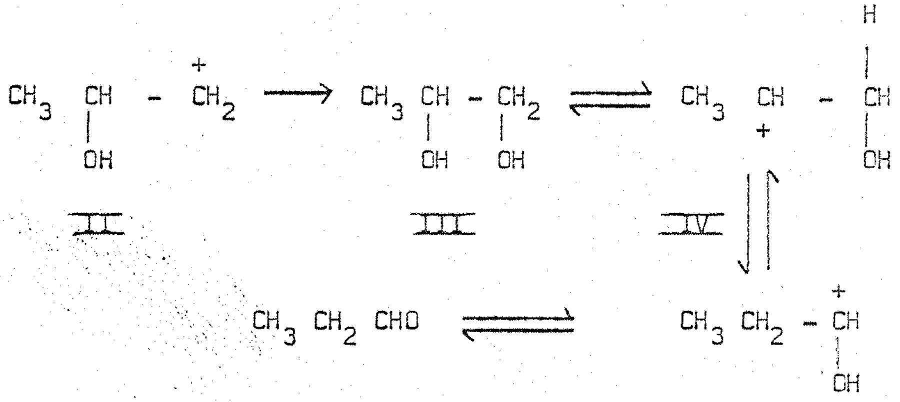
II

Mechanism I

This reaction is very similar to the pinacol-pinacolone rearrangement[77] in which a carbonium ion formed by the dehydration of a substituted diol in strong acid rearranges via an alkyl shift to give a ketone



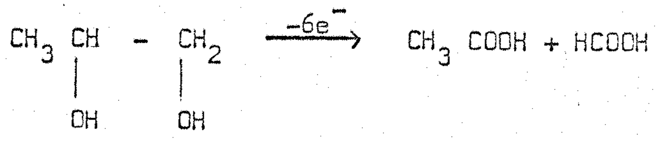
The second mechanism also involves the carbonium ion II but as can be seen the hydroxyl group first of all 'migrates' via the formation of a diol and this reaction is then followed by a hydride shift. The hydroxyl group is removed from the middle of the molecule to give carbonium ion IV as this is a secondary carbonium ion and more stable than the primary carbonium ion II.



Mechanism II

The series of equilibria between species II, III and IV will be weighted in favour of ion IV as this is a secondary carbonium ion and thus more stable than the primary carbonium ion II.

This mechanism also provides an alternative route for the production of acetic and formic acids to that outlined above via acetone. Species III - propane 1,2 diol could oxidise on the electrode with cleavage of the diol to give acetic and formic acids

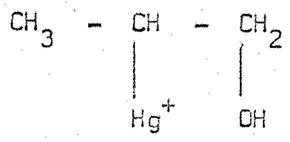


$$CH_3\underset{OH}{\underset{|}{CH}} - \underset{OH}{\underset{|}{CH_2}} \xrightarrow{-6e^-} CH_3COOH + HCOOH$$

III

If this mechanism did occur it might be expected to find at least traces of the diol amongst the products but, although the solution was carefully analysed for diol, none was found.

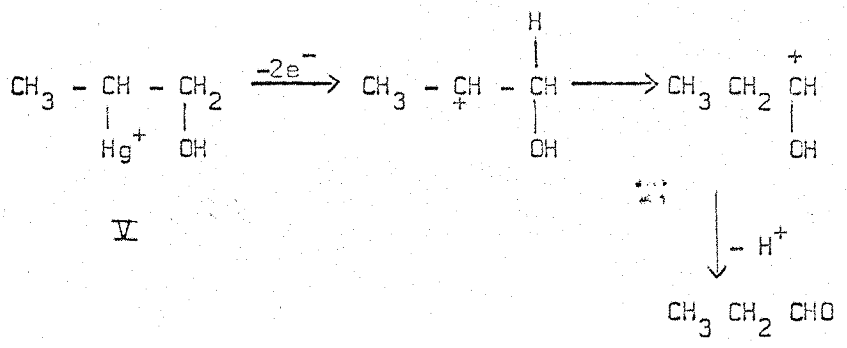
The third mechanism involves a different carbonium ion. Whereas the ion I can be described as being rormed by Markovnikov[72] addition of Hg - OH to the double bond another ion V could be formed by anti-Markovnikov addition of the Hg - OH.



$$CH_3 - \underset{Hg^+}{\underset{|}{CH}} - \underset{OH}{\underset{|}{CH_2}}$$

V

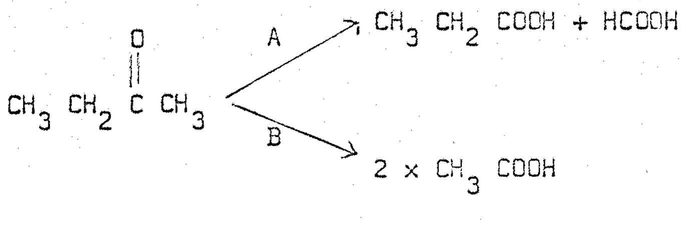
This ion, on oxidation at the electrode, would then give carbonium ion IV and then propionaldehyde via hydride shift and loss of a proton.



Mechanism III

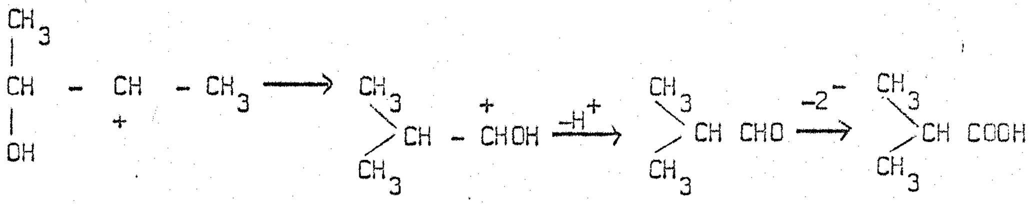
The propionaldehyde, whichever mechanism explains its formation, is, like acetone, formed close to the electrode and can be oxidised directly on the electrode to give propionic acid or diffuse into the bulk of the solution.

The results for any of the other α - olefins will also fit either mechanism I or III but they seem to indicate that if mechanism II does occur it is, at least, not the dominant reaction path. Taking but-1-ene as an example the ketone found here is methyl ethyl ketone which can split in two different ways on oxidation giving either two molecules of acetic acid or one of propionic and one of formic acid



All three acids are found but as can be seen from Table V the dominant route is route B as only small amounts of propionic and formic acids are found. If, however the mechanism involving diol formation (Mechanism II) occurred the butane 1,2 diol formed as an intermediate would cleave to give predominantly propionic and formic acids and not two molecules of acetic acid. Similar arguments hold for the other α olefins so that Mechanism II does not seem important for them.

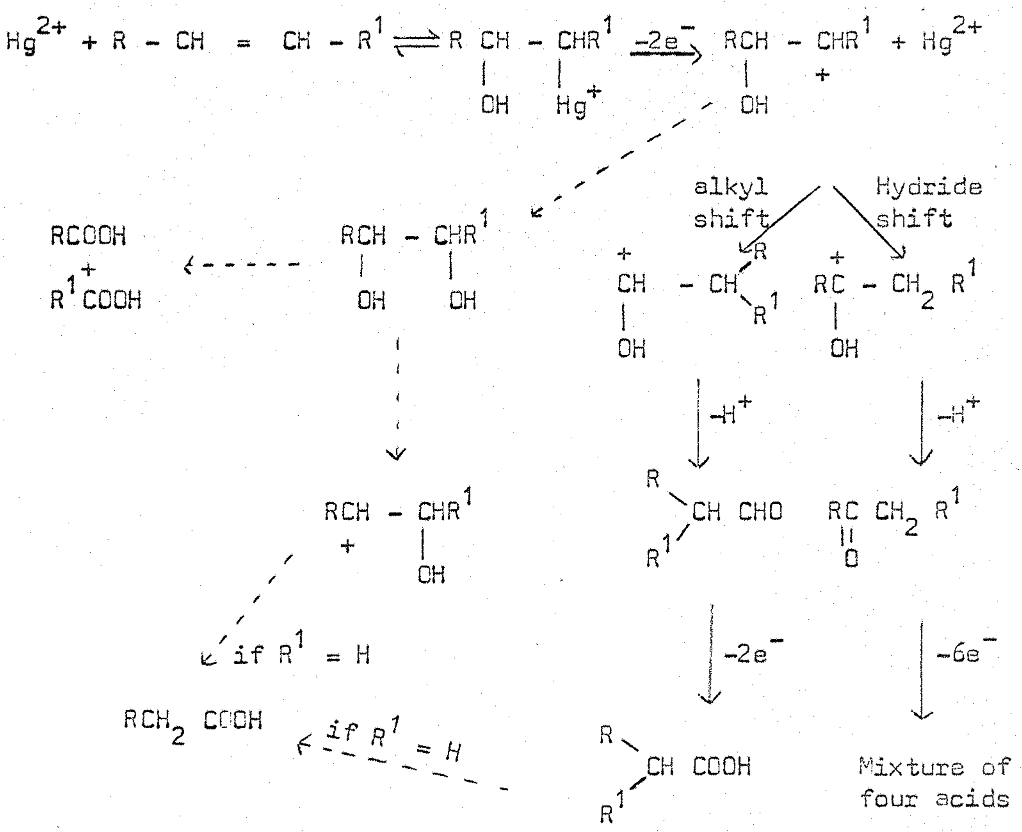
For the β-olefins, such as but-2-ene there is only one possible mechanism which can explain the isomerisation of the carbon skeleton which occurs to give isobutyric acid - Mechanism I. Mechanism I can be rewritten for but-2-ene as



According to this mechanism it would be expected that isobutyraldehyde would be amongst the products. None could be detected on the v.p.c., however, showing that its further oxidation to isobutyric acid must be rapid. The other acid products can be thought of as coming from methyl ethyl ketone (as for but-1-ene) which has been formed by the competing hydride shift. Some of the acetic acid may come from the oxidation of butane 2,3 diol which would be formed as shown in Mechanism II. Analysis of the products, however, reveals no traces of diol to support this theory. Pent-2-ene and hex-2-ene, the other two β-olefins studied give products which can be explained in a similar manner.

The only mechanism which is directly supported by the results which have been discussed so far is the alkyl shift mechanism, Mechanism

I. There is some circumstantial evidence that the diol mechanism, Mechanism II, also occurs in at least some cases but no direct evidence, in the form of diols amongst the products exists. Mechanism III, the mechanism involving anti-Markovnikov addition also has only circumstantial evidence to support it as, like Mechanism II it cannot explain the alkyl shift found in the case of the β-olefins. It is the less likely of the two alternative mechanisms as, although examples of anti-Markovnikov addition are known in organic chemistry, this is not a common reaction. From this evidence it is possible to suggest an overall mechanism for the reaction - Mechanism IV

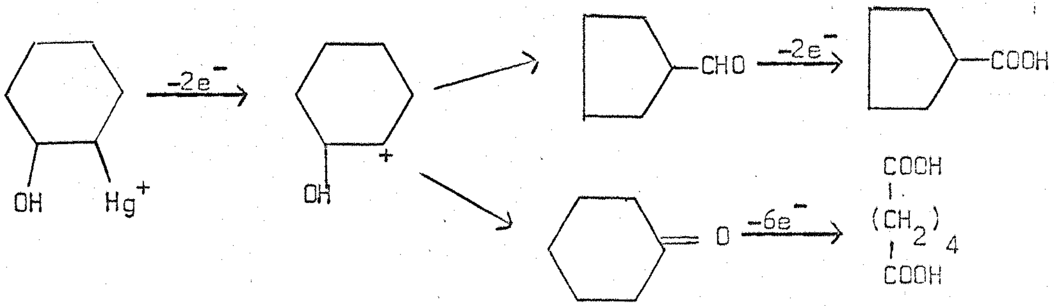


R, R^1 = H or alkyl

Mechanism IV

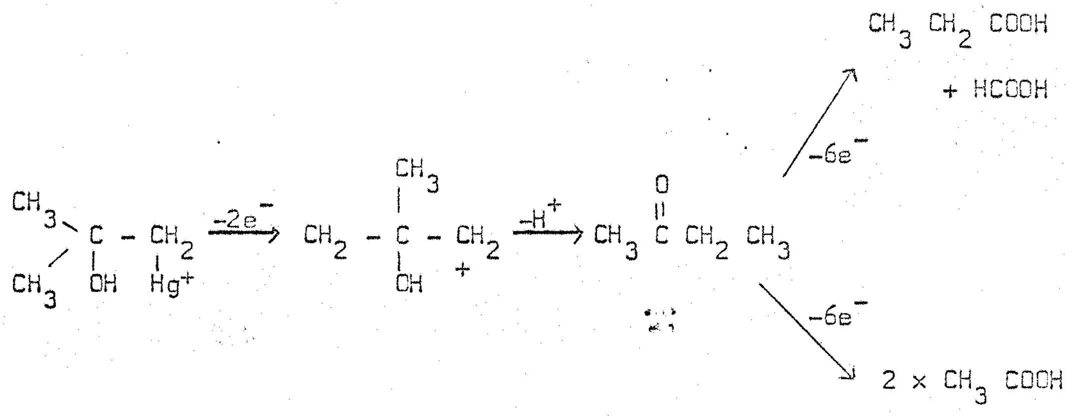
There are three olefins whose results have not yet been discussed - ethylene, cyclohexene and isobutene. Ethylene is a special case as there is only one carbonyl compound which can be formed (acetaldehyde) and no possibility of an alkyl shift. Thus the only products should be acetaldehyde and acetic acid. Significant amounts of formic acid are, however, found which can only be accounted for by Mechanism II, i.e. the formation of ethylene glycol and its oxidation at the electrode. There is no more direct evidence for this mechanism as no traces of ethylene glycol were found on a careful analysis of the products.

Cyclohexene was the only cyclic olefin studied. If the alkyl shift reaction can be thought of an a ring contraction in this case then the following products would be predicted.

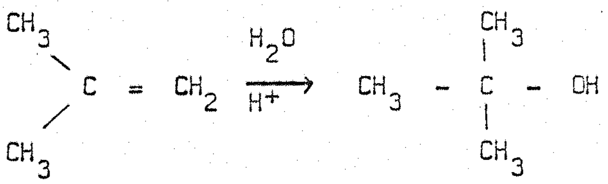


These predicted products are in fact those which are found, although in rather low current yields.

Isobutene - the only branched chain olefin studied - would be expected from Mechanism IV to give methyl ethyl ketone and its further oxidation products



These are the products which are found, the major one being acetic acid. Another product, tert butanol, which is found in quite large quantities is the result of a non-electrochemical, non oxidative hydration of the olefin



If this reaction occurs for isobutene it might also be expected to occur for the other olefins. If this is so it either occurs to a very small extent or the alcohol produced is rapidly oxidised as no appreciable quantities of alcohol were found in the products. This would, however, be expected since the alcohol produced would be a secondary alcohol which would be readily oxidised to a ketone.

A notable feature of the oxidation of the complexes of the higher olefins - pentenes, hexenes and octene is the large amount of acetic acid which is found. The amount of acetic acid which should be present can be calculated from the amount of the other acid which is

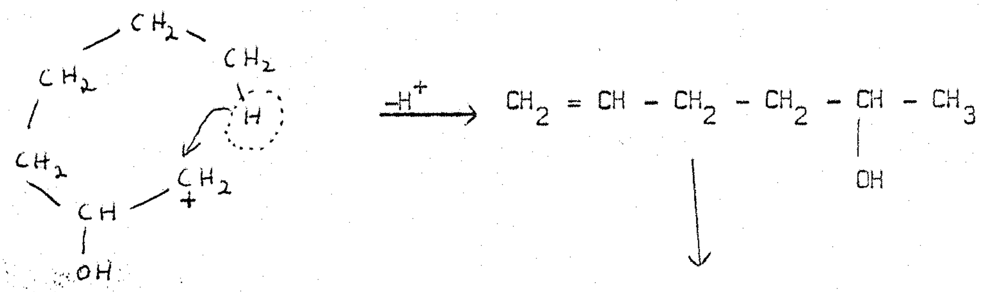
TABLE VI

Major products expressed as mole % of total organic products

Olefin	Products
ethylene	acetic acid 51%, acetaldehyde 32%, formic acid 10%
propene	acetic acid 33%, formic acid 30%, propionic acid 24%
1-butene	acetic acid 44%, n-butyric acid 33%
2-butene	acetic acid 70%, isobutyric acid 16%
isobutene	acetic acid 97%
1-pentene	acetic acid 36%, n-pentanoic acid 26%, n-butyric acid 14%, formic acid 14%
2-pentene	acetic acid 43%, propionic acid 28%, methylethylacetic acid 25%
1-hexene	n-hexanoic acid 33%, propionic acid 27%, n-pentanoic acid 15%, formic acid 25%
2-hexene	acetic acid 38%, propionic acid 27%, methylpropylacetic acid 16%, n-butyric acid 12%
cyclohexene	cyclopentane-aldehyde 72%, cyclopentanecarboxylic acid 22%
1-octene	acetic acid 59%, propionic acid 19%

found with it. Thus in the case of pent-2-ene the oxidation of n-propyl methyl ketone gives one molecule of acetic acid for every molecule of propionic acid and thus these two acids should be found as equal mole % of the total organic products (see Table VI). In this case there is 50% more acetic acid than can be accounted for by such a mechanism. It has been shown[83] that during the ozonolysis of organomercurials a similar wide spread of acid products is obtained. The situation is similar for pent-1-ene and the hexenes, but the effect is much more marked for oct-1-ene as almost 60% of the organic products are accounted for by acetic acid, and another 20% by propionic acid which is not predicted by Mechanism IV at all.

It is obvious that for these higher olefins some other mechanism is involved which results in the almost complete degradation of the carbon skeleton. A probable mechanism involves the formation of cyclic intermediates which would allow migration of the double bond and subsequent degradation of the molecule, e.g. for hex-1-ene



at least 2 molecules of acetic acid.

Such a mechanism would explain why this degradation is more obvious with larger molecules as they would much more readily form cyclic intermediates than molecules with only a few carbon atoms.

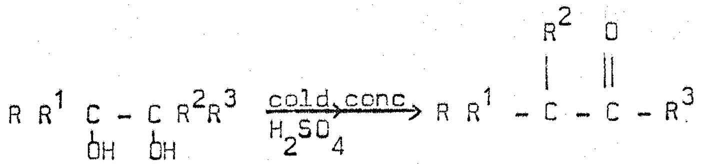
At the high potentials which are required for this reaction it is remarkable that the carboxylic acids which are the major products do not undergo the Kolbé reaction.[73] It is possible that some of them do undergo the Kolbé reaction but the proportion of the acid products which are degraded in this way particularly in the case of the lower olefins, must be very small as the current yield of products for these olefins is almost 100%. The reason for this absence of the Kolbé or any other decarboxylation reaction is probably that the surface conditions necessary - such as that of vacant adsorption sites - are not fulfilled. This lack of the necessary surface conditions could be due to the adsorption of the complex or other organic molecules on the surface. Another reason could be that the potentials under consideration lie within the 'inhibition region' of the Kolbé reaction. This region is normally below 2 volts but the conditions used here are not those normally associated with the Kolbé reaction - the pH is lower and the concentration of the organic acid is much lower than that normally used for this reaction. In addition anions other than those of the organic acid are present in large quantities and these, in particular perchlorate and sulphate, have been shown to have a marked effect on decarboxylation reactions. These factors could all combine to make it impossible for the Kolbe reaction to occur under the conditions existing during the electrolysis.

The 'Alkyl Shift'

The ratio of the quantity of products formed by the alkyl shift to the quantity formed by the hydride shift is shown in Tables I, III, IV and V. Two features stand out.

1) From Tables I, III and IV it can be seen that over a range of potentials (2.1 to 2.55 V) the ratio remains constant within the experimental error. (The errors associated with the measurement of the ratio are fairly large (± 10%)). It should be noted, however, that there is a marked falling off in the ratio for the butene complexes at high potentials (2.7 volts). This can be attributed to the fact that the amount of acid formed by an alkyl shift reaction which is found is less than would be expected from the amounts of the other products.

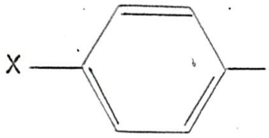
2) From Table V which shows the ratio for a number of different migrating groups it can be seen that there is a tendency for the ratio to increase with the increasing size of the group. The migrating aptitudes of aryl groups have been widely studied but there is very little information in the literature on the migrating aptitudes of alkyl groups. The reaction most studied in the case of aryl groups is the pinacol - pinacolone type of reaction



$$R\,R^1\,\underset{OH}{C}-\underset{OH}{C}\,R^2R^3 \xrightarrow[H_2SO_4]{cold, conc} R\,R^1-\overset{\overset{R^2}{|}}{C}-\overset{\overset{O}{\|}}{C}-R^3$$

where R, R^1, R^2 and R^3 are various substituted aryl groups.

The migratory aptitude of the various aryl groups depends on the ability of that group to stabilise a positive charge i.e. the more electron donating the substituent the more readily the group migrates. The migrating ability is, in fact, very closely related to the susceptibility of the group to electrophile attack. This can be seen from the following figures for groups of the type

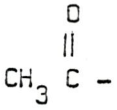
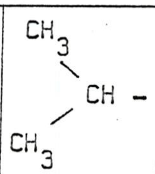


where X is the electron donating substituent.

The figures quoted are rates relative to the phenyl group.

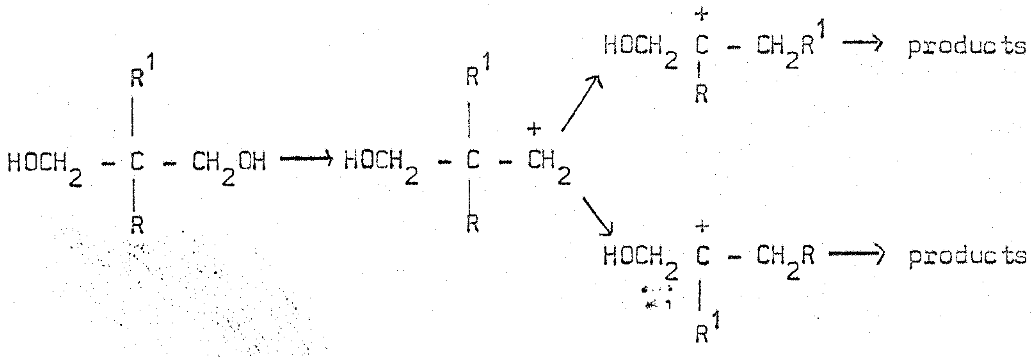
(X = H)

TABLE VII[74]

X	 $CH_3\overset{\overset{O}{\|}}{C}-$	CH_3-		 $(CH_3)_2CH-$	C_2H_5	F	I
relative rate	40	12-15	12.5	9	5	1.86	1

The rearrangement of triphenyl ethylene glycol has also been studied in a variety of solvents and the ratio of phenyl to hydride shift obtained. Figures of 7.33 in concentrated sulphuric acid and 0.44 in dilute acid are quoted[75].

Some work has recently been done on the migrating aptitudes of alkyl groups by Yvernault and Mazet[76] who studied the migration of alkyl groups during the dehydration of 2,2 disubstituted propene 1,3 diols in concentrated sulphuric acid.



Yvernault and Mazet do not quote any values of the ratio of alkyl to hydride shift, only relative rates of alkyl shift and comparing these figures with those calculated from the electrochemical experiments shows reasonably good agreement when the relatively large percentage errors on both sets of results are taken into consideration

TABLE VIII

	average ratio according to Yvernault & Mazet	average ratio from electrochemical results
Et/Me	1.42	1.82
n - Pr/Me	1.95	1.89
n - Bu/Me	2.82	3.1

Both sets of results in Table VIII show the same trend as is found in the case of aryl groups (see Table VII) i.e. the more electron donating the group (in the case of alkyl groups this means the larger the group) the greater its migratory aptitude. These ratios, both for aryl and alkyl migrating groups are only apparent ratios, the real ratios being masked by several effects.

1) It has been shown that the products of the pinacol-pinacolone rearrangement are affected by the configuration of the diol. If the configuration of a diol (or amino alcohol) is fixed by large groups hindering rotation about the carbon-carbon bond between the two 'ends' of the molecule, only the group which is trans to the leaving group will migrate[77]. Although only these extreme cases of totally hindered rotation are known it is possible that if the rotation of the molecule were slightly hindered this could have an effect on the products.

2) As the rearrangement of the molecule is a series of reversible steps it is possible for a factor such as the insolubility of one of the products, or an irreversible step in the reaction producing one of the products to affect the observed ratio.

3) As it is known that an aldehyde will rearrange in acid solution to give a ketone[77] it is possible that this affects the ratio of acetone to propionaldehyde (including their respective oxidation products) found from propene oxidation, masking the true alkyl to hydride shift ratio.

The cyclohexene complex represents a special case of this alkyl shift mechanism as an 'alkyl shift' here shows itself as a ring contraction (see Table V). It is found that the products resulting from this ring contraction are the dominant products with only small amounts of the other products. An explanation for this may be found in the sterochemistry of the complex. It has been shown by n.m.r.[34] spectroscopy that in the complex the mercury and hydroxyl are trans dicquatorial. Thus the direction of attack of the alkyl group and the carbon-mercury bond are trans allowing an almost planar transition state to be realised. This makes the formation of ring contraction products much more favourable than the formation of the hydride shifted products.

B. In Sulphate Solutions

Mercuric sulphate is less soluble in water than mercuric perchlorate. It is, however, possible to obtain solutions which are molar in mercuric sulphate and molar in sulphuric acid, such a solution being used for the preparative work. This solution absorbed propene as rapidly as the perchlorate solution allowing a solution of the complex to be obtained by bubbling propene through the mercuric salt solution.

Polarisation Curves

Polarisation curves were run for propene over the concentration range 0.01 M to 1 M complex (see Figs. XX and XXI), the sulphate ion concentration being kept constant at 2.0 M. The plots obtained are very similar to those obtained for propene in perchlorate except in the low potential range (< 1.4 volts) where there is, in sulphate, an oxidation wave of low current density. The explanation of this wave is probably the same as that for the waves found during the oxidation of the but-1-ene and but-2-ene complexes in perchlorate i.e. it is either the oxidation of a small amount of free olefin, or the oxidation of a hydration product of the olefin. In the region between 1.4 and 2.3 volts the current density decreases with increasing complex

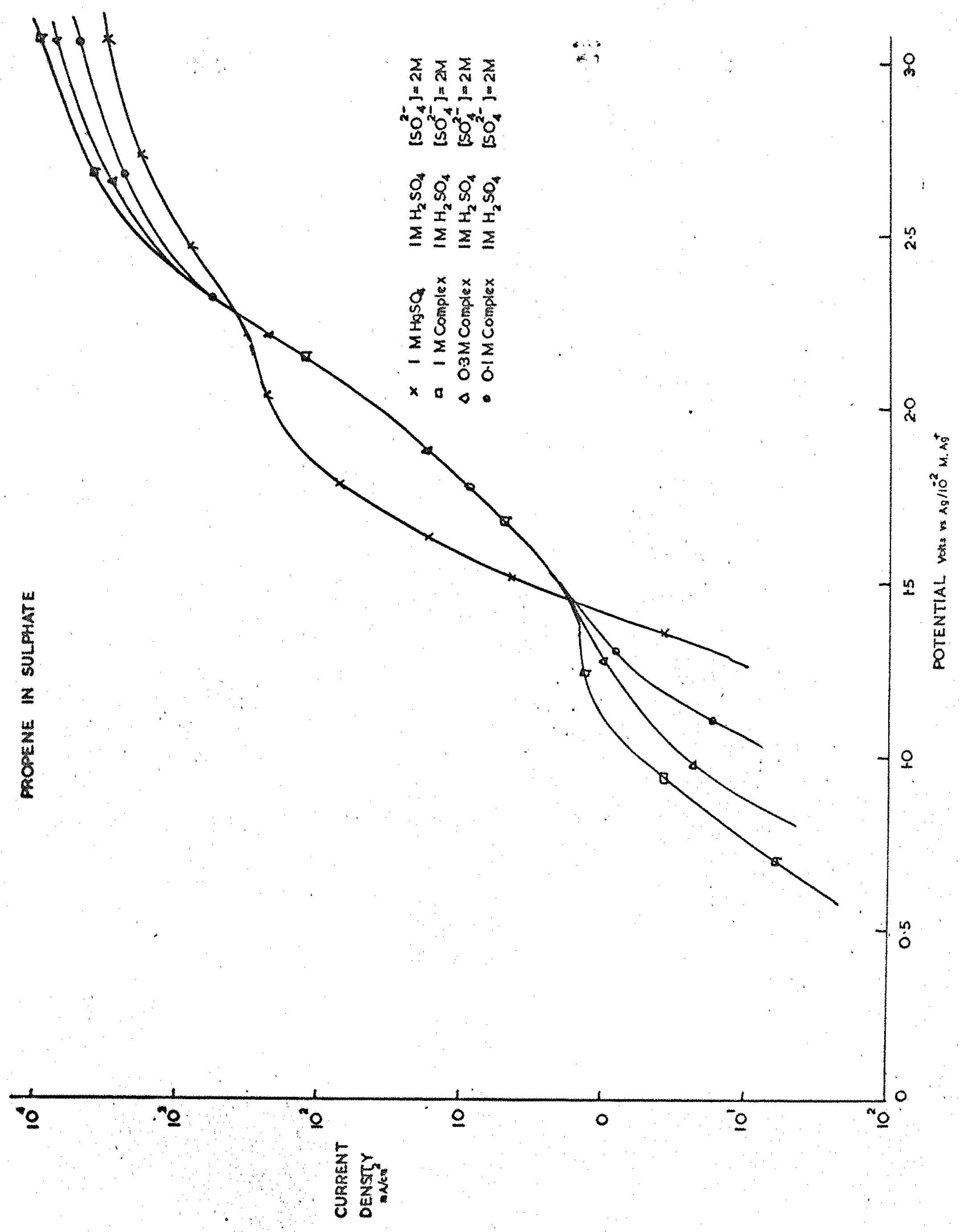

PROPENE IN SULPHATE
CURRENT DENSITY mA/cm²
10⁴
10³
10²
10
0
10⁻¹
10⁻²
0
0·5
1·0
1·5
2·0
2·5
3·0
POTENTIAL Volts vs Ag/10⁻² M.Ag⁺
× 1 M HgSO₄ 1 M H₂SO₄ [SO₄²⁻] = 2M
□ 1 M Complex 1 M H₂SO₄ [SO₄²⁻] = 2M
△ 0·3 M Complex 1 M H₂SO₄ [SO₄²⁻] = 2M
● 0·1 M Complex 1 M H₂SO₄ [SO₄²⁻] = 2M

Figure XX

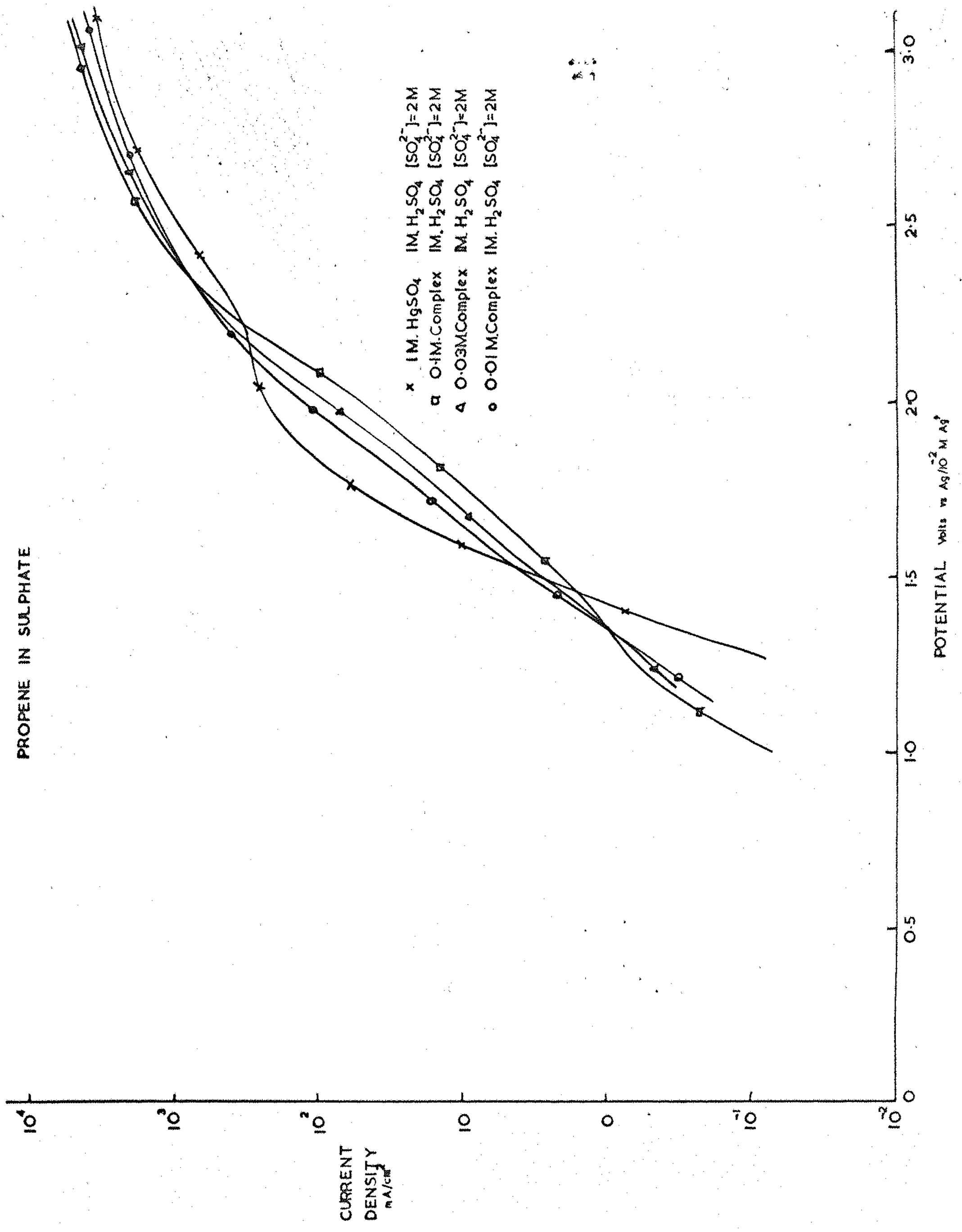

PROPENE IN SULPHATE
CURRENT DENSITY mA/cm^2
10^4
10^3
10^2
10
0
10^{-1}
10^{-2}
0
0·5
1·0
1·5
2·0
2·5
3·0
POTENTIAL Volts vs Ag/10^{-2}M Ag$^+$
× 1M. HgSO$_4$ 1M. H$_2$SO$_4$ [SO$_4^{2-}$]=2M
□ 0·1M.Complex 1M. H$_2$SO$_4$ [SO$_4^{2-}$]=2M
△ 0·03M.Complex 1M. H$_2$SO$_4$ [SO$_4^{2-}$]=2M
○ 0·01M.Complex 1M. H$_2$SO$_4$ [SO$_4^{2-}$]=2M

Figure XXI

concentration up to a concentration of 0.1 M (see Fig. XXI). This decrease must be due to strong adsorption, probably of the complex, interfering with the oxidation of water to oxygen. Higher concentrations (0.1 - 1.0 M) of the complex give currents which are zero order with respect to the concentration of the complex in this range of potentials, indicating maximum coverage of the electrode by adsorbed species. At higher potentials the current shows a first order dependance on complex concentration although this effect is somewhat masked by ohmic potential drop due to the high current densities (< 1 A/cm^2) in this region. It seems possible, from the magnitude of the current that the reaction becomes diffusion controlled in this region.

The product of the electrode reaction

From the evidence of the polarisation curves the complex is obviously oxidised at potentials above 2.3 volts as the current density here is higher than for the base electrolyte alone. Although there is no direct indication from the polarisation curves oxidation probably also occurs at lower potentials. Controlled potential electrolyses were therefore carried out at potentials of 2.1, 2.25 and 2.5 volts, the results of which are shown in Table IX. The products were readily identified by vapour phase chromatography as being the same as those found from the oxidation in solutions containing perchlorate ions.

TABLE IX

Variation of current yield of products with potential for propene in sulphate.

Potential / Product	2.1	2.25	2.5
Acetone	10	8	8
Propionaldehyde	1.2	1	0.8
acetic acid	4.1	59	52
propionic acid	12	18	16
Total current yield	64	86	77
apparent alkyl/hydride shift ratio	0.36	0.44	0.43

Formic acid was once again identified as a product using a spot test[71] but was not analysed quantitatively. No additional products were found.

From the results in Table VIII it can be seen that although the products are the same as those found from the oxidation in perchlorate solutions (Table I, p.40) there is a slight difference in the apparent alkyl/hydride shift ratio, which is somewhat lower in sulphate than in perchlorate solutions. The difference is, however, fairly small (20%) and is best considered along with the differences found for the oxidation in nitrate solutions.

C. In Nitrate solutions

The solubility of mercuric nitrate in water is very high allowing high concentrations of the mercuric ion to be attained in solutions containing nitric acid, a solution molar in mercuric nitrate and molar in nitric acid being used for preparative work. Such a solution, as was the case with the perchlorate and the sulphate, absorbs olefins rapidly and quantitatively to give a 1 : 1 mercury - olefin complex. Thus solutions of the complex may be made by bubbling the olefin through a solution of mercuric nitrate.

Polarisation curves

Polarisation curves were run for propene over the concentration range 0.01 M to 1.0M complex (see Figs. XXII and XXIII). These polarisation curves show a completely different behaviour to those in perchlorate and sulphate solutions. Below 1.4 volts there is an oxidation wave of low current density which is probably due to oxidation either of a small amount of free olefin or of a hydration product of the olefin. In the potential range 1.4 - 1.9 volts the curves show a zero order concentration dependance on the complex and lie on top of the base electrolyte curve. Thus there is no evidence for the oxidation of the complex in this region and as the current is not changed there is probably no adsorption. Above 1.9 volts the curves begin to separate, the current density increasing with increasing complex concentration, but due to the very high current densities reached in this region (almost 10 A/cm^2) it is difficult to see if the

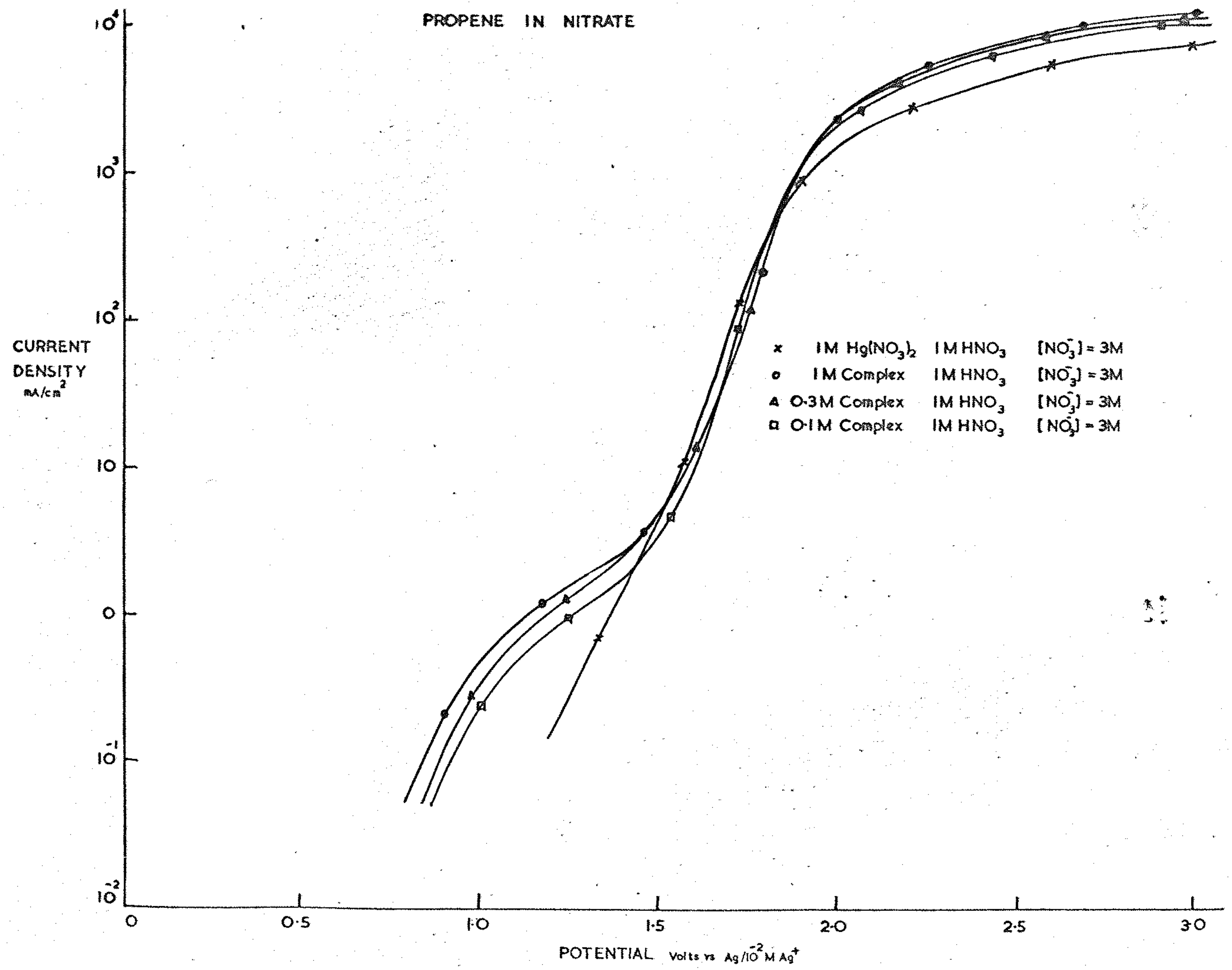

PROPENE IN NITRATE
CURRENT DENSITY mA/cm^2
10^4
10^3
10^2
10
0
10^{-1}
10^{-2}
0
0·5
1·0
1·5
2·0
2·5
3·0
POTENTIAL Volts vs Ag/10^{-2}M Ag$^+$
× 1M Hg(NO$_3$)$_2$ 1M HNO$_3$ [NO$_3^-$] = 3M
o 1M Complex 1M HNO$_3$ [NO$_3^-$] = 3M
▲ 0·3M Complex 1M HNO$_3$ [NO$_3^-$] = 3M
□ 0·1M Complex 1M HNO$_3$ [NO$_3^-$] = 3M

Figure XXII

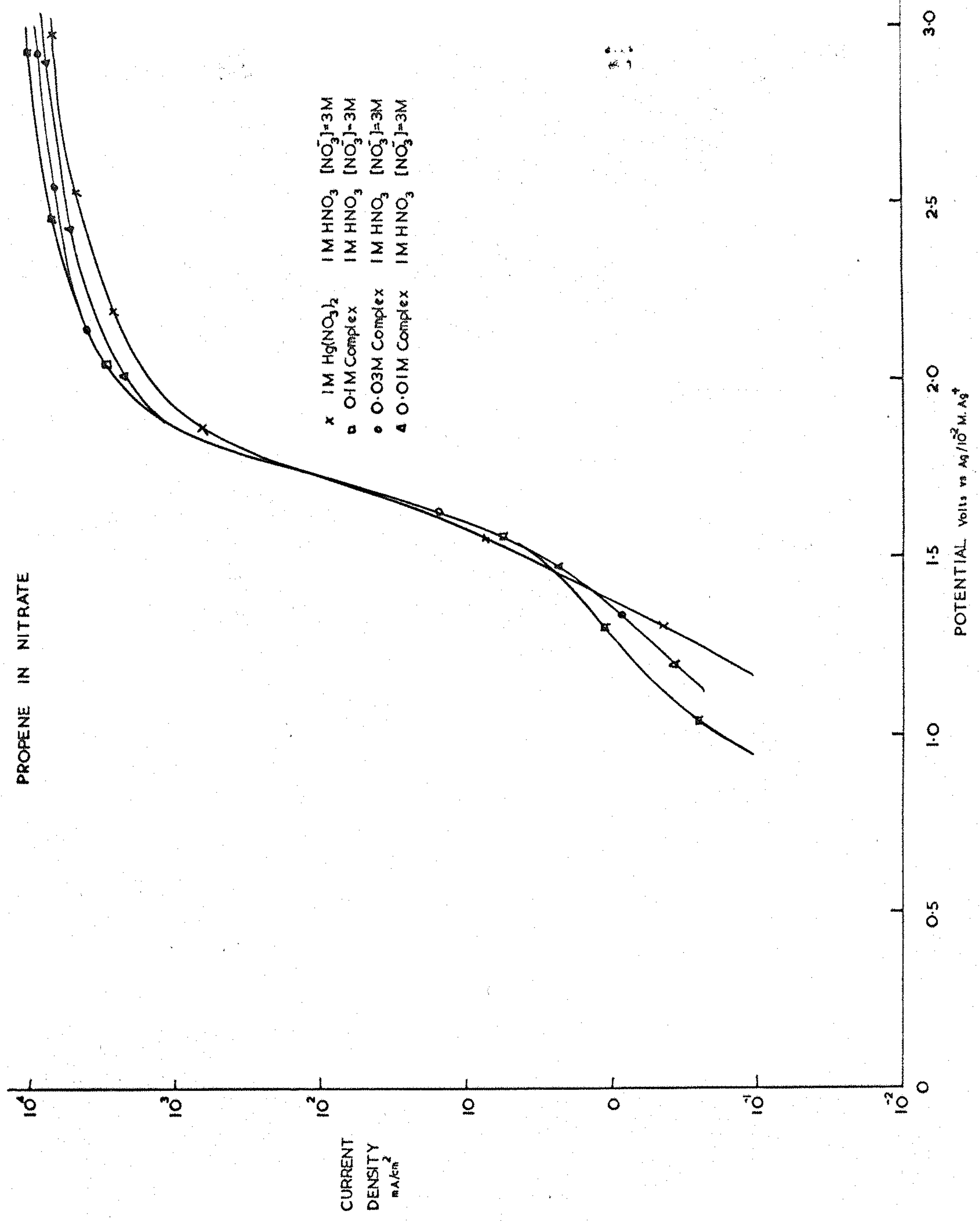


Figure XXIII

concentration dependance does become first order. Due to ohmic potential drop it is also difficult to see if there is a limiting current region here which would indicate diffusion control of the electrode process, although the magnitude of the current density seems to indicate that the complex oxidation should be almost diffusion controlled at 3.0 volts.

The products of the electrode reaction

Controlled potential electrolyses were performed for the propene and but-2-ene complexes. The results for the propene complex are shown in Table X. The major products were shown to be the same as for the propene complex in perchlorate and sulphate solutions by vapour phase chromatography. Formic acid was shown to be present by a spot test[2] but was not analysed quantitatively. An extra product was found from

TABLE X

Variation of current yield of product with potential for propene in nitrate.

Product \ Potential	1.80	2.10	2.40	2.70
Acetone	6	9	5	3.6
Acetonyl acetone	0.6	-	-	-
Acetic acid	11	16	34	27
Propionic acid	8.5	24	24	18
Total current yield	26	49	63	49
Apparent alkyl/hydride shift ratio	0.5	1.0	0.9	0.9

the oxidation at 1.8 volts and was shown to be acetonyl acetone (hexane -2,5 -dione). It is interesting to note that the complex is oxidised at this potential although it is well within the zero order region of the polarisation curves where these curves for the complex lie on top of the polarisation curve for the base electrolyte. As can be seen from Table X the ratio of alkyl to hydride shift is almost twice as large in nitrate as in perchlorate solutions. It was thus decided to examine the oxidation of the complex of a secondary olefin, but-2-ene for which an alkyl shift was definitely shown to occur.

The results for the but-2-ene complex are given in Table XI

TABLE XI

Variation of current yields of products with potential for but-2-ene in nitrate.

Potential / Product	2.10	2.40
Methylethyl ketone	18	6.3
Acetic acid	31	42
Propionic acid	6	3
iso Butyric acid	27	11.5
n Butyric acid	5.5	4
Total current yield	87	67
Apparent alkyl/hydride shift ratio	0.5	0.33

The products were shown to be the same as for the but-2-ene complex in perchlorate by vapour phase chromatography with the exception of n-butyric acid which was found in small amounts.

The mechanism of the electrode reaction

Three important features emerge from Table X:

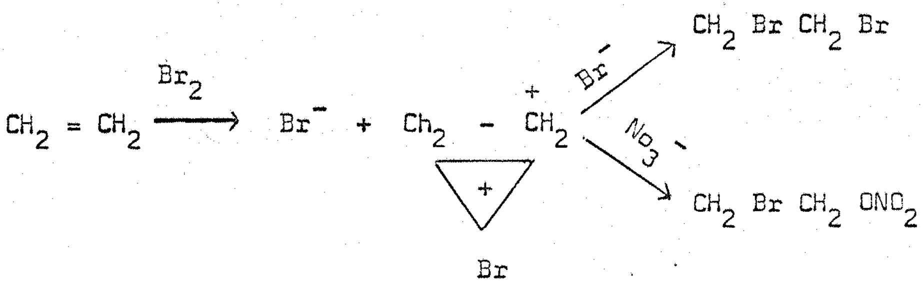
1) the presence of a new product, only formed at a low potential. The most probable route for the formation of acetonyl acetone is by the dimerisation of acetone by a radical process. The acetonyl radicals necessary for this process could be formed by hydrogen abstraction from acetone, possibly by nitrate radicals. If the acetonyl radicals are formed by hydrogen abstraction it might be expected that hydrogen abstraction would also occur from acetic acid resulting in succinic acid as a product.

2) the total current yields of organic products are much lower than is the case in perchlorate or sulphate solutions. This can be explained by the lack of any obvious adsorption allowing a greater amount of oxygen evolution to occur.

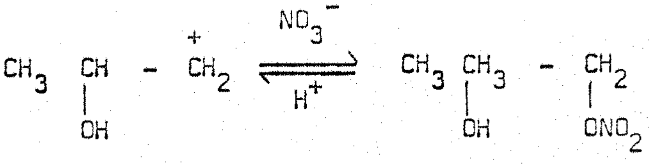
3) the apparent ratio of alkyl to hydride shift obtained for propene in nitrate solution is much higher than in perchlorate or sulphate solutions.

If the alkyl and hydride shift reactions were simple intra molecular rearrangements then the ratio of their rates would be indepdent of the anion present and depend only on the migrating group. The ratio, however, varies with the anion present, being similar for perchlorate and sulphate but considerably different for nitrate. It should, therefore, be possible to explain this change in the ratio using a property which is a feature of nitrate, but not of perchlorate or sulphate ions.

A property which is important only for nitrate ions is their ability to form organic nitrates if reactions involving carbonium ion intermediates are performed in solutions containing the nitrate ion. Thus, if ethylene is brominated in an aqueous solution containing sodium nitrate some 2-bromo ethyl nitrate is found amongst the products.[78] As bromination is known to occur via the formation of a bromonium ion the following is the most probable reaction mechanism



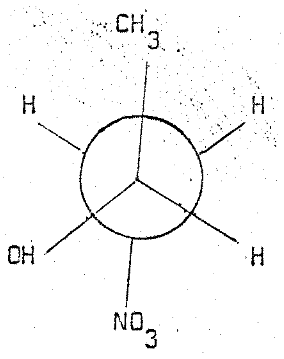
If, therefore, the carbonium ion II (see Mechanism IV, p^{46}) has an appreciable lifetime it may, by analogy with the mechanism shown above, form a nitrate. These aliphatic nitrates are not very stable in acid solution as their decomposition to a carbonium ion and nitrate is acid catalysed. Thus the nitrate will exist in an equilibrium concentration



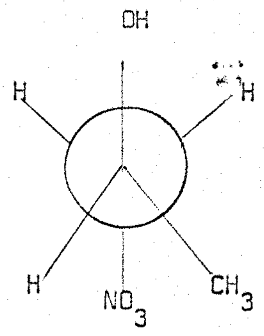
$$CH_3\ \underset{\displaystyle OH}{\underset{|}{CH}} - \overset{+}{CH_2} \xrightleftharpoons[H^+]{NO_3^-} CH_3\ \underset{\displaystyle OH}{\underset{|}{CH_3}} - \underset{\displaystyle ONO_2}{\underset{|}{CH_2}}$$

VI

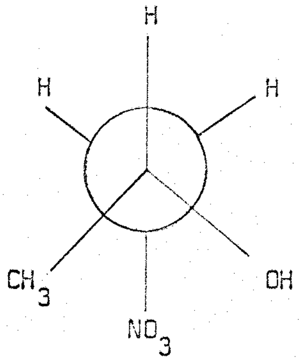
the equilibrium being forced towards production of the nitrate (VI) by the high concentration of nitrate ions (3M) in the solution. There are three possible configurations of the nitrate (VI).



VI A

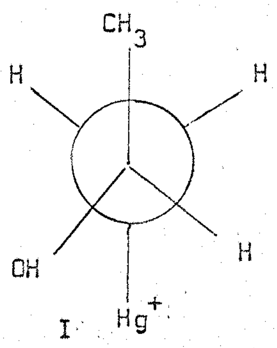


VI B



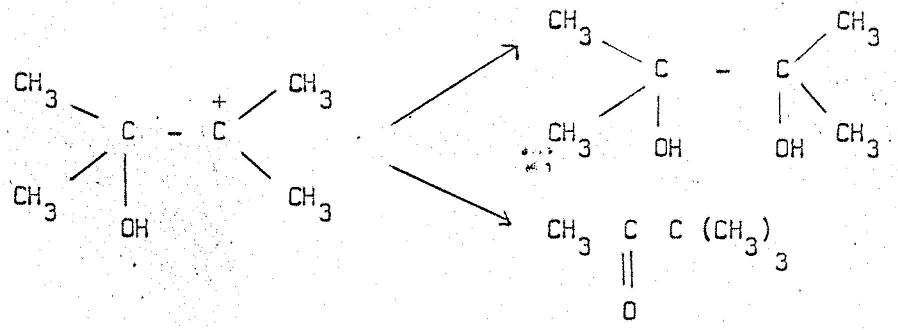
VI C

Of these three configurations VI A, with the largest groups (methyl and nitrate) trans to each other would be preferred and this is also the configuration which favours the alkyl shift as the migrating and leaving groups are trans to each other. Thus in this reaction path at least some of the carbonium ion would be held in a configuration favourable for the alkyl shift so that if the shift was concerted with the loss of nitrate a larger amount of the product resulting from an alkyl shift should be found than if the shift occurred in a 'free' carbonium ion. As the ion I would have a similar configuration to VI A it is therefore necessary, if the explanation given above is to be valid, to assume that the carbonium ion II which is produced by the oxidation of I is free for a sufficient length of time to lose its configuration. This time would only be that required for one rotation about a carbon-carbon bond, which is very short.



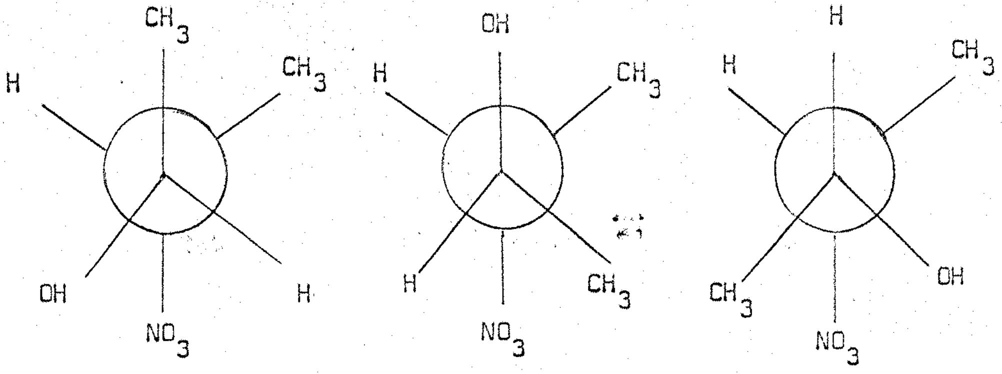
I

It has been shown that for the reaction[12]



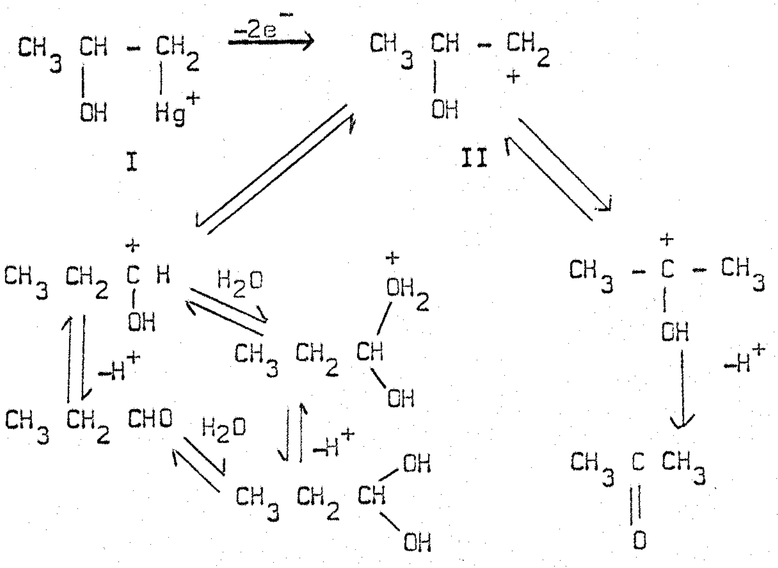
the products are produced in the same ratio whatever the source of the carbonium ion (it may be produced by opening of the epoxide, from the chlorhydrin, from the amine via a diazo salt or from the diol) indicating that the carbonium ion is 'free' for a sufficient length of time for the departing group to have no effect on the course of the reaction. However the lifetime of the carbonium ion II might be expected to be somewhat shorter than the lifetime of this more highly substituted ion.

This mechanism can, therefore, explain the fact that there is a difference in the measured methyl : hydride shift ratio for propene in perchlorate and nitrate solutions even if only a fraction of the carbonium ions do, in fact, form nitrate compounds. It cannot explain this difference in quantitative terms nor does it explain the difference in the ratio between perchlorate and sulphate solutions. As far as can be seen from the figures in Table XI and Table IV there is very little difference between the alkyl : hydride shift ratios observed for but-2-ene. This might be expected as, if the projections are examined for the nitrate compound, all three configurations seem to have approximately equal probability, so that little change in the ratio



would indeed be expected.

Another possible explanation for the difference in alkyl shift ratios observed for the different anions could lie in the fact that acid solution will convert aldehyde into ketones[77] whereas the reverse reaction does not take place. Thus the reaction scheme producing acetone and propionaldehyde should probably be shown as below



Aldehydes are known to form hydrates in aqueous acid solution so that the complex series of equilibria producing the gem-diol will exist in the electrolysis solution. Any factor which could disturb any one of these equilibria to cause stabilisation of propionaldehyde or its hydrate would affect the equilibrium producing propionaldehyde from the ion II and thus the observed alkyl : hydride shift ratio. The ionic strength of the solution is known to have an effect on these hydration[79] and protonation/deprotonation equilibria but it is only small and could only explain the small difference found between the ratio in perchlorate and sulphate solutions where there is a difference in ionic strength (there is no difference in ionic strength between the perchlorate and nitrate solutions). If, however, the base strengths of perchlorate and nitrate ions were appreciably different this could be sufficient to disturb the equilibria involving deprotonation and thus affect the observed alkyl : hydride shift ratio.

D. The electrolysis under pulse conditions

It has been shown by Fleischmann et al[80,81,82] that the kinetics of the fast steps in a sequence of reactions at an electrode can be determined by examing the variation in the yield of products with the length of oxidation pulse. This was done for the Kolbé reaction for which a reaction mechanism of several steps involving adsorption on oxide layers has been proposed. The integral yield of the products was determined for various oxidation pulse lengths the on:off ratio of the pulses being kept constant at 1.10 and the potential during the 'off' period being sufficiently low to remove all adsorbed species. As the duration of the oxidation pulse decreases the integral yield begins to deviate from the steady state value and it is possible to define, from the pulse length at which this occurs, a relaxation time for the reaction which involes the rate constants of the fast steps.

As the electrochemical oxidation of mercury-olefin complexes is believed to be a reaction involving adsorption on the electrode an attempt was made to use this method to examine the reaction mechanism. The attempt was not successful as it was found to be impossible to obtain consistent results at any given pulse length. The difficulties which were found with this method for studying the reaction were mostly instrumental. When an oxidation pulse was applied an initially very high current was obtained which rapidly fell off to a low value. Even when a very small electrode was used the initial current was limited to some extent by the potentiostat. Furthermore the use of such a small electrode meant that the average current was only 10 - 20 mA and as 300 - 400 coulombs had to be passed to produce an analysable amount of product the electrolysis had to be run for a long time (5 - 10 hrs). An electronic integrator was used to determine the number of coulombs passed but in order to prevent it from subtracting the cathodic coulombs from the anodic coulombs a modification had to be made to the system which seriously limited the performance of the potentiostat.

Oxidation pulses of lengths varying from 100 m sec to 100 μ sec were applied to the electrode and from several sets of results two trends could be seen. The first was that the total yield of products decreased with decreasing pulse lengths. This suggests that the yield of oxygen increases as the pulse length is shortened, as is found in studies of acetate oxidation (Kolbé and Hofer-Moest reactions) under similar conditions. Thus it seems possible that an order of events similar to that found for acetate oxidation occurs in the oxidation of mercury-olefin complexes. Thus the initial step would be the formation of an oxide layer on the electrode which would then be followed by oxygen evolution. After a certain length of time the electrode becomes covered with organic intermediates which limit oxygen evolution and give the observed organic products. The second trend (which was less obvious) was that the amount of acetone relative to the acids which were detected seemed to increase slightly as the pulse length decreased. This might be expected if one of the primary products of the reaction is a precursor of acetone (such as its protonated form) which could either undergo further oxidation on the electrode or deprotonate to give acetone in solution. An interesting consequence of this is that by careful control of the conditions it should be possible to produce good yields of a substance which is only partially oxidised i.e. acetone instead of the fully oxidised acids which are the usual products.

An important point in which the study of this reaction differed from the corresponding study of acetate oxidation was in the lowest potential which could be used for the 'off' pulse to remove platinum oxide and adsorbed species from the electrode. In the acetate oxidation reactions very low potentials could be used without affecting any of the species in solution and thus the platinum oxide could be removed rapidly. In this case, however, the mercury-olefin complexes which are present reduce readily below + 300 mV so that the lowest potential which could safely be used was + 400 mV and at this potential oxide reduction is relatively slow and incomplete.

CONCLUSION

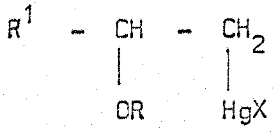
It has been shown in this thesis that the mercury II-olefin complexes of a variety of olefins, formed in each case by the simple rapid reaction of mercuric ions with the olefin in acid solution, are oxidised at a smooth platinum electrode. The concentration of olefin which can be achieved by dissolving it as a complex of mercury is more than 1000 times the solubility of the free olefin in aqueous acid allowing the oxidation to be carried out at high current densities. Although the reaction takes place at high anodic potentials, in most cases the organic products isolated account for almost 100% of the current. The electrode reaction regenerates the mercuric ion which can therefore be regarded as a catalyst since the complex can be regenerated by simply bubbling olefin through the solution. This reaction is interesting as it is the first reported example of an electrochemical oxidation of a complex resulting in the fission of a metal-carbon bond. The principal products which are observed are carboxylic acids together with small amounts of aldehydes and ketones which, it has been shown, are probably the first products of the electrode reaction.

The effect of pH (for the propene complex) and of electrode potential (for the propene, but-1-ene and but-1-ene complexes) on the products of the reaction was investigated. The products of the oxidation of the complexes of a large number of olefins were determined at one fixed potential.

A mechanism, which involes the rearrangement of a carbonium ion - via the migration of an alkyl group to give some of the products and via a hydride shift to give the others - has been suggested for the reaction. The ratio of the products formed by these two routes has been shown to depend on the size of the migrating alkyl group and, for propene, on the anion present, the alkyl migration being more favoured in nitrate than in perchlorate or sulphate solutions. Values of several alkyl to hydride shifts observed were obtained in perchlorate solutions and the relative alkyl to alkyl shift ratios calculated from these were compared with values in the literature.

Because of its nature this oxidation is, chemically, an interesting reaction but the major products - the lower carboxylic acids - have insufficient commercial value to make this reaction attractive economically in the form in which it is described. It may, however, be possible to modify the reaction to obtain products of greater commercial interest, such as diols, in one of two ways:

1) By trapping the carbonium intermedaites - a method which has not yet met with any success.
2) By modifying the complex, and thus the carbonium ion formed. This is possible by working in non-aqueous solvents. Thus in an alcohol[39] the complex has the form



$$R^1-\underset{\displaystyle OR}{CH}-\underset{\displaystyle HgX}{CH_2}$$

The oxidation of complexes of this type is currently being investigated.

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