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KINETICS AND ADSORPTION IN THE ELECTROCHEMICAL REDUCTION OF AROMATIC KETONES

BY

Eric James Rudd

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Ottawa, Canada

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B.E. Conway
Professor of Chemistry
Research Supervisor

Eric James Rudd
Ph.D. Candidate

This thesis was typed, proof-read and oft-times "criticised" by my wife, Jacqueline Ann. The time required to complete it has been endured by my son, Andrew, and by my daughter, Carrie Elena.

To these three people this labour is dedicated.

PREFACE

The progress of electro-organic chemistry following the studies of Faraday and Kolbe early in the nineteenth century was perhaps highlighted in 1900 by the detailed investigations of the electro-reduction of nitrobenzene by Haber, where it was shown that the nature of the reduction products found could be determined by controlling the electrode potential. Since then interest in electro-organic chemistry appears to have branched into two main fields.

(i) The study of organic electrode processes by polarographic methods, i.e., at a dropping mercury electrode or a hanging mercury drop electrode. Much of the emphasis has until recently been placed upon the chemistry of the electrochemical reactions rather than the nature of the reaction occurring at the electrode surface.

(ii) The development of electro-organic syntheses (including, in recent years, stereospecific ones) and industrial electro-organic chemistry in which the "electron" has essentially been employed as a powerful chemical reagent, but often without the careful control demonstrated by Haber in his early studies of organic electrode processes where the important effect of potential was first demonstrated.

During the last decade, interest in fuel cells and energy conversion systems of various types has stimulated a great deal of research in the electrochemistry of anodic (electro-oxidation) processes. In fundamental aspects of such work, the emphasis has been placed on understanding the nature of the reaction which occurs in the interfacial region at the electrode, the role of the adsorption of reactants, products and intermediates in the overall mechanism, the effect of the nature of the electrode material, etc. In this way, fundamental ideas regarding the mechanism of the electrode process have been developed.

Although polarographic studies have provided an extensive literature of electro-reduction reactions, the method is limited from a kinetic viewpoint by the necessity of working under largely diffusion-controlled conditions over the potential range of the reaction. Furthermore, in these reduction processes little attention has been given to the question of quantitative correlation between the adsorption of products and reactants and the electrochemical kinetics. The mercury electrode provides an ideally polarisable electrode over a wide range of cathodic potentials and has been much used in the study of the adsorption behaviour of many organic compounds, but not specifically in relation to reaction kinetics and studies of mechanism. One of the principal aims of the present work has therefore been to correlate the kinetic behaviour observed in the electro-reduction of the aromatic ketone, acetophenone

at mercury, with the adsorption behaviour of that ketone, and of the product of the reaction, directly determined thermodynamically by means of electrocapillary measurements over a range of potentials, and reactant and product concentrations.

In Chapter I an introductory review is presented which includes a brief summary of the principles of electrochemical kinetics in so far as they are involved in the present work and also some aspects of adsorption processes at a mercury electrode. The present state of knowledge of the mechanism of the electro-reduction of carbonyl compounds (in particular aromatic ketones), which has been obtained mainly from polarographic studies, is also discussed in an attempt to provide a perspective for the work described in this thesis. The experimental techniques used to study the electrode kinetics and the adsorption behaviour of the chosen ketone(s) are presented in Chapter II. The results and discussion of the results comprise Chapters III and IV.

Part of the work described in this thesis was presented at the Discussion of the Faraday Society in England (1968) and published as follows:

"Reaction Order and Adsorption in the Kinetics of Organic Electrode Reactions"

B.E. Conway, E.J. Rudd and L.G.M. Gordon, Disc. Farad. Soc., 45, 87 (1968).

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For creating the opportunity to pursue doctoral studies,
For the interest in the experimental work which has formed the "backbone" of this thesis,
For the discussion from which the thesis has evolved,
But more importantly,
For the friendship during all this time;

"Thank you, Dr. Conway".

The adsorption studies, which are recorded in the experimental section of this thesis, were carried out by Mr. L.G.M. Gordon as part of his own graduate studies.

The author wishes to express his appreciation to Dr. Halina Kozlowska for the constructive criticism and discussion of many aspects of the experimental work. The recently graduated members and the present members of the Electrochemistry Group will be remembered for the "electric atmosphere" which has been created in Room 151.

The author also wishes to thank Mr. A.J. Hancock who kindly provided facilities for thin-layer chromatographic studies and Mr. G. Desbarats for the preparation of several of the compounds used in this work.

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ABSTRACT

In the study of organic electrode processes it is desirable to complement kinetic and polarographic information by direct adsorption studies in relation to data on reaction orders and Tafel slopes.

The electro-reduction of acetophenone in acidic media (pH < 3) has been shown to yield only 2,3-diphenylbutane-2,3-diol (acetophenone pinacol) with a high coulombic efficiency. Furthermore, the electrode reaction occurs at cathodic potentials sufficiently removed from those at which currents attributed to the evolution of hydrogen are significant, so that in the potential range studied, only a single Faradaic process occurred.

This electrochemical reaction has therefore been studied in relation to (a) the adsorption and orientation of the ketone at the mercury electrode surface (b) the kinetic behaviour of the electrode reaction, and (c) the adsorption of the pinacol and its effect, if any, upon the kinetics of the electrode process.

Studies of the electrode kinetics comprised both potentiostatic steady-state and potentiodynamic non-steady state measurements employing a "triangular" potential sweep and a potential step procedure. Limiting current behaviour was consistently observed in the steady-state measurements and was attributed to the overall rate of reaction being determined ultimately by the rate of diffusion of the ketone

to the electrode surface. This conclusion was supported by the results of the analysis of current-potential curves obtained from potentiodynamic studies. A potentiostatic "potential step" technique was introduced as a complementary method of study in an effort to obtain current-potential relations at very short time intervals after the electrode potential had been established. However, oscillatory behaviour of the current was observed for a few milliseconds after the application of the potential step and this effect limited the value of this method in the study of the electrode process.

The electrochemical reaction was shown to be sensitive to the composition of the aqueous-organic solvent (experiments were conducted in methanol-sulphuric acid and in methanol-water-sulphuric acid mixtures) and to the concentration of hydrogen ions in the solution. However, the absence of a significant H/D primary isotope effect indicated that the proton was not critically involved in the rate-determining step.

Adsorption studies have been made by a new electrocapillary procedure and from the electrocapillary curves obtained, surface excess quantities and surface pressures have been derived. Both acetophenone and its reduction product, the pinacol, were found to be strongly adsorbed at the mercury surface and it was also shown that the presence of

pinacol in the solution inhibited the adsorption of the ketone. The dependence of K upon surface coverage (where K is the adsorption equilibrium constant in a Langmuir-type isotherm) indicated the presence of interaction effects in the adsorbed layer. The results were therefore examined in terms of an isotherm which included an interaction parameter, e.g., a Frumkin isotherm. Over an appreciable range of concentration and at intermediate coverages, $0.2 < \theta < 0.8$, "Temkin" adsorption behaviour was limitingly found.

The kinetic reaction order R was derived from potentiostatic, steady-state log[current]-potential curves and examined in relation to isotherms for reactant adsorption. Theoretical cases were considered for the evaluation of R as a function of the coverage θ for various types of isotherm. Since an electrochemical reaction is a heterogeneous process, an apparent surface reaction order R_s was first calculated. It was found that initially R_s increased with increasing surface concentration of reactant (Γ) but then reached an approximately constant value at high surface concentrations.

The electrochemical behaviour of the pinacol has also been examined and it was found that an adsorbed layer of the pinacol facilitated the evolution of hydrogen from the solution at the mercury surface. This is believed to involve a protonated form of the pinacol (*cf.* H_3O^+ and $MeOH_2^+$ species)

from which proton discharge occurs in the hydrogen evolution reaction.

The mechanism of the electro-reduction of acetophenone at mercury is discussed in the light of the complementary results of the adsorption and kinetic studies. Evidence is provided that the electroactive species is the protonated form of the ketone and the protonation is essentially a surface reaction. Calculations indicated that the presence of adsorbed acetophenone pinacol at the electrode surface, even at low surface coverage, was inevitable in virtually all the steady-state experiments. Its presence may only be avoided, or the effects minimised, in experiments employing very fast potentiodynamic sweeps ($\frac{dE}{dt} > 100$ V. sec^{-1}) or by the use of a potential step technique at an electrode with a renewable mercury surface, providing that oscillatory behaviour of the resulting current could be virtually eliminated.

CHAPTER I

INTRODUCTORY REVIEW

1. INTRODUCTION AND ELECTROCHEMICAL KINETIC PRINCIPLES

Early in the nineteenth century the oxidation of acetic acid by Faraday (1) demonstrated the power of the electric current to effect decomposition of organic substances. A few years later, Kolbe (2) anodically decomposed trichloromethylsulphonic acid, an acid which at that time had proved stable to the most powerful chemical oxidising reagents, and by the end of the century Gatterman, Kolbe, Haber and others had widely extended the field of electro-organic chemistry.

In 1900 Haber (3) indicated the several steps involved in the electro-reduction of nitrobenzene to aniline*

Despite the limited electrical equipment then available, Haber seems to have been the first to realise the importance of control of the electrode potential, a factor which unfortunately has been ignored in many later electro-organic syntheses. This situation becomes all the more curious when it is realised that a number of chemical reductions are in fact electrochemical in nature, and proceed effectively under

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* This reaction was recently studied electrochemically using conventional potentiostatic techniques, as well as controlled potential electrolyses and pulse-potential electrolyses, to investigate the electrochemical behaviour of the various intermediates (4).

conditions of controlled potential, e.g., the Clemmensen reduction (Zn/Hg) and reductions with Na/Hg or Mg/Hg*. It is true that potentiostatic reductions can be slow and this may have been the reason for the persistent use of a large current, even if controlled, in many electro-organic syntheses (5).

Although a great many organic electrode reactions have been studied, few have been examined in detail with regard to electrochemical mechanisms and the role of the adsorption of reactants and products. The introduction of polarography in 1922 by Heyrovsky and co-workers (6), and its subsequent development has led to an extensive literature of information upon organic electrode processes. This type of approach is, however, limited from a kinetic viewpoint by the necessity of operating under diffusion-controlled conditions over most of the potential range in which the reaction proceeds at significant rates. Nevertheless, the polarographic half-wave potential (characteristic of a particular redox process) can indicate an organic compound which may be suitable for an electrochemical study of both the kinetic and adsorption behaviour.

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* Here a mixed potential is established which corresponds to both the corrosion of the amalgam and reduction of the organic compound (itself adsorbed at the surface of the amalgam) occurring at equal rates.

(a) General Representation of an Electrochemical Reaction

The basic kinetic step in an electrochemical reaction is the transfer of electrons to or from an ion or a molecule at an electrode. Essentially such reactions can be considered in four steps:

Step I. Transport of the electroactive species to the electrode;

Step II. Adsorption at the electrode-solution interface*;

Step III. Charge transfer, which may, and usually does, occur to the adsorbed species;

Step IV. Subsequent reactions which may be chemical in nature, together with desorption of the products from the interface.

Transport from the bulk solution (step I) can occur by diffusion, by electrolytic migration or by convection. Net diffusion is a consequence of the reaction of the electroactive species at the surface, giving rise to a concentration gradient between the reaction layer and the bulk of the solution due to consumption of the reactant at the interface. It is this condition that is realised in polarography. Migration is the movement of charged particles

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* That adsorption is necessarily a pre-requisite for all electrochemical reactions has been recently questioned by Zuman et al. (7,8). Indeed, the reduction of several aromatic carbonyl compounds, effected at a mercury electrode, required electrode potentials beyond that at which the organic molecule was electrostatically desorbed from the interfacial region.

under the influence of an electric field and such transport is absent for all organic molecules and relatively slow for organic ions of appreciable molecular weight.

Following transport of the electroactive species to the electrode, an adsorption equilibrium is established (step II). That this process of adsorption should involve some type of chemisorption is open to question, particularly for adsorption at non-catalytic metals. Chemisorption is certainly not a necessary condition for the electrochemical process to occur, but an orientation of the molecule in the surface layer is likely and the energy for such a process may vary in a manner related to changes of the energy of adsorption with electrode potential. Considerations of this kind may explain the apparent "slow" electron transfer step observed in certain electrochemical reactions when the actual charge transfer event must surely be fast.

The electro-reduction of organic molecules usually involves protons (or molecules which are proton sources such as water or an alcohol) and the primary product of the electrode process may be a radical or a radical ion. Subsequent reactions e.g., dimerisation, dismutation, or abstraction, may occur at the electrode surface or in the solution near to the electrode (in the latter case the reactions are homogeneous).

(b) Mechanisms of Electro-reductions

It is possible to consider the electro-reduction of organic molecules in one of the following general ways:

(i) Electrochemical Hydrogenation: Electron transfer produces atomic hydrogen at the electrode surface and a subsequent heterogeneous reaction with the organic molecules effects reduction. Such processes will occur mainly at those electrodes at which there is appreciable surface coverage by adsorbed hydrogen atoms even at low cathodic potentials e.g., at platinum or palladium.

The formation of propane and isopropanol in the electro-reduction of acetone at a platinised platinum electrode was recently shown to occur by independent pathways, both involving chemisorbed ketone molecules (9,10) and dissociatively chemisorbed hydrogen atoms.

(ii) Electron Transfer/Proton Transfer: In this case electron transfer is considered to occur directly to the organic molecule. The electroactive species may be protonated prior to charge transfer or alternatively a radical ion can be the primary product of the electrode reaction and the protonation step follows. This type of electrode process probably occurs at metals where surface coverage of hydrogen atoms is low over a wide cathodic potential range and at which chemisorption of the reactant is unlikely, e.g., at mercury and cadmium.

The two mechanisms clearly reflect the catalytic and non-catalytic properties of certain electrode materials. A similar division is shown in the results of studies on the hydrogen evolution reaction in acidic solutions, and in the values of the exchange current density (i_o) obtained by extrapolation of the linear Tafel region to the reversible potential for the redox process. The non-catalytic metals give low i_o values (10^{-9} to 10^{-13} A. cm.$^{-2}$) whereas for platinum and palladium the value is much higher (10^{-3} to 10^{-4} A. cm.$^{-2}$).

The rate-determining step in the hydrogen evolution reaction is also dependent upon the nature of the electrode material (11,12,13,14), and appears to involve atom-atom recombination [mechanism (i)] for catalytic metals and an electrochemical discharge step [mechanism (ii)] for mercury, cadmium or lead.

Hence electrode processes may be highly specific with regard to the nature of the electrode surface; this specificity arises mainly from the adsorptive and catalytic properties of that surface, and is also manifested particularly in organic electro-reductions in regard to adsorption of reactants and products (15,16).

(c) Kinetic Formulation of Electrochemical Reactions

In so far as electrode reactions are heterogeneous processes their rates will be influenced by:

(1) the concentration of reactant at the surface, which is related to the bulk concentration by an adsorption isotherm;

(2) the activation energy for the heterogeneous reaction at the surface;

(3) the presence of adsorbed intermediates and/or products on the electrode,

and

(4) the potential difference across the metal-solution interface.

The effect of the electrode potential arises in two principal ways. Firstly, the surface concentration can be related to the bulk concentration by an electrochemical distribution function, which is dependent upon the electrochemical free energy of adsorption $\Delta \bar{G}^{o}_{ads}$. Secondly, this potential difference modifies the electrochemical standard free energy of activation $\Delta \bar{G}^{o\ddagger}$; this energy term will include (a) any chemical effects associated with the "activation" of the reactant particle e.g., configurational changes, bond deformation, and (b) changes of the electrical energy experienced by the particle in its progress along the reaction co-ordinate. Hence $\Delta \bar{G}^{o\ddagger}$ is analogous to the

chemical free energy of activation $\Delta G^{o\ddagger}$ and will be dependent on the electrochemical nature of the reactant and the catalytic and adsorptive properties of the surface.

(i) Rate Equations: Consider the simple redox process,

$$R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O + ze^-$$

where k_f and k_b are heterogeneous, potential-dependent rate constants for the forward and reverse electrochemical reactions. The reversible electrode potential $E=E_r$ can be written as

$$E_r = E_r^o + \frac{RT}{zF} \ln \left\{ \frac{(C_R)_s}{(C_O)_s} \right\} \qquad (I, 1)$$

where E_r^o is the standard reversible potential for the electrode process. For simplicity, surface concentrations $(C_R)_s$ and $(C_O)_s$ are used in place of surface activities.

At this equilibrium potential the current density corresponding to the cathodic reaction (i_c) is equal to that of the reverse reaction (i_a) so that the net current is zero. However the velocity of the forward or backward reaction can be expressed in terms of the exchange current density (i_o),

$$i_o = zF(C_R)_s (1-\theta)\ k \exp \left\{ - \frac{(\Delta G^{o\ddagger} - \beta E_r zF)}{RT} \right\} \qquad (I, 2)$$

where k_f (or k_b) is replaced by the single rate constant k.

The term $k \exp\left\{-\frac{\Delta G^{o\ddagger}}{RT}\right\}$ is the chemical rate constant at the particular condition $E_r = 0$, although the potential at which this situation is realised cannot in practice be known. In most cases the condition of zero charge density at the electrode surface does not correspond to zero metal-solution potential difference; this situation arises on account of surface potential effects and the specific adsorption of certain ions.

A geometrical factor $(1-\theta)$ gives the specific fractional area available for further electrochemical reaction, since θ refers to the steady-state coverage of intermediates or products adsorbed on the surface when the overall rate of reaction is υ. Usually θ depends upon the rate of reaction, but does not generally include coverage by solvent molecules, which normally cover initially more or less the whole surface of the electrode but are easily displaced by reaction products or intermediates.

To establish a net current, some potential E ($>E_r$) must be applied and the resulting current can be represented as

$$i = zF(C_R)_s(1-\theta)\, k \exp\left\{-\frac{\Delta G^{o\ddagger}}{RT}\right\} \exp\left\{\frac{\beta EzF}{RT}\right\} \quad (I, 3)$$

Since $E - E_r$ is often referred to as the overpotential (η)

then $E = (E_r + \eta)$ and

$$i = zF(C_R)_s(1-\theta)\ k \exp\left\{\frac{-\Delta G^{o+}}{RT}\right\} \exp\left\{\frac{\beta E_r zF}{RT}\right\} \exp\left\{\frac{\beta \eta zF}{RT}\right\}. \qquad (I, 4)$$

and therefore $i = i_o \exp\left\{\frac{\beta \eta zF}{RT}\right\}$. (I, 5)

(ii) Tafel Slopes: The logarithmic form of equation (I, 5) is the familiar Tafel relation

$$\eta = \frac{RT}{\beta zF} \ln i - \frac{RT}{\beta zF} \ln i_o \qquad (I, 6)$$

where the second term is a constant, characteristic of the kinetics of the reaction at $E = E_r$. $\frac{RT}{\beta zF}$ is the so-called Tafel slope, usually denoted by b. For certain favourable cases this parameter can provide a diagnostic criterion for the mechanism of an electrochemical process.

(iii) The Parameter β in b: This parameter can be interpreted in several ways, reflecting:

(a) the average charge on the activated complex;

(b) the fraction of the metal-solution potential difference which operates between the initial and activated states;

(c) the relative position of the activated state along the reaction co-ordinate; or

(d) the relative slopes of the potential energy profiles for the initial and final states in the region where the configuration of the particles almost corresponds to that of the activated state.

Bauer (17) has recently discussed the somewhat loose interpretations of the parameters α and β, often used in rate equations for electrode processes. Theoretically, Marcus (18) recognised that α or β could be potential dependent but in practice for most electrochemical reactions this effect is negligible. However, it has been shown (19) that for the reduction of chromium (III) to chromium (II) at a mercury electrode there is significant dependence of α upon the electrode potential.

The close correlation between the β-factor and Brønsted's α-factor (20) in acid-base proton transfer processes was pointed out by Frumkin (21).

(iv) Reaction Orders: The reaction order, which is determined experimentally, is obtained from the variation of the rate of a reaction with the concentration of a particular reactant.

The significance of reaction orders in some ionic electrochemical processes has recently been discussed by Vetter (22), and later by Conway and Salomon (23) who considered the problem for various conditions of ionic adsorption in the hydrogen evolution reaction. The derivative $\frac{d\ln i}{d\ln c}$, when measured at constant outer layer potential* and

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* Here, the potential referred to is that at the inner limit of the diffuse layer, i.e., where non-specifically adsorbed cations are normally situated at the electrode interface (see II (i), p. 13).

constant electrode potential, is the chemically significant reaction order. This derivative characterises the dependence of the current (and therefore the rate of reaction since $\upsilon = \frac{i}{zF}$) upon the reactant concentration in the absence of complicating double-layer effects. As in many chemical processes, the reaction order of electrode processes is not necessarily identical with the molecularity of the reaction (i.e., in electrochemical reactions, the molecularity of the surface reaction) particularly for cases of consecutive reactions which involve adsorbed intermediates.

2. ELECTROCHEMICAL ADSORPTION OF ORGANIC MOLECULES AT MERCURY

In general, the chemisorption of reactants and products is an important factor in electrode kinetics, particularly at catalytic metal electrodes (12,24); in this section, however, only adsorption at a mercury electrode will be considered. Adsorption processes both at a gas/solid interface and at an electrode surface can be divided according to the type of adsorption involved, namely physical adsorption and chemisorption. For most organic compounds (with the possible exception of organic sulphur compounds) the adsorption is physical and orientation and electric polarisation arises at the electrode/solution interface. A convenient starting point is perhaps to briefly discuss the electrical double-layer, in order to provide a

"molecular" picture of the electrode/solution interface.

(a) The Electrical Double Layer

The modern qualitative picture of the interface is based on a model proposed by Grahame (25), which itself is a modification of an earlier concept (26). This model comprises three main regions:

(1) the metallic phase, which bears a net electrical charge arising from an excess or a deficit of electrons,

(2) an inner layer, only a few molecular diameters thick, which is located next to the metal surface and contains adsorbed oriented solvent molecules (or other neutral molecules), and

(3) an outer or diffuse layer, a three dimensional region extending into the bulk of the solution and representing the ionic atmosphere conjugate to the charge on the electrode, with an inner limit of the ionic distribution determined by the distance of closest approach of solvated cations to the electrode surface.

In many electrolyte solutions, the inner layer will also contain a fractional monolayer of anions which are said to be specifically adsorbed. Grahame et al. (27) considered that some degree of covalent bonding existed between specifically adsorbed anions and the surface, but

it has recently been suggested that other factors are more important, e.g., the electrical image energy (28) and the degree and type of solvation (29,30).

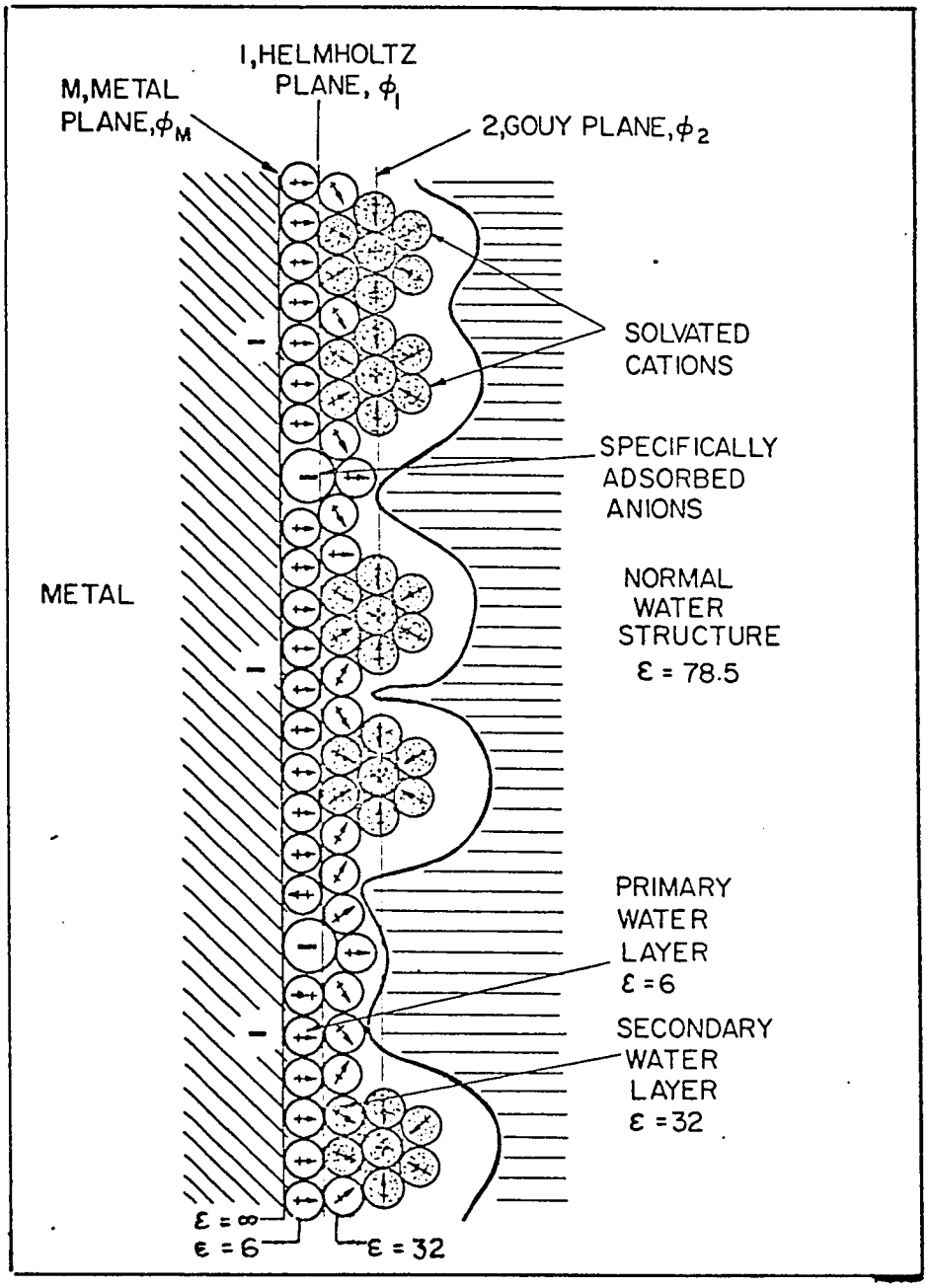
(b) The Effect of the Electric Field in the Interfacial Region

In the interfacial region at an electrode, the strength of the electric field is 10^6-10^7 V. cm.$^{-1}$.

An applied electrical field causes a distortion of the distribution of electrical charge in a molecule, thereby creating an induced dipole moment. The magnitude of this dipole depends on the field strength and on the polarisability of the molecule (determined by the degree to which the electrons and the positively charged nuclei are displaced by the action of the field). Molecules already possessing a permanent dipole moment will rotate in order to align themselves parallel to the applied field and thus minimise their electrical energy, but are also temporarily polarised so that the total polarisation is the sum of the two effects.

The electric field in the interfacial region must strongly orient the layer of solvent molecules at the surface and therefore cause appreciable dielectric saturation. A recent model (Figure 1) of the distribution of ions and solvent dipoles in the electrical double layer (29) clearly shows the effects which lead to dielectric saturation in the

Figure 1. Solvent adsorption model of the double-layer according to Bockris, Devanathan and Muller (29).


1,HELMHOLTZ
PLANE, ϕ_1
M,METAL
PLANE,ϕ_M
2,GOUY PLANE,ϕ_2
SOLVATED
CATIONS
SPECIFICALLY
ADSORBED
ANIONS
METAL
NORMAL
WATER
STRUCTURE
ε = 78.5
PRIMARY
WATER
LAYER
ε =6
SECONDARY
WATER
LAYER
ε =32
$\varepsilon = \infty$
ϵ = 6
ε = 32

inner layer, where a value of the dielectric constant is assumed which approaches the limiting Maxwell value. The solvent dipoles are regarded as adsorbed in either an "up" or a "down" configuration, i.e., with the negative end of the dipole oriented towards or away from the electrode surface depending upon the charge at that surface. The effect of the electric field is also somewhat significant in the diffuse layer ($\varepsilon \simeq 40$).

(c) Adsorption at an Electrode Surface

Two important and fundamental differences between adsorption from the gas phase and that at an electrode surface are evident from the model of the electrical double layer. Firstly there is the existence of a layer of adsorbed solvent molecules at the electrode surface and the possibility of specific adsorption of most anions and certain cations. Hence a displacement process must always occur at the surface of the electrode, a neutral organic molecule being adsorbed at a site (or at several sites, depending upon the relative molecular sizes of the solvent and the adsorbate) previously occupied by a solvent molecule. Observed values of ΔH^{o}_{ads}, ΔS^{o}_{ads} and ΔG^{o}_{ads} can only be related to the type of electrode-particle interactions involved if:

(a) similar thermodynamic quantities are known for the solvent, and

(b) if an estimate can be made of the number of solvent

molecules replaced by the molecule of adsorbate which is adsorbed.

Secondly, the electrode potential will usually affect the apparent standard free energy of adsorption. However, the presence of the adsorbed layer of solvent molecules at the surface will have a levelling effect upon the distribution of site energies along the surface, so that differences between these sites may be apparently less pronounced than in the corresponding gas-solid adsorption process (31-33).

(d) Methods for the Study of Adsorption of Organic Compounds

Adsorption of organic compounds can be studied directly by determination of the decrease in the concentration of the adsorbate in a dilute solution, e.g., by radiotracer techniques (34,35) or by a spectrophotometric method (36).

Frumkin and co-workers (37,38) have developed a theory to describe polarographic maxima of the second kind*, from which conclusions can be drawn regarding the adsorption of organic compounds at a dropping mercury electrode. Adsorption also causes a significant decrease in the capacity current of the supporting electrolyte and its effects can

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* This effect is associated with a pre-wave, observed at potentials less cathodic than the main reduction wave and is attributed to the facile reduction of an adsorbed layer. At low concentrations of reactant, the wave-height is concentration dependent, but a limiting height is reached which is thought to correspond to monolayer coverage of the electrode surface.

be observed on a d.c. polarogram. Measurements of this type have provided an indication of the potential range over which adsorption of a particular organic molecule is observed. The recent development of a.c. and oscillographic polarography have provided additional information concerning adsorption and desorption at a mercury electrode and their importance in electrochemical reductions (39).

The principal data on the effect of the field at the electrode-solution interface upon the adsorption of organic molecules have been obtained either from the electrocapillary method or from measurements of the differential capacity of the double layer.

In the presence of organic compounds, the electrocapillary curve (which represents the change in the interfacial tension at a mercury electrode with applied potential) lies below that obtained with the solution of supporting electrolyte. The observed decrease in the interfacial tension reaches a maximum in the vicinity of the potential of zero charge but decreases with increasing negative surface charge for both aliphatic and aromatic neutral molecules. When the surface becomes appreciably positively charged, a relatively sudden desorption of aliphatic molecules occurs but this is not observed in the case of aromatic compounds, e.g., pyridine, phenol.

Another significant feature is the shift in the electrocapillary maximum, which according to Lippmann's equation for constant chemical potential μ of substances in solution,

$$q = -\left\{\frac{d\gamma}{dE}\right\}_{\mu}$$

(where E is the electrode potential with respect to the potential of zero charge) corresponds to the condition of zero surface charge (q = o).

(e) Orientation of the Adsorbed Molecules

A shift in the potential of zero charge is usually associated with the change in the electric moment at the surface as organic adsorbate molecules are substituted for the oriented solvent dipoles*. Thus when the adsorbed

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* Frumkin proposed that the adsorption of a neutral molecule should be considered in terms of the change in the capacity of the double layer (40). This change was attributed to two effects;

(1) a decrease in the dielectric constant due to the presence of the adsorbed organic substance and a related change in the thickness of the interfacial region as the neutral molecule, upon being adsorbed, replaces solvent molecules;

(2) the change of dipole moment across the interfacial region as solvent molecules are replaced by the organic adsorbate.

A more explicit treatment was given by Butler (41,42) who considered the change of adsorption with change of electrode potential as a "salting out" type of effect involving the neutral adsorbate in the interfacial region.

dipoles are oriented in the interfacial field, an adsorption potential is built up which corresponds to the shift in the potential of zero charge. Adsorption potentials similar in magnitude and identical in sign have been observed in the adsorption of oxygenated aliphatic compounds at air/solution interfaces (43-45). Qualitatively this suggests that the organic molecules are oriented with the hydrocarbon chain in the direction of the metal/solution interface (since the chain is hydrophobic in nature it would tend to be displaced from the solvent phase towards the metal surface or towards the air in the other case). The orientation of the C-O bond gives rise to a positive potential difference between the outer phase and the bulk solution.

A similar comparison between the adsorption behaviour of aromatic compounds revealed considerable discrepancies in both the magnitude and the sign of the adsorption potential. Gerovich et al. (46-48) found that in the adsorption of benzene and naphthalene the shift in the potential of zero charge was to more cathodic potentials. Since adsorption of aromatic compounds is significant when the surface is positively charged, it was postulated that π-electron interaction with the surface was involved and was facilitated by the orientation of the aromatic ring (it was thought that the ring was flat at the electrode surface).

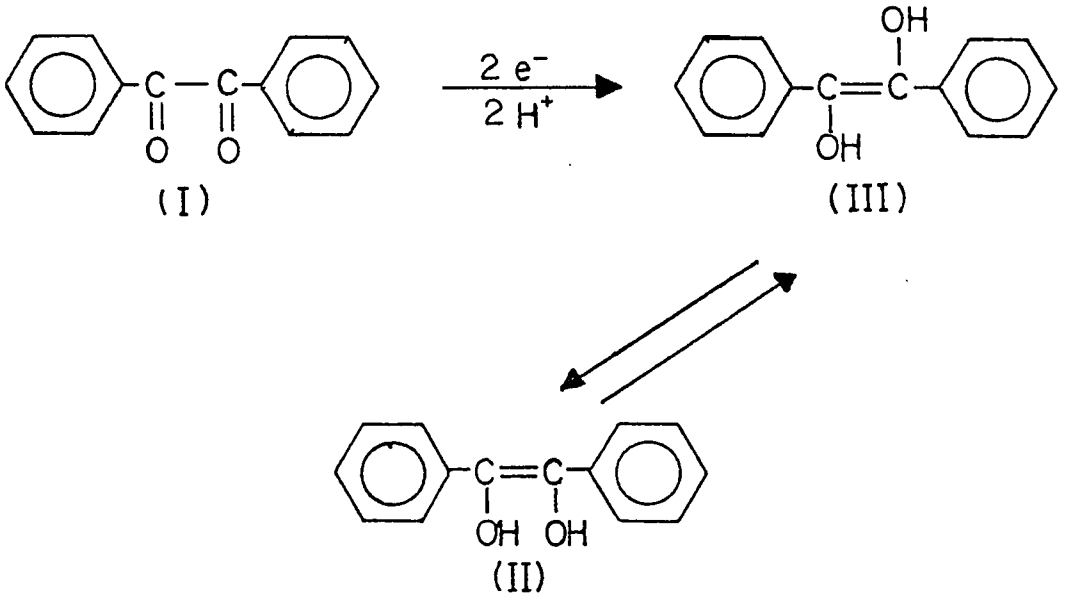
Studies of the adsorption behaviour of a series of aromatic amines in acid solution showed that it was the protonated species RNH_3^+ that was predominantly adsorbed, and that the adsorbed molecules lay flat on the electrode surface (49). Adsorption on the positive branch of the electrocapillary curve was determined both by coulombic and π-electron interaction whereas the coulombic forces became predominant when the surface charge was negative. Similar results were obtained in studies of the adsorption of heterocyclic bases in acid solution (43).

The values of Γ_{max} (the surface excess corresponding to full coverage of the electrode surface) obtained in the adsorption of heterocyclic bases in neutral solution were, however, best explained by an orientation of the adsorbed species <u>perpendicular</u> to the surface (43). Since the interaction of π-electrons with the surface can be neglected in this configuration, the standard electrochemical free energy of adsorption $\Delta \bar{G}^{o}_{ads}$ was shown to decrease linearly with $\theta^{3/2}$ (where θ is the fraction of surface covered), in accord with significant dipole-dipole interactions.

(f) <u>Stereochemical Specificity in Electrode Processes</u>

A factor which has not been widely appreciated in studies of electrochemical reactions is that the electrode potential will not only determine the surface excess of

neutral molecules, but may specifically orient the adsorbed molecule (or the functional groups in that molecule) at the surface. Thus a recent study (50,51) of the cathodic reduction of benzil (I) at a mercury electrode, revealed a strong potential-dependence of the ratio of the products, viz., cis and trans-stilbene diol (II and III, respectively).



(I) (III) (II)

Other factors which affect the strength of the electrical field in the double layer were also shown to be significant e.g., temperature, pH and the nature of the supporting electrolyte. It was suggested that the initial product of the electrochemical reaction, the trans-stilbene diol, rapidly isomerised at the electrode surface since the activation energy for this process was lowered by the electrical field, on account of the higher overall dipole moment of II.

In the electro-reduction of 2-phenyl-2-chloro-propionic acid (50), an optically active product was obtained with almost total inversion of the asymmetric centre, suggesting the occurrence of a stereospecific electrode process. Analagously to homogeneous substitution, at least three mechanisms have been proposed for this type of electro-reduction, i.e., the cathodic substitution of a halogen X by a hydrogen atom H (52-57).

S_N1 process*	$R\text{-}X \longrightarrow R^+ + X^-$
	$R^+ + 2e^- \longrightarrow R^-$
	$R^- + H^+ \longrightarrow RH$
S_N2 process	$R\text{-}X + 2e^- \longrightarrow R^- + X^-$
	$R^- + H^+ \longrightarrow RH$
Free Radical (S_R) process	$R\text{-}X + e^- \longrightarrow R^\bullet + X^-$
	$R^\bullet + e^- \longrightarrow R^-$
	$R^- + H^+ \longrightarrow RH$

In electrode kinetics it is difficult to distinguish between S_N1 and S_N2 mechanisms (56, 58) and a general term is used, i.e., ionic mechanisms, in contrast to the free radical process. The two mechanisms S_R and S_N1 should, however, lead mainly to racemisation or retention of the configuration, whereas an S_N2 mechanism results in an inversion

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* It has recently been suggested (59) that the reduction of some halogenated aromatic hydrocarbons in non-aqueous solvents involved a negatively charged potential-determining transition state and therefore cannot proceed by an S_N1 mechanism.

at the reaction centre. It is usually postulated that the charge transfer step occurs to the carbon atom of the carbon-halogen bond which is oriented perpendicularly to the electrode surface (56,60). However, in the electro-reduction of some halogenated compounds it has been suggested that the reaction may involve a parallel orientation of the C-X bond at the surface (61).

(g) Summary

The more important factors in the adsorption of organic molecules* at the electrode/solution interface can be briefly summarised:

(1) The surface charge has been shown to affect differently the adsorption of aliphatic and aromatic compounds, particularly when that charge is positive. Orientations of the adsorbed species may be different at a strongly charged surface from those at or near the potential of zero charge; this is an important factor in the understanding of the conditions for electro-reduction at very cathodic potentials (43,62,63).

(2) Molecular structure may be a significant factor in several ways;

(a) the polarisability of the adsorbed molecule under the influence of the strong electrical fields of the interfacial region will be an important factor

* The adsorption of organic molecules is the subject of two recent reviews by Frumkin and Damaskin (64,65).

determining the electrostatic energy of adsorption;

(b) the presence of π-electrons can markedly affect the orientation of the molecule, particularly at positive surface charge when a "flat" orientation will be favoured;

(c) polar molecules will tend to be oriented in the field at the electrode surface, which may lead to the occurrence of stereospecific electrochemical reactions;

(d) the relative size of the adsorbate and solvent molecules will be important since the process of adsorption is in effect a displacement reaction. Here, as in (a), the relative polarisability of the solvent and the adsorbate will be a factor.

3. POLAROGRAPHY AND RELATED ELECTROCHEMICAL TECHNIQUES

When polarography was first developed the term denoted an electrolytic method based on the measurement of the dependence of an average current upon controlled potential at a dropping mercury electrode. Thus classical polarography may, in fact, be regarded as a potentiostatic method for a given drop where the average current is determined. Polarography nowadays refers to the interpretation as well as the measurement of such current-potential relationships and is the most well-known and experimentally important example of techniques based on the evaluation of diffusion-controlled currents at a non-stationary surface.

Since the concentration of the reducible species may be varied from 10^{-6} to perhaps 10^{-3} mole. litre^{-1}, and if the rate of electron transfer is "fast", then the current becomes limited by the rate of diffusion of the electroactive species to the surface. Such conditions give rise to the so-called reversible waves. Although the Ilkovic equation for diffusion-controlled processes (66) has not been fully satisfactory (67,68), it can be shown that relations based on this simple equation (I, 7) are valid, if polarographic currents are obtained in the usual way:

$$i_{lim.} = 607\ nm^{2/3}\ t^{1/6}\ D_R(C_R)_b \qquad (I, 7)$$

where n is the number of electrons involved in the process, t is the drop time, m is the drop weight, $(C_R)_b$ is the concentration of reactant in the bulk solution and D_R is the diffusion coefficient of the reducible species. The limiting current is independent of potential and is directly proportional to the concentration of the reducible substance (hence the analytical importance of polarography). The half-wave potential ($E_{\frac{1}{2}}$) is that potential for which the condition

$$i = \frac{i_{lim.}}{2}$$

is realised, and it is this parameter which is characteristic of a particular redox system.

However, only a few organic compounds behave in a polarographically reversible manner, though many may involve a reversible electron transfer step followed by irreversible chemical reactions. Irreversible processes are those for which the current is mainly limited by the rate of the electrode process itself. The theory of such polarographic currents is based on the work of several authors and an approximate form of the exact solution is given as equation I, 8.

$$\frac{i}{i_{lim.}} = \frac{0.886\,\lambda}{1+0.886\lambda} \qquad (I, 8)$$

and

$$\lambda = k_1 D_R^{-\frac{1}{2}} + k_2 (D_R t)^{-\frac{1}{2}}$$

where k_1, k_2 are the rate constants for the forward and reverse reactions. A value of approximately 2×10^{-3} cm. $sec.^{-1}$ represents the upper limit of the rate constant which can be evaluated, but faster reactions can be studied at shorter drop times*.

Classical polarography makes possible a rapid assessment of an electrode process over a wide range of potentials, and the process at any potential is not influenced by the pre-history of the electrolysis, as is found with other methods. There is, however, little possibility of ascertaining

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* In a typical polarographic study, the drop time is usually 3-4 seconds.

the nature of intermediates or of the final products of an electrode reaction, although some conclusions can be drawn from the dependence of $E_{\frac{1}{2}}$ upon drop-time and upon the concentration of the reactant if a reversible wave is obtained. If the overall reaction is polarographically irreversible, nothing is known of the product of the electron transfer process (except the number of electrons consumed, as determined from the wave-height).

In most cases the electrode processes studied in organic polarography do not consist of a simple electron transfer, but may involve mass transfer, preceding or subsequent chemical reactions and adsorption-desorption phenomena. Therefore no single method can fully elucidate the organic electrode process and information must be obtained from several approaches in order to identify the partial steps in the reaction (69), e.g.,

(a) from polarographic waves. Conclusions regarding the nature of the electroactive species can be drawn from the presence of, and changes in, diffusion-controlled or kinetic currents, and from the effect of pH or solvent upon the half-wave potential. It is also possible to establish participation of preceding, parallel or consecutive chemical reactions;

(b) from preparative methods;

(c) from other electrochemical techniques*.

The voltage sweep method introduced by Matheson and Nichols (70) and considerably improved by Randles (71) and Sevcik (72) is considered a logical step in the evolution of polarography, being a potentiostatic method using linear or triangular impulses of potential. At a hanging mercury drop electrode** both single sweep and multi-sweep studies originally provided qualitative information upon the nature of intermediates or products of the reaction. Recent developments of the theory of cyclic voltammetry at a stationary mercury electrode (73-75) has led to the quantitative resolution of electrochemical and preceding or succeeding chemical steps in electrode processes. These techniques have been extended to include studies of the adsorption behaviour of electroactive molecules (76).

Other developments include a.c. polarography (77-79), which is a galvanostatic method, square-wave polarography and the commutator method introduced by Kalousek (80). Measurements by these techniques can give information upon adsorption effects and upon the reversibility of the electron transfer step.

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* These techniques have been the subjects of several reviews, e.g., see "Progress in Polarography", Vols. I and II.

**Many efforts have been made to introduce new types of indicator electrodes into polarography and related electrochemical measurements. The hanging mercury drop electrode is particularly successful in analysis of the nature of the reaction products in an electrode process.

Although the renewability of the electrode surface is often considered to be a necessary prerequisite for useful analytical procedures, current-potential curves have been obtained with a stationary pool electrode (81,82); with stirring, measurements can be made at concentrations as low as 5×10^{-7} mole. litre^{-1}. The curves were shown to be similar to those obtained by a single sweep method at a dropping mercury electrode, i.e., they exhibited characteristic maxima, the heights of which varied linearly with the concentration of the reactant. It is found that at scan-rates comparable to those used in classical polarography ($\sim$400 mV min.$^{-1}$) and at comparable current densities to those encountered in a polarographic wave, the curves recorded at a stirred mercury pool electrode are quite reproducible.

The comparison of polarographic curves with the current-potential curves obtained at a stirred mercury pool is considered to be important in the identification of products of electrolysis. In most cases the number, the shape and the half-wave potentials of the waves are identical, e.g., as in the behaviour of p-diacetylbenzene referred to by Zuman* (69). However, cases have been reported in which differences are observed and in some there is no resemblance at all between the results obtained at a dropping mercury electrode and at a stationary mercury pool.

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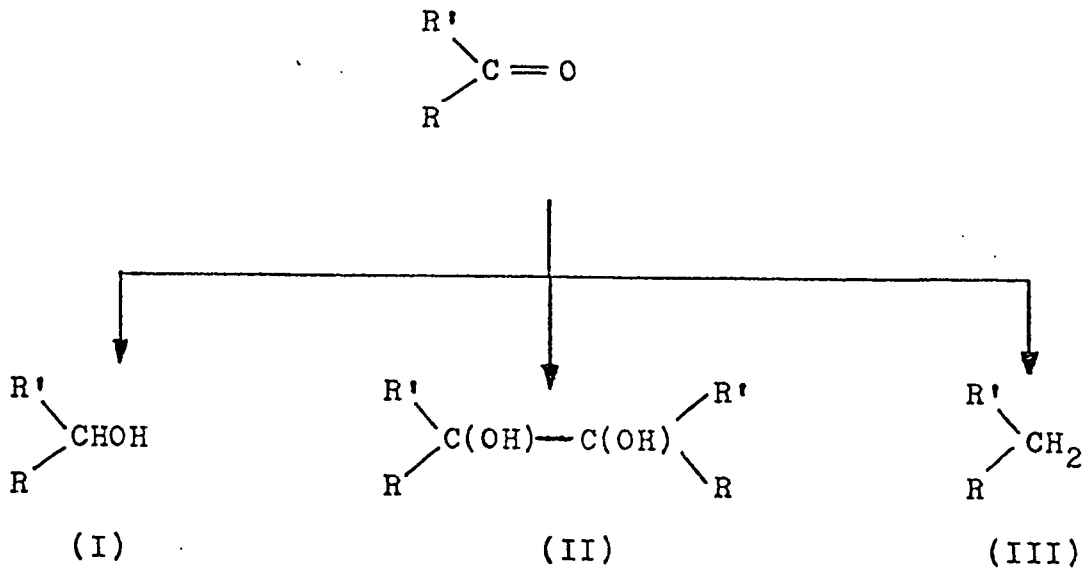
* These results have not as yet been published.

4. ELECTRO-REDUCTION OF CARBONYL COMPOUNDS

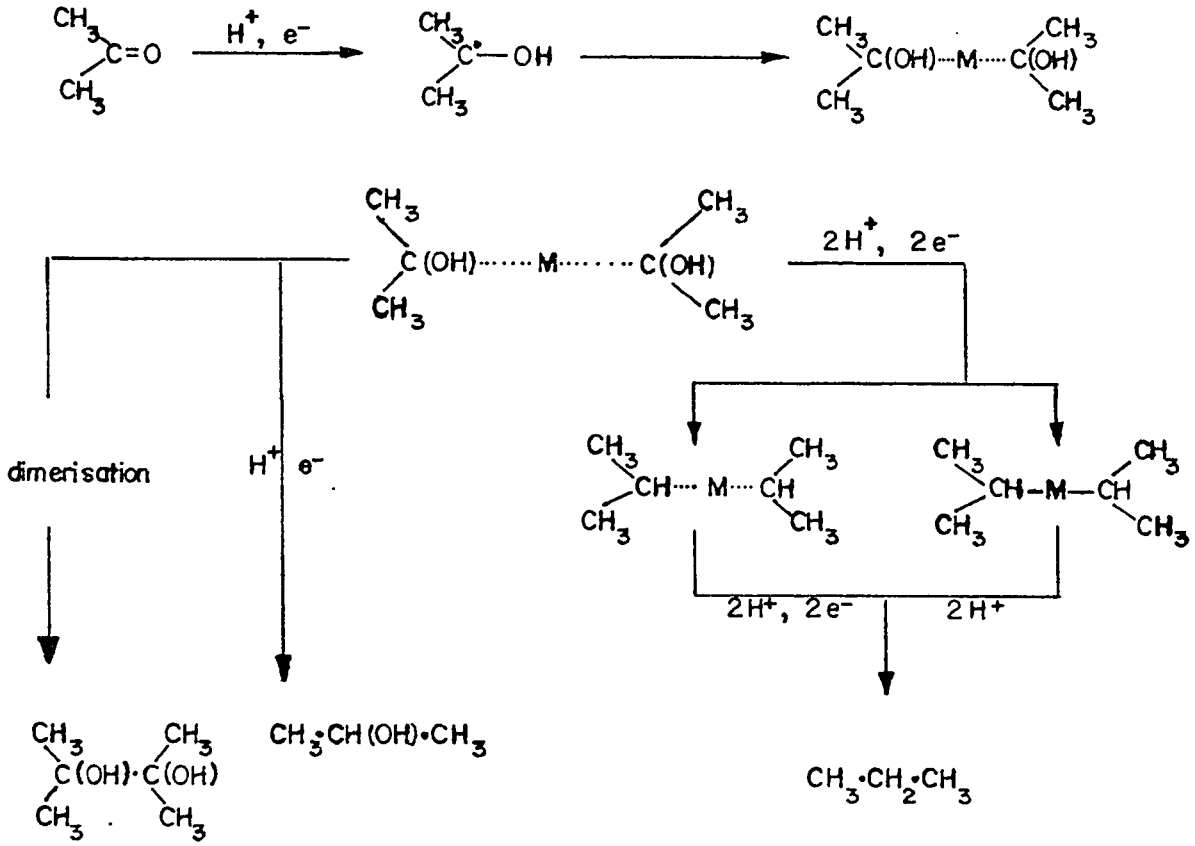
Early studies of the electro-reduction of aromatic and aliphatic carbonyl compounds indicated that the products and yields were dependent upon both the cathode material and the pH of the medium. Generally mixtures of alcohol (I), pinacol (II) and hydrocarbon (III) were obtained (83-86).



In a review of the electrochemical reduction of the carbonyl group to a methylene moiety (cf. III), Swann (87) concluded that a hydrocarbon was formed only in strongly acidic solutions and that amalgamated zinc appeared to be the most active cathode material for this reaction, (cf. the Clemmensen reduction, $\rangle C{=}O \longrightarrow \rangle CH_2$ with Zn/Hg in acid solution). That organometallic compounds had been observed in electrochemical reactions (88), and later suggested as

an intermediate in the reduction of menthone to menthane (89), formed the basis of a tentative mechanism for the reaction in which the cathode metal was involved.

More recently (90-92), the formation of organometallic compounds has been proposed to explain the products obtained in the electrochemical reduction of acetone. Controlled potential studies using different electrode materials* yielded various mixtures of isopropanol, butane-2,3-diol and propane. Di-isopropyl mercury and di-isopropyl lead were also isolated and hence the following mechanism was proposed:



* These studies were carried out in acetone (80 volume %) -water mixtures containing sulphuric acid (0.25 M) and at a controlled potential, -1.1 V. vs the normal hydrogen electrode.

From electrocapillary measurements, Brown and Lister (93) established that in acid solution, acetone is strongly adsorbed at the mercury electrode over the whole potential range of the Faradaic process. The reduction of the ketone was believed to involve the transfer of one electron and one proton to an adsorbed ketone molecule to form an adsorbed radical, the precursor of the diverse products obtained (Table I)*.

Table I

Controlled potential electrolyses of acetone (4M) sulphuric acid (0.5M) solution (93)

	product analysis: current efficiences %		
electrode potential (volts. vs N.H.E.)	isopropanol	pinacol	di-isopropyl mercury
- 1.03	22	2.5	17
- 1.06	21	2.1	28
- 1.135	27	1.1	11

(a) Polarographic Reductions of the Carbonyl Group

Since the early study of the behaviour of nitro-

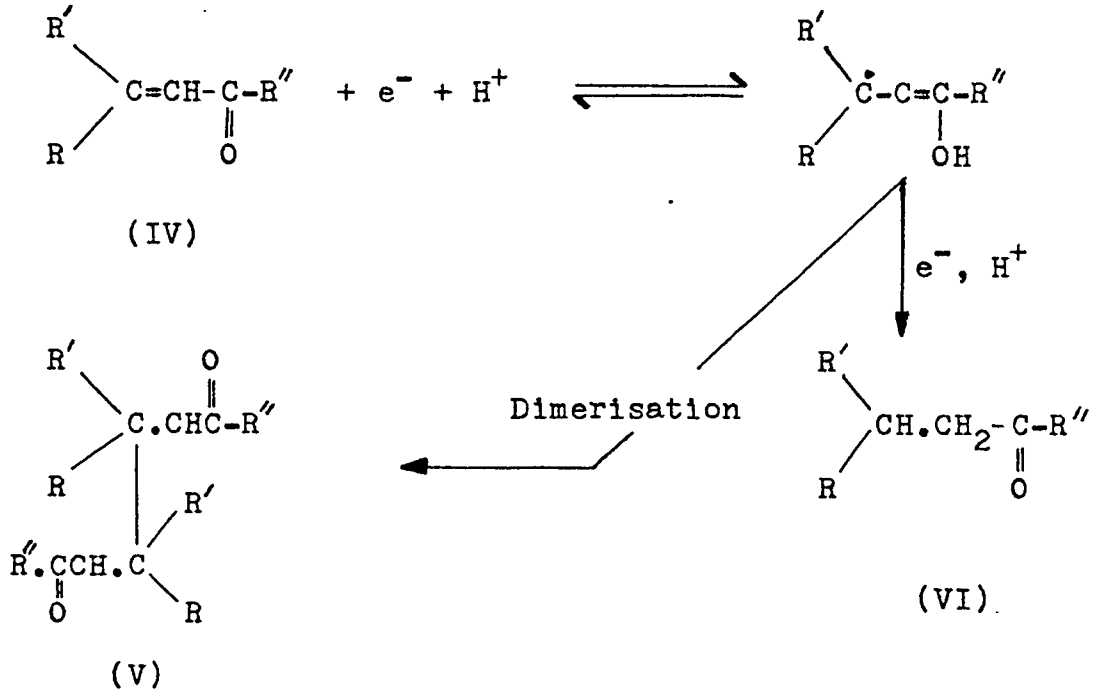
* It is to be noted that evolution of hydrogen was in fact the major reaction obtained at all the potentials.

benzene by Shikata (94,95), the field of organic polarography has advanced considerably (96-99) and has included extensive studies of the electro-reduction of carbonyl compounds. This section will therefore include a review of the polarography of only aliphatic and aromatic ketones.

(i) Aliphatic Ketones: For a wide variety of aliphatic ketones the polarographic waves corresponding to reduction of the $\rangle C{=}O$ group are completely masked by hydrogen evolution (100). However, in the presence of tetramethylammonium iodide, reduction of methyl ethyl ketone, acetone and cyclohexanone was shown to occur at very cathodic potentials (> -2.0 V. vs the normal hydrogen electrode) (52,101). The adsorption of the R_4N^+ cation at the electrode surface is known to inhibit markedly the hydrogen evolution reaction. The formation of derivatives, in situ, provides a suitable analytical technique for aliphatic carbonyl compounds, e.g., an acidic solution of acetone containing hydrazine shows two one-electron waves which are attributed to reduction of the azomethine group, $\rangle C{=}N$.

(ii) $\alpha\beta$-unsaturated Ketones: Conjugation of an olefinic group and the carbonyl function facilitates reduction at a dropping mercury electrode. Based on the results of polarographic studies and controlled potential electrolyses obtained with mesityl oxide (IV, $R, R', R'' = CH_3$.), a general mechanism was proposed for the reduction of these molecules (102)

viz:

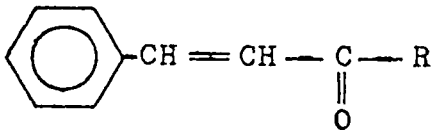


In acid solutions, the dimeric ketone (V) was obtained whereas at high pH the product was almost exclusively the ketone (VI). The generality of this mechanism is questionable since it was found that the electro-reduction of methyl vinyl ketone yielded an organo-mercury compound (103).

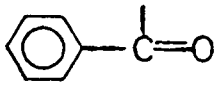
The reduction of certain $\alpha\beta$-unsaturated steroidal ketones yielded a normal pinacol, the expected β dimerisation to a saturated keto-steroid probably being prevented by steric hindrance (104). Furthermore, the pH of the solution was shown to be a significant factor in the controlled-potential electrolyses of these compounds (105),

pinacols of different stereochemistry being obtained in acid or in alkaline conditions*. It was suggested (106) that the intermediate radical is probably neutral in acid solution, whereas at high pH it is the ketyl anion ($>C^{\cdot}-O^{-}$) which undergoes dimerisation so that repulsion between the negatively charged oxygen atoms can affect the configuration of the product.

Unsaturated ketones which are conjugated with an aromatic ring, e.g., chalcone (VIII, R=Ø), benzalacetone, (VIII, R=CH_3)



(VIII)

show similar behaviour to that observed with mesityl oxide (107), except that the product of the reduction of chalcone contains a  structure which is further reduced at the electrode potentials involved (cf. acetophenone, benzophenone).

(iii) Aromatic Ketones. Reduction in Acid Solution: Although conclusions were based on the concept of "reduction potentials"**, early studies of the polarographic reduction of

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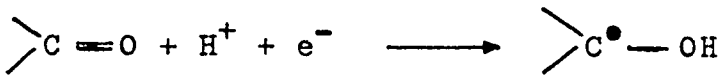
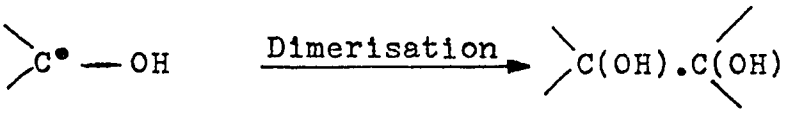
* A pinacol may have a dl- or a meso-configuration.

**These have been described as the potential at which the "step" commences and have also been referred to as the deposition potential or the depolarisation potential. The reduction potential could be derived by one of several empirical methods (e.g., see Kolthoff and Lingane "Polarography" p.623) but were soon replaced by the half-wave potential. The most outstanding shortcomings of these methods were that the potentials changed with concentration of the reducible compound, with drop time and even with the sensitivity of the galvanometer.

aromatic ketones and aldehydes at low pH indicated that two one-electron steps were involved (108-110), and it was suggested that electron transfer occurred to a protonated species. A pinacol is the product of controlled potential electrolysis at a potential corresponding to the first plateau (102) and it has been observed (111,112) that the derivative $\left(\frac{dE_{\frac{1}{2}}}{dpH}\right)$ is -0.06 volts for the first wave. The reaction corresponding to this wave was therefore thought to be one involving a single electron and a proton:



(IX)



Elving and Leone (112) considered that proton transfer to the ketone occurred in the diffusion layer at the electrode surface and is facilitated by polarisation of the carbonyl group by the electric field at the surface. The carbonyl group is visualised as oriented at the electrode with the carbon atom towards the metal surface. The simultaneous transfer of an electron completed the reduction reaction. It was observed that changes in the ionic strength of the medium had little effect upon the polarographic reduction of acetophenone and it was concluded that diffusion of a charged species from the bulk solution to the electrode was not a

significant process in the overall reaction.

The equilibrium constant for the protonation of acetophenone in strongly acidic solutions has been measured spectrophotometrically (113) and a value $K = 10^{-6}$ was obtained. It can be seen therefore that the concentration of the protonated species in the bulk solution is negligibly small even in strongly acidic solutions.

In recent studies of the reduction of acetophenone at a dropping mercury electrode (114,115) it was observed that with increasing pH the limiting current of the first wave* became kinetic in character rather than purely diffusion controlled. Furthermore, at constant pH and constant ionic strength, the limiting current decreased with decreasing buffer capacity, suggesting that the rate of reduction was proportional to the rate of protonation of the carbonyl group in the interfacial layer. Finally at pH 5.5 the limiting current was shown to be <u>independent</u>** of the concentration of ketone (at concentrations greater than 6×10^{-3} moles. litre^{-1}).

Mairanovskii (115) concluded that the protonated ketone was the electroactive species at the electrode surface. The limiting current of the first polarographic wave observed

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* Other investigators (116) have also shown that with increasing pH the half-wave potential of this wave becomes more cathodic and, more significantly, the height of the wave markedly decreases.

**A non-linear dependence of limiting current upon ketone concentration had been previously observed (117).

in these reductions was therefore limited by the rate of protonation of the ketone at the electrode surface rather than by diffusion of the neutral ketone to the surface.

The shape of the first polarographic wave is not described by the theoretical equations for either a rate-limiting electron transfer (118) or a reversible electron transfer with subsequent, irreversible dimerisation (119). It was suggested (120) that since neither step is strictly rate determining, the rate of re-oxidation of the ketyl radical (IX) may be comparable to the rate of dimerisation.

For some ketones, the transfer of the first electron is considered to be a reversible process (121-125) and in the reduction of acetophenone (112,113) it was shown that at low concentrations of ketone ($< 5 \times 10^{-4}$ moles. litre^{-1}) the reaction did in fact correspond to a reversible electron transfer followed by an irreversible dimerisation. However, the rate of the electrochemical reaction may not be very fast and may, in fact, be easily diminished by accumulation of the strongly adsorbed pinacol at the electrode surface, so that the reaction becomes irreversible as the concentration of the ketone is increased.

The second polarographic wave observed in acid solutions is generally accepted as being independent of pH*

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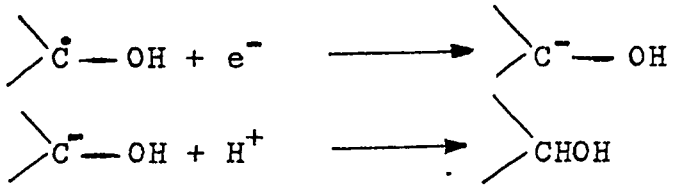
* In the polarographic reduction of benzophenone a slight pH dependence of this second wave was observed and attributed to partial reversibility of the overall reaction (120). It was suggested that an acid-anion equilibrium may be involved, i.e., that between the ketyl radical and its protonated form $>\dot{C}-OH_2^+$

and is attributed to the irreversible reduction of the ketyl radical (111,112,126):



A secondary alcohol is usually the major product of controlled potential electrolysis at the potential corresponding to the plateau of the second wave (102).

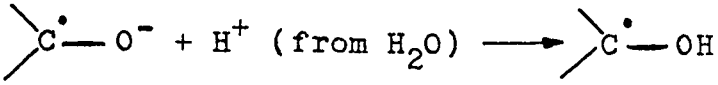
Proton abstraction from either a solvent molecule or from the hydronium ion is possible in the reduction of aromatic ketones; this situation is hence unlike that for aromatic hydrocarbons where only the water molecule is regarded as an effective proton donor (127).

(iv) Aromatic Ketones. Reduction in Approximately Neutral Solutions: As the pH of the medium increases, the two waves normally observed in acid solution finally merge and produce a single two-electron wave. That the reduction process in neutral solution is a two-electron process is verified by controlled potential coulometry (112) and the product is a secondary alcohol.

The electroactive species in these solutions is most probably the neutral ketone and the product of the electrode reaction is initially a ketyl anion (X) which is sufficiently basic to abstract a proton from a solvent molecule.

Since the electron affinity of the neutral radical is greater than that of the anion (128) it is further reduced.

(X)



Mairanovskii (129) has pointed out that a composite wave is probably observed in neutral solution, corresponding to reduction of both a protonated species (protonated by a solvent molecule) and the ketone itself. The polarographic wave for the reduction of acetophenone in a solution of pH 7.2 was resolved into two waves*, the first of which showed kinetic character.

(v) Aromatic Ketones. Reduction in Alkaline Solutions: A decrease in the diffusion-limited current of the combined wave is observed at still higher pH and the wave-height approaches that for a one-electron process; this is verified by controlled potential coulometry (112). A new wave is formed at more cathodic potentials, sometimes so negative that the wave can be masked by the current from the supporting electrolyte; this behaviour

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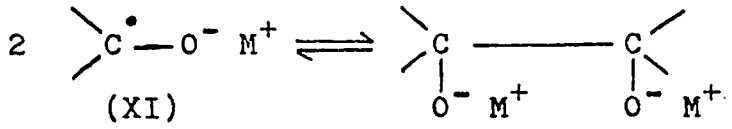
* A third wave was observed, attributable to the reduction of the ketyl radical.

corresponds to formation of a secondary alcohol.

Again the first wave is regarded as corresponding to the reduction of the ketone to a ketyl anion (112,120) which is not protonated within the lifetime of the mercury drop and therefore diffuses away into the bulk solution where proton abstraction and dimerisation yields a pinacol.

The decrease in height of the single wave, and the appearance of a new wave, has been the subject of much speculation. A metal ketyl (XI)



(XI)

was postulated as a reaction intermediate, the monomeric and dimeric forms of which were regarded as being in equilibrium at the electrode surface (111), with the extent of dissociation of (XI) being dependent upon the nature of the cation* through ion pair formation. The reduction of the monomer occurred at very cathodic potentials and the wave separation depended upon the position of the monomer-dimer equilibrium.

The possibility of the formation of a metal ketyl in aqueous media has been questioned by Elving and Leone (112) and the ketyl anion (X) was suggested as a more

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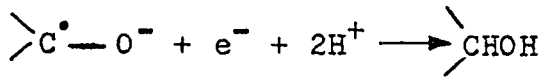
* Experimentally it was observed that the half-wave potential for this wave was sensitive to the nature of the cation (111,112).

likely intermediate. This anion was also assumed to be an intermediate in the electro-reduction of benzaldehyde at high pH (130):



The ion is not reduced as soon as it is formed since it tends to be repelled from the electrode surface and electron transfer must occur to a region of increased electron density.

A qualitative explanation of the cation effect referred to above is based (124,131,132) upon the effect of structure on the equilibrium proposed by Ashworth (see p.41) yet not necessarily involving formation of a metal ketyl*. Separation of the waves will then be maximal when substituents cannot sufficiently stabilise the radical anion so that dimerisation may occur.

(vi) Summary: In a recent review (133) and in a more extensive paper presented to the Faraday Society in England (1968), Zuman et al. (134) have pointed out that although the polarographic reduction of aldehydes and ketones has been extensively studied, in most investigations attention has been paid to only a particular aspect of the problem.

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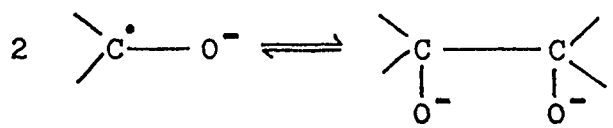
* Equilibrium between monomeric and dimeric forms of the ketyl anion is possible:



By studying the polarographic behaviour of carbonyl compounds showing a wide variation in structure, a general mechanism has been developed to describe:

(a) reduction in acid, neutral and alkaline solutions, and

(b) the effect of substituents in side-chains (α or β) or in the aromatic nucleus.

The observed polarograms of aryl alkyl and diaryl ketones in acid media are explained by a sequence of individual reduction steps: proton-electron-electron-proton, e.g.,

$$\text{>C=}\overset{+}{\text{O}}\text{H} \rightleftharpoons \text{>C=O} + \text{H}^+$$

$$\text{>C=}\overset{+}{\text{O}}\text{H} + \text{e}^- \xrightarrow{E_1} \text{>}\dot{\text{C}}\text{-OH} \qquad i_1$$

$$\text{>}\dot{\text{C}}\text{-OH} + \text{e}^- \xrightarrow{E_2} \text{>C}^-\text{-OH} \qquad i_2$$

$$\text{>CHOH} \rightleftharpoons \text{>}\bar{\text{C}}\text{-OH} + \text{H}^+$$

The products of the reaction are accounted for by chemical reactions subsequent to the first electron transfer (E_1, i_1), e.g.,

$$2\ \text{>}\dot{\text{C}}\text{—OH} \longrightarrow \text{dimers}$$

$$\text{>}\dot{\text{C}}\text{-OH} + \text{Hg} \longrightarrow \text{organomercury compound}$$

$$\text{>}\dot{\text{C}}\text{-OH} + \text{solvent} \longrightarrow \text{products}$$

In alkaline solutions it has been shown that the reduction process is sensitive to the kind and concentration of the cations present in the supporting

electrolyte (108,109,129). For solutions of low ionic strength ($\mu < 0.1$) containing only lithium ions, Zuman has described the reduction in terms of a sequence: electron-electron-proton-proton, viz.

$$\rangle C{=}O + e^- \xrightarrow{E_3} \rangle \dot{C}{-}O^- \qquad i_3$$

$$\rangle \dot{C}{-}O^- + e^- \xrightarrow{E_4} \rangle C{-}O^= \qquad i_4$$

$$\rangle CHOH \rightleftharpoons \rangle C{-}O^{2-} + 2H^+$$

The effect of the kind and the concentration of metal ions is also explained by a reaction scheme involving an entity* $\rangle \dot{C}{-}OM$, the product of the interaction between the metal cation and the radical anion.

5. CHOICE OF SYSTEM FOR STUDY OF ELECTROCHEMICAL KINETICS AND ADSORPTION BEHAVIOUR

It has already been pointed out that although a large number of organic electrode processes have been studied, little attention has been paid to simultaneous and related studies of both the kinetic and the adsorption behaviour of the reactants and products. For such an electrochemical study, the choice of a particular system must be made with

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* The structure of this product was not elucidated i.e. it may involve a covalent bond, it may resemble a complex, a charge-transfer complex or an ion pair.

several factors in mind:

(1) the suitability of the system for determination of the adsorption behaviour;

(2) choice of reactant and conditions so that the Faradaic process occurs within a convenient range of potentials;

(3) choice of conditions so that other competitive Faradaic processes are negligible e.g., hydrogen evolution in acidic solutions, deposition of cationic species in neutral or alkaline solutions, and finally

(4) that preferably a single product is obtained in high coulombic yield.

Reference to the several available text books and reviews on electro-organic chemistry (83,135-137) reveals that a wide range of electrode materials has been used (with equally widely varying degrees of success). At catalytic, low hydrogen-overpotential metals such a platinum, palladium, nickel or copper, evolution of hydrogen must be a significant, concomitant process and controlled potential studies cannot ensure the formation of perhaps a single product in high coulombic yield. Furthermore, only limited techniques are available for the study of adsorption behaviour at solid metals (138), and none has the reliability of electro-capillary measurements.

The use of amalgamated electrodes or possibly metal alloys has proved successful in electro-organic syntheses,

but this introduces an unnecessary complication in the interpretation of the results of kinetic studies, namely the actual nature of the electrode surface.

Data on the electro-reduction of many organic molecules at a dropping mercury electrode are readily available and mercury certainly provides the most convenient electrode for adsorption studies. It is obviously one of the few metals suitable for electrocapillary measurements and the thermodynamic principles of such adsorption studies are based on the concept of an ideally polarised electrode*. Furthermore, since mercury is a so-called high hydrogen-overpotential metal, then a wide range of cathodic potentials is available for the study of the reduction of an organic molecule before hydrogen evolution currents become significant. In aqueous/organic solvent mixtures, the use of which is often necessary because of the limited solubility of many organic compounds in water, this range may well be reduced.

Many polarographic studies are carried out in the presence of large organic ions which are known to be specifically adsorbed at the electrode surface, e.g., tetraalkylammonium salts. The complicating double-layer effects which may arise

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* This concept is realised in practice by a mercury electrode over a wide range of potential, 0.00 to -0.90 V. vs the normal hydrogen electrode.

in the above-mentioned systems can be avoided by the use of simple acids* or bases. This is a factor which is particularly important in the interpretation of electrochemical reaction orders.

On the basis of the above considerations, it is therefore possible to select a system where both the electrochemical kinetics and the adsorption behaviour can be studied. Experimental conditions can usually be modified (as indicated above) to allow these studies to be carried out using concentrations of the reactants from approximately 0.01 to 1.00 mole litre^{-1}.

A study of the kinetics of electrochemical reduction and the related question of adsorption behaviour of carbonyl compounds at mercury was considered. The polarographic behaviour of saturated aliphatic ketones indicated that their reduction would occur together with substantial hydrogen evolution (unless specifically adsorbed cations such as $(CH_3)_4N^+$ were used as a supporting electrolyte) and the coulombic efficiency of the process would therefore be low.

However, the reduction of both $\alpha\beta$-unsaturated ketones and aromatic ketones can be conveniently studied at the mercury electrode. The simple alkyl aryl ketone, acetophenone,

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** It should be remembered that even halide ions, particularly Br^- and I^-, are specifically adsorbed to a significant extent at a mercury electrode at low cathodic potentials from aqueous solution where $[X^-] > 2$ g.ion litre^{-1}.

was selected as the model compound [half-wave potential approximately -0.85 volts (vs the normal hydrogen electrode) at pH 1.5], so that reduction will occur in a potential range suitable for the study of both the kinetic and adsorption behaviour. The product of controlled potential electrolysis in acidic solution is the pinacol, 2,3-diphenylbutane-2,3-diol in almost quantitative yield.

6. AIMS OF THE PRESENT WORK

In the last decade much interest has been shown in the electrochemistry of anodic processes such as the oxidation of formic acid and the formate ion, the Kolbe reaction, and particularly the oxidation of hydrocarbons and alcohols of low molecular weight, (in this case interest was in the development of a practical, commercially feasible and economic fuel cell). The studies of the electrode kinetics of these reactions, which are usually carried out at noble-metal electrodes, have been complemented by studies of the adsorption of the reactants, intermediates and the products at the electrode surface. The involvement of chemisorbed oxide species and hydrocarbon residues in the electrode processes is now well-established.

On the "negative side" of the potential of the reversible hydrogen electrode, the electro-reduction of many organic molecules has been studied by polarographic techniques at a dropping mercury electrode or at a hanging mercury drop electrode. Much of this work has been concerned with the chemistry of the electrochemical reactions, that is to say studies in which polarography or cyclic voltammetry is used to elucidate the mechanisms of processes in which charge transfer is a fundamental process, but in which various prior and/or subsequent chemical steps occur and determine the nature of the ultimate product(s) of the electrochemical reaction. The physical adsorption of neutral organic molecules

has been extensively studied by electrocapillary methods and more recently by a.c. capacity techniques. Although chemisorption is not likely at a mercury electrode, except in the case of some S or N compounds, certainly physical adsorption or an electrical orientation of the reducible species must be a prerequisite for electro-reduction in many cases. Furthermore, the product of the reaction will also usually be adsorbed or oriented at the electrode surface and its presence at the surface may lead to inhibition or acceleration of the rate of the electro-reduction.

The present work is an effort to correlate systematically the kinetic and the adsorption behaviour of an organic compound in an electro-reduction reaction. In acid solutions, acetophenone can be reduced electrochemically to a single product, acetophenone pinacol, in a high coulombic yield. The kinetics of this electrochemical reduction and the adsorption behaviour of the ketone and the corresponding pinacol were both studied at a mercury electrode and in the same solvent system, i.e., a solution of water (20 mole %) in methanol containing sulphuric acid.

In this way the kinetic results obtained from both steady-state and non steady-state (potentiodynamic) studies may be interpreted in the light of the known adsorption behaviour of the reactant and the product over the same range of electrode potentials. In particular, the question of the significance

of the kinetic reaction order in relation to the adsorption behaviour is of basic importance.

It is realised that molecular structure must be an important factor in both the adsorption behaviour and kinetics of an electrode process, but the information obtained from this study may provide a general model for the electro-reduction of aromatic ketones under the chosen experimental conditions.

CHAPTER II

EXPERIMENTAL

1. INTRODUCTION

The interdependence of the electrode potential and electrical current can provide an insight into the mechanism of an electrochemical process. The current is a measure of the overall rate of a reaction and the electrode potential can affect this rate as well as the adsorption behaviour of the reactants and products at the electrode surface. Under certain conditions, the slope of the current-potential relation ($\log[i]$ vs E) can lead to mechanistically significant conclusions, and from a series of such $\log[i]$-E curves obtained at various concentrations of the reactant, the electrochemical reaction order can be determined.

The kinetics of the electro-reduction of acetophenone and other aromatic ketones were studied by both potentiostatic steady-state and potentiodynamic non-steady state measurements. Potentiostatic conditions were preferred to galvanostatic conditions since the structure of the limiting current region could then be more conveniently discerned. The measured electrode potentials were corrected for ohmic overpotential (iR drop) particularly in the regions of high current density.

From potentiodynamic linear sweep studies, qualitative information can be obtained regarding the reversibility of the electrode reaction, the adsorption-desorption phenomena, the role of diffusion and activation control and the nature

of the products of the reaction. With such factors in mind, this method has been applied to the study of the electro-reduction of acetophenone and the electrochemical behaviour of the reaction product, acetophenone pinacol.

If a stepwise change of potential is suddenly applied to the working-electrode, the resulting non-steady state current can be recorded virtually instantaneously and also after longer times as it then approaches a new steady-state value. Such potential-step studies have been used in the present work but oscillatory effects were encountered and these possibly arise from the "relatively slow" response of the potentiostat to the applied potential-step signal (139). The oscillations tended to obscure the shape of the current-time transient over the first few milliseconds.

In this chapter, the above experimental procedures will be described in some detail but first a general account of the techniques used for preparation and purification of the electrolytic solutions, the construction of the cells and electrodes, etc. will be given.

2. SOLUTIONS

(a) Water

"Once distilled" water was redistilled from alkaline potassium permanganate in a still provided with three spray traps. This water was then refluxed for a short time in a stream of purified nitrogen gas, primarily to remove

dissolved oxygen, and then redistilled.

(b) Deuterium Oxide (D_2O)

Deuterium oxide (Atomic Energy of Canada, 99.75 mole %) used in a study of kinetic isotope effects in the reduction reaction, was redistilled in an atmosphere of dry nitrogen.

(c) Methanol

Methanol (Fisher Spectrograde), used as the solvent or co-solvent in many of the experiments, was refluxed in 500 ml. quantities with sodium borohydride (1g) and magnesium turnings (1g) for two hours in an atmosphere of nitrogen, and then distilled through a short fractionating column, discarding the first few millilitres of the distillate.

(d) Methanol-d (CH_3OD)

After redistillation, deuterium oxide (160g; 8 moles) was added slowly to sodium methoxide (438g; 8.1 moles) and the flask sealed from the atmosphere before the mixture was gently shaken for several hours. The slurry was then distilled *in vacuo*, the distillate being condensed in a receiver immersed in a mixture of acetone and solid carbon dioxide (at approximately $-70^{\circ}C$).

Methanol-d was redistilled in an atmosphere of nitrogen before further use.

(e) Deuterosulphuric Acid (D_2SO_4)

A liquid form of sulphur trioxide (20 g) (Allied Chemical Co.) was distilled *in vacuo* and condensed into

deuterium oxide (5g) in a receiver immersed in an acetone/ "drikold" slurry. The mixture was allowed to warm slowly to room temperature in a sealed flask.

The concentration of deuterosulphuric acid was found to be 16.8 M. The acid was used in kinetic isotope studies described in a later section.

(f) Preparation of the Electrolyte

(i) Methanol (80 mole %)-Water-Sulphuric Acid (1 M): For convenience a dry, clean volumetric flask (250 ml) was used in the preparation of the electrolyte.

Sulphuric acid (B.D.H. Micro-analytical Reagent, 98% H_2SO_4) (14 ml.) was diluted to 250 ml. with a solution of triply-distilled water (27g) and purified methanol (192g). This solution was poured into a specially designed glass apparatus (see Figure 4) and deaerated for approximately thirty minutes by the passage of nitrogen gas before being transferred to the cell*.

The concentration of sulphuric acid in the electrolyte was determined by titration against a standardised solution of sodium hydroxide, using methyl orange as an internal indicator.

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* This procedure was followed for all solutions prepared for the electrochemical kinetic studies.

(ii) Nominally Anhydrous Methanol-Sulphuric Acid (1 M): Sulphuric acid (14 ml.) was diluted to 250 ml. with purified methanol and this solution was deaerated and transferred to the cell in the manner described above.

(iii) Methanol-d (80 mole %)-Deuterium Oxide-Deuterosulphuric Acid (1 M): Deutero-sulphuric acid (15 ml.) was diluted to 250 ml. with a solution of deuterium oxide (30g) in methanol-d (198g).

(iv) Pre-electrolysis: Since the behaviour of an electrode is sensitive to traces of electro-reducible and adsorbable impurities, the electrolyte in the working-electrode compartment of the cell was further purified by cathodic pre-electrolysis using a mercury pool electrode (geometric area approximately 5 cm^2). The electrode was withdrawn from the solution before experimental measurements were made.

During pre-electrolysis the potential of this electrode was controlled potentiostatically at -0.7 volts vs E_H [see section 4(c)] for twenty to twenty-four hours, during which time nitrogen was continuously bubbled through the solution.

(g) Acetophenone, Benzophenone and Fluorenone

Acetophenone (Fisher reagent grade) was redistilled at reduced pressure, b.p. 70-71°C/1 mm.

Benzophenone (Fisher reagent grade), m.p. 47-48°C and Fluorenone (Eastman Kodak), m.p. 82°C were both recrystallised from a methanol (80 mole %)-water solution.

(h) Addition of Ketone

Small volumes of ketone* were added only to the working-electrode compartment and the solution was agitated vigorously by a rapid stream of nitrogen before any measurements were taken.

When studies on any one solution were completed, a sample of the electrolyte was removed and the concentration of the ketone was determined by ultra-violet spectrophotometry [see section 5(c)].

(i) A Study of the Effect of the Concentration of Water in the Electrolyte

"Titration" of nominally anhydrous methanol containing sulphuric acid (1M) [section 2(d) (ii)] with aqueous sulphuric acid (1M), prepared by dilution of concentrated sulphuric acid with triply distilled water, provided a range of concentrations of water in the electrolyte. Addition of the aqueous acid was made only to the solution in the working-electrode compartment which also contained a known concentration of acetophenone. Further ketone was added to maintain a constant concentration since the volume of the solution in the working-

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* Acetophenone was added directly, but in the experiments with benzophenone and fluorenone, aliquots of a solution of the ketone made up in the electrolyte were used.

electrode compartment increased during the experiment.

The resulting solution was drawn into the Luggin capillary from the reference-electrode compartment to minimise changes in the composition of the solvent close to the electrode surface arising from diffusion processes. Since only the solution in the Luggin capillary and not that in the reference-electrode compartment was replaced, the potential of the reference electrode remained essentially constant throughout the experiment.

(j) A Study of the Effect of Change of pH of the Electrolyte

In most of the work, experiments at a relatively high concentration of hydrogen ions were carried out, so that a constant pH was easily maintained during the kinetic studies (although the hydrogen ion is actually a co-reactant in the electro-reduction reaction). The acid solution also acted as the supporting electrolyte, allowing the passage of fairly large currents (10^{-3} - 10^{-2} A).

However, in a special experiment designed to show the effect of change of pH upon the electro-reduction of acetophenone, the initial solution contained approximately 5×10^{-3} g.ion litre^{-1} of hydrogen ions as $HClO_4$, so that it was necessary to use sodium perchlorate as a supporting

electrolyte*. Conditions of constant ionic strength were maintained.

Sodium perchlorate (30g) and perchloric acid (0.2g) (BDH Analar Reagent, 72% aqueous solution) were diluted to 250 ml. with a solution of triply distilled water (27g) and purified methanol (192g), and this solution was deaerated and transferred to the cell.

The solution was pre-electrolysed for 24 hours using a mercury pool electrode, the potential of which was controlled potentiostatically at -0.7 volts (measured against a hydrogen electrode in the same solution). Acetophenone (2g) was added to the solution in the working-electrode compartment and, after mixing, a sample was removed for determination of (a) the concentration of ketone by ultra-violet spectrophotometry and (b) the concentration of hydrogen ions by titration against a standard solution of sodium hydroxide.

The concentration of acid in the solution in the working-electrode compartment was progressively <u>increased</u>, (pH decreased), by "titration" with a solution of perchloric acid (21g) and sodium perchlorate (9.7g) in methanol (40g)**

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* Since the simple inorganic sulphates are only sparingly soluble in methanol, sodium perchlorate was chosen as the inert electrolyte and therefore perchloric acid was used as the proton source.
Anhydrous sodium perchlorate (Anachemia Chemicals Ltd.) was recrystallised from methanol by partial evaporation of the solvent.

**The concentration of methanol in the solution was 80 mole % since water is present in the perchloric acid (approximately 28% w/w). The concentrations of sodium perchlorate and acetophenone were kept essentially constant throughout the experiment.

containing acetophenone (0.6g), after first removing an equal volume of the solution already in the compartment. Following each addition of acid, the concentration of both ketone and hydrogen ions was determined.

(k) Controlled Potential Electrolysis of Acetophenone Solutions

(i) Electrolysis in Methanol-Water (20 mole %)-Sulphuric Acid (1 M): Sulphuric acid (14 ml.) was diluted to 250 ml. with a solution of triply distilled water (27g) in purified methanol (192g) and this solution was deaerated and transferred to a three-compartment cell in the usual way.

Acetophenone (4.5g) was added to the working-electrode compartment and the solution was electrolysed for forty-eight hours at a large mercury pool electrode (approximate area 14 cm^2), the potential of which was controlled potentiostatically at -0.65 volts vs E_H. A copper coulometer was connected in series with the counter-electrode and the total charge passed during electrolysis was determined from the weight of copper deposited at a platinum cathode. The decrease in the concentration of acetophenone as the reaction proceeded was followed by ultra-violet spectrophotometric analysis.

After electrolysis the solution was neutralised and then steam-distilled to remove the organic solvent. A thin-layer chromatogram of the crude product showed the

presence of only two compounds (acetophenone and acetophenone pinacol) which were separated by a solvent mixture of chloroform and diethyl ether (20:1). A separation of the same two compounds was also obtained in a more polar solvent mixture than that originally used [in this case the solvent mixture was chloroform and diethyl ether (9:1)].

The residue was extracted with hot benzene and the solution diluted with n-pentane to isolate a crystalline product which was shown to be optically inactive. The product was recrystallised from ethanol (96%) and identified from its ultra-violet and infra-red spectra as the expected 2,3-diphenyl-butane-2,3-diol (acetophenone pinacol) m.p. 120-121°C.

(ii) Electrolysis in Methanol-Sulphuric Acid (1 M): The controlled potential electrolysis of acetophenone in a solution of sulphuric acid (1M) in nominally anhydrous methanol was carried out in order to establish that acetophenone pinacol was again the only product of the electro-reduction.

Sulphuric acid (14 ml.) was diluted to 250 ml. with purified methanol and this solution was deaerated and transferred to the cell in the usual way. Acetophenone (2g) was added to the working-electrode compartment and the solution was electrolysed for twenty-four hours at a large mercury pool electrode (E= -0.65 V. vs E_H). The total charge passed during electrolysis was again determined coulometrically.

After electrolysis the solution was neutralised and the crude product was extracted. A thin-layer chromatogram of this product showed the presence of only the pinacol and unreacted acetophenone.

(1) A Study of the Electrochemical Behaviour of Acetophenone Pinacol

In experiments to show the kinetic effects of the addition of the pinacol and in regard to the adsorption behaviour of this compound (the reaction product of the electrochemical reduction of acetophenone in acid media), it was necessary to prepare solutions of known concentration of the pinacol from the pure compound.

(i) Preparation of Acetophenone Pinacol: Acetophenone pinacol was prepared by the condensation of a Grignard reagent, methyl magnesium iodide, with benzil in anhydrous ether. The reaction mixture was decomposed in the usual way with dilute hydrochloric acid and the product was extracted with n-pentane. The crude material was twice recrystallised from ethanol (96%).

(ii) Electrochemical Behaviour of Acetophenone Pinacol: Pure sulphuric acid (14 ml.) was diluted to 250 ml. with a solution of triply-distilled water (27g) and purified methanol (192g). The solution was deaerated, transferred to the cell in the usual way and then pre-electrolysed at -0.7 volts vs E_H overnight.

Acetophenone pinacol (0.25 g) was added to the solution in the working electrode compartment and electrochemical measurements were made after prolonged agitation with nitrogen gas to ensure complete dissolution

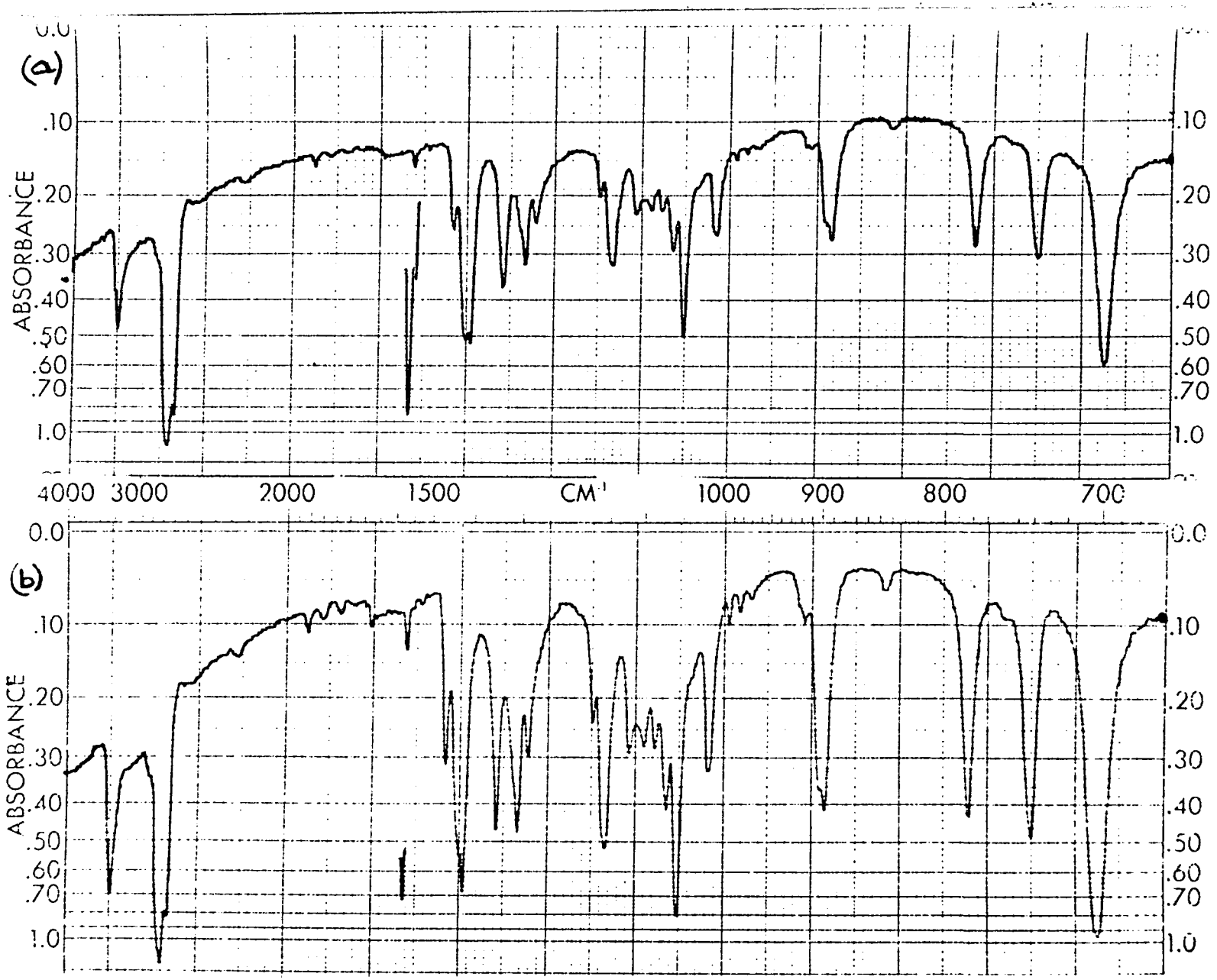
of the pinacol. Two other solutions containing higher concentrations of the pinacol were similarly studied. Acetophenone (3g) was then added to the solution and measurements were made to determine the effect of the pinacol, if any, upon the kinetics of electro-reduction of the ketone.

(iii) Rearrangement of Acetophenone Pinacol in Acid Solution: In order to determine if a pinacol-pinacolone rearrangement was likely to occur to a significant extent during the experiments in acidic solutions, the following investigation was made. Acetophenone pinacol (2g) was dissolved in a solution of methanol (80 mole %) and water containing sulphuric acid (1 M), and an ultra-violet spectrum (from 240-300mμ) was determined on a sample of this solution [see later, section 5(c)]. The solution was allowed to stand at room temperature for several days and a second ultra-violet spectrum was then determined. After neutralisation and evaporation of the solvents, a crude product was extracted from the residue and the infra-red spectrum obtained.

The infra-red spectra of the pure pinacol [Figure 2(a)] and of the "rearranged" product [Figure 2(b)] were not significantly different, particularly in the spectral region corresponding to carbonyl absorption, i.e., 1670-1750 $cm.^{-1}$. Furthermore, the ultra-violet spectra of both solutions (before and after) showed no absorption

Figure 2. (a) Infra-red spectrum of 2,3-diphenylbutan-2,3-diol (acetophenone pinacol)

(b) Infra-red spectrum of the residue extracted from a solution of acetophenone pinacol in methanol-water-sulphuric acid.


(a)
ABSORBANCE
.10
.20
.30
.40
.50
.60
.70
1.0
4000
3000
2000
1500
CM⁻¹
1000
900
800
700
(b)
0.0

between 275 and 285 mμ, the wavelengths at which carbonyl absorption is usually found. It was therefore concluded that under these conditions rearrangement did not occur to any significant extent.

3. CELLS

A three-compartment pyrex-glass cell was used (Figure 3).

The main compartment contained the working electrode and a second mercury pool electrode, used for pre-electrolysis. An additional gas inlet was provided in order to ensure complete mixing of the solution after addition of the ketone by bubbling nitrogen.

The counter-electrode compartment was separated from the main compartment by a closed, solution-sealed stopcock to prevent diffusion of reactant away from this main compartment; the stopcock also prevented contamination of the catholyte by oxidation products formed at the anode.

A detachable reference-electrode compartment was used which allowed the solution in the Luggin capillary to be replaced with that in the main compartment, since the catholyte composition may be significantly changed during certain experiments. Again a closed, solution-sealed stopcock was used which effectively separated the two compartments yet allowed electrolytic contact between them.

A second cell (Figure 4) was constructed to allow the surface of the mercury pool electrode to be renewed

Figure 3. Photograph of the experimental cell.

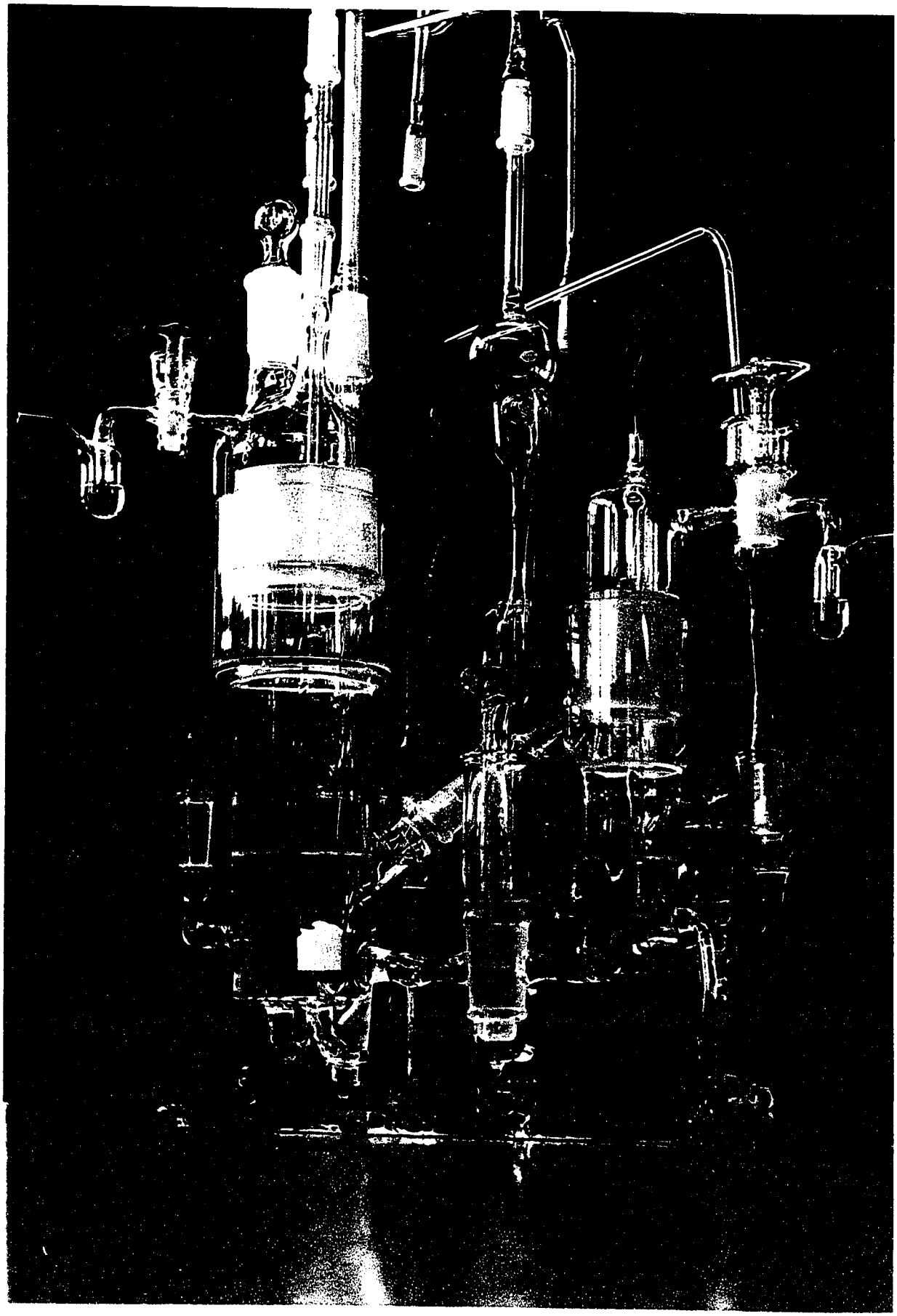
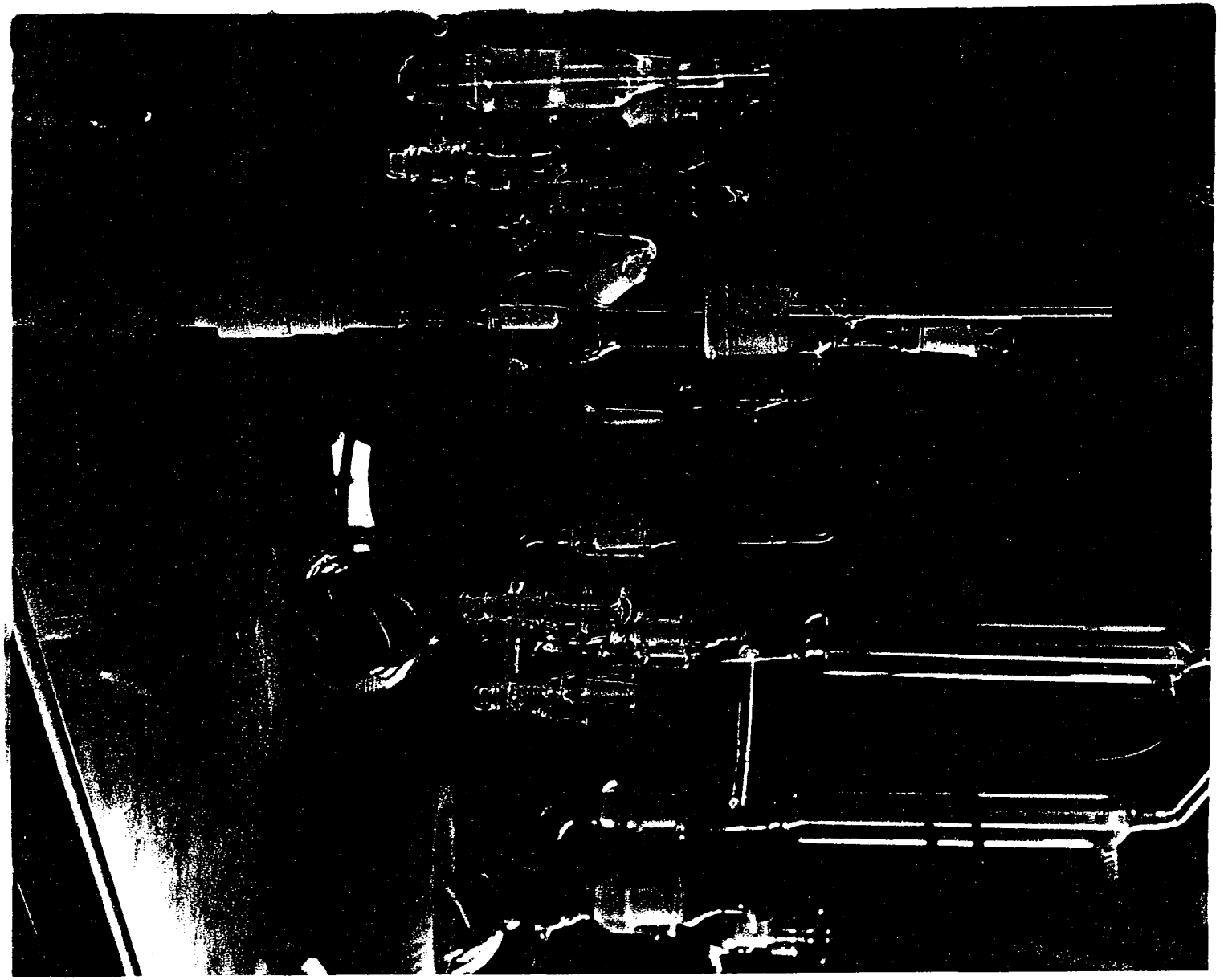


Figure 4. Photograph of the experimental cell for studies using a mercury electrode with a renewable surface. Also in the photograph is the apparatus from which the electrolyte is transferred to the cell.



[section 4a (ii)]; again a detachable reference-electrode compartment was used.

Pre-saturators for both nitrogen and hydrogen gases were used in order to avoid changes of composition of the electrolyte during an experiment. This is of particular importance when using methanolic solutions, which are relatively volatile.

4. ELECTRODES

(a) Working Electrode

(i) Stationary Mercury Electrode: In preliminary experiments a simple glass capillary "U-tube" containing mercury was used, the capillary being sealed at one end together with a platinum wire to provide electrical contact. However, it was found that penetration of the electrolyte at the mercury/glass interface resulted in partial displacement of the mercury and eventual loss of electrical contact, particularly at high cathodic potentials (> -0.8 volts vs E_H). The surface area of the electrode obviously changed with time and furthermore the electrode potential inside the capillary would probably not be that measured at the surface. This arrangement was hence unsatisfactory.

A hydrophobic silicone coating on the inside of the glass capillary has been widely used in polarography, particularly with the hanging drop mercury electrode (140). However, this was considered to be undesirable in the present

work since it was felt that slow hydrolysis of the coating may occur in the electrolyte, leading to contamination of both the electrode and the solution.

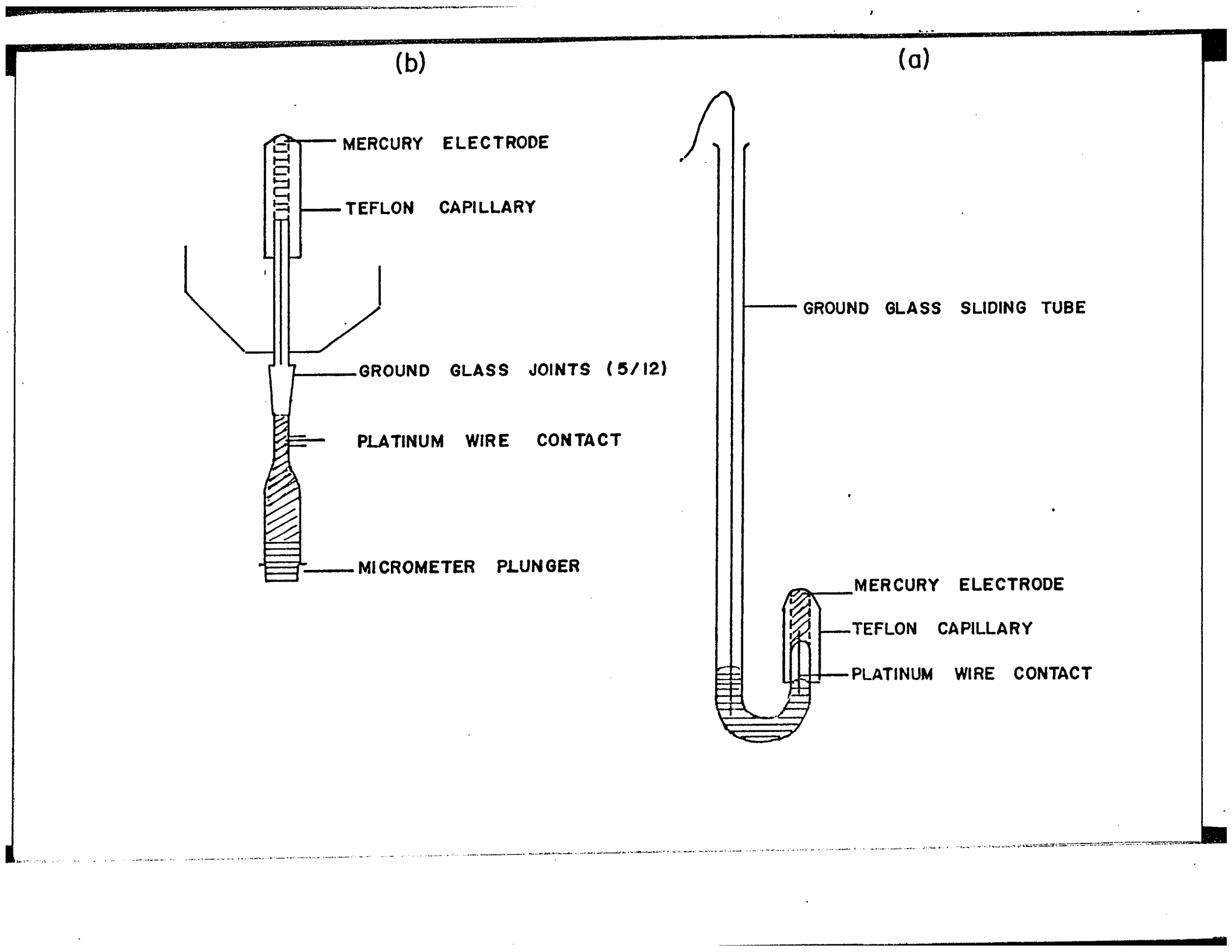
It was found that mercury contained in a Teflon capillary provided a convenient stationary pool electrode and penetration effects were avoided even when prolonged experimental measurements (e.g. 1-2 days) were involved and high cathode potentials were studied.

The design of this electrode is shown diagrammatically in Figure 5(a). The glass stem is in part a ground-glass sliding tube, the counterpart being attached to the top of the working electrode compartment; this arrangement ensured exclusion of air and yet provided an adjustable electrode. A platinum wire was sealed into the other end of the glass tube and the tip smoothly ground before the unsymmetrical "U"-tube was formed. The Teflon capillary was then fitted tightly over the short arm of this "U"-tube and the "well" filled with triply-distilled mercury (Johnson and Matthey) to give a pool electrode having a geometric area of approximately 0.1 $cm.^2$

(ii) Stationary Mercury Electrode with a Renewable Surface: An alternative mercury pool electrode arrangement was constructed in order to allow repeated changing of the electrode surface during an experiment [Figure 5(b)].

Figure 5. (a) Diagram of the stationary mercury pool electrode

(b) Diagram of the stationary mercury pool electrode with renewable surface.


(b)
MERCURY ELECTRODE
TEFLON CAPILLARY
GROUND GLASS JOINTS (5/12)
PLATINUM WIRE CONTACT
MICROMETER PLUNGER
(a)
GROUND GLASS SLIDING TUBE
MERCURY ELECTRODE
TEFLON CAPILLARY
PLATINUM WIRE CONTACT

A short glass capillary was sealed into the base of the working electrode compartment of a second cell and a Teflon mercury "reservoir" was again fitted tightly on to this glass capillary. A micrometer syringe unit [volume 2 ml., with a Teflon barrel and plunger, the barrel being calibrated to permit extrusion of 0.002 ml. of a liquid] was joined from the outside of the cell using two ground-glass joints (5/12 male and female). The syringe was filled with triply-distilled mercury and inverted to expel residual air before being fitted to the cell. Mercury was then forced into the Teflon capillary by rotating the micrometer barrel until a pool electrode was obtained (geometric area approximately 0.025 $cm.^2$). The formation of a stable spherical drop, i.e., a "sessile" mercury drop, proved difficult since the mercury tended to fall away unpredictably when the solution was agitated or when sudden changes of the electrode potential were made. However, the surface of the mercury pool was easily and reproducibly renewed by expelling a small volume of mercury.

(b) Counter Electrode

A platinum gauze of large surface area was used as the counter electrode, and hydrogen gas was bubbled continuously through the solution in the compartment in order to minimise anodic oxidation of the electrolyte.

(c) Reference Electrode

Potentials of the working electrode were measured against a hydrogen electrode* established in a solution initially the same as that in the working-electrode compartment.

From the Nernst equation:

$$E_H = E^o - \frac{RT}{F} \ln\left[a_{H^+}\right]$$

where E^o is the standard potential of the reversible hydrogen electrode taken arbitrarily as zero. If activities are replaced by concentration terms, then at 25°C the equation becomes

$$E_H = -0.059 \log[H^+]$$

Unless otherwise stated, all values of electrode potentials quoted in this thesis are with reference to E_H, the potential of the hydrogen electrode in the particular electrolyte used in the kinetic runs.

5. INSTRUMENTATION AND TECHNIQUE

(a) Instruments

Potentials were controlled by a Wenking short rise-time potentiostat and measured on a Radiometer pH-mV meter.

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* The electrode was freshly prepared for each experiment by electrodeposition of platinum at a platinum gauze (approximate geometric area 1 $cm.^2$) from a solution of chloroplatinic acid containing traces of lead acetate (141).

In the programmed potentiodynamic and potential-step experiments, a signal of the required form was applied to the reference input of the potentiostat from a function generator. In other cases, this input was shorted so that the working electrode could be made cathodic with respect to the counter electrode.

For galvanostatic measurements, a conventional divided resistance arrangement was used, the source of power being a 90-120 V. D.C. Power supply (Dressen-Barnes Corp. Model 22-110).

Linear sweep potentiodynamic measurements were made using a "Servomex" function generator (Type L.F. 141).

The steady-state currents were measured on a "Sensitive Research" milliammeter connected in series with the counter electrode. Transient currents in potentiodynamic and potential-step experiments were passed through a calibrated resistance and the resulting potential difference recorded on an oscilloscope or a Moseley high impedance X-Y recorder (Model 2D-2AM).

All transients arising from open circuit e.m.f. decay, potentiodynamic sweeps ($\frac{dE}{dt} > 0.1$ V. sec^{-1}) and potentiostatic step-charging experiments were photographed from the screen of a Tektronix dual-beam oscilloscope using a 35 mm. reflex camera. The electrode signal was passed through a Tektronix operational amplifier (Type "O"), set up

as a high input impedance cathode follower, before being recorded. This eliminated significant current drain from the working electrode/reference electrode system.

(b) Electrochemical Procedures

(i) Potentiostatic Steady-state Kinetic Measurements: In the experimental arrangement for the potentiostatic polarisation of the electrode, the working electrode, which was grounded, was made cathodic with respect to the counter electrode. Polarisation was commenced just after immersing and adjusting the position of the electrode in the solution so that the tip of the Luggin capillary was as close as possible to the surface of the mercury. Measurements were made both with and without nitrogen gas bubbling through the solution in the vicinity of the electrode.

To obtain a log[i]-E relation for a particular solution the potential was changed by successive increments of 10 mV and the resulting current recorded thirty seconds after each adjustment of potential. This procedure was followed in an ascending (i.e., more cathodic) and descending direction over a range of electrode potentials in which the Faradaic process was known to occur, e.g., in the electro-reduction of acetophenone the potential range usually studied was from -0.4 to -1.0 volts vs E_H.

(ii) Correction of Measured Potential for iR Drop: In the steady-state kinetic runs, the electrode was polarised

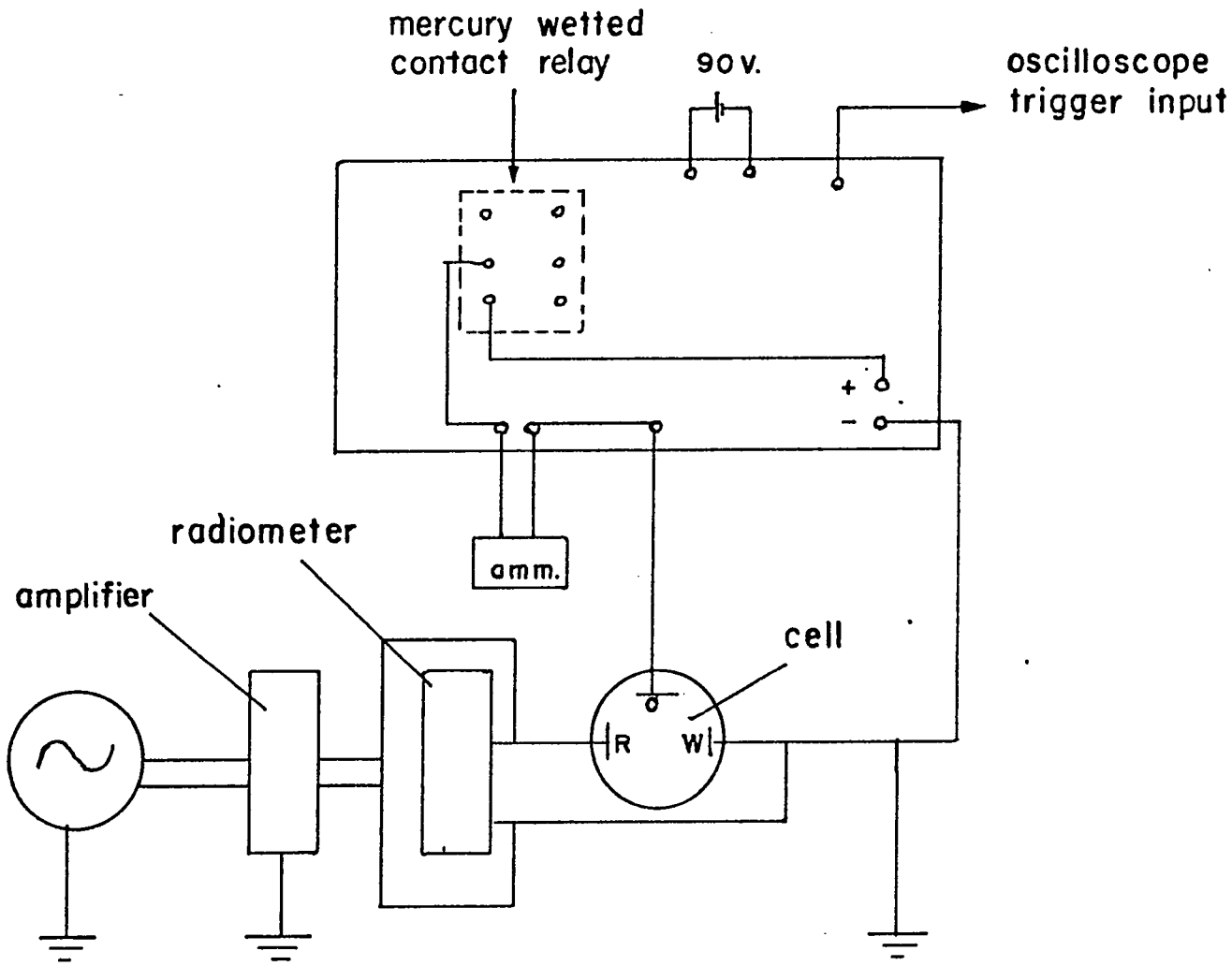
potentiostatically into a region of current densities where ohmic overpotential could be significant. The electrochemical reaction may show regions of potential in which the current flowing is limited either by an activation-controlled process or simply by diffusion (cf. polarographic conditions) and it was therefore important to establish the magnitude of iR effects at high cathodic currents.

iR corrections were therefore made at all high current densities by observing the virtually instantaneous initial drop of potential when the electrode potential was allowed to decay on open-circuit. The transient was photographed on an oscilloscope and the ohmic overpotential determined from the picture after appropriate enlargement.

The circuit diagram for open-circuit decay measurements is shown in Figure 6.

(iii) Potentiodynamic Repetitive and Single Sweep Experiments: The shape of the current-potential transient depends on the nature of the potential programme and on the electrochemical behaviour of the process under investigation. In the present potentiodynamic experiments a symmetrical "triangular" wave form was used. The characteristics of the diffusion-controlled peak, i.e., peak potential (E_p) and cathodic peak current (i_p), which corresponded to the electro-reduction of the ketone were determined as a function of sweep-rate over a constant range of potential. The

Figure 6. Schematic diagram of the circuit for open circuit decay measurements.


mercury wetted
contact relay
90v.
oscilloscope
trigger input
+
−
radiometer
amm.
amplifier
cell
R
W

presence or absence of anodic peaks corresponding to the re-oxidation of intermediates or products formed in the electrode process was also investigated.

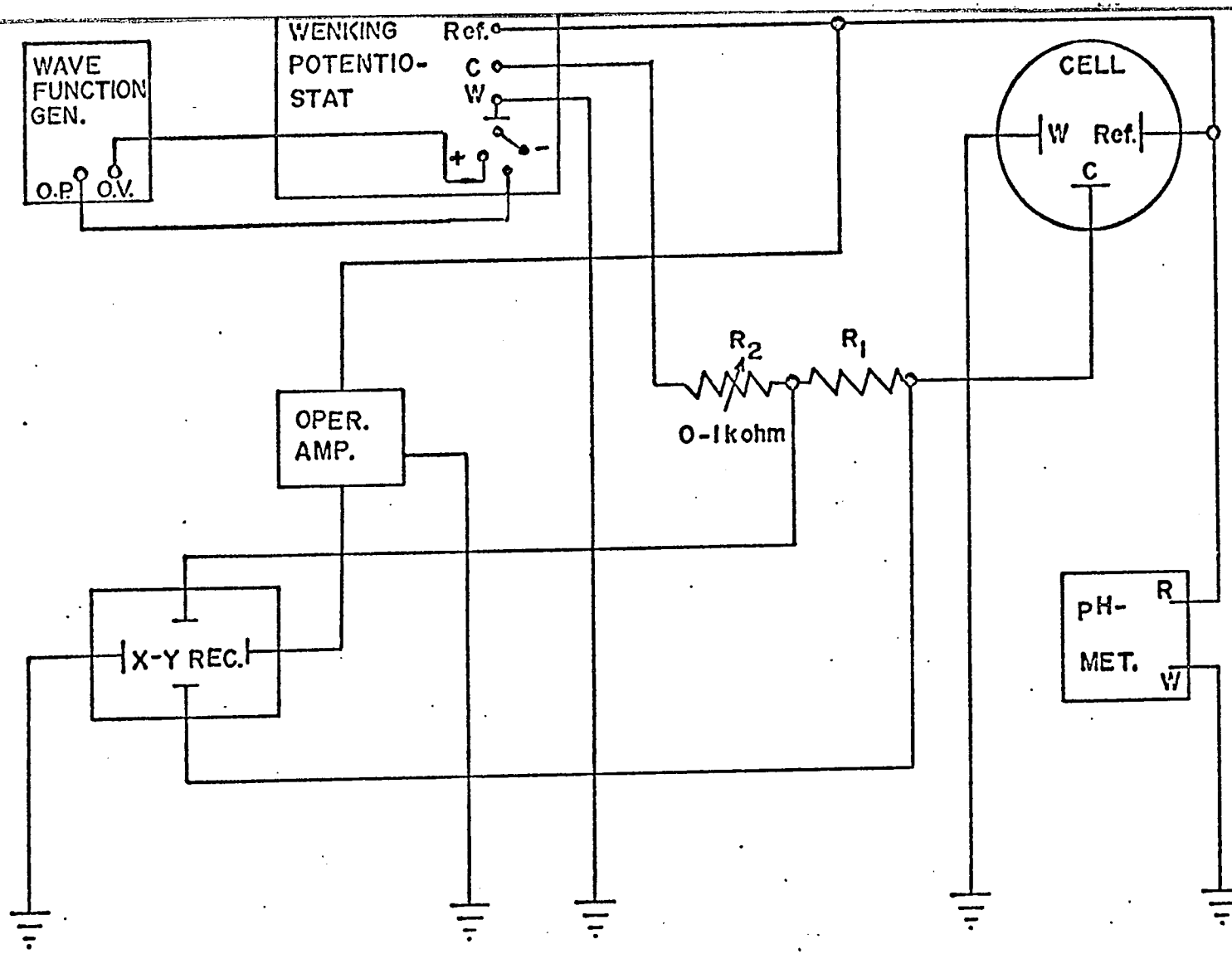
The circuit diagram for potentiodynamic studies is shown in Figure 7.

A reference signal drawn from the output of a wave function generator is applied to the reference input of the potentiostat. The potential of the working electrode, which varies according to the selected signal, is suitably amplified and recorded on the X-axis of an X-Y recorder (for slow sweep-rates, viz., $\frac{dE}{dt} < 0.1$ V. sec^{-1}) or on an oscilloscope. When a current flows in the cell (corresponding to the potential applied to the working electrode) a potential difference is developed, in proportion, across the decade resistance (R_1) which is connected in series with the counter electrode. This potential difference is recorded on the Y-axis of the oscilloscope or the recorder.

Thus the transient current (i_t) passing through the cell at a given moment, arising from the selected change of electrode potential, is measured as a potential difference $(\Delta E)_t$ where

$$(\Delta E)_t = i_t R_1$$

Figure 7. Schematic circuit diagram for potentiodynamic repetitive and single sweep experiments.


WAVE
FUNCTION
GEN.
O.P
O.V.
WENKING
POTENTIO-
STAT
Ref.
C
W
+
-
CELL
W
Ref.
C
R_2
R_1
0-1kohm
OPER.
AMP.
X-Y REC.
pH-
MET.
R
W

Any noise in the Y-axis signal is suppressed by using an input filter (Hewlett Packard Model 17106 A). For optimum conditions the working electrode, the operational amplifier and the oscilloscope were grounded. The range of potentials over which the electrochemical process was studied could be adjusted by appropriate settings on the potentiostat and the function generator.

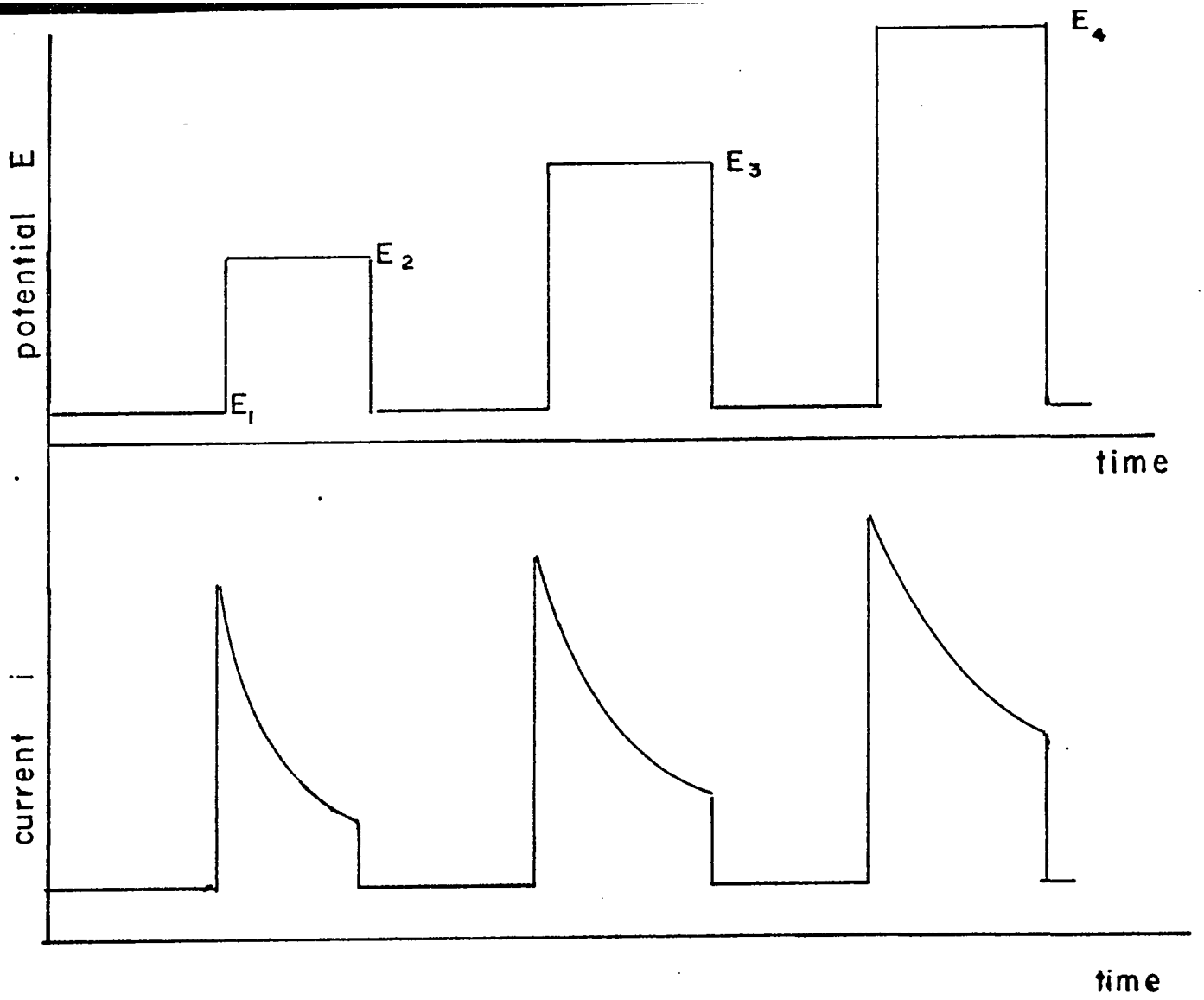
(iv) Potential-Step Measurements: The principle of these measurements is shown in Figure 8.

The electrode was polarised at a potential, E_1, which was known to be in an electro-inactive or non-Faradaic region with respect to the electro-reduction of the ketone. After a few seconds, the potentiometer was switched in through a fast-acting mercury vacuum relay to give a preset, more cathodic value of potential, E_2. This condition was maintained for various intervals of time and the corresponding current was developed across a calibrated decade resistance, the resulting potential difference being recorded photographically on an oscilloscope. The potentiometer was then switched out.

This procedure was repeated for successive values of potential over the range of potentials where steady-state log[i]-E relations indicated that the Faradaic process was occurring. A renewed mercury surface was used for each potential step [see section 4a (ii)].

In this manner, a series of current-time

Figure 8. Schematic representation of current vs time and potential vs time profiles in potential-step technique.


potential E
E1
E2
E3
E4
time
current i
time

transients were obtained which comprised both the virtually instantaneous non-steady state currents as well as the currents which passed after longer times and then approached the steady-state values.

A circuit diagram is shown in Figure 9.

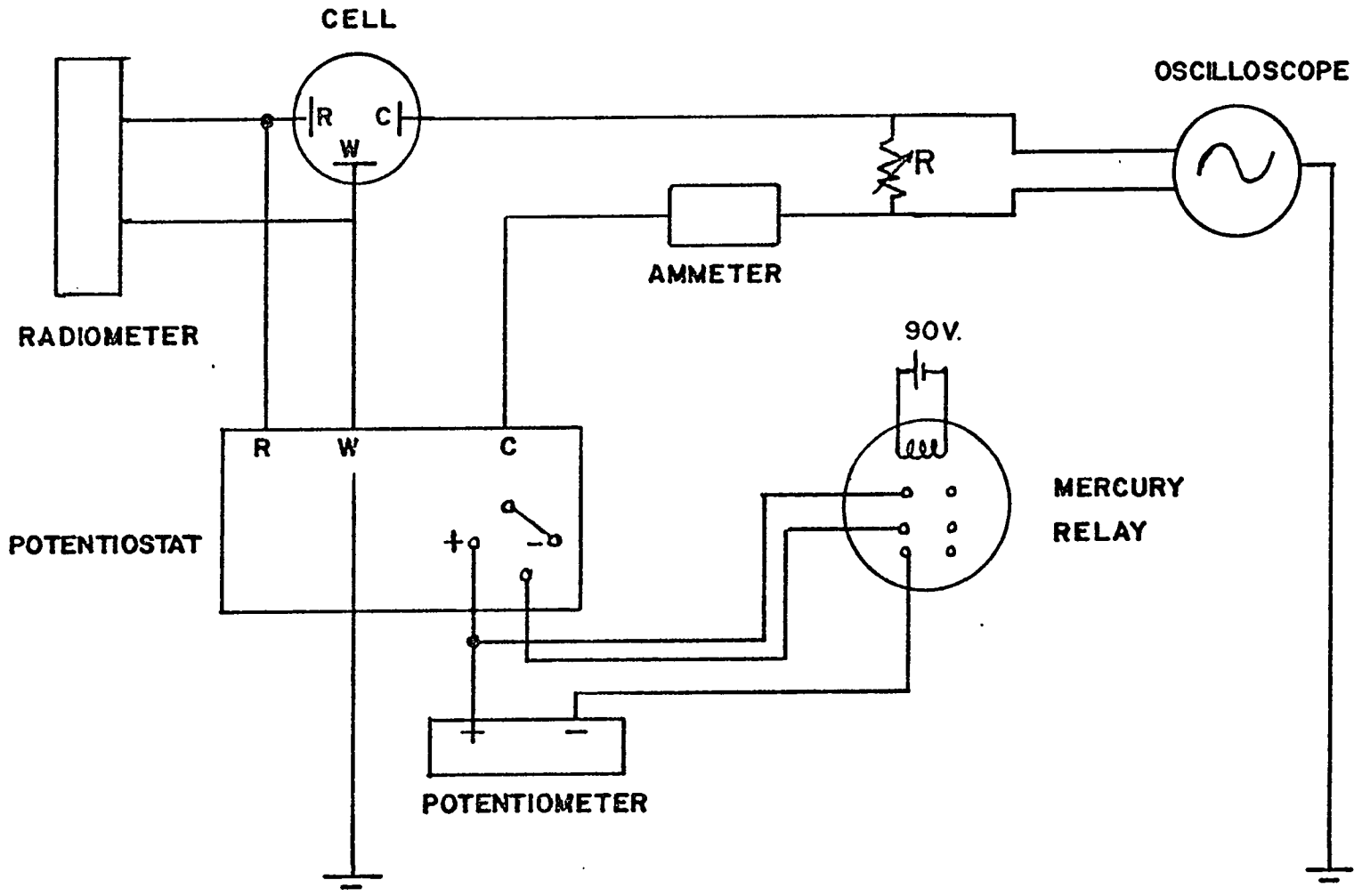
(c) Ultra-Violet Spectrophotometric Analyses

The electrolyte (approximately 0.05g) containing the ketone was weighed accurately into a volumetric flask (25 ml.) and dissolved in methanol. From the optical density of this solution at 280 mμ, the concentration of the ketone was determined by reference to a previously prepared calibration curve for that ketone.

It was shown that acetophenone pinacol was optically transparent at 280 mμ, even when present in the electrolyte at concentrations as high as 5×10^{-2} moles. litre^{-1}. Acetophenone could therefore be determined after reduction experiments in the presence of significant quantities of the reduction product formed during the electrolysis.

The method was found to be reproducible to $\pm$ 2%.

Figure 9. Schematic circuit diagram for potential-step studies.


CELL
R
C
W
OSCILLOSCOPE
R
AMMETER
RADIOMETER
90V.
R
W
C
MERCURY
RELAY
POTENTIOSTAT
+
−
+
−
POTENTIOMETER

6. THE ADSORPTION BEHAVIOUR OF THE REACTANT AND THE PRODUCT: POTENTIOSTATIC ELECTROCAPILLARY STUDIES

Recent modifications (142) to the capillary electrometer technique have been introduced in which the determination of (a) the position of the fine thread of mercury in the capillary and (b) the height of mercury in the manometer has been considerably simplified. For studies of equilibrium electrochemical adsorption at mercury, the use of the Lippmann electrometer is particularly valuable when slow adsorption processes may be involved, as in the case of organic adsorbates.

The adsorption behaviour of acetophenone and 2,3-diphenyl-2,3-butanediol (acetophenone pinacol) in a solution of methanol (80 mole %) and water containing sulphuric acid (1 M) was studied by this method. Three types of solution were used:

(a) those containing acetophenone alone,

(b) those containing acetophenone in the presence of a small, fixed amount of the pinacol,

and

(c) those containing only pinacol.

Hence information is obtained regarding the adsorption of the reactant and the product separately, and of the reactant in the presence of the product.

Thus both the adsorption behaviour and the electrochemical kinetics were studied in the same electrolyte, at a mercury electrode and at the same concentrations of acetophenone and pinacol.

CHAPTER III

RESULTS

1. INTRODUCTION

In order to study the kinetics of an electrochemical reaction, the products of that reaction should first be well-defined. For many simple electrode processes the coulombic efficiency is almost 100% but this is not always the case, particularly for many organic electrode reactions. The difficulty may be further complicated by a dependence of the type of product formed upon the electrode potential, e.g., the electro-reduction of nitrobenzene (4), and upon the cathode material.

In the present work, it was found that under certain conditions the electro-reduction of acetophenone gave practically the theoretical yield of the corresponding pinacol. It has been observed (102) that in acid solutions (pH < 3) other aromatic ketones were also exclusively reduced to pinacols in similarly high coulombic yields. The overall reaction pathway for the electro-reduction of an aromatic ketone in acidic solutions is therefore well characterised.

In the study of electrode kinetics by steady-state methods, the rate of reaction is measured directly in terms of the current, i, as a function of the electrode potential, E. In the steady-state kinetic analysis of the electrochemical reduction of the chosen aromatic ketones, $\log[i]$-E

curves have been evaluated for ascending and descending directions of change of electrode potential. The reaction order at several electrode potentials has been determined from a series of log[i]-E curves, obtained from steady-state potentiostatic experiments with solutions containing different concentrations of the aromatic ketone. The effect of change of pH and change of solvent composition upon the electrode kinetics have also been studied by steady-state methods. The results obtained from an experiment using a deuterated solvent system (methanol-d, deuterium oxide and deutero-sulphuric acid) have indicated that the proton is not critically involved in the rate-determining step of the reaction.

The magnitude of the contribution of ohmic overpotential to the measured potential of the working electrode was determined by open circuit e.m.f. decay measurements, and the steady-state log[current]-potential curves were corrected appropriately. It was found that iR effects were significant at high current densities, e.g., in a solution containing acetophenone (0.42 M) an iR drop of 10 mV. was observed at a current density of 5×10^{-2} A. cm.$^{-2}$

Non-steady state current-potential curves have been obtained by potentiodynamic studies (triangular sweep method) and the dependence of (a) the peak potential, E_p, and (b) the peak current, i_p, upon the rate of change of potential in the

applied potential sweep has been determined. In this way, additional qualitative conclusions have been made regarding nature of the electrochemical reduction of acetophenone. Further information has also been obtained by potential-step studies.

For convenience, all current densities reported in this thesis are referred to the geometric area of the mercury pool electrode. In order to evaluate this area, the double-layer capacity of the electrode was estimated from the current-potential profiles obtained from a potentiodynamic experiment. In a solution of methanol (80 mole %) and water containing sulphuric acid (approximately 1M), and at an electrode potential E = -0.04 V. vs E_H, the double-layer capacity of the actual electrode was found to be 2.5 μF so that* the area was approximately 0.1 cm^2. This electrode was used for all the steady-state measurements.

In a particular solution, the current-potential curves, which were obtained by both steady-state and non-steady state methods were found to be very reproducible.

2. COULOMBIC YIELD AND CHARACTERISATION OF THE PRODUCT OF THE ELECTRO-REDUCTION OF ACETOPHENONE

During a controlled potential electrolysis of acetophenone in a solution of methanol and water (20 mole %) containing sulphuric acid (1 M), the decrease in the concentration of the

* It has been shown that in methanol the capacity of the compact double layer, $C_{d.l.}$, at a mercury electrode is generally smaller than that in aqueous solutions (143). The differential capacity of a mercury electrode in a solution of potassium fluoride (0.66 M) in methanol is approximately 18 μF. $cm.^{-2}$ at -0.3 V. vs normal calomel electrode. In an aqueous solution of potassium fluoride, $C_{d.l.}$ = 28 μF. cm^{-2} at the same electrode potential.

ketone was followed by ultra-violet spectrophotometric analysis. The total charge passed during the electrolysis was determined from the weight of copper deposited at the platinum cathode of a copper coulometer.

The results are shown in Table II.

The current efficiency was based upon the amount of acetophenone which had reacted rather than the amount of product formed since quantitative isolation of the pinacol from the reaction mixture was difficult. Furthermore the amount of the pinacol in the solution could not be determined by ultra-violet spectrophotometry, due to the presence of acetophenone.

The only product of the reaction (see Chapter II, p. 60-61) was identified from its ultra-violet and infra-red spectra, these being compared with the corresponding spectra of 2,3-diphenylbutane-2,3-diol (acetophenone pinacol), which was prepared by the well known reaction of methylmagnesium iodide and benzil [see Chapter II, Section 2(b)].

It was established that rearrangement of the pinacol to give a pinacolone did not occur to any significant extent. [See Chapter II, Section 2(l)].

A controlled potential electrolysis of acetophenone in a solution of sulphuric acid (1 M) in methanol was found to yield only acetophenone pinacol. The coulombic efficiency of the electrolysis was 91%, this value being based on the

Table II

Controlled Potential Electrolysis of Acetophenone: E= -0.65 V. vs E_H

Time (hours)	Current (A.)	Moles ketone present	Grammes ketone
0	2.3×10^{-2}	0.037	4.44
17.6	1.9×10^{-2}	0.019	2.28
20.2	1.7×10^{-2}	0.017	2.04
24.2	1.5×10^{-2}	0.0145	1.74
41.4	1×10^{-2}	0.009	1.08
48	8.5×10^{-3}	0.0085	1.02

Total weight of ketone apparently reduced	3.42 grammes
No. of coulombs passed during electrolysis	2660
Corresponding weight of ketone electrochemically reduced	3.35 grammes
Coulombic efficiency	96%

amount of acetophenone which had reacted. The weight of the crude product after the neutralisation and steam-distillation of the electrolyte was 1.8 g. Recrystallisation of the crude product from n-pentane gave acetophenone pinacol (1.67 g).

3. KINETIC STUDIES ON THE ELECTRO-REDUCTION OF ACETOPHENONE: POTENTIOSTATIC STEADY-STATE MEASUREMENTS

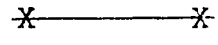
(a) Studies of the Reaction in Methanol (80 mole %)-Water-Sulphuric Acid

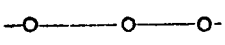
(i) The log[i]-E Curve: A typical log[i]-E curve obtained for the electro-reduction of acetophenone is shown in Figure 10.

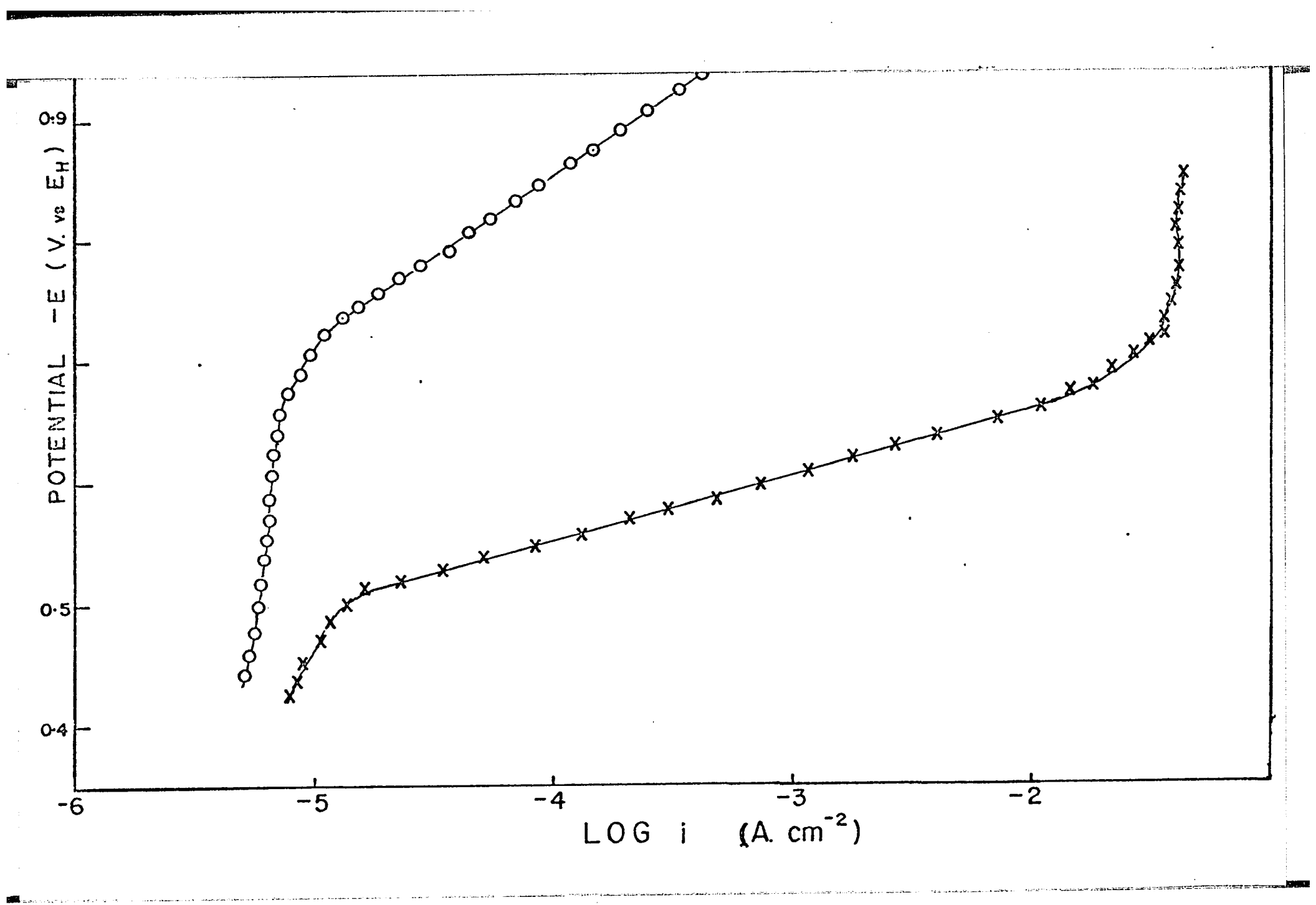
Measurements were made at successive potentials under potentiostatic conditions in a solution of methanol (80 mole %) and water containing sulphuric acid (0.97 M) and acetophenone (0.49 M), in the absence of agitation of the solution near to the working electrode by the passage of nitrogen gase.

The electrochemical reduction of acetophenone occurs at potentials more cathodic than -0.5 V. vs E_H and the kinetics of this reaction are characterized electrochemically by the linear (Tafel) region of the log[i]-E curve, b=52 mV. and by a limiting current at potentials above ca. -0.7 V.

Figure 10. A typical potentiostatic steady-state log[i]-E curve obtained for the electro-reduction of acetophenone in methanol (80 mole %)-water-sulphuric acid (0.97 M) solution
Concentration of acetophenone 0.49 mole. litre^{-1}


Electro-reduction of acetophenone


Hydrogen evolution reaction in the solution in the absence of ketone.


POTENTIAL -E (V. vs E_H)
0·9
0·5
0·4
-6
-5
-4
-3
-2
LOG i (A. cm^{-2})

The steady-state current-potential behaviour for the background solution in the absence of acetophenone is shown by the broken line in Figure 10. It can be concluded that the current due to the discharge of protons, i.e., the hydrogen evolution reaction, is not significant in the region of potential in which acetophenone is reduced. However, the limiting current which is observed at potentials below -0.45 V may possibly be attributed to the electro-reduction of an impurity in the solution. This current must contribute to the total current measured at a given potential during the reduction of acetophenone. The log[i]-E curves were therefore corrected (Figure 11) and it was found that the Tafel slope was a little lower (Table IIIa) than originally observed.

(ii) The Effect of Agitation of the Solution in the Working Electrode Compartment: Agitation of the solution near the working electrode markedly affected (as expected) the regions of potential in which limiting currents were observed. The limiting current at potentials above -0.7 V. vs E_H, which may be attributed to the reduction of the ketone, was found to increase with this agitation (Figure 12) and hence the rate of reaction in this potential region is probably controlled by the rate of diffusion of the electroactive species to the electrode. The observed (corrected) Tafel slope was not significantly affected by

Figure 11. Potentiostatic steady-state log[i]-E curves obtained for the electro-reduction of acetophenone: Correction of the total current at a given potential.

o——o 0.03 mole. litre^{-1} acetophenone

•——•——• 0.21 mole. litre acetophenone.

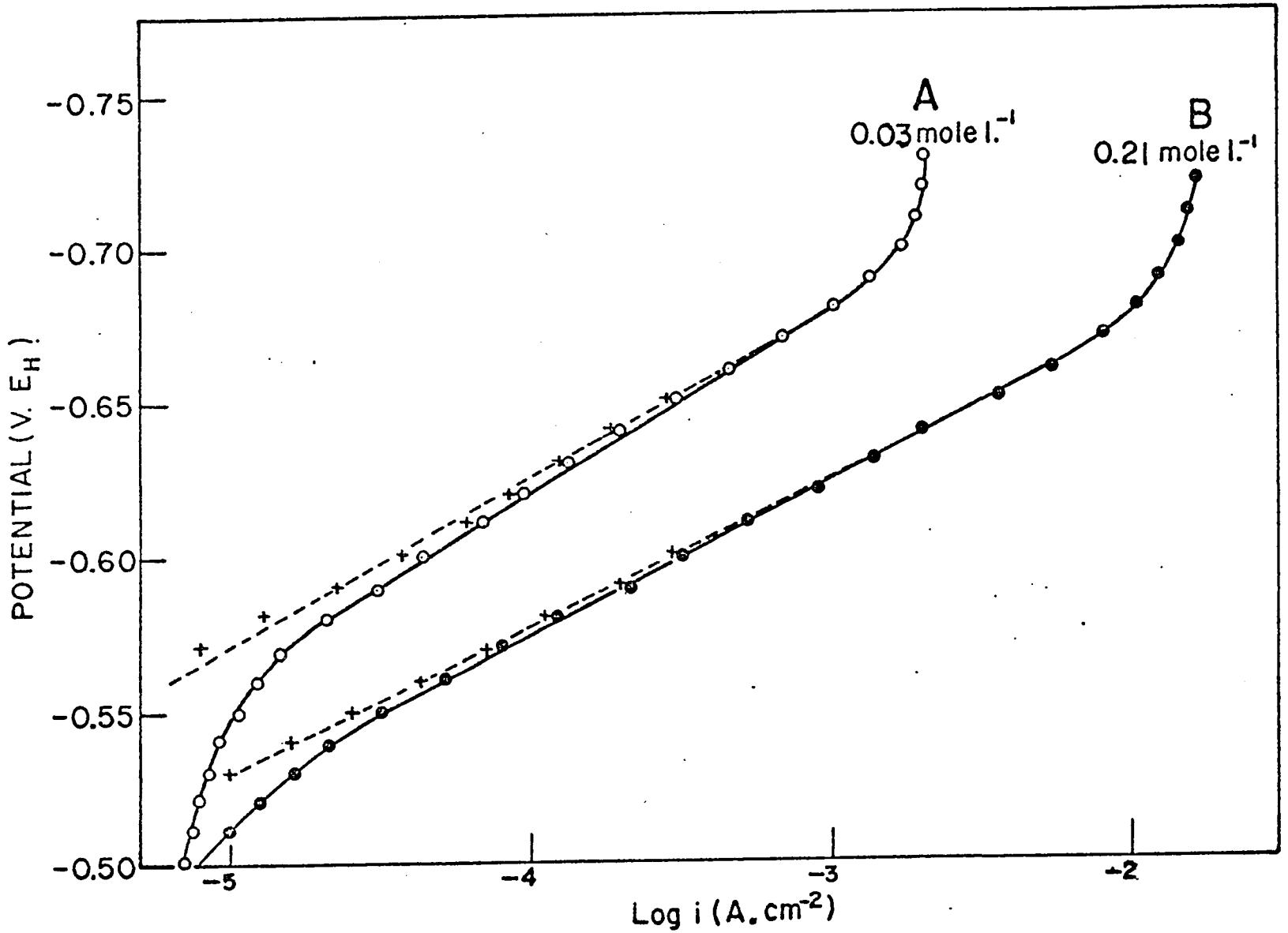
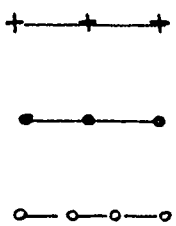

A
0.03 mole l.-1
B
0.21 mole l.-1
-0.75
-0.70
-0.65
-0.60
-0.55
-0.50
POTENTIAL (V. E_H)
-5
-4
-3
-2
Log i (A. cm-2)

Figure 12. The effect of agitation of the solution near to the working electrode.



0.014 mole. litre^{-1} acetophenone

0.03 mole. litre^{-1} acetophenone

Hydrogen evolution reaction in the solution in the absence of ketone.

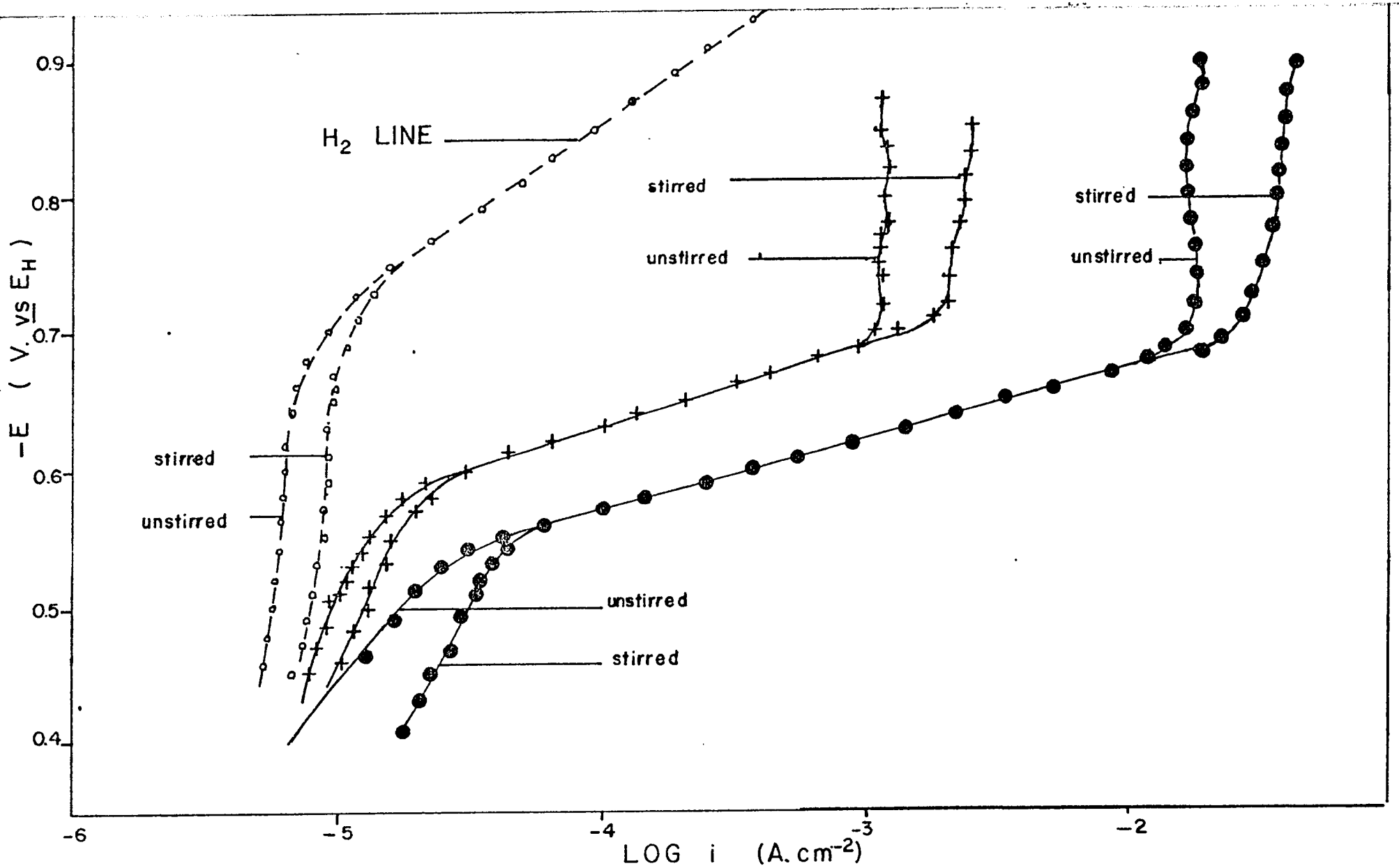

0.9
0.8
0.7
0.6
0.5
0.4
-E (V. vs E_H)
H_2 LINE
stirred
unstirred
stirred
unstirred
stirred
unstirred
unstirred
stirred
-6
-5
-4
-3
-2
LOG i (A.cm^{-2})

Table III

(a) Effect of the Presence of an Impurity in the Electrolyte: Correction of the Tafel Slope, b, for Residual Currents

Concentration of ketone (mole. litre^{-1})	b (uncorr.) mV	b (corr.) mV
0.03	60	55
0.21	53	51

(b) Primary Isotope Effect

Concentration of ketone (mole. litre^{-1})	i_{H_2O}/i_{D_2O} (E= -0.5 to -0.8 V vs E_H)	i_{H_2O}/i_{D_2O} for H_2/D_2 evolution
0.2	0.95	2.5 - 3.1
0.59-0.74	0.99	
1.1 -1.25	1.29	

(c) Tafel Slope in Relation to Water Content in Methanolic Solutions Containing Sulphuric Acid (0.95 M)

Mole % H_2O	b (mV.)
"0"	85
1	78
2	70
5	57
10	54
15	52
20	52
50	51

agitation of the solution.

(iii) Reaction Order: A series of potentiostatic log[i]-E curves at various concentrations of acetophenone is shown in Figure 13. The currents corresponding to the hydrogen evolution reaction in the solution in the absence of the ketone are again indicated by the broken line.

It was found that the Tafel slope, b, decreased with increasing concentration of acetophenone over the concentration range 0.014 to 0.15 moles litre^{-1} [Table IV (a)], but further increase of concentration did not further change the slope.

The slope of the relation between log[i] and log $(C_R)_b$ (Figure 14) gives the reaction order, $\left\{\frac{d \log i}{d \log (C_R)_b}\right\}_E$. A value of 0.95 was obtained at potentials in the Tafel region of the log[i]-E curves. As expected, in the limiting current region R tended towards a value of unity.

A more detailed study of the reaction order at the potential, E = -0.65 V. vs E_H, was carried out by a "titration" method* The results, based on a relatively large number of points (Figure 15), indicated that the reaction order, like the Tafel slope showed a dependence upon the concentration of the ketone.

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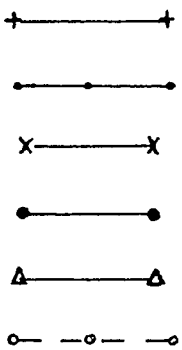
* In this experiment the potential of the working electrode was kept at -0.65 V. vs E_H. Small volumes of acetophenone were added from a burette to the solution in the working-electrode compartment and the corresponding current recorded after prolonged agitation of the solution by the passage of nitrogen gas.

Figure 13. Potentiostatic steady-state log[i]-E curves at different concentrations of acetophenone in methanol (80 mole %)-water-sulphuric acid (0.97 M) solution.



0.014 mole. litre^{-1} acetophenone

0.082 mole. litre^{-1}

0.15 mole. litre^{-1}

0.285 mole. litre^{-1}

0.49 mole. litre^{-1}

Hydrogen evolution reaction in the solution in the absence of ketone.

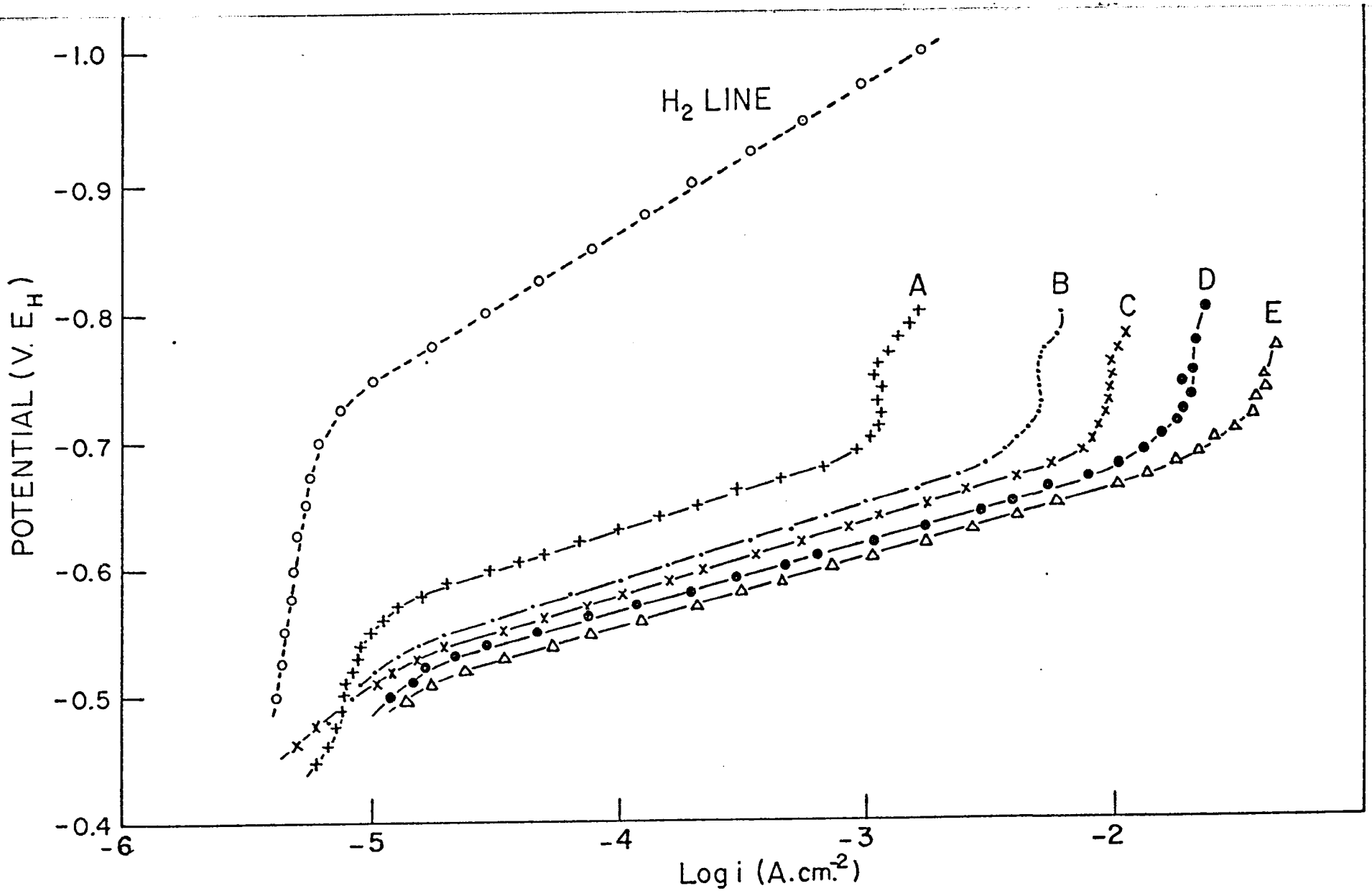

H2 LINE
A
B
C
D
E
-1.0
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
POTENTIAL (V. EH)
-6
-5
-4
-3
-2
Log i (A.cm-2)

Figure 14. Reaction order $\left\{\frac{d\log i}{d\log(C_R)_b}\right\}_E$ for the electro-reduction of acetophenone in methanol (80 mole %)-water-sulphuric acid (0.97 M) solution.

×——× E = -0.6 V. vs E_H

+——+ E = -0.65 V. vs E_H

●——● E = -0.75 V. vs E_H

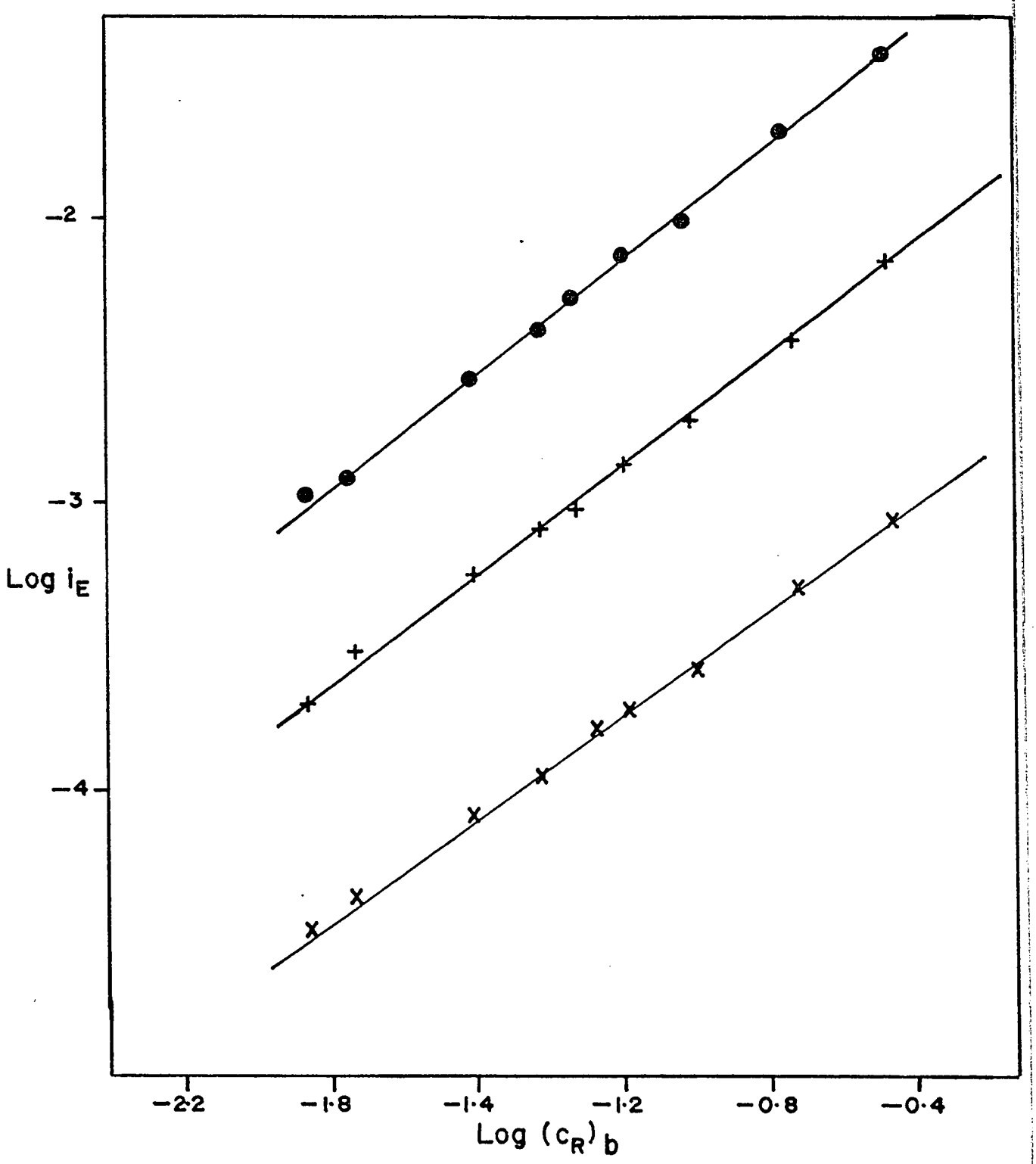

-2
-3
-4
Log i_E
-2·2
-1·8
-1·4
-1·2
-0·8
-0·4
Log $(c_R)_b$

Figure 15. Reaction order $\left\{\frac{d\log i}{d\log(C_R)_b}\right\}_E$ for the electro-reduction of acetophenone at E = -0.65 V. vs E_H in methanol (80 mole %)-water-sulphuric acid (0.97M).

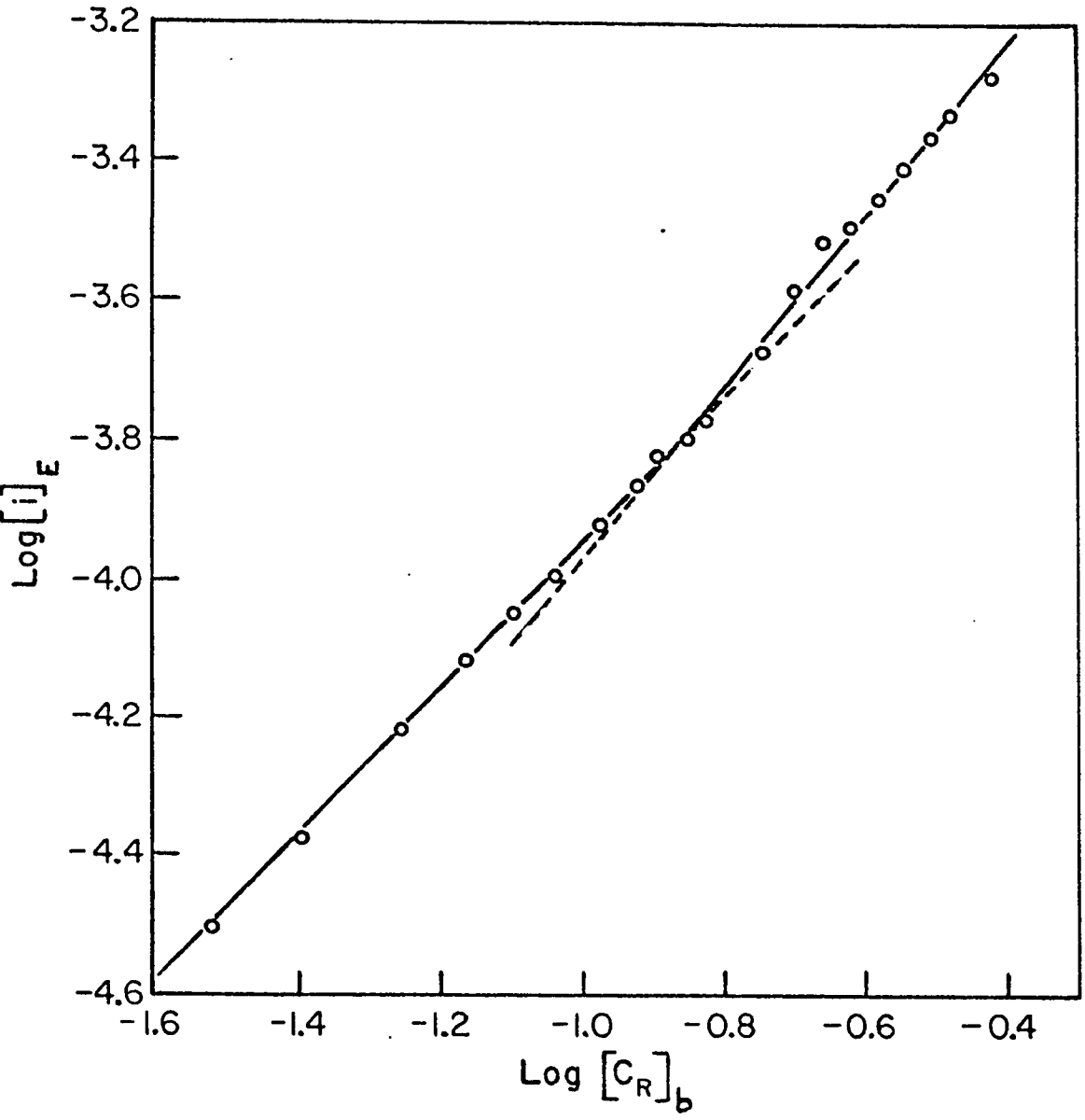

-3.2
-3.4
-3.6
-3.8
-4.0
-4.2
-4.4
-4.6
Log[i]ε
-1.6
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
Log [CR]b

Table IV

Dependence of the Tafel Slope, b, upon the Concentration of Acetophenone

(a) Electro-reduction in Methanol (80 mole %)-Water-Sulphuric Acid Solution

Concentration of ketone (mole. litre^{-1})	b (mV)
0.014	58
0.017	58
0.039	56
0.075	55
0.082	54
0.104	53
0.14	52
0.15	52
0.285	50
0.49	50

(b) Electro-reduction in Methanol-Sulphuric Acid Solution

0.045	86
0.06	85
0.165	83
0.2	81
0.36	80
0.46	77

The results for R are summarised below.

Concentration of ketone (mole. litre^{-1})	R (E = -0.65 V)
> 0.14	1.2
< 0.14	1

(b) Studies of the Reaction in Nominally Anhydrous Methanol

A steady-state kinetic study of the reduction was also carried out in "nominally" anhydrous methanol containing sulphuric acid (0.95 M), and a series of log[i]-E curves were obtained at various concentrations of acetophenone (Figure 16).

These curves exhibit the same general shape as that of the log[i]-E relationships found when the reaction proceeds in a partially aqueous solution. Again agitation of the solution brought about an increase in the limiting currents observed at potentials more cathodic than those corresponding to the linear log[i]-E region. Both the background current, i.e., the log[i]-E curve for the hydrogen evolution reaction in this solution, and currents obtained in the electro-reduction of the ketone were found to be substantially larger than those obtained in the partially aqueous solution.

The Tafel slope, b, was higher than that observed in the solution containing water but again showed a small

Figure 16. Potentiostatic steady-state log[i]-E curves for the electro-reduction of acetophenone in methanol-sulphuric acid (0.95 M).

A 0.045 mole. litre^{-1} acetophenone

B 0.06 mole. litre^{-1}

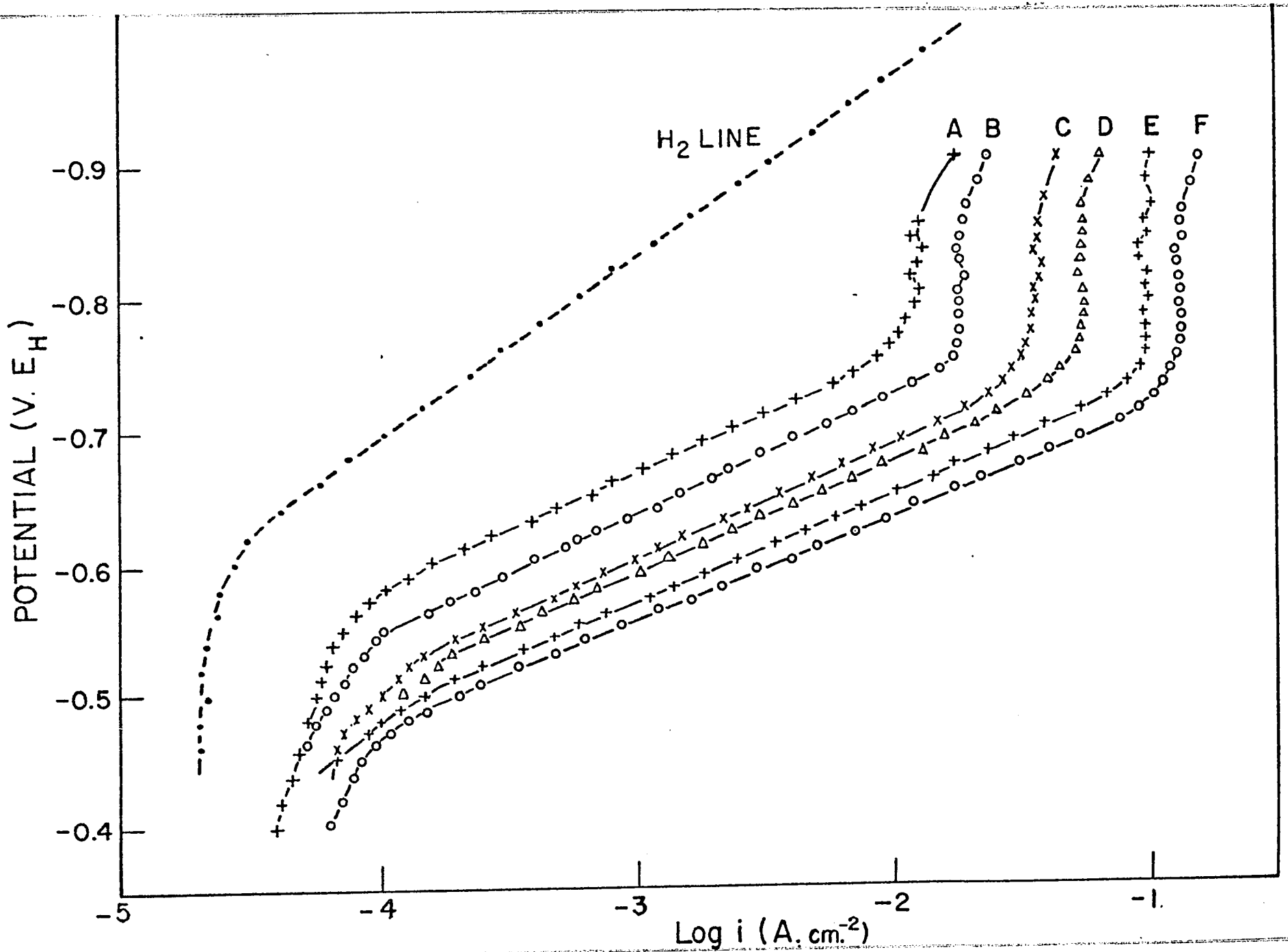
C 0.165 mole. litre^{-1}

D 0.2 mole. litre^{-1}

E 0.36 mole. litre^{-1}

F 0.46 mole. litre^{-1}

– – – – – – – – Hydrogen evolution reaction in the solution in the absence of ketone.


H2 LINE
A
B
C
D
E
F
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
POTENTIAL (V. EH)
-5
-4
-3
-2
-1
Log i (A. cm-2)

dependence upon the concentration of the ketone [Table IV (b)]. The reaction order in the Tafel region was found to be 1.1 (Figure 17).

(c) H/D Primary Isotope Effect

The kinetic H/D isotope effect observed in the electrochemical reduction of acetophenone in a methanol/water/sulphuric acid solution and in a deuterium oxide/methanol-d/deuterosulphuric acid solution was close to unity [Table III (b)]. The hydrogen evolution reaction in the background solutions, in the absence of the ketone, gave values of the isotope effect which are usually observed (ca. 3).

(d) The Effect of Change of pH

Steady-state log[current]-potential curves were obtained from potentiostatic measurements on solutions containing different concentrations of hydrogen ions but at a constant concentration of acetophenone (0.27 M) and ionic strength to eliminate double layer kinetic effects with changing pH. The results are shown in Figure 18.

The Tafel slope was found to be independent of the concentration of hydrogen ions in the solution and a value of 51 mV was obtained which is consistent with values observed in other parts of the work (see Table IV). In solutions of pH $>$ 1, a reaction order of unity, with respect to the hydrogen ion, was obtained at potentials in the limiting current region, but with further decrease in pH the reaction order rapidly

Figure 17. Reaction order $\left\{\frac{d\log[i]}{d\log(C_R)_b}\right\}_E$ for the electro-reduction of acetophenone in methanol-sulphuric acid (0.95 M).

+——+——+ E = -0.65V. vs E_H

o——o——o E = -0.6 V. vs E_H

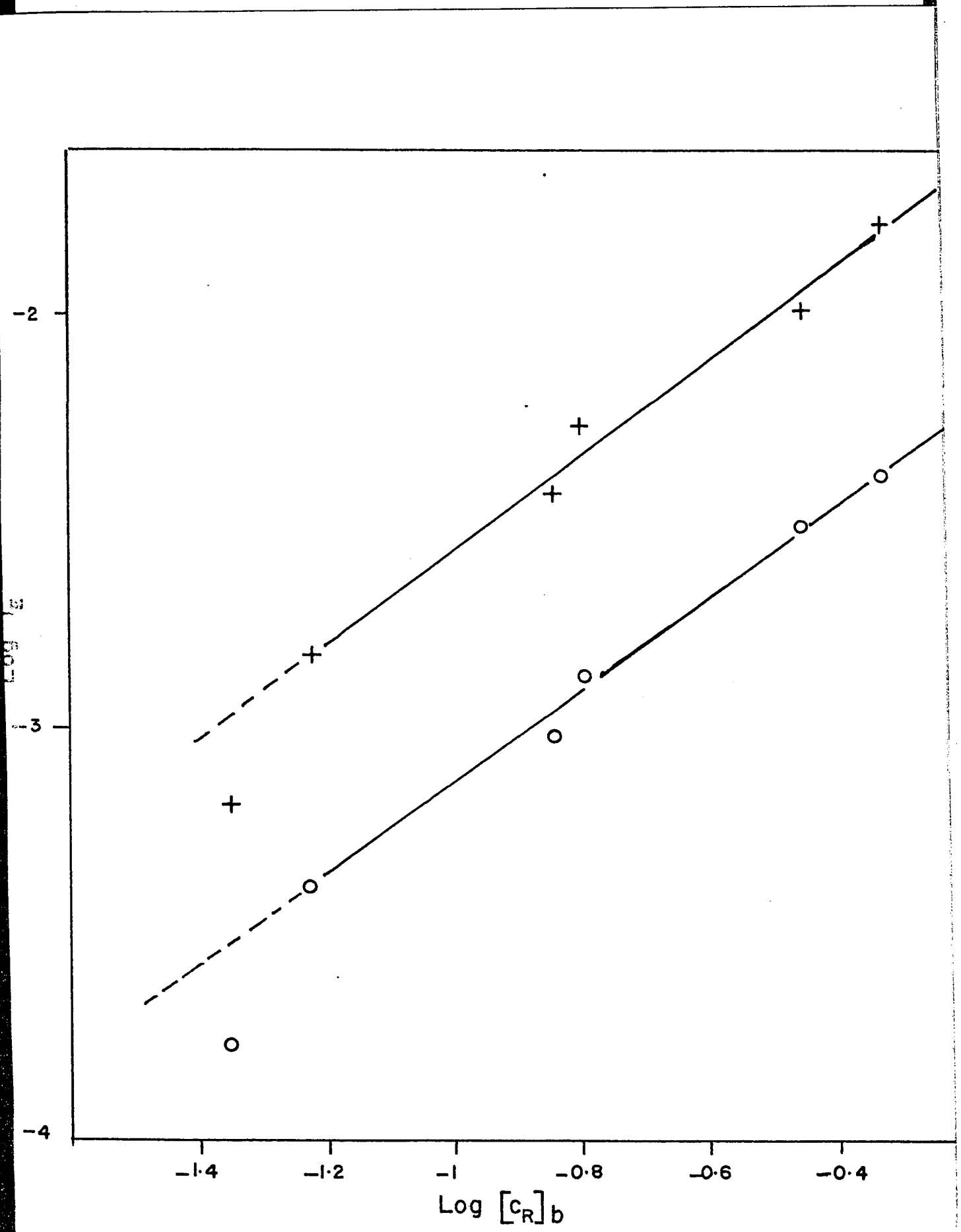
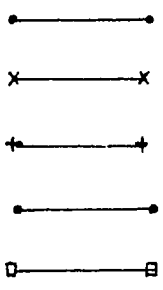

-2
-3
-4
Log i_p
-1·4
-1·2
-1
-0·8
-0·6
-0·4
Log $[C_R]_b$

Figure 18. Potentiostatic steady-state log[i]-E curves for the electro-reduction of acetophenone (0.27 M) in methanol (80 mole %)-water solutions of different pH



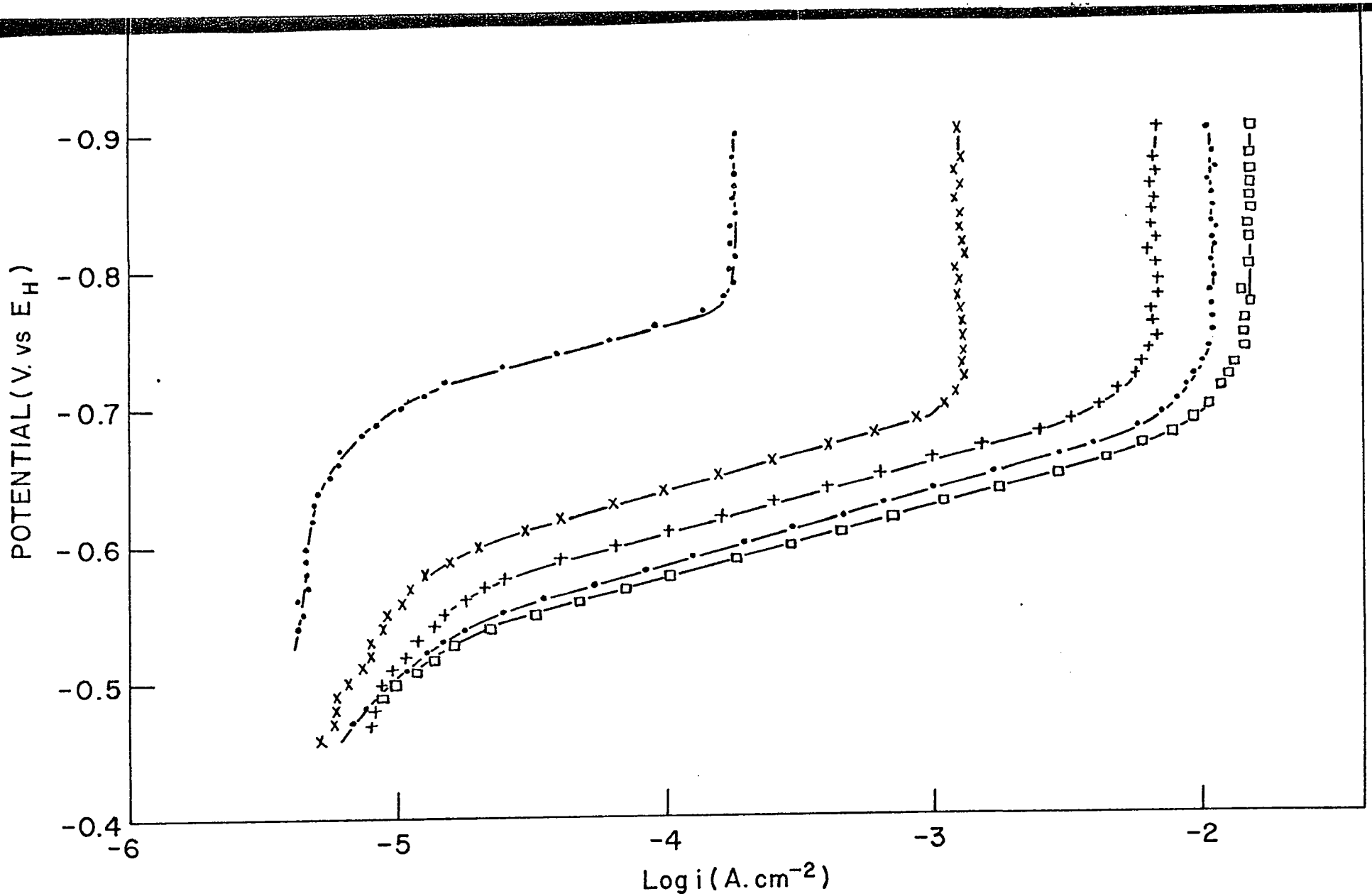
pH 2.3

pH 1.47

pH 0.7

pH -0.04

pH -0.26


POTENTIAL (V. vs E_H)
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
-6
-5
-4
-3
-2
Log i (A. cm^{-2})

tended towards zero. At potentials in the Tafel region $(R)_H^+$ was ca. 0.7 (Figure 19).

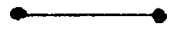
Agitation of the solution by the passage of a stream of nitrogen gas markedly increased the limiting currents observed, particularly at pH $>$ 1. As expected, the currents at potentials in the Tafel region were not affected (cf. behaviour observed in the other kinetic studies at constant pH).

(e) The Effect of Change of Solvent Composition

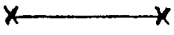
The reduction of acetophenone was also studied in solutions containing varying concentrations of water. Potentiostatic steady-state log[i]-E curves (Figure 20) were obtained over the range of water concentrations referred to in Table IIc, the concentration of acetophenone being kept constant throughout the experiment.

In nominally anhydrous methanol, the Tafel slope was found to be 85 mV., in agreement with the earlier results in this solvent system, and the slope decreased rapidly with the addition of water to the solution until a Tafel slope of 52 mV was obtained (corresponding to 20 mole % water). An additional large increase of the water concentration did not significantly lower the Tafel slope any further [Table III (c)]. The magnitudes of the limiting currents were found to decrease with increasing concentration of water. This effect was also observed previously [see Section (b)], and probably arises from the change of viscosity.

Figure 19. Reaction order $\left\{\frac{d\log i}{d\log[H^+]}\right\}_E$ for the electroreduction of acetophenone.



E = -0.8 V. vs E_H



E = -0.65 V vs E_H

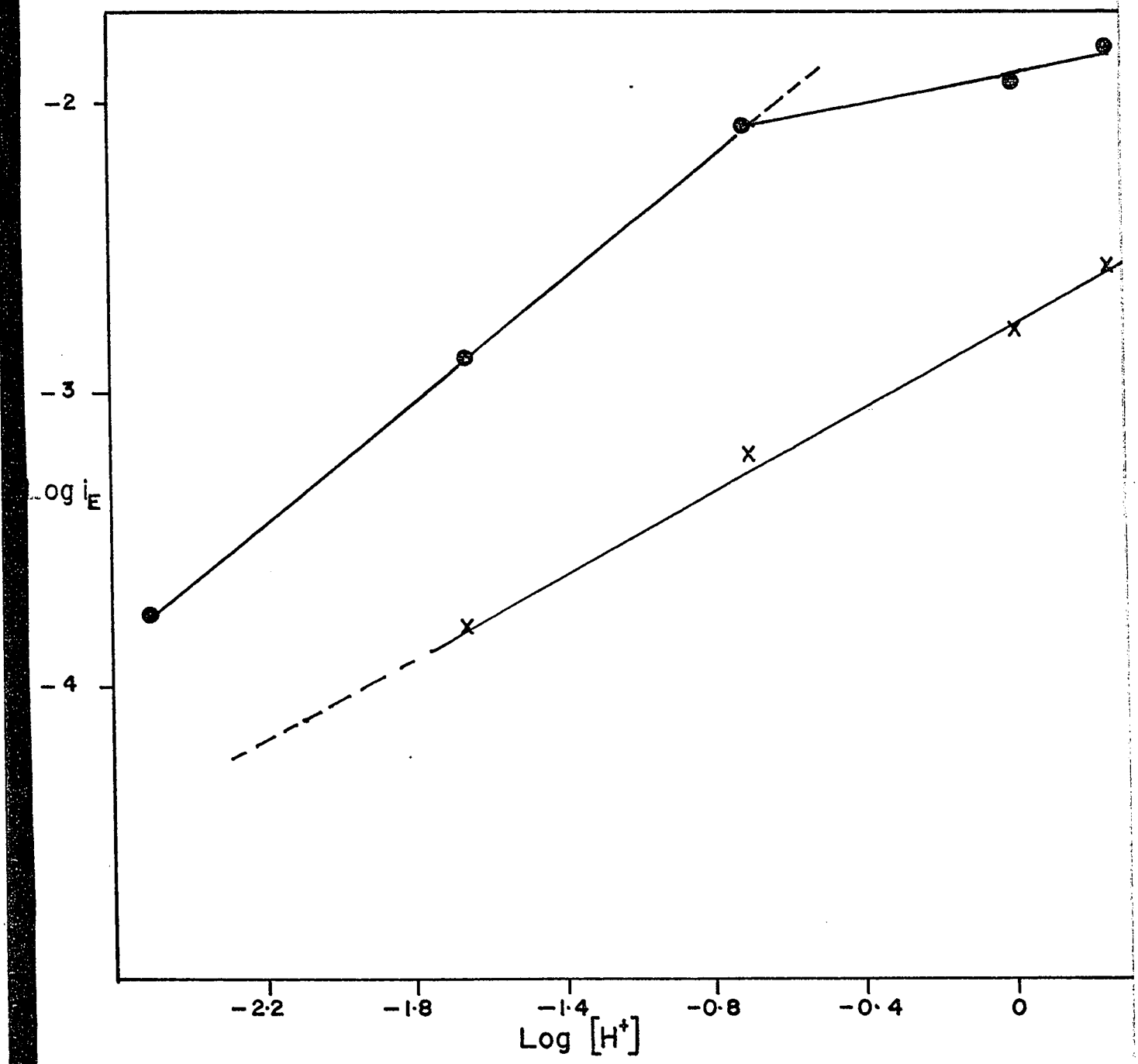
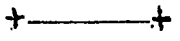
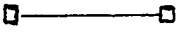

-2
-3
-4
Log i_E
-2·2
-1·8
-1·4
-0·8
-0·4
0
Log [H⁺]

Figure 20. Potentiostatic steady-state log[i]-E curves for the electro-reduction of acetophenone (0.15 M) in solutions containing different amounts of water.

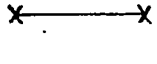
Nominally anhydrous methanol containing sulphuric acid (0.95 M)



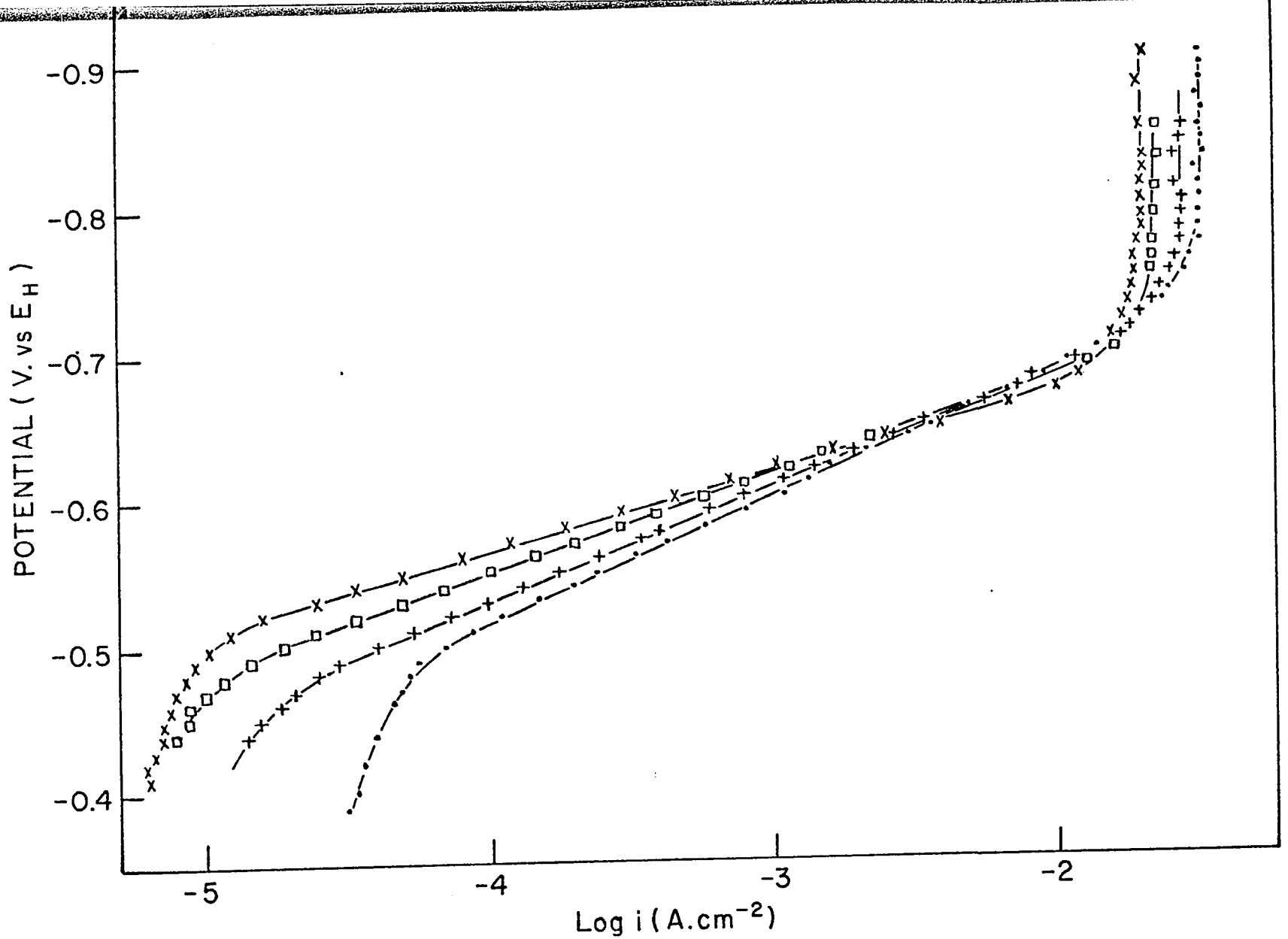
1 mole % water



5 mole % water



20 mole % water.


-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
POTENTIAL (V. vs E_H)
-5
-4
-3
-2
Log i (A.cm^{-2})

4. KINETIC STUDIES OF THE ELECTRO-REDUCTION OF ACETOPHENONE: POTENTIODYNAMIC MEASUREMENTS

Potentiodynamic sweep measurements involve the use of an electronically programmed "triangular" wave signal which is applied to the working electrode.

There are two types of potentiodynamic (non-steady state) current-potential curves:

(a) those obtained when the electrode reaction involves the oxidation and/or reduction of intermediates adsorbed (probably chemisorbed) at the surface.

(b) those obtained when the reaction rate may become limited by the rate of diffusion of the electroactive species to the electrode.

It is the latter case (b) that is involved in the present work.

From a kinetic viewpoint, the current-potential profile obtained for a diffusion-controlled reversible process shows a cathodic and an anodic peak for which the peak potentials, $(E_p)_{anodic}$ and $(E_p)_{cathodic}$, differ by 56 mV. and are independent of the sweep-rate (144). With increasing irreversibility of the electrode process the anodic peak is displaced to less cathodic potentials. Although it is unlikely that the electrochemical reduction of organic molecules at a mercury electrode involves chemisorbed species, triangular sweep studies have been used to give information upon adsorption and desorption processes at the electrode surface (76).

(a) Studies of the Reaction in Methanol (80 mole %)-Water-Sulphuric Acid

A typical series of current-potential relations obtained at different scan rates ($\frac{dE}{dt}$) over two ranges of potential are shown in Figure 21, from which the peak current density, (i_p) and the cathodic peak potential, $(E_p)_{cathodic}$, have been determined [see Table V (a)].

In Figure 22 the following relationships are shown:-

(i) i_p vs $\frac{dE}{dt}$

(ii) i_p vs $\sqrt{\frac{dE}{dt}}$

(iii) $(E_p)_{cathodic}$ vs log $(\frac{dE}{dt})$

The linear dependence of the peak current upon $\sqrt{\frac{dE}{dt}}$ and of the peak potential upon log $\left\{\frac{dE}{dt}\right\}$ indicates that the electode process is irreversible and diffusion controlled.

Conventional log[i]-E curves were constructed from the current-potential profiles obtained by slow potentiodynamic sweeps and compared with a potentiostatic steady-state curve determined in the same solution (Figure 23). The Tafel slope for each curve was 53 mV. indicating good agreement between the results of the two methods.

Similar results were obtained from potentiodynamic studies of solutions containing different concentrations of acetophenone. Comparison of the results obtained from these experiments showed that at a given scan rate the cathodic peak

Figure 21. Potentiodynamic studies of the electro-reduction of acetophenone: Typical current-potential profiles at different sweep-rates.
Concentration of acetophenone 0.11 mole. litre^{-1}

(a) Potential Range -0.42 V to -0.91 V. vs E_H	
Curve No.	$\left\{\frac{dE}{dt}\right\}$ mV. sec.$^{-1}$
1	2.45
2	4.9
3	9.8
4	24.5
5	49
6	98
(b) Potential Range -0.105 V. to -0.905 V.	
1	4
2	8
3	16
4	40
5	80

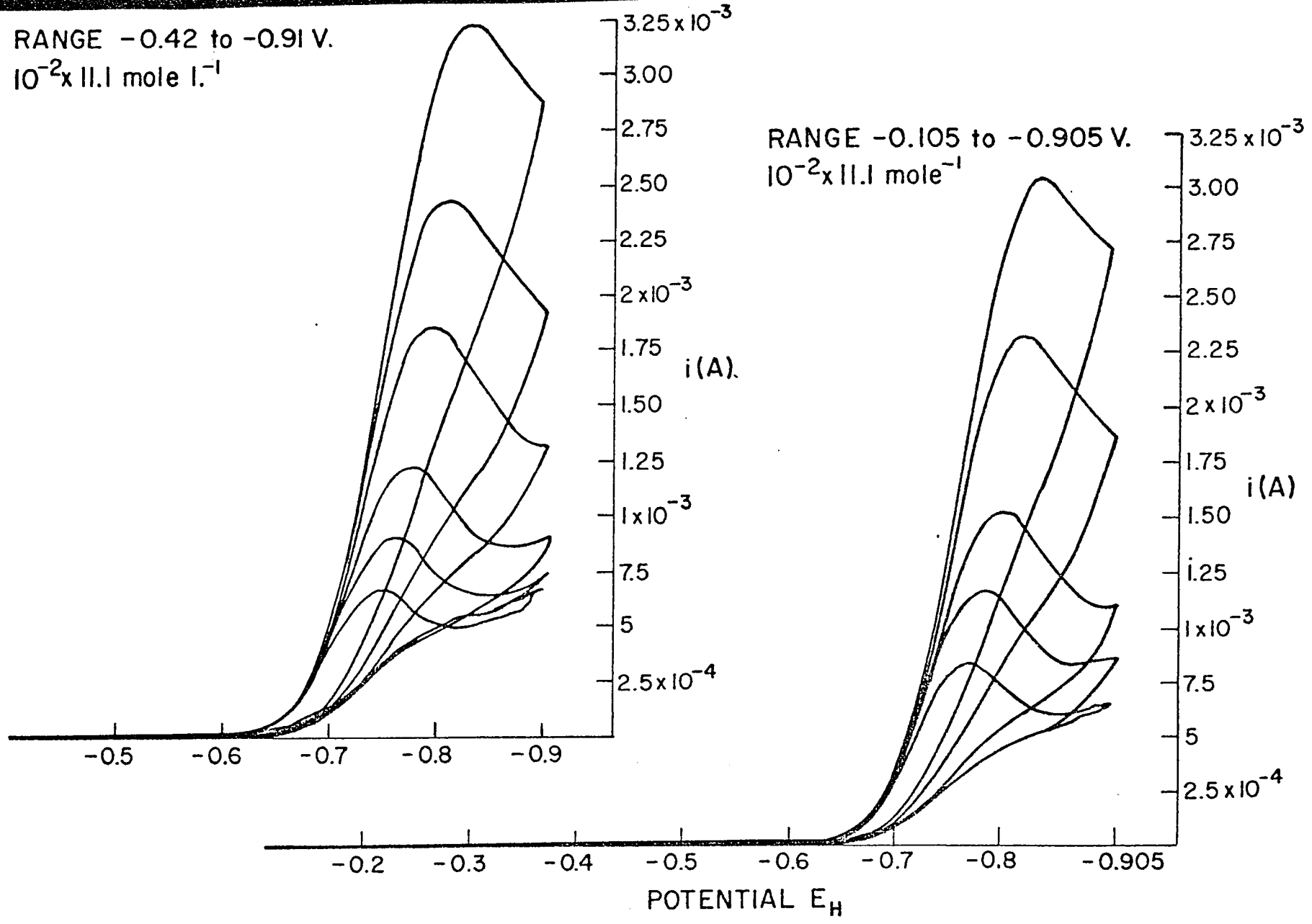

RANGE −0.42 to −0.91 V.
10^{-2}x 11.1 mole $l.^{-1}$
3.25 x 10^{-3}
3.00
2.75
2.50
2.25
2 x 10^{-3}
1.75
i (A).
1.50
1.25
1 x 10^{-3}
7.5
5
2.5 x 10^{-4}
−0.5
−0.6
−0.7
−0.8
−0.9
RANGE −0.105 to −0.905 V.
10^{-2}x 11.1 mole^{-1}
3.25 x 10^{-3}
3.00
2.75
2.50
2.25
2 x 10^{-3}
1.75
i (A)
1.50
1.25
1 x 10^{-3}
7.5
5
2.5 x 10^{-4}
−0.2
−0.3
−0.4
−0.5
−0.6
−0.7
−0.8
−0.905
POTENTIAL E_H

Figure 22. Potentiodynamic studies of the electro-reduction of acetophenone.

Dependence of peak current (i_p) and peak potential (E_p) upon the sweep-rate

Plots of (i) i_p vs $\frac{dE}{dt}$

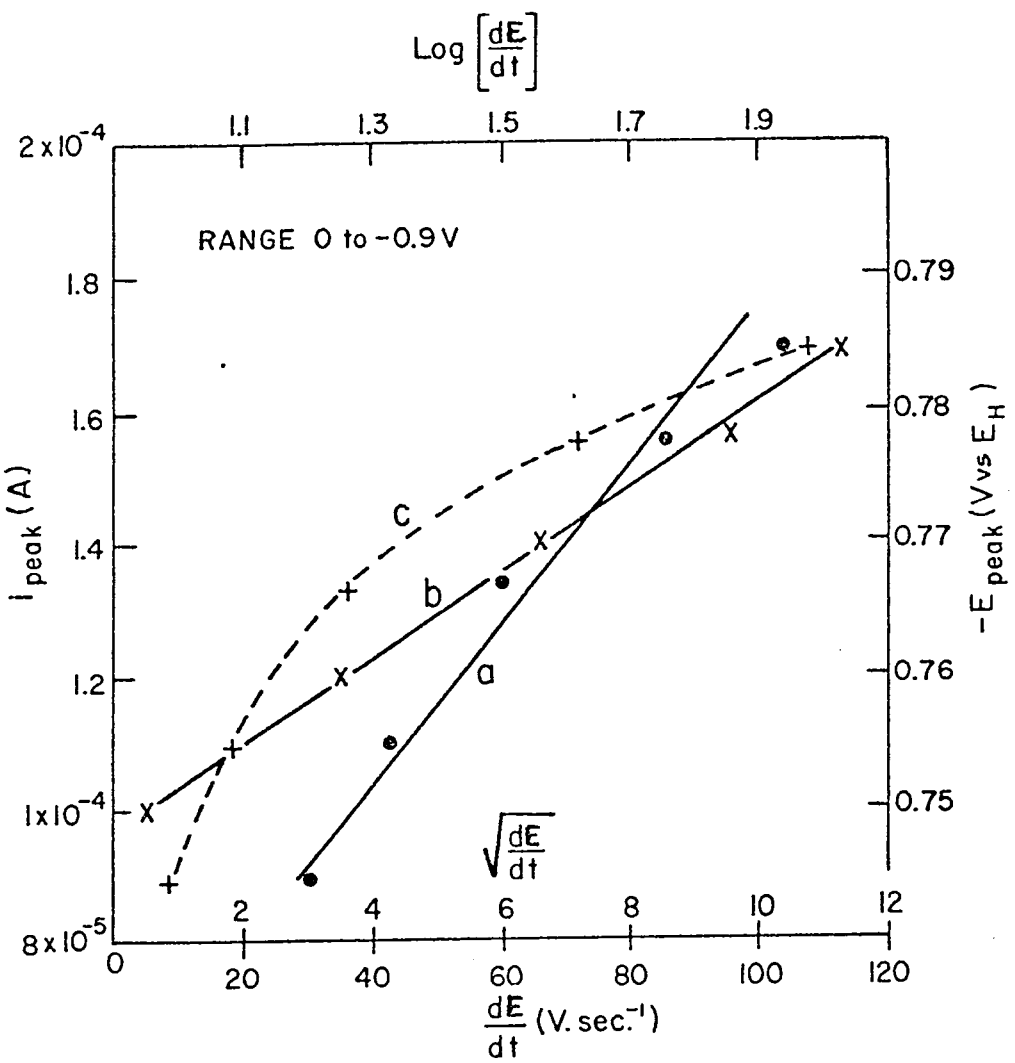
(ii) i_p vs $\sqrt{\frac{dE}{dt}}$

(iii) E_p vs $\log\left\{\frac{dE}{dt}\right\}$

(a) Potential range 0 to -0.9 V. vs E_H

(b) Potential range -0.4 to -0.9 V. vs E_H

Concentration of acetophenone 6.4×10^{-3} mole. litre^{-1}.


Log [dE/dt]
RANGE 0 to -0.9V
I_{peak} (A)
$-E_{peak}$ (V vs E_H)
$\sqrt{\frac{dE}{dt}}$
$\frac{dE}{dt}$ (V. sec.$^{-1}$)
a
b
c

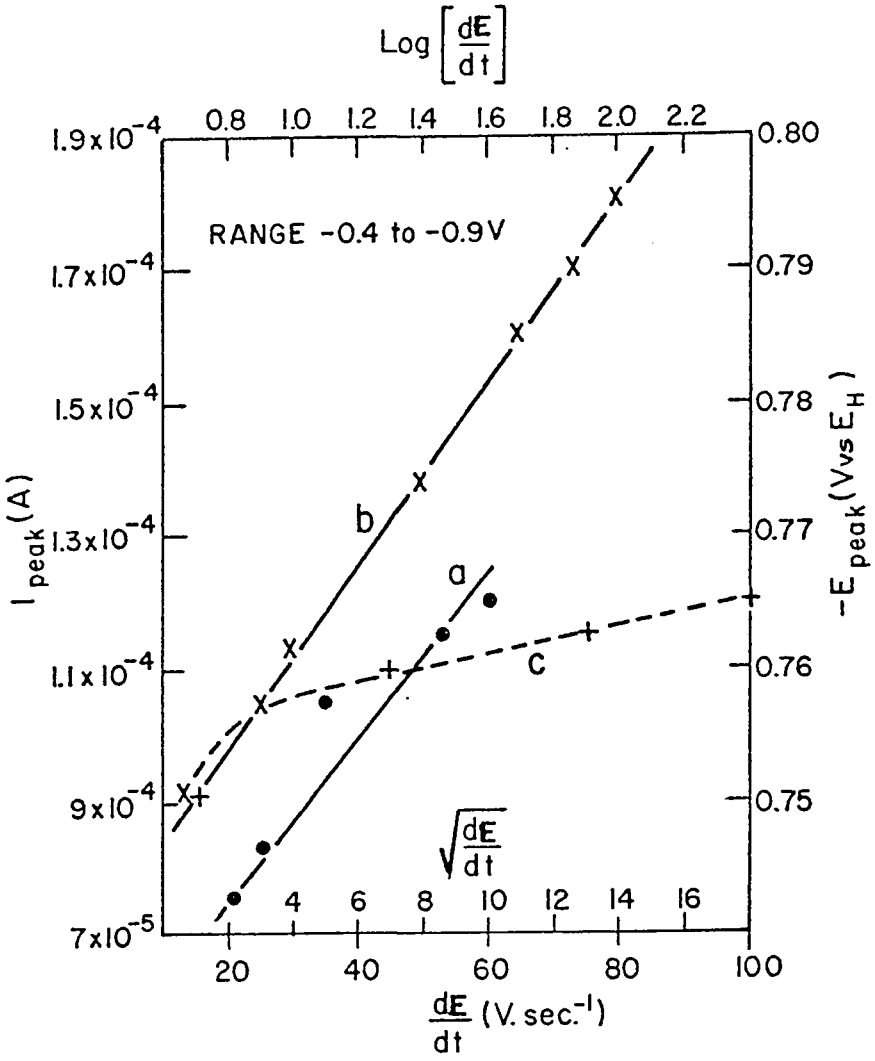

Log [dE/dt]
RANGE -0.4 to -0.9V
I_{peak} (A)
$-E_{peak}$ (V vs E_H)
$\sqrt{\frac{dE}{dt}}$
$\frac{dE}{dt}$ (V. sec.$^{-1}$)
a
b
c

Figure 23. A comparison between log[i]-E curves obtained

(i) by potentiostatic steady-state measurements and

(ii) from potentiodynamic current-potential profiles

●——● log[i]-E curve constructed from i-E profile obtained at $\frac{dE}{dt}$ = 50 mV.sec^{-1}

▲——▲ log[i]-E curve constructed from i-E profile obtained at $\frac{dE}{dt}$ = 10 mV.sec^{-1}

×——× Potentiostatic steady-state log[i]-E curve.

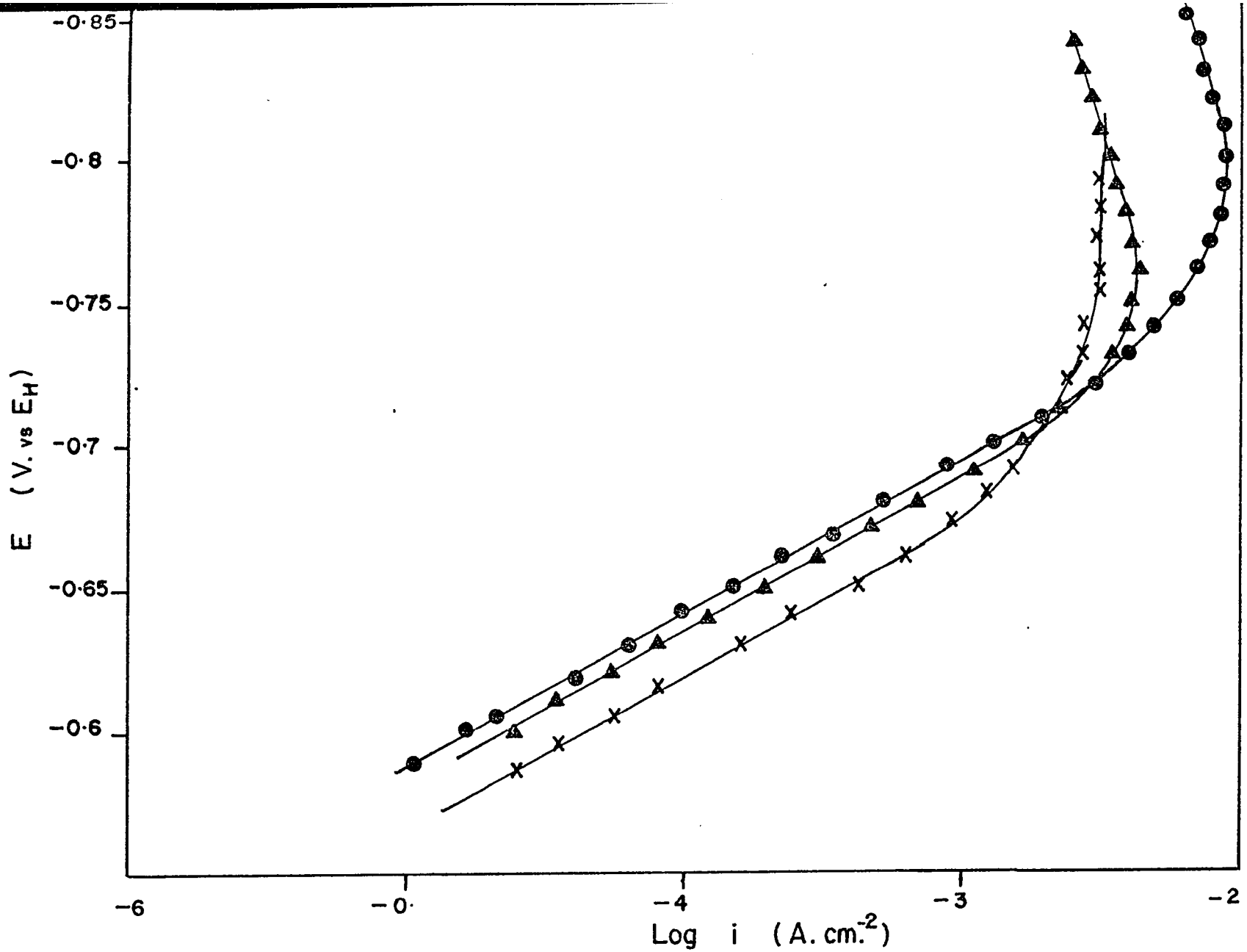

-0·85
-0·8
-0·75
-0·7
-0·65
-0·6
E (V. vs E_H)
-6
-0·
-4
-3
-2
Log i (A. cm.$^{-2}$)

Table V

Dependence of i_p and $(E_p)_{cathodic}$ upon the Sweep-Rate

(a) In Methanol (80 mole %)-Water-Sulphuric Acid:

Potential Range V. vs E_H	dE/dt mV. sec^{-1}	$(dE/dt)^{\frac{1}{2}}$	log(dE/dt)	$i_p \times 10^3$ A.$cm.^{-2}$	E_p V. vs E_H
	4	2	0.6	8.5	-0.77
	8	2.83	0.9	11.7	-0.78
-0.11	16	4	1.2	15.3	-0.8
to	40	6.33	1.6	23	-0.82
-0.91	80	8.94	1.9	30.3	-0.83
	2.45	1.57	0.39	6.8	-0.745
	4.9	2.21	0.69	9.3	-0.76
-0.42	9.8	3.13	0.99	12.5	-0.775
to	24.5	4.95	1.39	18.8	-0.795
-0.91	49	7	1.69	24.5	-0.815
	98	9.9	1.99	32.5	-0.83

(b) In Methanol-Sulphuric Acid:

	6	2.45	0.78	1.35	-0.82
-0.44	12	3.46	1.08	1.88	-0.85
to	30	5.48	1.48	2.92	-0.9
-1.04	60	7.75	1.78	3.8	-0.94
	90	9.49	1.95	4.4	-0.96

potential was dependent upon the concentration of ketone in the solution (Table VI).

A wide potential range below the Faradaic region (from E = +0.6 to -0.5 V. *vs* E_H) was studied in both the presence and absence of acetophenone. The two series of i-E profiles were found to be virtually superimposable (Figure 24). It would appear that the product of the reaction is not re-oxidised in this potential range or alternatively diffuses away from the electrode surface before its re-oxidation potential is reached in the reverse direction of the sweep.

An anodic current corresponding to the oxidation of the intermediate ketyl radical (the primary product of the electrode process) was, however, not observed at high sweep rates ($\frac{dE}{dt}$ = 2 to 20 V. sec^{-1}). Re-oxidation of the fluorenone ketyl, formed by the electro-reduction of fluorenone at mercury, was observed by Grabowski *et al.* (145) since in this case the ketyl radical can be more resonance-stabilised.

(b) Studies of the Reaction in Nominally Anhydrous Methanol

The analysis of current-potential curves, which were obtained from a potentiodynamic study of the reduction in nominally anhydrous methanol containing sulphuric acid (0.95 M), indicated that the reaction again corresponded to a diffusion-controlled irreversible process. The results are shown in Table IV (b).

Figure 24. Potentiodynamic studies of the electro-reduction of acetophenone: Potential sweep study over a wide range of potential <u>below</u> the Faradaic region. Potential range +0.6 V. to -0.5 V. <u>vs</u> E_H

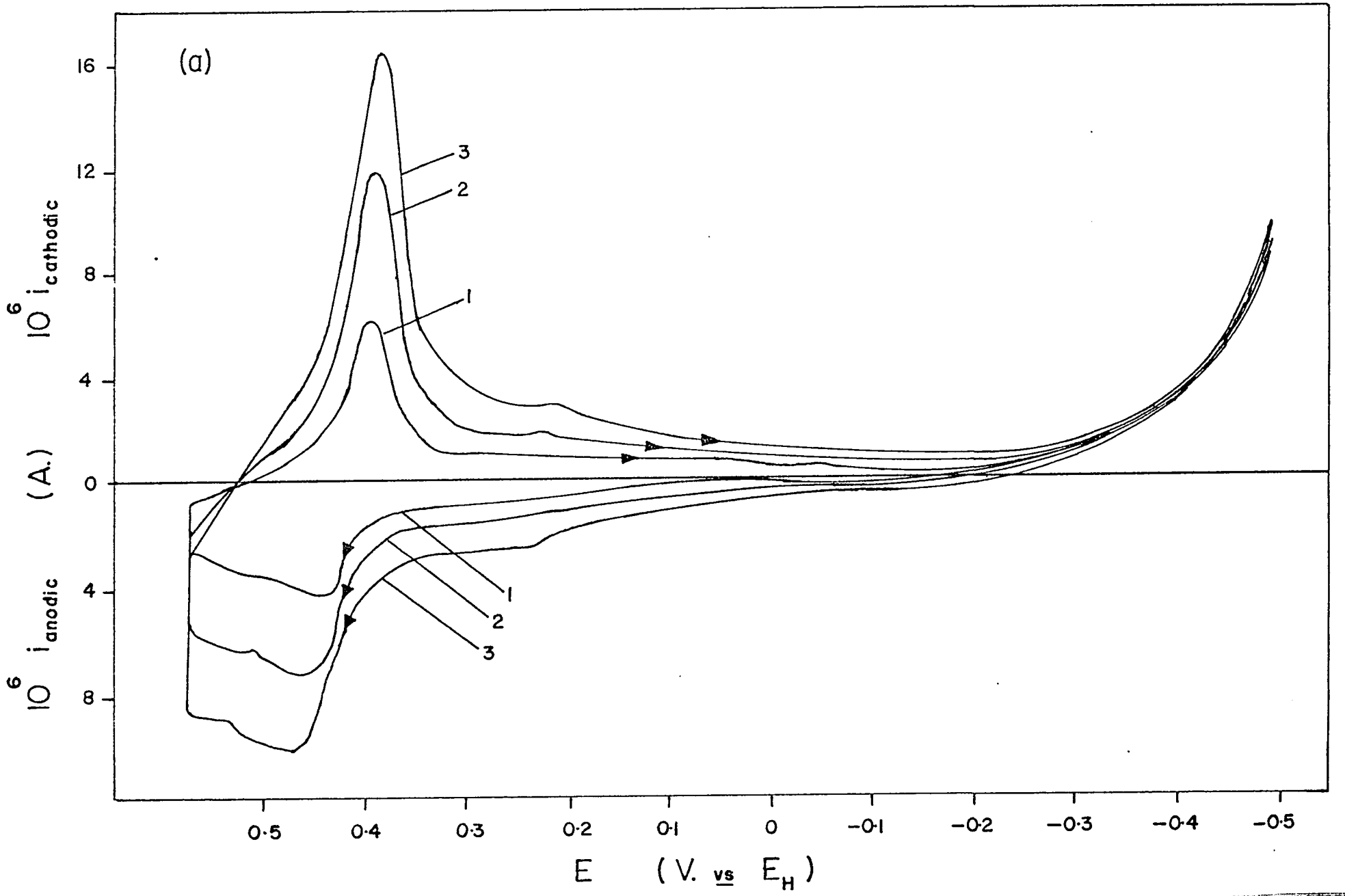
Concentration of Acetophenone

(a) 0.11 mole. litre^{-1}

(b) zero

Sweep rates

Curve	$\frac{dE}{dt}$ mV. sec^{-1}
1	22
2	44
3	88


(a)
16
12
8
4
0
4
8
10^6 $i_{cathodic}$
(A.)
10^6 i_{anodic}
3
2
1
1
2
3
0·5
0·4
0·3
0·2
0·1
0
-0·1
-0·2
-0·3
-0·4
-0·5
E (V. vs E_H)

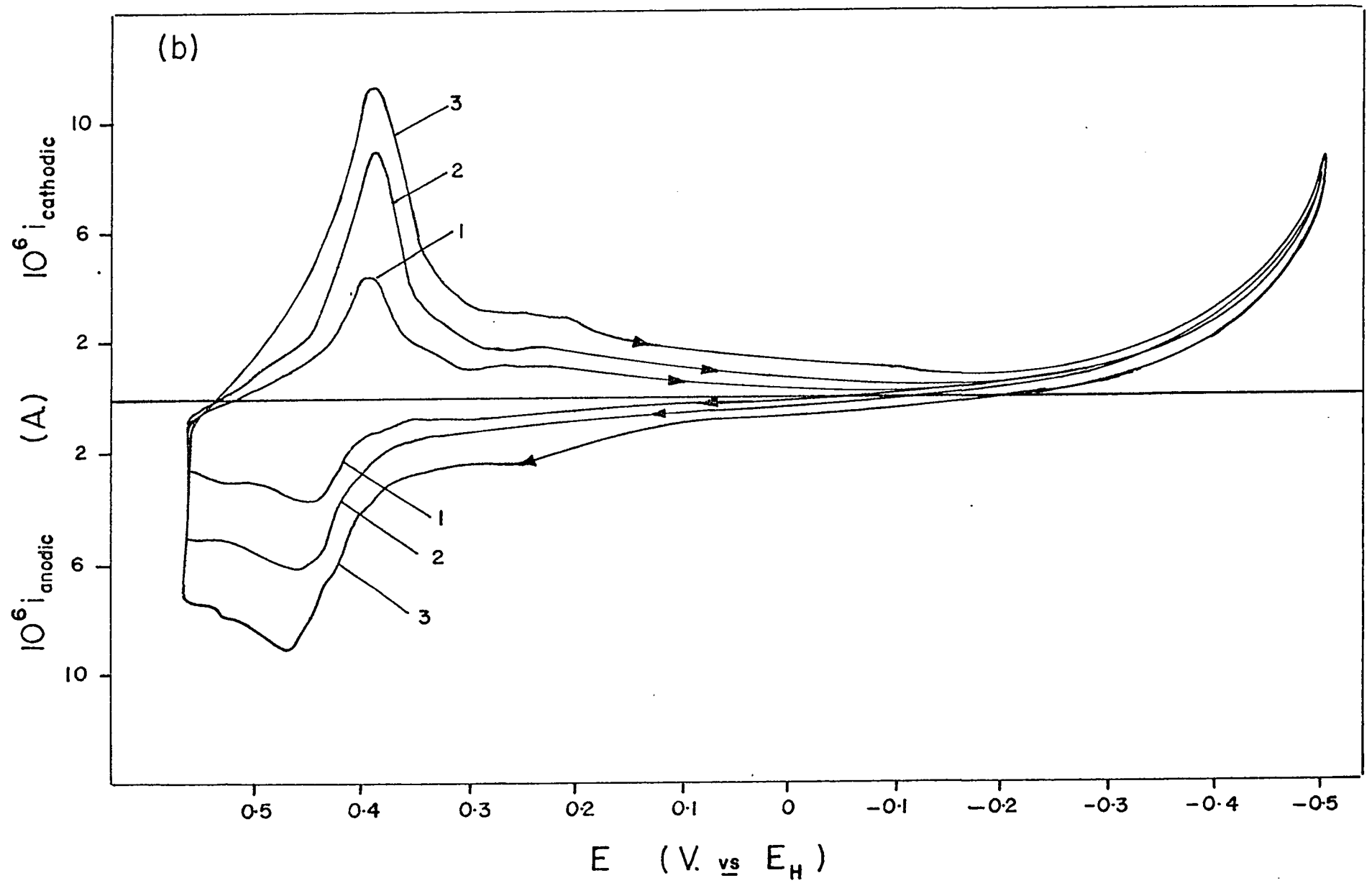

(b)
$10^6 i_{cathodic}$
$10^6 i_{anodic}$
(A)
10
6
2
2
6
10
1
2
3
1
2
3
0·5
0·4
0·3
0·2
0·1
0
−0·1
−0·2
−0·3
−0·4
−0·5
E (V. vs E_H)

Table VI

Dependence of $(E_p)_{cathodic}$ upon the Bulk Concentration of Acetophenone

Scan Rate $\frac{dE}{dt}$ mV. sec^{-1}	$(E_p)_{cathodic}$ V.	Concentration of ketone mole. $litre^{-1}$
8	-0.76	0.039
	-0.77	0.094
	-0.78	0.11
40	-0.79	0.039
	-0.8	0.094
	-0.82	0.11
80	-0.8	0.039
	-0.81	0.094
	-0.83	0.11

It can be seen that the peak potential again becomes more cathodic with increasing sweep-rate but the magnitude of this change (120 mV for a ten-fold increase in $\frac{dE}{dt}$) is much larger than that observed in the similar studies carried out in the partially aqueous system.

5. KINETIC STUDIES: POTENTIAL-STEP RELAXATION MEASUREMENTS

This method involves the measurement of the virtually instantaneous current which results from a sudden change of potential applied to the working electrode. Under these conditions the magnitude of the current (and hence overall rate of reaction) is not affected by the formation and adsorption of the product at the electrode surface. Furthermore at the short time intervals used [in favourable cases these may be less than 100 μ secs. (93,139)] the rate of reaction cannot become limited by the rate of diffusion of the electroactive species to the electrode.

Each potential step was made at a clean mercury surface (a new drop) and the electrode potential was changed from a value in the electro-inactive region to one at which the electro-reduction was known to occur. From the recorded current-time profiles,

(i) a non-steady state current could be determined at a time just longer than that required to charge the double layer at the electrode surface, and

(ii) a "new" steady-state log[i]-E curve could be constructed.

(a) Studies of the Reaction in Methanol (80 mole %)-Water-Sulphuric Acid

A series of log[i]-E curves were constructed which described the steady-state behaviour in solutions containing different concentrations of ketone, using the same mercury surface throughout the experiment. As had been previously observed in this work, the Tafel slope was dependent upon the concentration of ketone and the reaction order R was 1.1-1.2.

The potential-step method was applied to the same solutions of acetophenone as were used in the steady-state measurements.

A number of the recorded current-time curves are shown in Figure 25. It can be seen that the initial oscillatory behaviour (ringing) of the current prevented measurements at very short intervals of time after the potential step had been applied. However, for all solutions and for all the applied potential steps the current after 5 m. sec was measured and hence a series of $\log[i]_{t=5m.sec.}$—E curves were constructed (Figure 26). It was not, however, possible to obtain values of the currents corresponding to a potential in the diffusion-controlled region. Below E = -0.7 V. vs E_H, Tafel behaviour is again observed with b = 60 mV. The reaction order at E = -0.65 V. vs E_H is 0.9.

Figure 25. Potential-step measurements.

Current-time transients recorded for several potential steps.

Initial potential -0.45 V. vs. E_H.

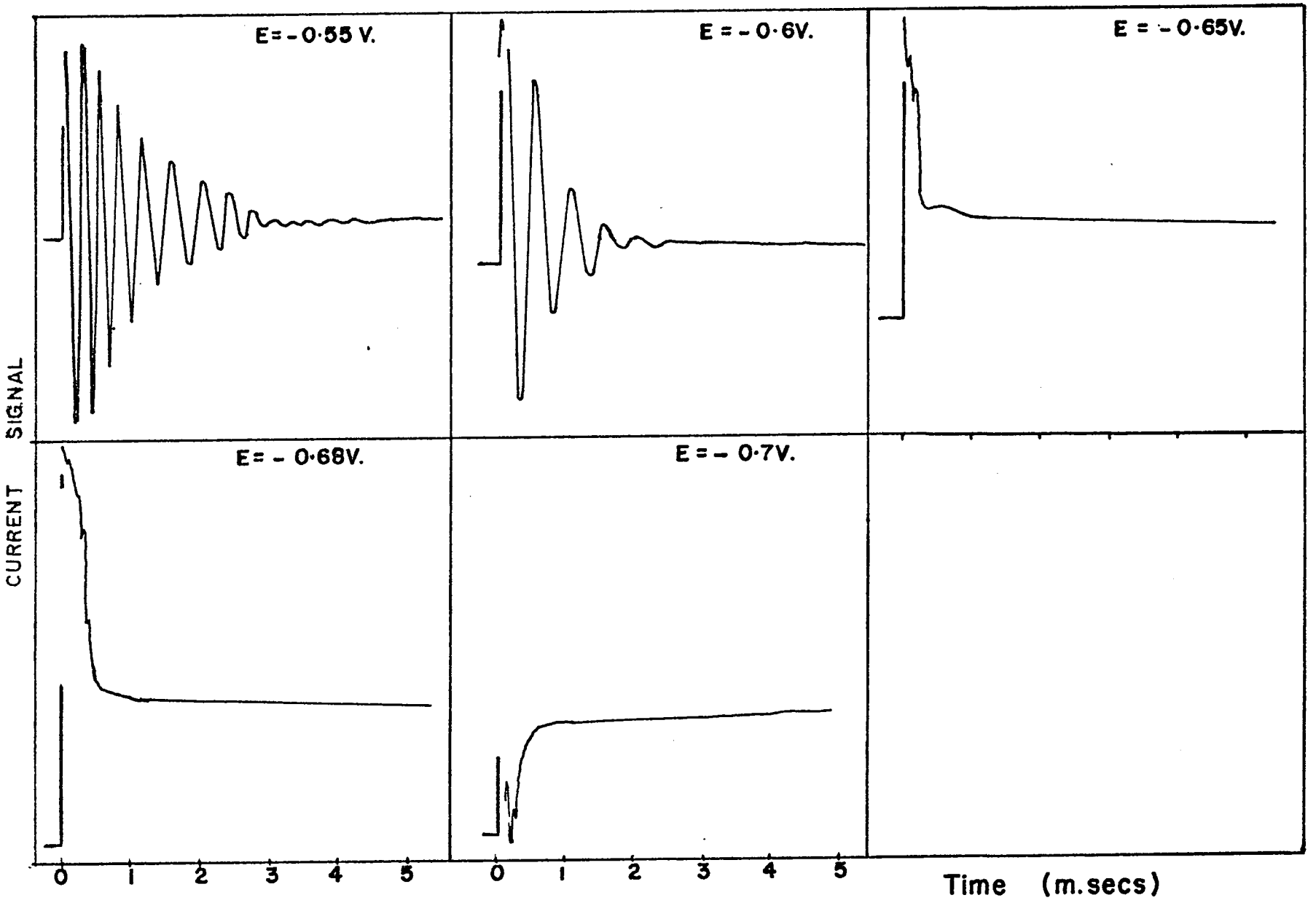

E = - 0·55 V.
E = - 0·6V.
E = - 0·65V.
E = - 0·68V.
E = - 0·7V.
CURRENT SIGNAL
0
1
2
3
4
5
Time (m.secs)

Figure 26. Potential-step studies: $Log[i]_{-t=5m.secs}$ $^{-E}$ curves constructed from current-time transients.

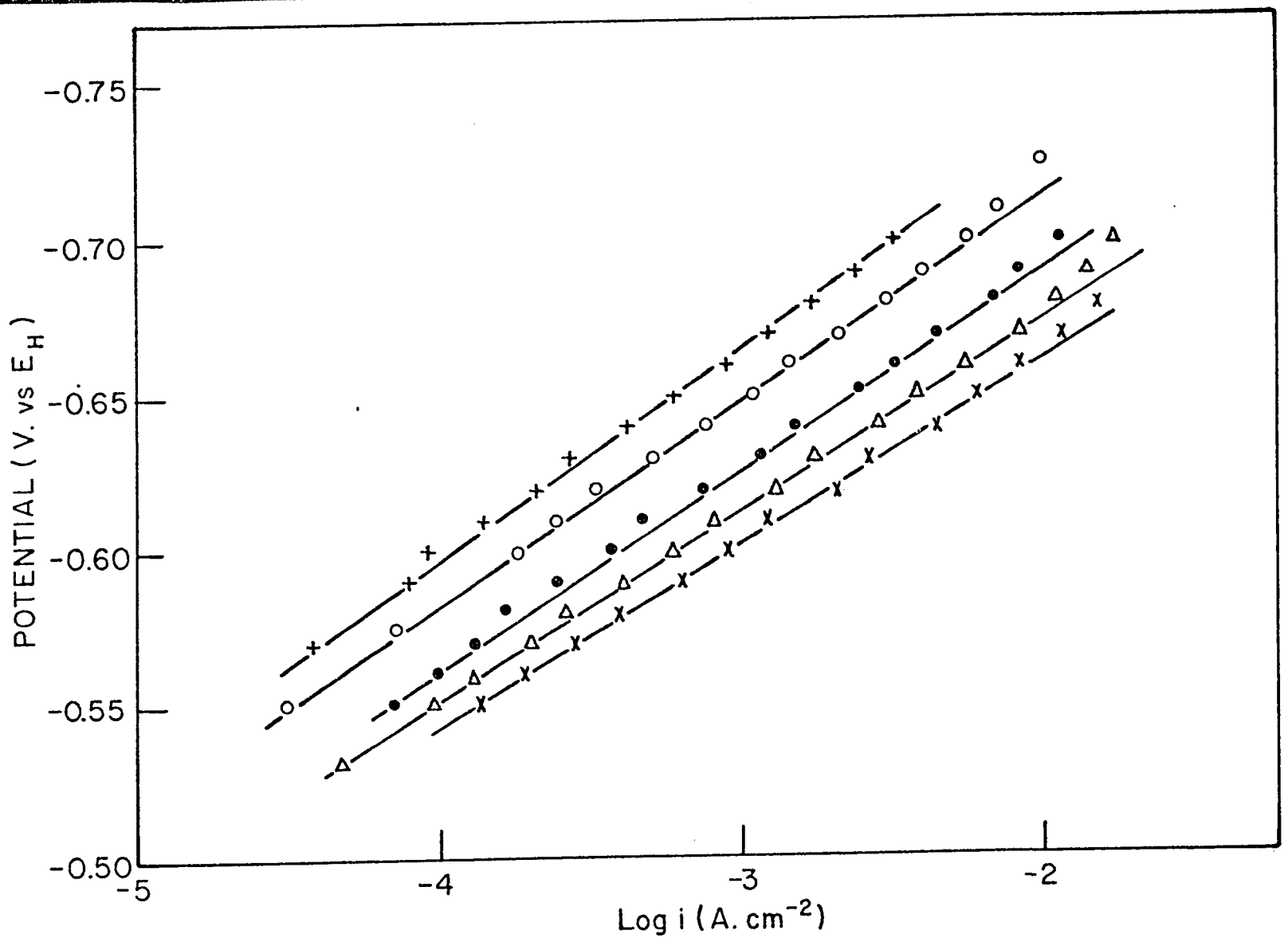
+—+—+ 0.03 mole. litre^{-1} acetophenone

o——o 0.062 mole. litre^{-1}

●—●—● 0.13 mole. litre^{-1}

Δ——Δ 0.25 mole. litre^{-1}

×—×—× 0.38 mole. litre^{-1}.


-0.75
-0.70
-0.65
-0.60
-0.55
-0.50
POTENTIAL (V. vs E_H)
-5
-4
-3
-2
Log i (A. cm^{-2})

A comparison of the log[i]-E curves obtained from the potential-step measurements with typical curves obtained by the steady-state method showed that at low concentrations of acetophenone, virtually identical Tafel slopes are found, but with a more concentrated solution of the ketone, the conventional log[i]-E curve has a significantly lower slope (50 mV, compared with 60 mV for the potential-step method).

6. ELECTROCHEMICAL BEHAVIOUR OF ACETOPHENONE PINACOL

Steady-state and potentiodynamic studies were carried out upon a solution of acetophenone pinacol (approximately 10^{-2} M) in methanol (80 mole %)-water and sulphuric acid (0.97 M) in order to examine if there were any further significant electrode processes occurring with the product of the acetophenone reduction.

(a) Steady-state log[i]-E Curve

Without agitation of the solution near to the electrode, steady-state currents and the corresponding potentials were measured under potentiostatic conditions. The evolution of a gas, presumably hydrogen, began at a potential of E = -0.75 V. *vs* E_H, which is considerably lower than that at which the evolution of hydrogen gas from the background solution is first observed ($E \simeq 1$ V. *vs* E_H).

A linear (Tafel) region, b = 120 mV, is however, found in the log[i]-E curve for the ascending direction of

the change of electrode potential (Figure 27) and this corresponds to the normal behaviour for H_2 evolution at mercury.

(b) Potentiodynamic Studies

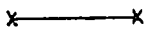
At slow scan rates ($\frac{dE}{dt} \simeq 8$ mV. sec^{-1}), a cathodic peak is observed [Figure 28 (a)] but with an increase in the rate of the potential sweep this peak begins to disappear [Figure 28 (b)]. A similar effect is obtained by repetitive sweeps even at slow scan rates [Figure 28 (c)]. Agitation of the solution by a rapid flow of nitrogen gas had no effect upon the peak currents [Figure 28 (d)].

(c) Addition of Acetophenone

The steady-state and non-steady state current-potential relations were determined upon the same solution of the pinacol but after addition of some acetophenone. The log[i]-E curves for the two concentrations of acetophenone exhibited the usual Tafel behaviour (with b = 52 mV.) for acetophenone reduction and a limiting current was again observed (Figure 27). The analysis of the results of potentiodynamic studies in one of these solutions gave the expected linearity between (i) i_p and $\sqrt{\frac{dE}{dt}}$, and (ii) $(E_p)_{cathodic}$ and $\log\left\{\frac{dE}{dt}\right\}$. The presence of a substantial concentration of the pinacol hence does not significantly modify the kinetics of the main reaction of acetophenone reduction.

Figure 27. Electrochemical behaviour of acetophenone pinacol: potentiostatic steady-state log[i]-E curves.

(1) Solution containing acetophenone pinacol ($\simeq 10^{-2}$ mole. litre^{-1})



(2) Solution containing pinacol + acetophenone (0.18 mole. litre^{-1})

(2)′ Solution containing pinacol + acetophenone (0.30 mole. litre^{-1})

— — — Hydrogen evolution reaction in absence of both pinacol and ketone.

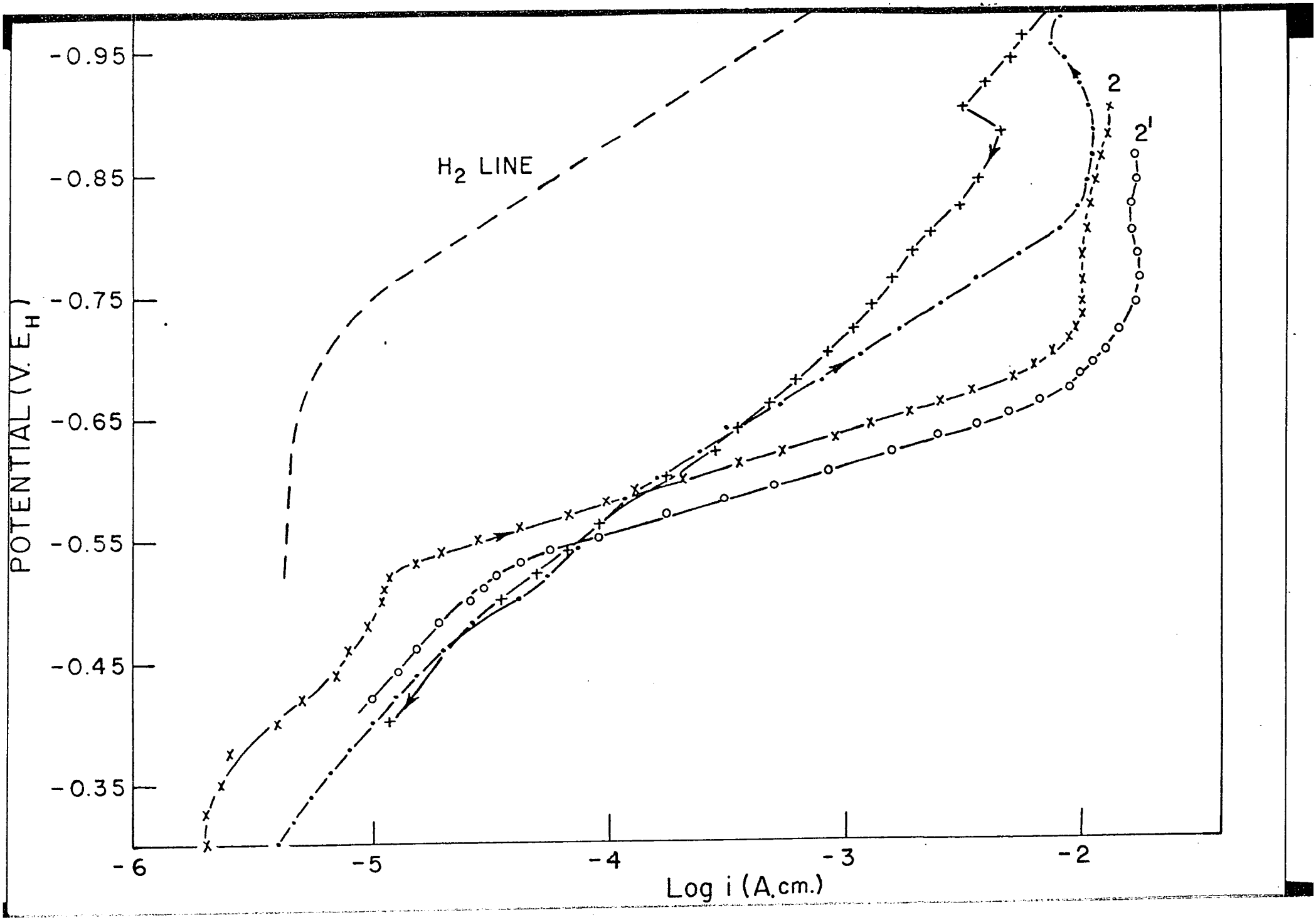

-0.95
-0.85
-0.75
-0.65
-0.55
-0.45
-0.35
POTENTIAL (V. E_H)
H_2 LINE
2
2'
-6
-5
-4
-3
-2
Log i (A.cm.)

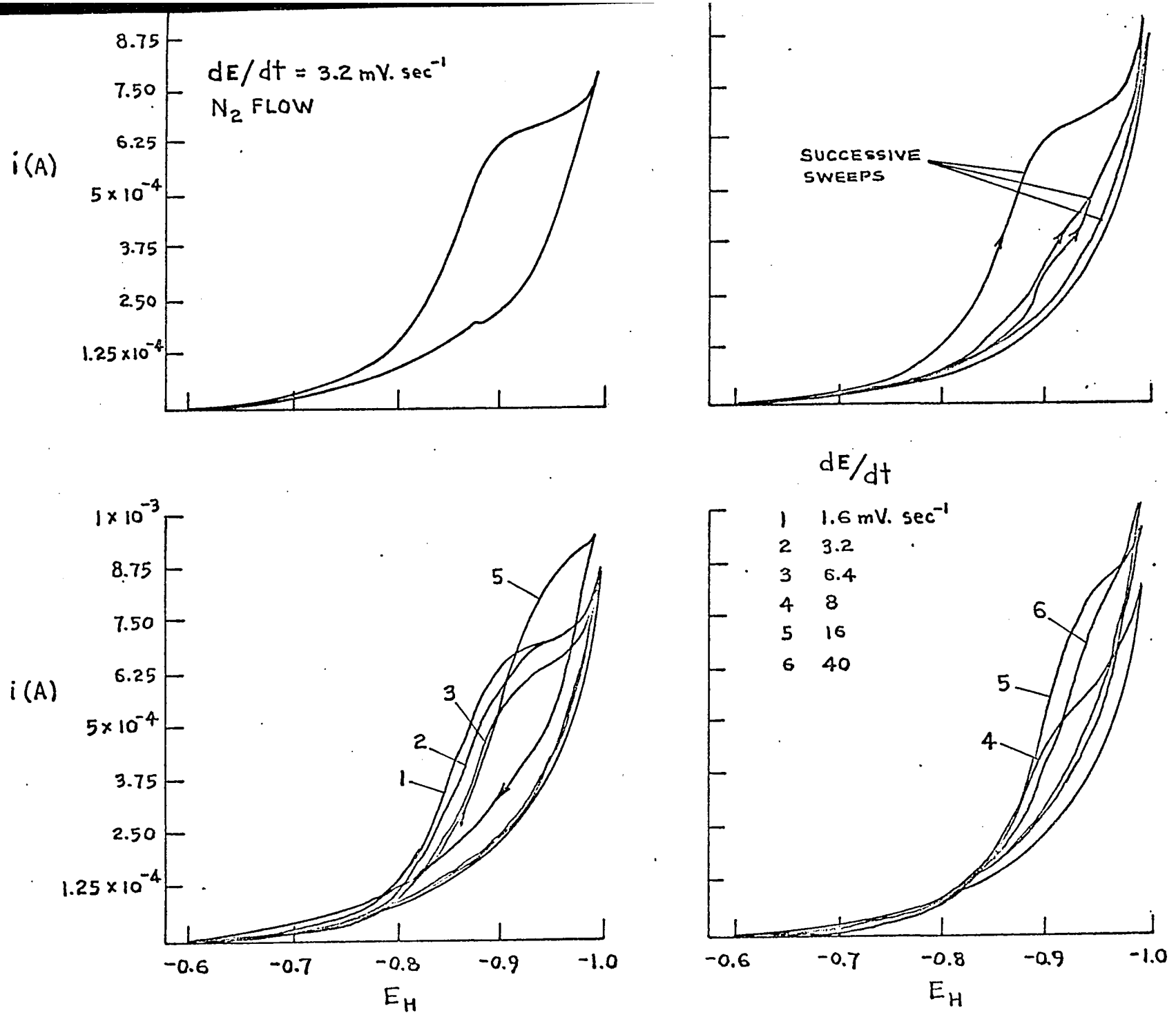
Figure 28. Electrochemical behaviour of acetophenone pinacol: potentiodynamic studies.

(a) and (b) Effect of change of sweep rate

Curve No.	$\left\{\frac{dE}{dt}\right\}$ mV. sec^{-1}
1	1.6
2	3.2
3	6.4
4	8
5	16
6	40

(c) Repetitive sweeps $\left\{\frac{dE}{dt}\right\}$ = 3.2 mV. sec^{-1}

(d) Sweep-rate 3.2 mV. sec^{-1} with nitrogen gas bubbled through the solution in the working-electrode compartment.


8.75
7.50
6.25
5 x 10^-4
3.75
2.50
1.25 x 10^-4
i (A)
dE/dt = 3.2 mV. sec^-1
N2 FLOW
SUCCESSIVE SWEEPS
dE/dt
1 1.6 mV. sec^-1
2 3.2
3 6.4
4 8
5 16
6 40
1 x 10^-3
8.75
7.50
6.25
5 x 10^-4
3.75
2.50
1.25 x 10^-4
i (A)
1
2
3
4
5
6
-0.6
-0.7
-0.8
-0.9
-1.0
E_H

The hydrogen evolution reaction at the mercury electrode is evidently facilitated by the presence of the pinacol, which is significantly adsorbed at the electrode surface even at low bulk concentrations (see Figures 32 and 33). This lowering of the overpotential of the hydrogen evolution reaction has also been observed in the presence of certain alkaloids and hetero-aromatic bases (146,147,148).

In the reaction the pinacol molecule adsorbed at the surface is acting as a catalyst for the electrochemical discharge of a proton (cf. discharge from $MeOH_2^+$ which occurs at lower overpotentials than the discharge of the H_3O^+ entity) and hence the species involved may well be the protonated form of the pinacol. The steady-state log[i]-E curve (Figure 27) shows a limiting current at potentials greater than -0.9 V. vs E_H, which is not usually observed in hydrogen evolution reactions. However, this may be explained by a slow desorption of the pinacol at the high cathodic potentials involved (Figure 28).

The potentiodynamic current-potential curves (Figure 28) show a peak which is independent of the bulk concentration of pinacol and is not affected by agitation of the solution. With increasing sweep rate ($\frac{dE}{dt} \longrightarrow 50$ mV. sec^{-1}) the peak is displaced and finally almost disappears ($\frac{dE}{dt} = 40$ mV. sec^{-1}).

This behaviour is consistent with the presence of an adsorbed layer which is slowly desorbed as E becomes increasingly

cathodic. It has been reported (149) that acetophenone pinacol is desorbed in a neutral solution at E = -1.3 V vs S.C.E.(i.e., -1.02 V. vs N.H.E.)

7. ADSORPTION OF ACETOPHENONE AND ACETOPHENONE PINACOL AT A MERCURY SURFACE: RESULTS OBTAINED FROM ELECTROCAPILLARY STUDIES

The electrocapillary curves showed no region in which either the reactant or the product is adsorbed or desorbed over a narrow potential range. A progressive increase of the surface concentration (Γ) at a given bulk concentration was found to occur with increasing cathodic potential so that the reactant is specifically adsorbed into the range of potential within which reduction occurs. The electrocapillary measurements were extended some way across the potential range in which appreciable reduction rates are measured but at these higher potentials the measurements become unsatisfactory due to the incomplete polarisability of the interface.

The surface excess quantities Γ, the coverage θ (where $\theta = \frac{\Gamma}{\Gamma_m}$; Γ_m is the surface excess corresponding to a surface monolayer), and the surface pressures ϕ for acetophenone and the pinacol were evaluated by standard procedures (25,150) for various values of electrode potential and surface charge.

Examination of the adsorption data was made in terms of the Langmuir isotherm and it was found, as expected, that

values of K were dependent upon the coverage θ, which indicated the presence of interaction effects in the adsorbed layer. The adsorption results were therefore examined, more realistically, in terms of an equation similar to Frumkin's relation, viz.

$$\frac{\theta}{1-\theta} = K(C_R)_b \exp[-r\theta] \qquad \text{(III, 1)}$$

with θ again expressed as Γ / Γ_m and r taken as an interaction parameter.

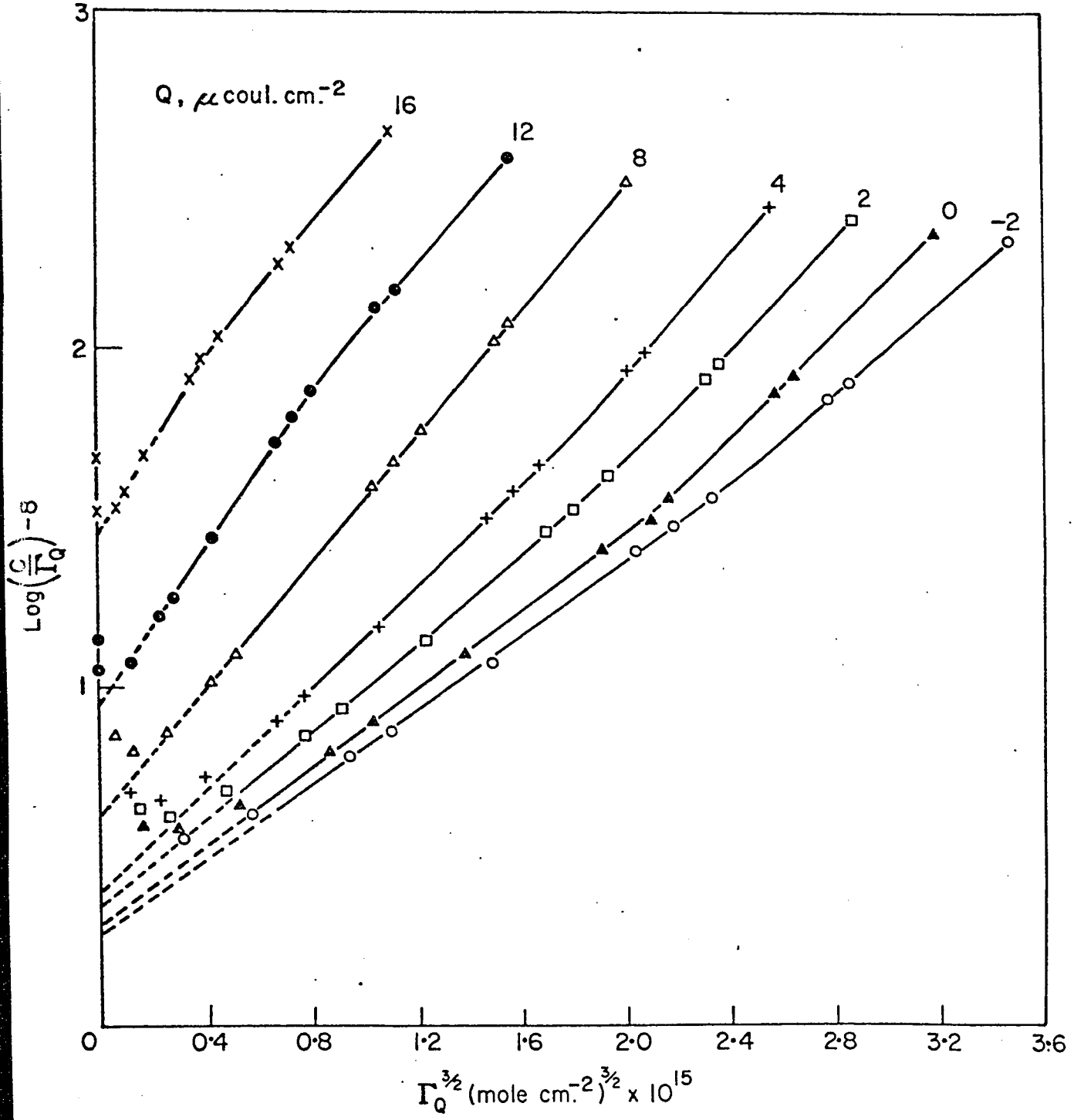
In an analysis of first order dipole-dipole repulsion effects, based on the treatment of Conway and Barradas (43,151), the following expression derived by Conway, Rudd and Gordon (152) may be used:

$$\log (C_R)_b/\Gamma = \frac{n\bar{\mu}^2\Gamma^{3/2}}{2\varepsilon kT} - \log K'\Gamma_m \qquad \text{(III, 2)}$$

in which n is a local two-dimensional co-ordination number, μ is the component of dipole moment of the adsorbate <u>normal</u> to the electrode surface, ε is the local dielectric constant and K' is an "initial" adsorption equilibrium constant appropriate for the data at low coverages, i.e., as $\theta \longrightarrow 0$, and analogous to K in equation (III, 1).

It was found that the adsorption of acetophenone at mercury showed a linear dependence of $\log \left[(C_R)_b/\Gamma\right]$ upon $\Gamma^{3/2}$ at constant charge at the electrode surface (Figure 29). Two distinct regions were indicated and the slopes of the

Figure 29. Adsorption of Acetophenone at Mercury: Tests of equation (III, 2) for an isotherm with first-order interaction effects due to dipole repulsion.


Q, μcoul. cm.⁻²
16
12
8
4
2
0
-2
3
2
1
0
0·4
0·8
1·2
1·6
2·0
2·4
2·8
3·2
3·6
$\log\left(\frac{c}{\Gamma_Q}\right) - 6$
$\Gamma_Q^{3/2}$ (mole cm.⁻²)$^{3/2}$ x 10^{15}

upper parts of the lines gave a reasonable value for $\bar{\mu}$ (= 1.26 D), [assuming hexagonal co-ordination and a surface dielectric constant of $\varepsilon = 6$ (29)]. The values of Γ_m corresponded to a molecular area of 66 $\mathring{A}^2$ for acetophenone and 110 $\mathring{A}^2$ for the acetophenone pinacol.

At intermediate θ values, and for sufficiently large r values, equation (III, 1) becomes similar to Temkin's logarithmic isotherm (see Chapter IV p.108). It was found that the adsorption of acetophenone from methanol-water-sulphuric acid solutions (Figure 30) and from methanol-sulphuric acid solutions (Figure 31), showed a logarithmic dependence upon the bulk concentration over an appreciable range of $(C_R)_b$ at certain electrode potentials.

Acetophenone and the corresponding pinacol were found to be strongly adsorbed at the electrode. The pinacol was not desorbed from the surface even at very cathodic potentials (Figure 32) and, as can be seen from the relationship between surface pressure ϕ and log $(C_R)_b$ (Figure 33), the presence of the reaction product lowers the surface excess (or extent of adsorption) of acetophenone, particularly at lower coverages.

Figure 30. Adsorption of acetophenone at mercury in methanol (80 mole %)-water-sulphuric acid (0.97 M): Surface excess (Γ_E) *vs* log(C_R) at various potentials (E *vs* the normal hydrogen electrode).

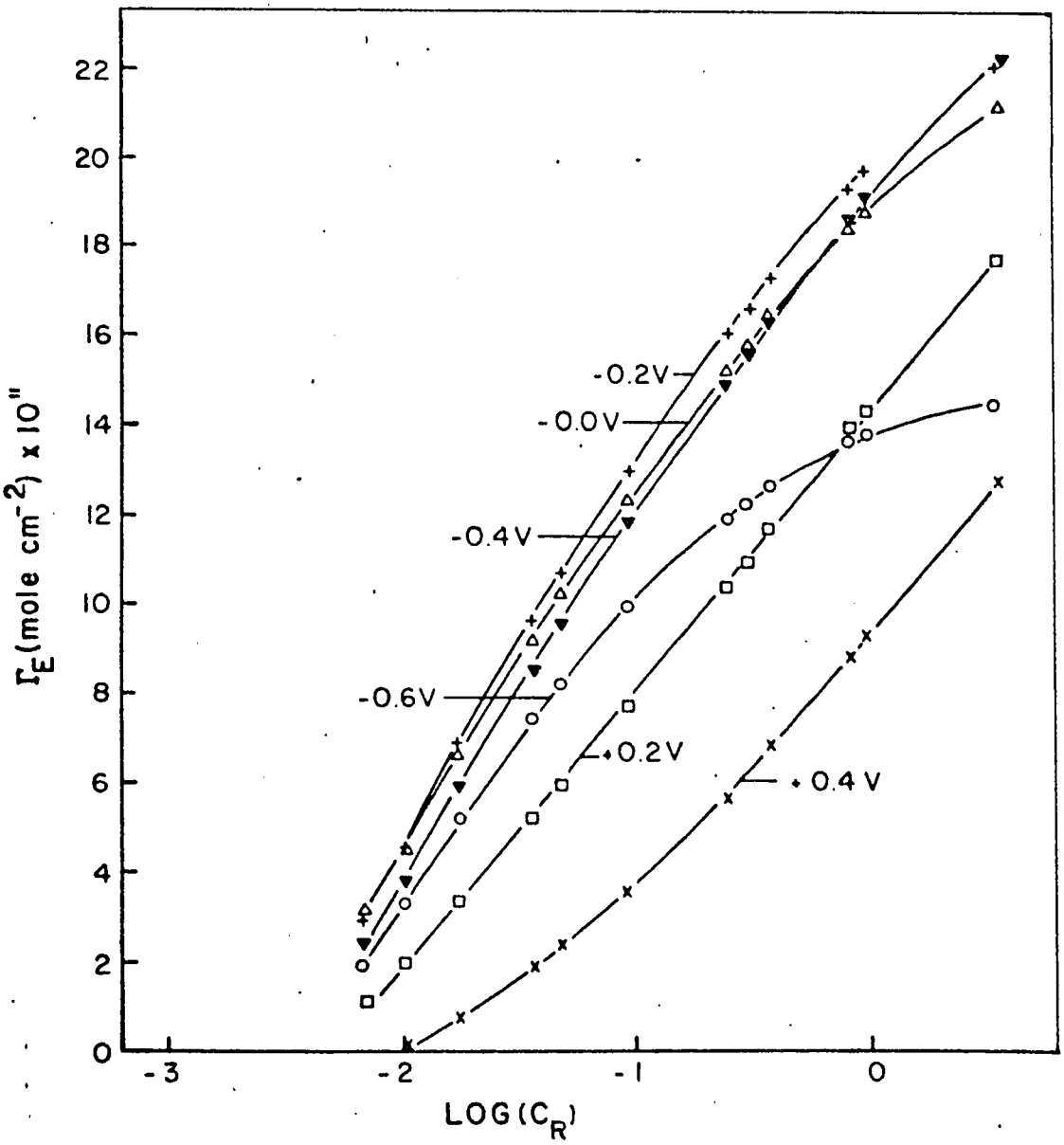

22
20
18
16
14
12
10
8
6
4
2
0
-3
-2
-1
0
Γ_E(mole cm^{-2}) x 10"
LOG(C_R)
-0.2V
-0.0V
-0.4V
-0.6V
+0.2V
+0.4V

Figure 31. Adsorption of acetophenone at mercury in methanol-sulphuric acid (0.97 M): Surface excess (Γ_E) *vs* $\log(C_R)$ at various potentials (E *vs* the normal hydrogen electrode).

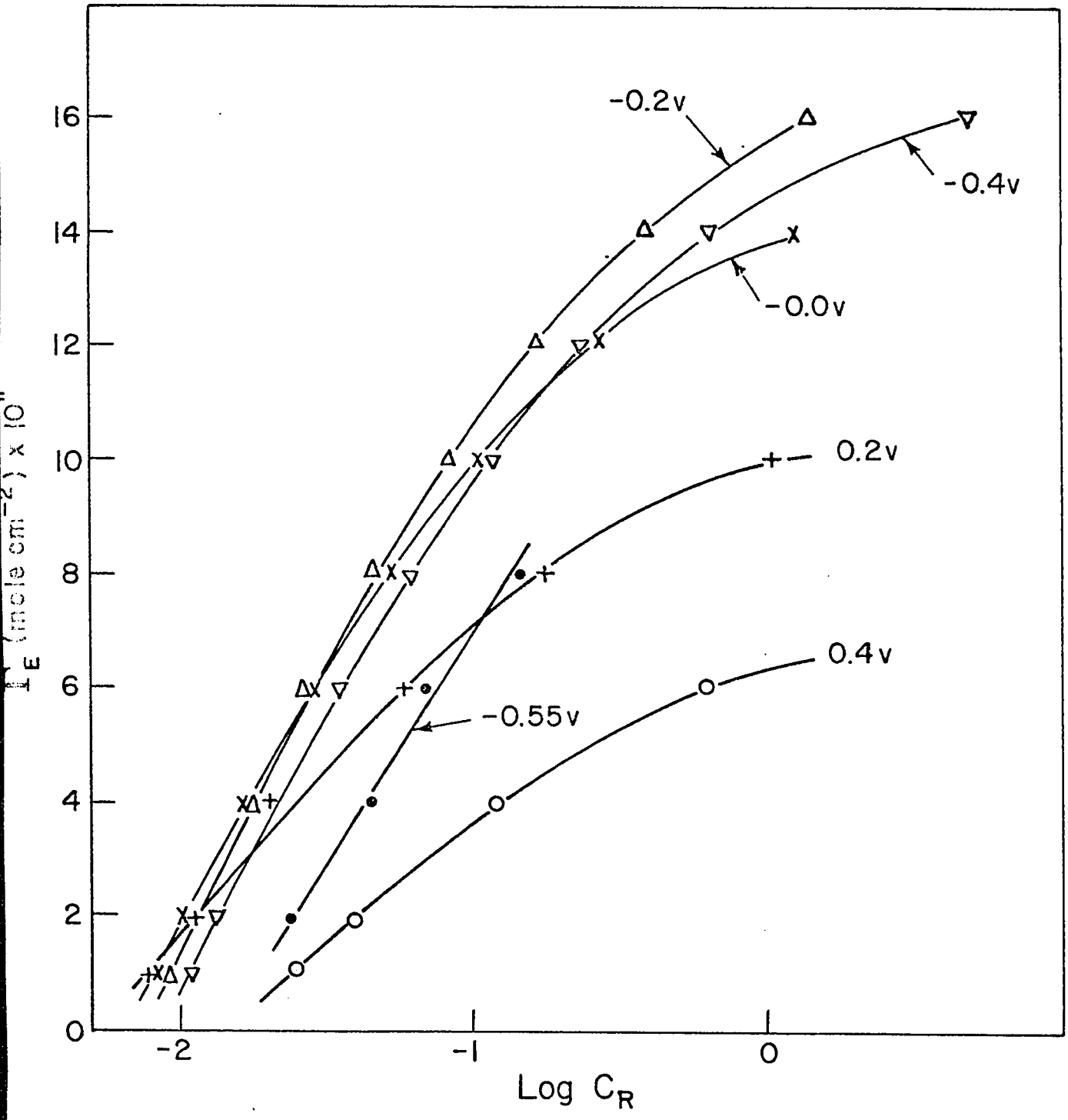

-0.2v
-0.4v
-0.0v
0.2v
0.4v
-0.55v
16
14
12
10
8
6
4
2
0
-2
-1
0
Log C_R
Γ_E (mole cm^{-2}) x 10^{10}

Figure 32. Adsorption of acetophenone pinacol at mercury in methanol (80 mole %)-water-sulphuric acid (0.97 M): Surface excess (Γ_E) vs log (C_R) at various potentials (E vs the normal hydrogen electrode).

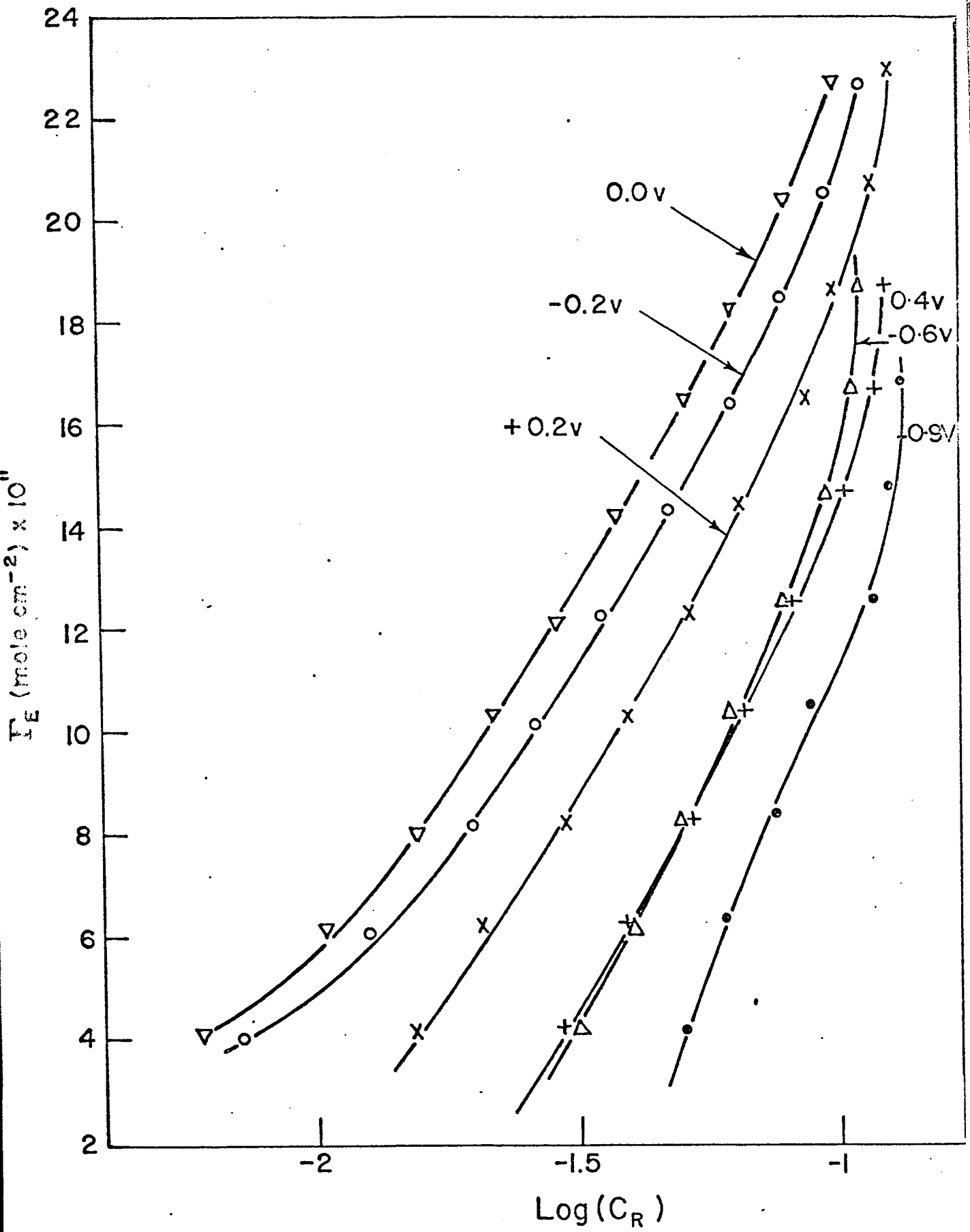
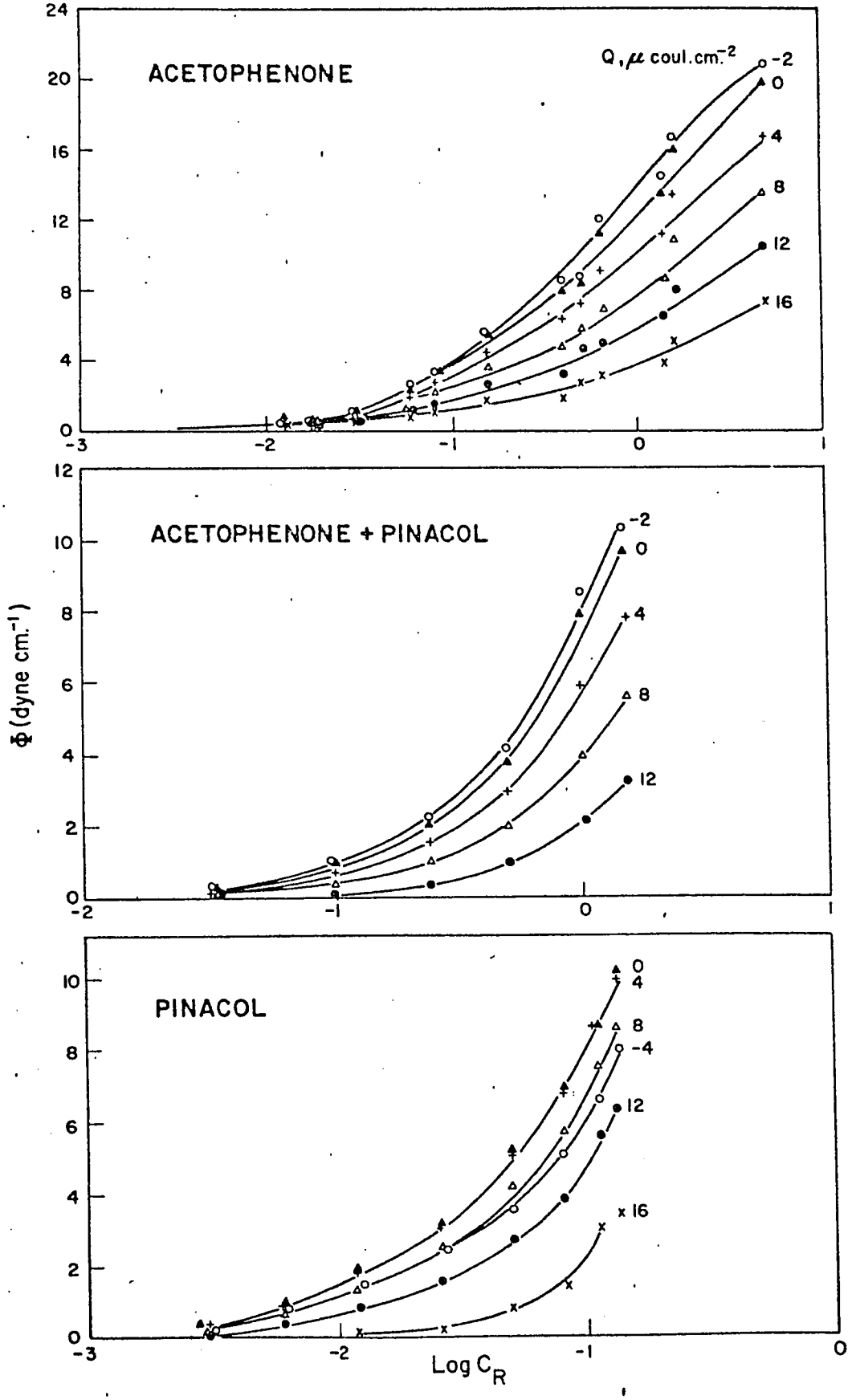

24
22
20
18
16
14
12
10
8
6
4
2
Γ_E (mole cm^{-2}) x 10^{11}
0.0 v
-0.2v
+0.2v
0.4v
-0.6v
-0.9V
-2
-1.5
-1
Log (C_R)

Figure 33. Adsorption of acetophenone and acetophenone pinacol and acetophenone in presence of pinacol: Surface pressure (ϕ) *vs* $\log(C_R)$ at various constant surface charges Q ($\mu C.cm.^{-2}$) in methanol (80 mole %)-water-sulphuric acid (0.97 M).


ACETOPHENONE
Q, μ coul.cm.⁻²
-2
0
+4
8
12
x 16
ACETOPHENONE + PINACOL
PINACOL
Φ (dyne cm.⁻¹)
Log C_R

8. BRIEF STUDIES OF THE ELECTRO-REDUCTION OF OTHER AROMATIC KETONES

(a) Electro-reduction of Fluorenone

The analysis of current-potential curves obtained from potentiodynamic studies on the electro-reduction of fluorenone showed a linear dependence of i_p upon $\sqrt{\frac{dE}{dt}}$ and of E_p upon $\log\left\{\frac{dE}{dt}\right\}$, which is again characteristic of an irreversible diffusion-controlled reaction. The peak potential, E_p, was also found to be dependent upon the concentration of the ketone becoming more cathodic as $(C_R)_b$ increased.

Even at relatively high sweep-rates ($\frac{dE}{dt}$ = 50 V. sec^{-1}), there was no evidence of an anodic current corresponding to the oxidation of an intermediate radical [a re-oxidation peak has been observed (145) at $\frac{dE}{dt}$ =100 Hz.]

The log[i]-E curves obtained by potentiostatic steady-state measurements were similar to those obtained for the electro-reduction of acetophenone, although the reaction occurred at less cathodic potentials. At low concentrations, $(C_R)_b = 7\times10^{-3}$ mole. $litre^{-1}$, the Tafel slope was found to be 65 mV but again decreased with increasing concentration of ketone (Figure 34).

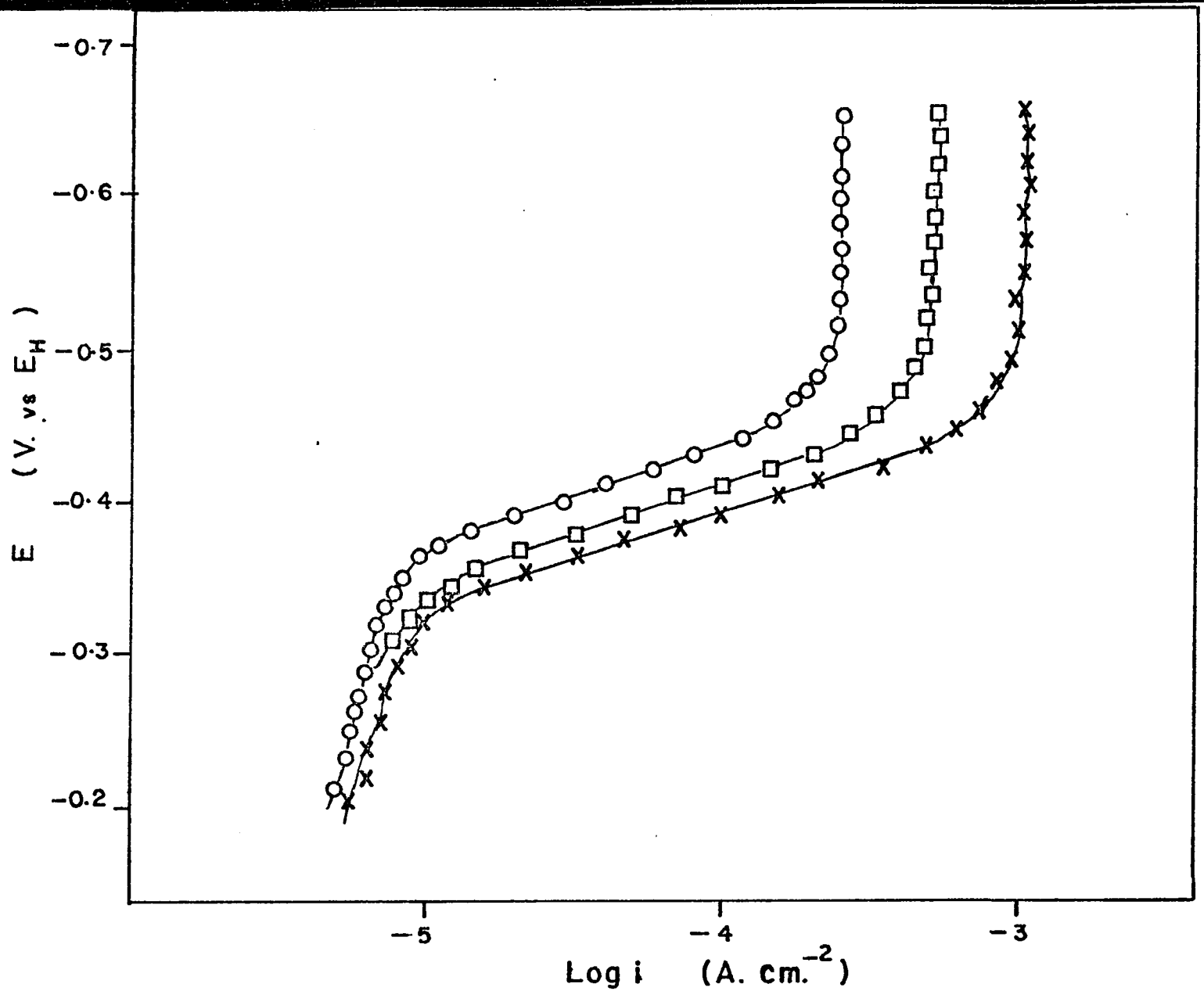
The reaction order was not determined over a wide range of concentrations of the ketone, but there is evidence that it is again close to unity in the Tafel (linear) region as in the case of acetophenone.

Figure 34. Electro-reduction of fluorenone: Potentiostatic steady-state log[i]-E curves at different ketone concentrations in a methanol (80 mole %)-water-sulphuric acid (0.95 M) solution

o——o 0.007 mole. litre^{-1} fluorenone

□——□ 0.015 mole. litre^{-1}

×——× 0.09 mole. litre^{-1}.

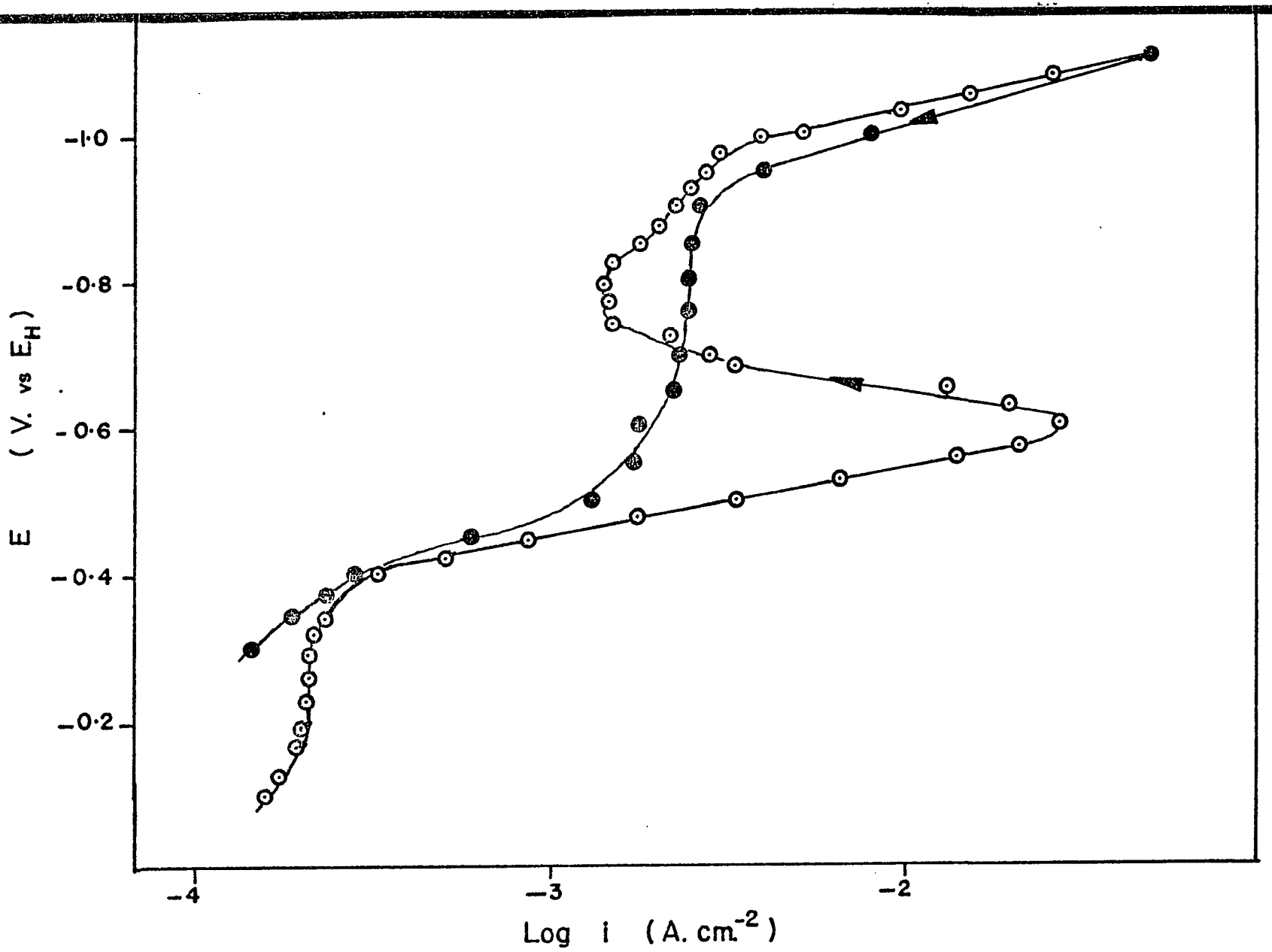

-0·7
-0·6
-0·5
-0·4
-0·3
-0·2
E (V. vs E_H)
-5
-4
-3
Log i (A. cm.$^{-2}$)

(b) Electro-reduction of Benzophenone

A log[i]-E curve obtained from steady-state measurements of the electro-reduction of benzophenone is shown in Figure 35. The marked inhibition of the reaction at potentials more cathodic than -0.6 V. *vs* E_H was caused by the formation of an insoluble film of benzophenone pinacol at the electrode surface. This film is visible to the eye and may be partially removed by physically "scraping" the mercury surface. Hydrogen evolution is not, however, suppressed by the presence of this film of pinacol.

The Tafel slope would appear to be 75 mV but inhibition effects will tend to give a high value and would be progressively more significant as the potential was increased in the cathodic direction. It is evident that satisfactory determination of a reaction order in the normal manner is not possible for this case.

Figure 35. Potentiostatic steady-state log[i]-E curve obtained for the electro-reduction of benzophenone (0.3 M) in methanol (80 mole %)-water-sulphuric acid (0.97 M).


-1·0
-0·8
-0·6
-0·4
-0·2
E (V. vs E_H)
-4
-3
-2
Log i (A. cm^{-2})

CHAPTER IV

DISCUSSION

1. REACTION ORDERS IN ORGANIC ELECTROCHEMICAL PROCESSES

The determination of the reaction order has been insufficiently considered in studies of organic electrochemical processes, yet it forms an important aspect of reaction kinetics in relation to criteria of mechanisms. It has already been shown (Chapter I, p.9) that in an electrochemical process the overall rate of reaction can be expressed in terms of the current obtained at a potential E appreciably displaced from the reversible potential for the electrode reaction; viz.,

$$i = zF\Gamma\,(1-\theta)\,\exp\left[-\frac{\Delta\bar{G}^{o\dagger}}{RT}\right]\exp\left[\frac{\beta z' EF}{RT}\right] \qquad (IV, 1)$$

where z' is usually unity for electron transfer in the transition state. Since an electrochemical process is heterogeneous in nature, the rate of reaction is dependent upon the surface concentration of the electroactive species (denoted here by the symbol Γ), which is related to the bulk concentration by an adsorption isotherm which can usually be expressed in a form related to that following:-

$$\Gamma = (C_R)_b \exp\left[-\frac{\Delta G^{o}_{ads}}{RT}\right] \qquad (IV, 2)$$

The quantities $\Delta\bar{G}^{o\dagger}$ and ΔG^{o}_{ads} have been discussed by Conway (11) in terms of a treatment of the electrical double-

layer and the adsorption of ionic and neutral species at an electrode surface.

Expressing equation (IV, 1) in a logarithmic form and introducing a bulk concentration term (IV, 2) gives:-

$$\ln i = \ln k' + \ln(C_R)_b - \frac{\Delta G^{o\ddagger}}{RT} - \frac{\Delta G^{o}_{ads}}{RT} + \frac{\beta z' EF}{RT} \quad \text{(IV, 3)}$$

where k' includes the constant terms and $(1-\theta)$ for convenience. The following characteristic derivatives may be obtained and derivative (a) is the chemically significant reaction order when the electrode potential is held constant, e.g., potentiostatically

$$\text{(a)} \quad \left\{\frac{d\ln i}{d\ln(C_R)_b}\right\} \phi_m, \psi_1$$

$$\text{(b)} \quad \left\{\frac{d\ln i}{d\ln(C_R)_b}\right\} E$$

$$\text{(c)} \quad \left\{\frac{dE}{d\ln(C_R)_b}\right\} i$$

The derivative (c) has usually been considered in papers on the double-layer effects in the kinetics of electrode processes (see ref.23). For most organic electrode processes it can be shown that use of an excess of supporting electrolyte virtually eliminates double-layer effects, and under potentiostatic conditions the reaction order $\left\{\frac{d\ln i}{d\ln(C_R)_b}\right\} E$ then depends on:

(a) The mechanism of the reaction;

(b) the type of isotherm required to describe the adsorption behaviour of the reactant; and

(c) the relative degree of surface coverage by the reactant.

2. ADSORPTION ISOTHERMS

It would appear that a wide variety of isotherms have been used to describe the experimental results obtained from studies of the adsorption of ions and molecules. The forms of a number of these isotherms are shown in Table VII.

Since a layer of solvent molecules is always present at the surface, adsorption at an electrode must be considered as a displacement reaction. Furthermore, in deriving an isotherm to describe adsorption behaviour, it would seem necessary to account for:-

(a) particle-particle interactions at the surface (this must include adsorbate-adsorbate, adsorbate-solvent and solvent-solvent interactions);

(b) intrinsic electrode-particle interactions;

(c) the effect of the electrode potential upon the electrostatic interaction of the adsorbate with the charged surface and in causing orientation; and

(d) "induced" surface heterogeneity (153).

However, as was pointed out earlier (Chapter I, p. 16), the solvent layer will have a levelling effect upon the distribution of site energies across a solid surface. It is

Table VII

The Forms of a Number of Adsorption Isotherms and the Corresponding Expressions for the Reaction Order $\frac{R}{n}$

	Isotherm	$\frac{R}{n}$
Henry's Law	$K(C_R)_b = RT\theta\Gamma_m$	1
Volmer	$K(C_R)_b = RT\frac{\theta\Gamma_m}{1-b\theta}\exp.\frac{b\theta\Gamma_m}{1-b\theta}$	$1+\frac{b\theta}{1-b\theta}_m+\frac{b\theta\Gamma_m}{(1-b\theta\Gamma_m)}$
Langmuir	$K(C_R)_b = \frac{\Gamma}{\Gamma_m-\Gamma} = \frac{\theta}{1-\theta}$	$1-\theta$
Flory-Huggins	$K(C_R)_b = \frac{\theta}{x(1-\theta)^x}$	$\frac{1-\theta}{1+(x-1)\theta}$
Virial	$K(C_R)_b = RT\theta\Gamma_m \exp\left[-r\theta\right]_m$	$\frac{1}{1-r\theta\Gamma_m}$
Frumkin	$K(C_R)_b = \frac{\theta}{1-\theta}\exp\left[-r\theta\Gamma_m\right]$	$\frac{1-\theta}{1-r\theta\Gamma_m+r\Gamma_m\theta}$
Temkin $0.2 < \theta < 0.8$	$K(C_R)_b = \exp\left[-r\theta\Gamma_m\right]$	$-\frac{1}{r\Gamma_m\theta}$

Γ is the surface concentration of adsorbate

Γ_m is the surface concentration corresponding to a monolayer at the surface

$K = \exp\left[-\frac{\Delta G_{ads}}{RT}\right]$

θ is the degree of coverage of the electrode surface by adsorbate, given by Γ/Γ_m.

x is the ratio of the relative sizes of the adsorbate and the solvent molecules

b is the molecular area of an adsorbate species

r is an interaction parameter characterising 2-dimensional attraction or repulsion in the adsorbed layer.

therefore possible that at low coverages of the adsorbate only electrode-adsorbate interactions contribute significantly to the standard free energy of adsorption. Under these conditions $\Delta \bar{G}^{o}_{ads}$ is constant and thus independent of the surface concentration of adsorbate so that Henry's law is applicable. In practice it is difficult to realise this ideal dilute state and adsorbate-adsorbate interactions are often significant ($\theta > 0.2$). The Virial equation is a modified form of Henry's law in which particle-particle interactions are accounted for by an empirical term, r (see Table VII). This term was first introduced by Frumkin (40) into the equation of state corresponding to the Langmuir isotherm. The parameter r is positive for attractive forces and negative for repulsive forces. The Langmuir isotherm applies strictly only to a fixed site adsorption on a lattice of identical sites, with no lateral interactions between adsorbed species. At first glance neither of these assumptions would seem likely to be physically realistic at a mercury surface where the ad-layer is probably mobile. Since adsorption must be a displacement process, a type of "fixed-site" adsorption nevertheless arises since the adsorbate can be regarded as replacing certain solvent molecule(s) at the surface (154,155). In a similar way, the Flory-Huggins* isotherm

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* So called after the analogous original treatment of Flory and Huggins for the thermodynamics of polymer solutions in terms of volume fractions and site occupancy fractions.

is more generally applicable since it accounts for the relative sizes of adsorbate and solvent molecules and that the adsorbed species may displace more than one solvent molecule.

The Temkin isotherm, which assumes a linear distribution of energies of adsorption with coverage, was originally introduced to account for experimentally observed deviations from Langmuir behaviour for the adsorption of certain gases at metal surfaces (156). However, it has been found (157) that this isotherm may be applied to a layer of interacting particles on a homogeneous surface, provided that the interactions lead to a linear decrease of $\Delta\bar{G}^{o}_{ads}$ with coverage.

Expressions for particle-particle interactions other than through the term $r\theta$ can be derived from corresponding treatments for adsorption processes at gas/metal interfaces (158). In the adsorption behaviour of some ionic and neutral species at a mercury electrode a dependence of $\Delta\bar{G}^{o}_{ads}$ upon $\theta^{\frac{1}{2}}$ (31) and upon $\theta^{3/2}$ (43) was found to occur at low and intermediate coverages, corresponding to ion-ion and dipole-dipole interactions in two-dimensions in the adsorbed layer.

3. DERIVATION OF THE REACTION ORDER FROM AN ADSORPTION ISOTHERM

Since both the rate of the reaction and the coverage θ are potential-dependent quantities, the values of the reaction order, R, must be considered at a constant electrode potential.

$$R = \left\{\frac{d\ln i}{d\ln(C_R)_b}\right\}_E = \left\{\frac{d\ln i}{d\ln\theta}\right\}_E \left\{\frac{d\ln\theta}{d\ln(C_R)_b}\right\} \qquad (IV, 4)$$

The second term of the product in (IV, 4) can be derived from the adsorption isotherm for the reactant, $\theta \sim f\left\{(C_R)_b\right\}$. Since $\frac{d\theta}{d(C_R)_b}$ can usually be readily obtained, the required logarithmic derivative can be obtained easily by multiplication of $\frac{d\theta}{d(C_R)_b}$ by $\frac{(C_R)_b}{\theta}$. If the current density is a linear function of θ^n, the reaction order can be written as

$$R = n\left\{\frac{(C_R)_b}{\theta}\right\}\left\{\frac{d\theta}{d(C_R)_b}\right\} \qquad (IV, 5)$$

or

$$\frac{R}{n} = \left\{\frac{(C_R)_b}{\theta}\right\}\left\{\frac{d\theta}{d(C_R)_b}\right\} = \left\{\frac{d\ln\theta}{d\ln(C_R)_b}\right\} \qquad (IV, 6)$$

with constant potential conditions being implicit.

One of the most generally applicable isotherms in electrochemical adsorption is that of Frumkin:

$$K(C_R)_b = \frac{\theta}{1-\theta}\exp\left[-r\theta\right] \qquad (IV, 7)$$

and this can be written in logarithmic form as

$$\ln K + \ln(C_R)_b = \ln\theta - \ln(1-\theta) - r\theta \qquad (IV, 8)$$

and then

$$\frac{d\ln(C_R)_b}{d\theta} = \frac{1}{\theta} + \left(\frac{1}{1-\theta}\right) - r$$

Since $\frac{d\theta}{\theta} = d\ln\theta$,

$$\frac{d\ln(C_R)_b}{d\ln\theta} = 1 + \frac{\theta}{1-\theta} - r\theta = \frac{1-r\theta\,(1-\theta)}{1-\theta} \qquad (IV, 9)$$

and $$\frac{R}{n} = \frac{1-\theta}{1-r\theta + r\theta^2} \qquad \text{(IV, 10)}$$

The expressions for $\frac{R}{n}$ which result from the selected isotherms are shown in Table VII.

4. ADSORPTION BEHAVIOUR OF ACETOPHENONE AND ACETOPHENONE PINACOL

The following general conclusions may be drawn from the results of electrocapillary studies of the adsorption of acetophenone and the corresponding pinacol at a mercury/solution interface.

(a) Acetophenone is strongly adsorbed over a wide range of electrode potentials and remains adsorbed to a significant extent in the potential region in which electro-reduction occurs. As might be anticipated from the simple consideration of relative solubility of acetophenone in methanol and in a water (20 mole %)-methanol solution, the surface concentrations (and therefore the extents of adsorption) of the ketone adsorbed from the solution in nominally anhydrous methanol are lower than those from the partly aqueous solution under otherwise similar conditions of potential and concentration.

(b) Acetophenone pinacol is also strongly adsorbed and an important observation from the adsorption studies is that there is no evidence of sudden desorption within the potential range over which the electro-reduction of the parent ketone occurs.

(c) The adsorption of both acetophenone and the pinacol is logarithmic in $(C_R)_b$ over an appreciable range of concentration for certain potentials, i.e., the adsorption follows, in form, the logarithmic isotherm proposed by Temkin.
(d) The presence of the pinacol in the solution, and therefore at the electrode surface, markedly inhibits the adsorption of the ketone particularly at low coverages (see Figure 33, where the results in terms of surface pressure are shown).

It has been pointed out that K, the adsorption equilibrium constant in the Langmuir isotherm, was found to be dependent upon the surface coverage of adsorbate. This behaviour indicates the presence of significant interaction effects in the adsorbed layer and this conclusion is further supported by the observed linearity between $\log \frac{(C_R)_b}{\Gamma}$ and $\Gamma^{3/2}$ (Figure 29) in agreement with equation (III, 2) which was obtained from an analysis for first-order dipole repulsion effects (43). The term in the $\frac{3}{2}$ power of Γ in this equation may strictly only be applied to an array of dipoles of constant effective moment in a two-dimensional lattice which is not disturbed by thermal motion (159). It seems unlikely that these conditions are exactly met in this particular case (although the use of the mean dipole component $\overline{\mu}$ normal to the surface may partly allow for thermal disorientation effects in the adsorbed layer) but although the "$\frac{3}{2}$" relation is undoubtedly an over-simplification it does, however, represent

the results rather adequately. A further limitation in the analysis is that towards full coverages ($\theta \longrightarrow 1$) changes in the interactions between solvent and adsorbate dipoles will probably become significant, i.e., the solvent cannot be regarded as an inert space-filling medium in the interphase (cf. the case of the Debye-Hückel treatment for ionic solutions when high ionic concentrations are involved so that changes of solvation arise).

The inflections in the relation between $\log \frac{(C_R)_b}{\Gamma}$ vs $\Gamma^{3/2}$ plotted at various surface charge (Q) values (Figure 31) may be attributed to the onset of extensive orientation in the field of the electrode [cf. the orientation effects observed in the adsorption behaviour of pyridine (43)]. A reasonable value for $\bar{\mu}$ is obtained from the slopes of the upper parts of the lines in Figure 29 and values of Γ_m are approximately 66 $\mathring{A}^2$ for acetophenone and 110 $\mathring{A}^2$ for acetophenone pinacol. Both of these figures are, as expected, larger than the minimum geometrical areas estimated from Courtauld space-filling models. In these calculations, the adsorbed layer was assumed to exist as a hexagonally co-ordinated lattice, with the aromatic nucleus "flat" on the electrode surface. The surface pressure ϕ vs $\log (C_R)_b$ relations for acetophenone and for the pinacol (Figure 33) are not superimposable by a simple

lateral shift on the scale of log $(C_R)_b$* which implies that a change of surface charge causes orientation of the dipoles in the adsorbed layer.

To a first approximation, the dipole moment in acetophenone can be regarded as being confined largely to the $\rangle C = O$ group (160) and it is the orientation of this dipole which occurs in the adsorbed layer with increasing surface charge. In the adsorption of the ketone, the surface pressure of the ad-layer varies least with log $(C_R)_b$ at potentials close to the potential of zero charge. This is presumably because of a more random configuration of the adsorbate dipoles at these potentials and dipole repulsion is therefore minimal. With increasing surface charge, dipole-dipole interactions and resultant lateral repulsion effects are indicated by an increase in the surface pressure, associated with orientation.

5. CORRELATION OF EXPERIMENTALLY DETERMINED REACTION ORDERS WITH THE ADSORPTION BEHAVIOUR

When the electro-reduction of acetophenone is carried out in a solution of methanol (80 mole %) and water containing sulphuric acid (0.97 M), the reaction order $\left\{\frac{d \log i}{d \log (C_R)_b}\right\}_E$ at E = -0.65 V. vs E_H (i.e., in the linear or Tafel region of

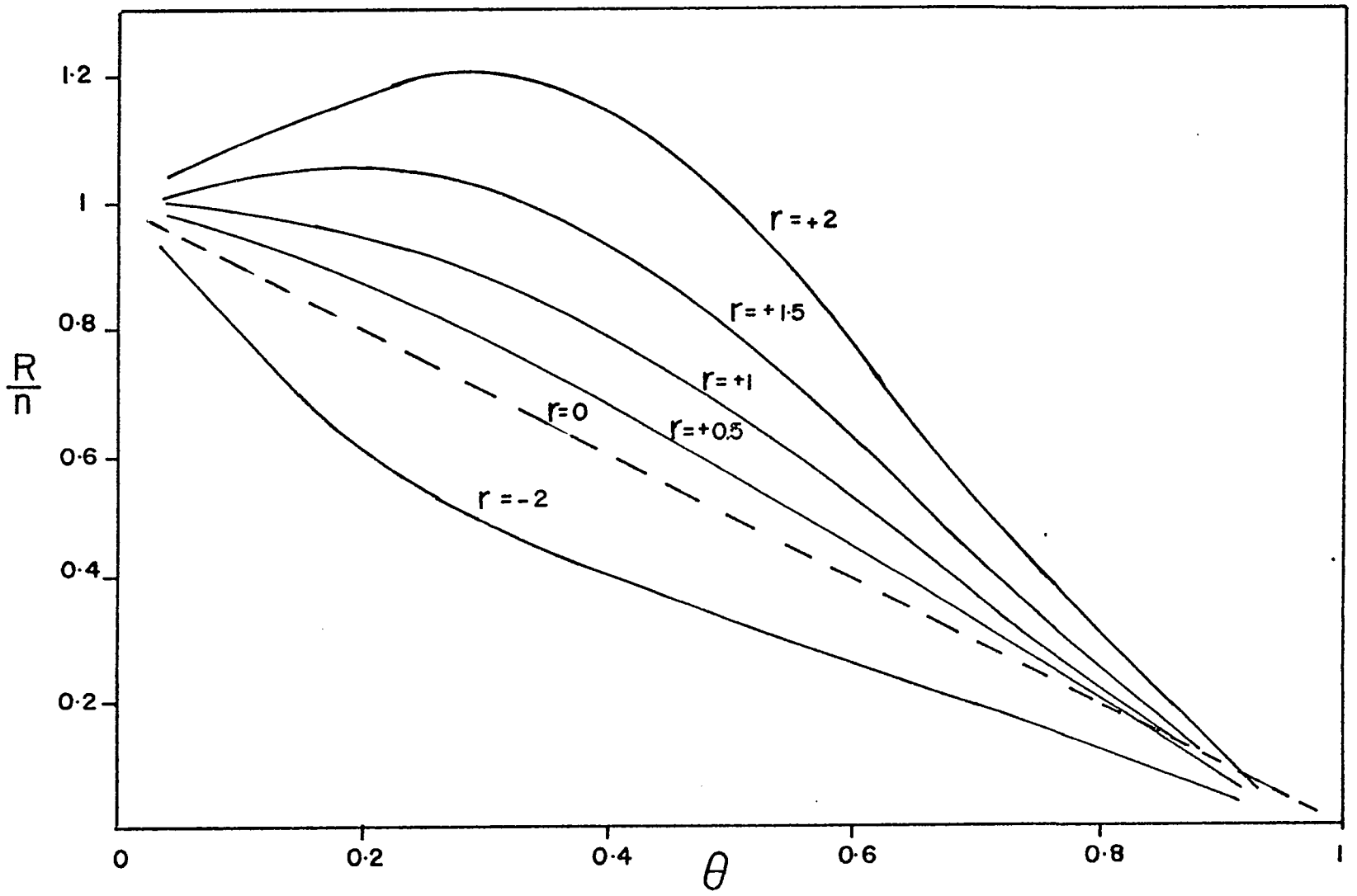
---

* Such behaviour is characteristic, for example, of the adsorption of thiourea. This compound is presumably adsorbed in a fixed orientation even at potentials near the p.z.c. and Hg-S chemisorption may be involved. (161,162).

the log[current]-potential relations) is found to be 1.2 over a fairly wide range of bulk concentration, but decreases to unity at $(C_R)_b < 0.1$ mole. litre. A similar value, R = 1.1, is obtained if the electro-reduction is carried out in nominally anhydrous methanol.

It will be useful to explore the dependence of the reaction order upon coverage (θ) or bulk concentration $(C_R)_b$ for the selected isotherms (Table VII). The relation between $\frac{R}{n}$ and θ for the Frumkin isotherm is shown in Figure 36. It can be seen that for negative values of the interaction parameter (i.e., repulsive interactions between the adsorbed dipoles) or with r = 0 the reaction order $\frac{R}{n}$ falls rapidly with θ. An interesting case arises when $r > 1$ (attractive interactions) and $\frac{R}{n}$ can then become larger than unity at low coverage and may remain near unity over an appreciable range of coverage. It might be expected that with increasing bulk concentration, the coverage at the electrode surface would also increase. However, as $\theta \longrightarrow 1$, the reaction orders deduced from the isotherm decrease rapidly in contrast to the experimentally observed behaviour where R remains relatively constant with changing Γ or θ. This problem is discussed further on pp. 115-118. Most of the other isotherms show similar trends, i.e., as $\theta \longrightarrow 1$, $\frac{R}{n}$ approaches zero. Henry's law gives a value of one over the whole range of coverage values but the modified form of this law (the Virial equation) is interesting. At small positive values of r (0.1 to 0.5) the reaction order changes slowly from one (at low θ) to 1.1 as full coverage is approached;

Figure 36. Dependence of the reaction order derivative $(\frac{R}{n})$ upon surface coverage (θ) for a Frumkin type isotherm using various r values including positive ones (attractive interactions).


1·2
1
0·8
0·6
0·4
0·2
R/n
r = +2
r = +1·5
r = +1
r = +0·5
r = 0
r = -2
0
0·2
0·4
θ
0·6
0·8
1

fuller details are shown in Table VIII.

However, it will be necessary to examine in more detail the significance of R and n for kinetics proceeding under "Temkin" type conditions (163-165). From log-log plots of Γ as a function of $(C_R)_b$ the term $\left\{\frac{d\ln \Gamma}{d\ln(C_R)_b}\right\}_E$ can be evaluated. From equation (IV, 6), this term in combination with the observed orders would normally give the molecularity n of the electrochemical surface reaction as

$$n = \frac{R}{\frac{d\ln \Gamma}{d\ln(C_R)_b}}$$

From the present results, the required quantities can be obtained for the reduction of acetophenone, e.g., at E = -0.4 V and -0.6 V vs E_H. In this way apparent values of n are given which can be referred to as the order of the surface reaction R_S. n is found to be greater than R and increases substantially as $\Gamma \longrightarrow \Gamma_m$. (See Table IX).

However, for a reaction which may proceed under "Temkin" conditions, the quantity $\left\{\frac{d\ln \Gamma}{d\ln(C_R)_b}\right\}_E$ in combination with the experimentally observed reaction order will still not give the true molecularity of the surface reaction. Thus, for a general rate equation with a coverage-dependent rate constant,

$$\nu = \frac{i}{zF} = k\,\theta^n \exp\left[\alpha' nr\theta\right] \exp\left[\frac{\alpha FE}{RT}\right] \qquad \text{(IV, 11)}$$

and

$$\ln i = \ln K' + n\ln\theta + \alpha' nr\theta + \frac{\alpha FE}{RT} \qquad \text{(IV, 12)}$$

where α' is a Brønsted factor pertaining to coverage effects on the activation energy, analogous to α or β.

Table VIII

Coverage Dependence of the Reaction Order $^{R}/_{n}$

derived from the Virial Isotherm

VIRIAL EQUATION $K(C_R)_b = RT\theta\,\Gamma_m \exp\left\{-r\theta\,\Gamma_m\right\}$

$$\frac{R}{n} = \frac{1}{1-r\theta\,\Gamma_m}$$

$\frac{R}{n}$							
	Attraction				no Interaction	Repulsion	
$\theta\,\Gamma_m$	r = 5	r = 1	r = 0.5	r = 0.1	r = 0	r = -0.1	r = -1
0.1	2	1.11	1.05	1.01	1	0.99	0.91
0.2	[∞]	1.25	1.1	1.02	1	0.98	0.83
0.3	-2	1.43	1.17	1.03	1	0.97	0.77
0.4	-1	1.67	1.25	1.04	1	0.96	0.71
0.5	-0.67	2	1.33	1.05	1	0.95	0.67
0.6	-0.5	2.5	1.43	1.06	1	0.94	0.63
0.7	-0.4	3.33	1.54	1.07	1	0.935	0.58
0.8	-0.33	5	1.67	1.08	1	0.93	0.55
0.9	-0.29	9.1	1.82	1.1	1	0.92	0.52
1	-0.25	[∞]	2	1.1	1	0.91	0.5

Table IX

Evaluation of the Apparent Surface Reaction Order R_s and true Molecularity n for Acetophenone Reduction for R = 1.1

(a) E = -0.4 V vs E_H									
$\log(C_R)_b$	-1.8	-1.6	-1.4	-1.2	-1	-0.8	-0.6	-0.4	-0.2
$\frac{d\log\Gamma}{d\log(C_R)_b}$	0.9	0.73	0.52	0.435	0.38	0.33	0.32	0.3	0.32
R_s	1.22	1.45	2.05	2.45	2.78	3.25	3.36	3.55	3.36
$\Gamma^{3/2}_{x10^{15}}$	0.21	0.41	0.62	0.86	1.15	1.5	1.85	2.3	2.8
(b) E = -0.6 V vs E_H									
$\frac{d\log\Gamma}{d\log(C_R)_b}$		0.75	0.58	0.43	0.38	0.37	0.34	0.32	0.33
R_s		1.47	1.9	2.54	3.01	3.01	3.25	3.48	3.38
$\Gamma^{3/2}_{x10^{15}}$		0.31	0.49	0.69	0.91	1.19	1.52	1.93	2.4

then $$\left\{\frac{d\ln i}{d\ln\theta}\right\}_E = n\,(1 + \alpha' r\theta) \qquad \text{(IV, 13)}$$

Thus the derivative gives the true n only as θ approaches zero. In the general case of finite surface coverage, n may be evaluated as

$$n = \frac{\left\{\frac{d\ln i}{d\ln\theta}\right\}_E}{(1+\alpha' r\theta)} \qquad \text{(IV, 14)}$$

and in terms of the experimental reaction order, R,

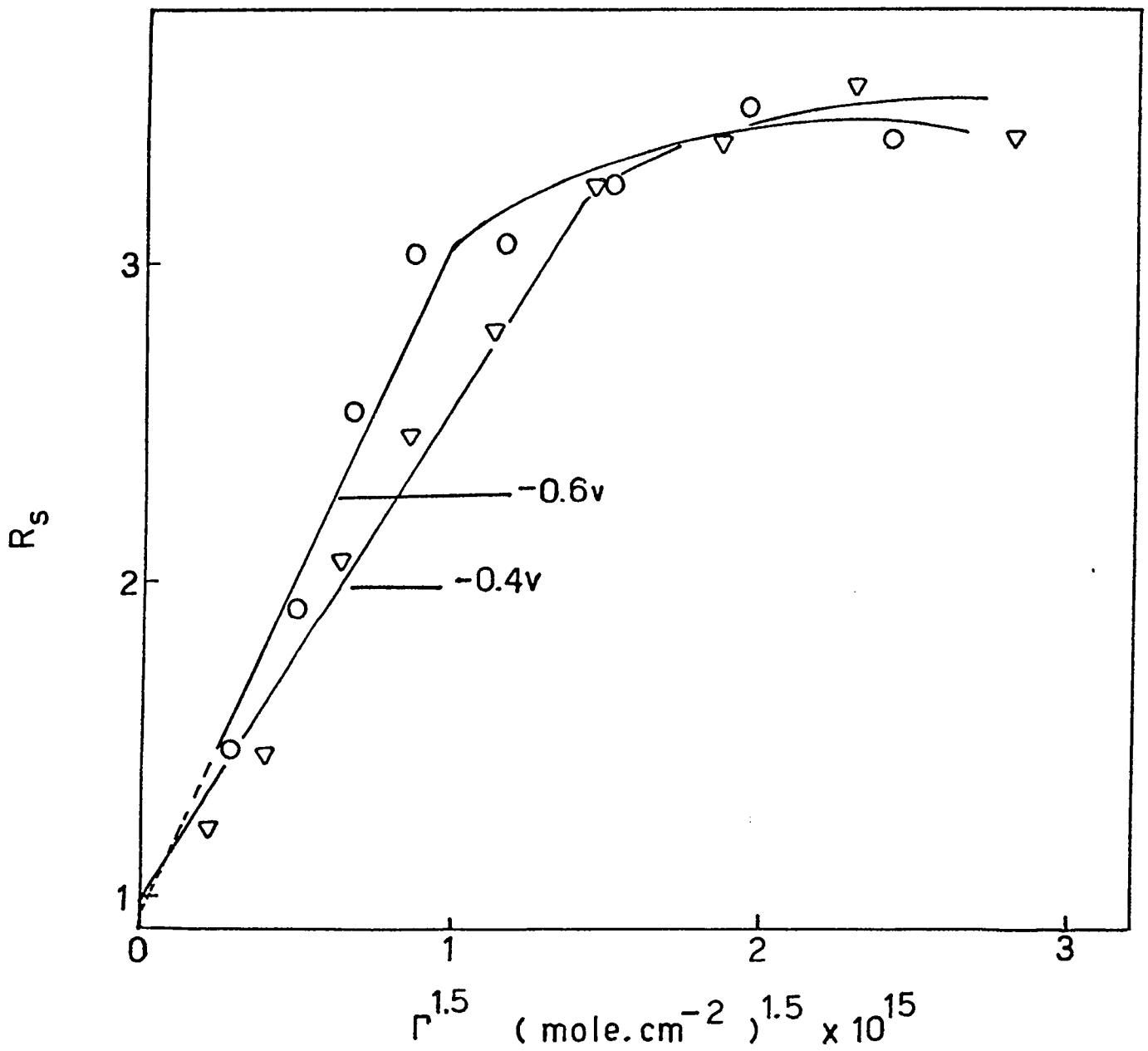
$$n = \frac{R}{\left\{\frac{d\ln\theta}{d\ln(C_R)_b}\right\}_E (1 + \alpha' r\theta)} = \frac{R_s}{1+\alpha' r\theta} \qquad \text{(IV, 15)}$$

In the present case, for nearest-neighbour dipole repulsion effects, the interaction term will have approximately the form $r'\theta^{3/2}$ and therefore

$$n = \frac{R_s}{(1+\frac{3}{2}\alpha' r'\theta^{3/2})} \qquad \text{(IV, 16)}$$

By plotting R_s against $\Gamma^{3/2}$ a linear relation is obtained in agreement with the predictions of equation (IV, 16) and the intercept then gives a value of 1 for the true molecularity of the surface reaction (see Figure 37), which is required in the interpretation of the kinetics.

Figure 37. Dependence of the apparent surface reaction order R_S upon the surface concentration of acetophenone $\Gamma^{3/2}$


R_s
3
2
1
0
1
2
3
-0.6v
-0.4v
$\Gamma^{1.5}$ (mole.cm^{-2})$^{1.5}$ x 10^{15}

6. THE SIGNIFICANCE OF THE LIMITING CURRENTS

The limiting currents observed at potentials more cathodic than those corresponding to the Tafel region may arise from one or from a combination of several factors, which may be summarised as follows:

(a) The current becomes limited either by the rate of diffusion of protons to the electrode surface or by the rate of protonation of the ketone at the electrode surface (here it is to be noted that two protons are consumed per mole of pinacol formed by the passage of two Faradays of charge).

(b) The overall rate of reaction is limited by the rate of diffusion of the ketone from the bulk solution to the electrode surface (cf. the condition which pertains in polarography, where the surface concentration of the reducible species is, limitingly, effectively zero).

(c) The product of the electro-reduction at low pH is the pinacol which is strongly adsorbed at the electrode surface and may consequently inhibit the progress of the reaction.

It has been shown (115,129) that over a certain pH range (from pH 5-7) the limiting current observed in the polarographic reduction of acetophenone (corresponding to the formation of the pinacol) is kinetically controlled, and the slow rate of protonation of the carbonyl group is thought to

be the limiting factor. In the present work, the steady-state rate of the electrochemical reaction was found to be strongly dependent upon the concentration of hydrogen ions in the solution, particularly at pH > 1 (Figure 18)*. The interesting result was also found that agitation of the solution increased the pH-dependent limiting currents which are observed at different pH values (Figure 18) although the ketone concentration was constant at 0.27 M. This indicates that the limiting currents at high pH values must be determined by the rate of diffusion of protons (involving either the species H_3O^+ or $MeOH_2^+$ depending on the solution) to the electrode surface. However, at pH < 1 the dependence of the rate of reaction upon the concentration of hydrogen ions rapidly diminishes and the reaction order with respect to the proton tends to zero (Figure 19 and see section 9 of this Chapter). Hence, under the usual experimental conditions i.e., pH = -0.3, the limiting current is essentially independent of the rate of diffusion of hydrogen ions to the electrode surface and then only determined by the concentration gradient of the ketone.

Mairanovskii (115,129) regards the protonated form of the ketone as the electro-active species in the polarographic reduction of aromatic ketones. Furthermore, it is suggested

* The study of the effect of change of pH upon the electro-reduction of acetophenone was confined to a range of concentrations of hydrogen ions greater than 10^{-3} g.ion. litre^{-1}, i.e., pH < 3 since in this pH-range only the pinacol is formed (102). Also it is preferable to avoid using other anions in higher pH buffers since such anions can introduce specific adsorption effects into the kinetics and thus obscure the significance of any effects which may be determined by changes of pH towards neutral values.

that protonation occurs essentially at the electrode surface, and for such a situation it would seem quite unlikely that agitation of the solution would affect the actual rate of that reaction occurring in the layer probably only 3-5 $\mathring{A}$ thick adjacent to the electrode surface. Hence the observed increase in the limiting current with agitation of the solution close to the working electrode probably reflects diffusion control.

In a recent polarographic study of the reduction of aromatic carbonyl compounds, Laviron (166) observed an anomalous dependence of the half-wave potential upon the logarithm of the bulk concentration of the ketone. He attributed this behaviour to the formation of a surface film of pinacol which may inhibit either the rate of dimerisation of the intermediate radicals or the rate of protonation of the carbonyl group at the electrode surface. Indeed, with benzophenone, it was observed in the present work that a visible film can be formed and similar observations have been made by Elving and Suzuki (120).

The molecular area of acetophenone pinacol has been determined (see p. 100) and for an electrode of surface area 0.1 cm.^{2} the concentration of pinacol in a monolayer (Γ_m) may be calculated as

$$\Gamma_m = \frac{10^{15}}{110 \times 6 \times 10^{23}} \text{ mole. cm.}^{-2}$$

$$= 1.52 \times 10^{-11} \text{ mole. cm.}^{-2}$$

and the charge required to form a surface monolayer will be 3.03 μC. With the passage of a steady current $i = 10^{-4}$ A, the time required to produce the monolayer of pinacol is therefore only 3.03×10^{-2} seconds. It can be seen that for steady-state measurements and in potentiodynamic studies at slow sweep-rates the electrode surface will probably always tend to be covered by pinacol. Significant diffusion of the product away from the surface (particularly since the bulk concentration of pinacol is effectively zero) will of course occur and the pinacol will also tend to become desorbed from the electrode interface as the potential becomes more cathodic, so that the surface concentration of pinacol will be reduced from saturation somewhat. Nevertheless, appreciable coverage may be anticipated.

This argument is supported by the observed lack of any effect of passage of nitrogen gas upon the current-potential profiles in the studies of the electrochemical behaviour of the pinacol (Figure 28), i.e., mass-transfer effects are absent.

Therefore, under the experimental conditions used in the present work, [i.e., with a stationary pool electrode and a bulk concentration of ketone greater than 10^{-2} mole litre^{-1} and with a hydrogen ion concentration approximately 2 g.ion litre^{-1}] it follows that the currents observed at potentials more cathodic than those in the Tafel region are limited mainly by the rate of diffusion of the ketone to the electrode surface.

7. REVERSIBILITY AND IRREVERSIBILITY OF ELECTROCHEMICAL REACTIONS

An electrochemical reaction occurring without any significant overpotential (η) is said to be reversible; conversely an electrode process involving a measurable over-potential is said to be irreversible. In diffusion controlled processes, as in polarography, the degree of reversibility of an electrode reaction can be regarded as depending upon

(a) the rate of transport of the electroactive species to the electrode and in particular, the limiting diffusion controlled rate, in relation to

(b) the overpotential associated with the rate of electron transfer required to produce the diffusion controlled flux of reactant.

Delahay (144) has pointed out that the distinction between reversible and irreversible electrode processes is somewhat artificial since a sufficiently large increase in current will, in any reaction, establish an overpotential and hence so-called irreversibility.

A criterion for the reversibility of polarographic processes has been discussed by Delahay (144). The distinction is based upon the value of the heterogeneous rate constant k (see Chapter I, p. 8) and it is concluded that with $k > 2 \times 10^{-2}$ cm. sec.$^{-1}$ the process is virtually reversible. Under these conditions, the rate of the electrochemical step is so high that the overall rate of reaction is diffusion limited. Hence the current and the electrode potential are then determined, through Nernst's equation, very largely by the surface concentration of the electroactive

species. As the value of k decreases, the shape of the polarographic wave changes and it becomes more "drawn out". It was calculated (144) that the effect of the reverse reaction can be neglected for any value of k less than 3×10^{-5} cm. sec^{-1} and the wave is then totally irreversible.

The magnitude of the exchange current density (i_o) may be regarded as an equivalent criterion of the reversibility or irreversibility of an electrochemical reaction, although it involves the additional factor of reactant concentration. Briefly, a high value of i_o is usually taken to indicate a reversible process, as in the hydrogen evolution reaction at platinised platinum ($i_o \simeq 10^{-3}$ A. cm^{-2}). Conversely, the very low i_o value (10^{-13} A. cm^{-2}) which is obtained for the same reaction at a mercury electrode reflects the irreversibility of the process under these conditions.

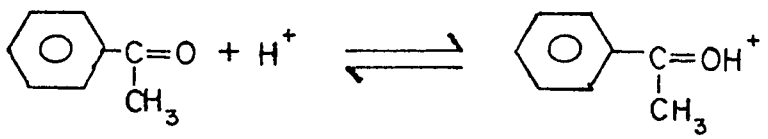
At currents appreciably displaced from the exchange current the rate of the reverse reaction of the process is negligible and the current is then essentially an exponential function of the potential. Consequently, the logarithm of the current varies linearly with the potential (Tafel behaviour). Extrapolation of the linear (Tafel) region of the relation between log[current] and potential to the condition $\eta = o$ gives the exchange current density i_o. This pre-supposes that the potential corresponding to this condition ($\eta = o$) is known, i.e., that the reversible potential for the electrode

reaction is known or can be determined e.g., from appropriate thermodynamic data. In the case of many organic electrode processes, however, the required thermodynamic data is not available and E_r cannot be calculated.

Under these circumstances the Tafel slope may be used to indicate another aspect of the degree of reversibility of the electrode reaction. Since a reversible reaction should occur essentially without significant overpotential, then not only should i_o be preferably large but the slope of the log[i]-E curve should be low, and large values of the Tafel slope would therefore reflect the irreversibility of the electrode process in another way.

8. THE SIGNIFICANCE OF THE EFFECT OF pH

It is generally considered that it is essentially the neutral ketone which diffuses to the electrode surface (112) and evidence which would indicate that protonation occurs at the surface to form the electroactive species has been presented and discussed in Chapter I (see p. 37-38). The equilibrium constant for the protonation of acetophenone in strongly acidic solutions has been measured spectrophotometrically (113); thus for the reaction



$$K' = \frac{[PhC(\overset{+}{O}H)CH_3]}{[PhCOCH_3][H^+]} = 10^{-6} \qquad (IV, 17)$$

so that

$$[PhC(\overset{+}{O}H)CH_3] = 10^{-6}\,[H^+][PhCOCH_3]. \qquad (IV, 18)$$

It is obvious that under the experimental conditions used, the concentration of the protonated ketone will be very small even at the surface where the hydrogen ion concentration is somewhat larger than in the bulk solution (possibly by a factor of 10).

The current obtained at a given potential may be represented as a composite one, comprising the sum of partial currents corresponding to electron transfer to both the neutral and the protonated species; viz.

$$i = k_K c_K e^{-E/b} + \left(k_{KH^+}\right)\left(c_{KH^+}\right)\, e^{-E/b} \qquad (IV, 19)$$

where k_K and k_{KH^+} are the rate constants for the electron transfer to the neutral and charged species, respectively. In this equation, $b = \frac{RT}{\beta F}$ and is regarded as being the same for both reactions (e.g., the same value of b is obtained in the hydrogen evolution reaction at nickel in aqueous acid and in alkaline solutions where sources of protons are H_3O^+ or H_2O).

Since $$C_{KH^+} = 10^{-6}\, C_K C_{H^+} \qquad (IV, 20)$$

$$i = k_K C_K e^{-E/b} + \left(k_{KH^+}\right).\left(10^{-6}\right)\left(C_K\right)\left(C_{H^+}\right) e^{-E/b} \quad \text{(IV, 21)}$$

It can be seen that if the rate of electron transfer to the protonated species contributes significantly to the overall rate of reaction (as measured by the current i) then $k_{KH^+} > 10^6 k_K$ and in this event the current should be markedly dependent upon the pH of the solution. This is experimentally observed (Figure 18) particularly above pH = 1 and it would therefore seem that the electroactive species is the protonated form of the ketone as indicated in related ways by the polarographic results. Furthermore, the reaction order with respect to hydrogen ions is unity in the limiting current region and is thus again in agreement with the equation (IV, 21).

In the Tafel region (at E = -0.65 V vs E_H), the reaction order with respect to $[H^+]$ is somewhat less than one. At pH = 2.3 the rate of the electro-reduction is diminished so that background currents (which were attributed to the electro-reduction of an impurity in the solvent or to presence of dissolved oxygen) mask the Tafel region until fairly high cathodic potentials are reached (Figure 20). Extrapolation of the linear region of the log[current]-potential curve at this pH value gives a current at E = -0.65 V vs E_H which is substantially lower than that expected if the reaction order were one with respect to hydrogen ion. In fact a direct comparison with the current obtained at this potential in a solution of pH = 1.47 would suggest a reaction order of 2.2.

It has been found that acetophenone pinacol facilitates the evolution of hydrogen from the 20% water-methanol solvent mixture and, as has been discussed in Chapter III, p, 97, this process may involve discharge from a protonated form of the pinacol (cf. H_3O^+ or $MeOH_2^+$). at the electrode surface. A surface layer of the product of the electro-reduction will therefore effectively lower the concentration of hydrogen ions in the double-layer but provide an alternative source of H^+ for discharge to H_2 as in the case of the catalytic effect of adsorbed alkaloids referred to in Chapter III. Certainly the rate of the electrochemical reaction is sensitive to the bulk concentration of hydrogen ions, but more realistically (since the kinetically significant protonation of the ketone occurs in the surface boundary layer) must be sensitive to the concentration of hydrogen ions in the double-layer. It would appear that there may be competitive protonation occurring at the surface, between ketone and the pinacol, and at a low concentration of hydrogen ions the presence of the pinacol may retard the protonation of the ketone to a relatively greater extent (in comparison with the situation at lower pH) and hence diminish the overall rate of the reaction.

In the limiting current region of the log[i]-E curve, the reaction order with respect to hydrogen ion decreases with decreasing pH (at pH $<$ 1) and the reaction appears then to become virtually independent of pH. At the high cathodic

potentials corresponding to the limiting current (E = -0.8 V and higher), it has been shown from potentiodynamic studies that the pinacol may be desorbed from the surface (see p. 97 and Figure 30). The protonation of the ketone would then be less retarded and the overall rate of reaction may no longer be limited by the rate of protonation but only by the rate of diffusion of the ketone to the surface.

9. THE SIGNIFICANCE OF TAFEL SLOPES OBSERVED IN THE ELECTRO-REDUCTION OF ACETOPHENONE

For certain favourable cases, the Tafel slope may be correlated with the nature of the rate-determining step and reaction order of an electrochemical reaction. For the discharge of a neutral or ionic species at an electrode surface, the well-known Tafel slope of approximately 118 mV ($\simeq \frac{2RT}{F}$) is usually obtained, e.g., in the hydrogen evolution reaction at a mercury electrode b = 118 mV in both acidic solutions (where the species discharged is the hydroxonium ion H_3O^+) and in alkaline solutions (where the neutral water molecule is involved). In relation to the comments in section 7 above, the electrochemical reduction of acetophenone is to be regarded as irreversible both on account of the appreciable Tafel slopes observed and the low exchange current density ($< 10^{-6}$ a.cm.$^{-2}$ since linear log[i]-E behaviour persists down to at least this current density).

In the case of electro-reduction of acetophenone, physical or electrostatic adsorption of the ketone is involved and orientation of the polar carbonyl group at the surface may be anticipated and is in fact indicated by the electrocapillary data. It has also been shown from the analysis of the electrocapillary data that interaction effects occur in the adsorbed layer and so-called Temkin adsorption behaviour is found. The product of the reaction, acetophenone pinacol, is strongly adsorbed at the electrode surface and the presence of this molecule may further complicate the reaction mechanism and electrode kinetic behaviour.

When the electro-reduction reaction is carried out in a partially aqueous solvent, the Tafel slope is found to be somewhat dependent upon the bulk concentration of the ketone but at $(C_R)_b > 0.2$ mole. litre^{-1}, a constant value of $b = 50$ mV ($\simeq \frac{RT}{F}$) is obtained.

In the absence of water (i.e., in nominally anhydrous methanol), a similar dependence of b upon the bulk concentration is found. However, the values of b are always significantly higher than those obtained in the partially aqueous system, and upon gradually increasing the water content (from 0 to 20 mole %) the Tafel slope gradually <u>decreases</u> to the value of 50 mV. In the presence of water in concentrations greater than 20 mole %, the Tafel slope is found, however, to remain at <u>ca.</u> 50 mV [see Table II (c)]. It is not easy to suggest

any unambiguous reason for this behaviour, but two possible explanations will be presented below. It is possible that the solvent composition at the interface may undergo significant changes as the water content in the bulk of the solution is increased.

At the cathodic potentials at which the reaction occurs, the desorption of methanol molecules from the electrode surface and their replacement by water molecules may affect either the rate of protonation in the interfacial region or the adsorption behaviour of the pinacol, or both.

The composition of the adsorbed layer of solvent molecules at a mercury electrode in solutions of water and methanol has been studied by Parsons and Devanathan (167). The relative surface excess of methanol was determined from electrocapillary curves and expressed as the function $[\ \Gamma_A - \frac{\Gamma_W x_A}{x_W}\ ]$, where Γ_A and Γ_W are the surface excess quantities and x_A and x_W are the mole fractions of methanol and water, respectively. At potentials E > -0.6 V. *vs* the hydrogen electrode in 0.1 N hydrochloric acid, the surface excess of methanol decreased markedly as x_M increased and it is of interest to note that this behaviour occurs over the potential range in which electro-reduction of acetophenone takes place. The authors attributed this effect to the fact that the polarisation of the methanol molecule increases less rapidly than that of water so that the methanol becomes

replaced at the interface as the strength of the electric field increases with increasing cathodic electrode potential.

The surface mole fraction of methanol $\frac{\Gamma_A}{\Gamma_A + \Gamma_W}$ at a given potential may also be calculated from the following expression (167)

$$\frac{\Gamma_A}{\Gamma_A + \Gamma_W} = \frac{\frac{x_A}{x_W} - S_W \left[\Gamma_A - \frac{\Gamma_W x_A}{x_W} \right]}{\frac{1}{x_W} + (S_A - S_W) \left[\Gamma_A - \frac{\Gamma_W x_A}{x_A} \right]} \qquad (IV, 22)$$

where S_A and S_W are the molecular areas of methanol and water, respectively. Using equation IV, 22 with the results of Parsons and Devanathan it may be shown that the surface mole fraction of methanol is greater than that in the bulk solution over the range of potentials E = -0.5 to -0.8 V. for solutions where $x_A > 0.7$.

Experimental evidence (168,169) indicates that methanol is a weaker base* than water, so that in pure methanol (or under conditions where a relative surface excess of methanol molecules is present in the adsorbed layer) the protonation

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* The value of a basicity constant r was determined by conductometric methods and a value of 0.25 (0.235) has been reported; r is defined by

$$r = \frac{[MeOH_2^+]\,[H_2O]}{[H_3O^+]}$$

of the ketone may be expected to be facilitated.

The change of the Tafel slope is relatively sharp as the water content in the solvent is increased, particularly at concentrations of water lower than 5 mole % (Figure 38). A similarly sharp change is shown in the dependence of b upon the surface mole fraction of methanol, which was calculated, as described above, from the data presented by Parsons and Devanathan (167). The relationship between the Tafel slope b and the bulk concentration of the $MeOH_2^+$ species* is also shown in Figure 38 and again a trend is observed which is parallel to those discussed above, although the change is more gradual (it is to be noted that the surface concentration of $MeOH_2^+$ cation species at the negatively charged electrode surface will be higher than the bulk concentration) and since b is probably more sensitive to the surface concentration, then the true dependence of b upon the kinetically significant concentration of the $MeOH_2^+$ species may not be obtained from the plot (curve 3 of Figure 38) expressed in terms of bulk concentration of $MeOH_2^+$ species .

It would appear that two effects may contribute to the observed change in the value of b with solvent composition.

(a) The increase in concentration of the species $MeOH_2^+$ at the surface as the water content decreases may lead

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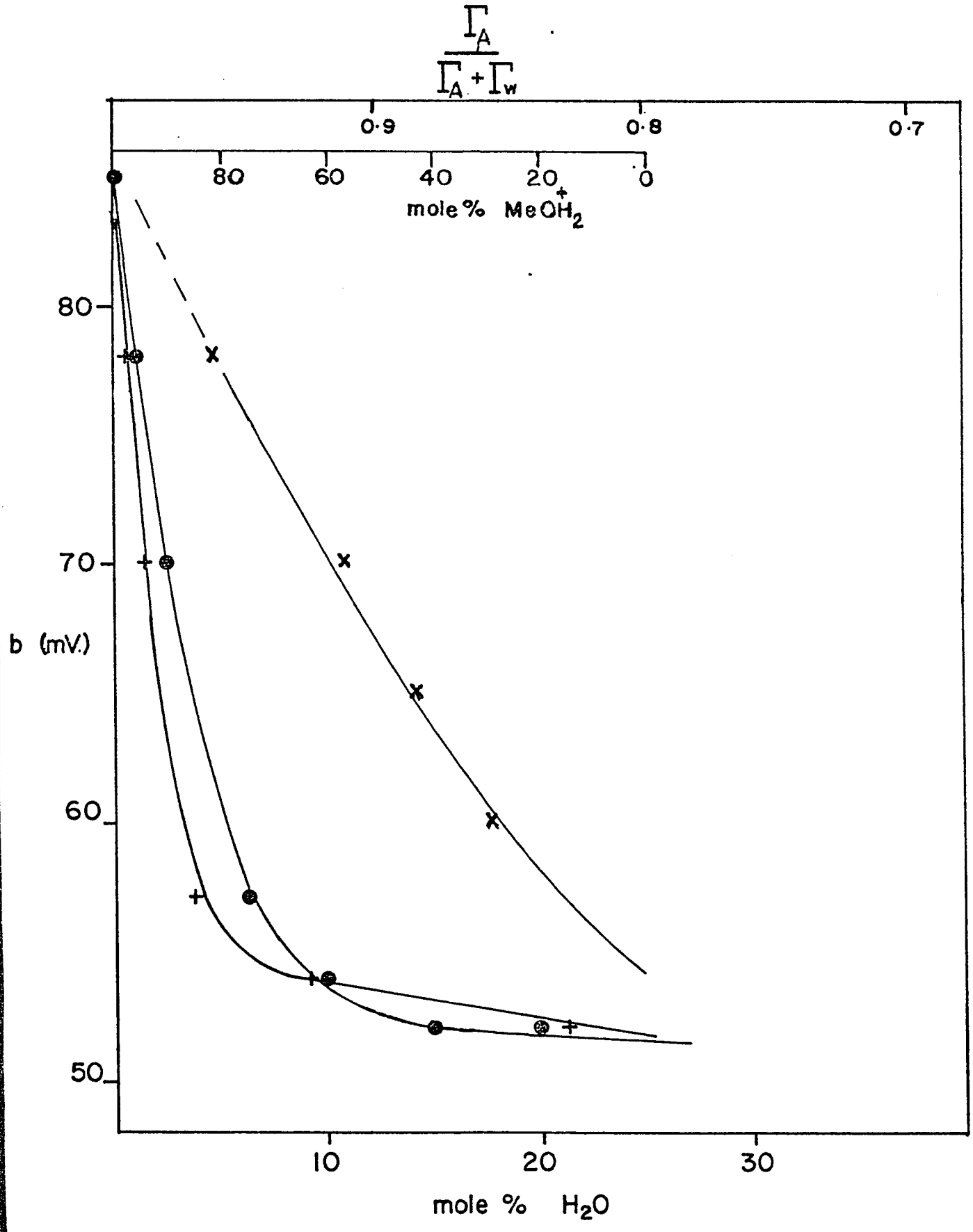
* The values of % $MeOH_2^+$ in the solution were obtained from calculations (170) on the distribution of protons in aqueous alcohol solutions.

Figure 38. Dependence of the Tafel slope b upon the solvent composition

(o) b *vs* mole % water

(+) b *vs* surface mole fraction of methanol

(×) b *vs* mole % $MeOH_2$ species.


$\frac{\Gamma_A}{\Gamma_A + \Gamma_w}$
0·9
0·8
0·7
80
60
40
20
0
mole % $MeOH_2^+$
80
70
60
50
b (mV.)
10
20
30
mole % H_2O

to an easier protonation of the ketone since $MeOH_2^+$ is a stronger acid than H_3O^+.

(b) The surface mole fraction of methanol increases and approaches unity both as the bulk mole fraction of methanol increases and as the potential becomes more cathodic. This may lead to a diminution of the surface concentration of both the reactant and the product.

Comparison of the relations between Γ and $\log(C_R)_b$ obtained from the electrocapillary studies in methanol-water solution and in nominally anhydrous methanol (Figures 30 and 31) indicates:

(a) that the surface concentration of the reactant is lower in the nominally anhydrous solutions, and

(b) that the linearity (Temkin adsorption behaviour) between Γ and $\log(C_R)_b$ holds only over a smaller range of bulk concentration in methanol than in the partially aqueous solution.

The net result of one or both of these effects is that electrochemical discharge could become the rate-determining step as discussed below and the Tafel slope would then approach a limiting value b = 118 mV in the complete absence of water in the solvent.

A change of the concentration of hydrogen ions in the bulk solution does not, however, change the Tafel slope (Figure 18) and it is likely that the electro-active species

at the electrode surface will be the same over the pH range which was studied; evidence leading to the identity of that species is given below, based upon the pH dependence of the rate of the reaction and the derived reaction order in H^+.

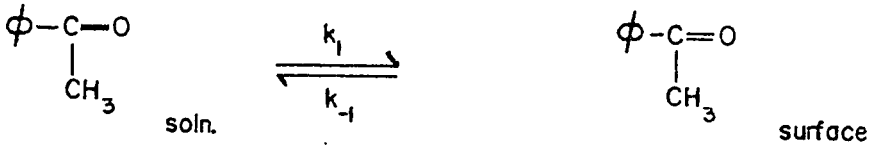
The unusual sensitivity of the electrode kinetics to solvent composition and to pH indicates that protons are involved in the overall reaction [cf. the pH-dependence of the half-wave potential of the first polarographic wave observed in the reduction of aromatic carbonyl compounds (112,115,120, 133,134)]. However, in the present work it has been found that the primary H/D isotope effect is small and much less than that for the hydrogen evolution reaction in acid solution at a mercury electrode. This clearly indicates that proton transfer is not critically involved in the rate-determining step of the mechanism. The small magnitude of the H/D isotope effect (near to unity) indeed supports the view that an equilibrium rather than a kinetic isotope effect is involved with the proton.

10. MECHANISM OF THE REACTION

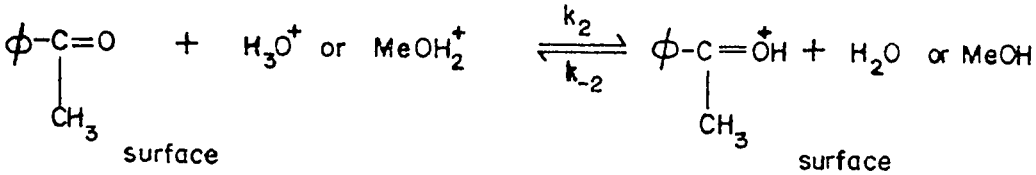
(a) General Aspects

The following mechanism will now be considered in relation to the above observations:

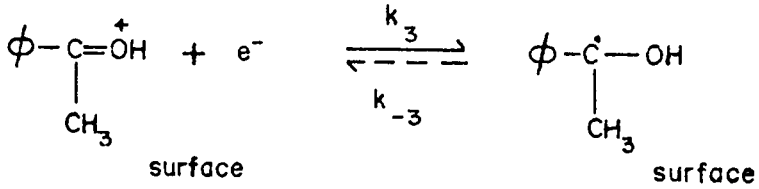
STEP I



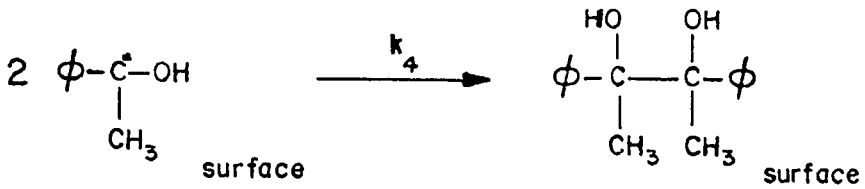
STEP II



STEP III



STEP IV



The recombination reaction (step IV) may occur at the electrode surface or the carbinol free radicals may diffuse into the solution and the recombination occur as a homogeneous process. The stereochemistry of the products of electro-reduction of benzaldehyde has been studied recently (171) and it was concluded that in the presence of specifically adsorbed ions, e.g., $(n\text{-}Bu)_4N^+$, the recombination step probably occurred at the surface. Elving and Suzuki (120) also concluded that the free radicals recombined at the surface in the polarographic reduction of benzophenone in acidic solutions.

It has been shown in the present study that acetophenone pinacol is strongly adsorbed at the mercury electrode and that it remains significantly adsorbed at high cathodic potentials (Figure 32). The pinacol molecule or the protonated form of the pinacol may then act as a specifically adsorbed blocking species at the electrode surface thus causing the recombination step to be rate-controlling.

(b) Recombination Mechanism and Tafel Slopes

The Tafel slope of 59 mV ($2.3 \frac{RT}{F}$) observed in the present work is an unusual one (it corresponds to an α factor of 1) and its variation towards a higher value as solvent composition is varied below 20 mole % water presents features of special interest.

The Tafel slope of $2.3\frac{RT}{F}$ (b = 59 mV. at 25°C) could arise for a rate-controlling surface recombination of the ketyl radicals under Temkin conditions of adsorption (cf. refs. 163-165). Thus, if the rate of recombination is given by

$$v_4 = k_4 \theta_k^2 \exp\left[\frac{2\beta' r\theta_k}{RT}\right] \qquad \text{(IV, 23)}$$

(where β' is a symmetry factor of ca. 0.5 analogous to β in a discharge step) and if the coverage θ_k is determined by a potential-dependent quasi-equilibrium in step III (characterised by a constant K_1), then

$$K_1\left(C_{KH^+}\right) = \exp\left[-\frac{(FE - r\theta_k)}{RT}\right] \qquad \text{(IV, 24)}$$

Substituting for C_{KH^+} in terms of C_K from equation (IV, 20) and expressing (IV, 24) in a logarithmic form gives

$$\ln K' + \ln k_1 + \ln C_K = \ln C_{H^+} + \frac{FE}{RT} = \frac{r\theta_K}{RT} \qquad \text{(IV, 25)}$$

and then

$$\ln v_4 = \ln k_4 + \ln\theta_k^2 + 2\beta' \ln K_1 + 2\beta \ln K' + 2\beta' \ln C_K + 2\beta' \ln C_H + \frac{2\beta' FE}{RT} \qquad \text{(IV, 26)}$$

which gives a reaction order of one with respect to both acetophenone and hydrogen ion ($\beta' \doteqdot 0.5$) and a Tafel slope of $\frac{RT}{F}$ (b = 59 mV) for significant coverage of the electrode

surface by acetophenone, i.e., $1 > \theta_K \gg 0$.

However, in nominally anhydrous methanol (and in solutions containing only small amounts of water, i.e., mole % $H_2O < 5\%$, so that the surface mole fraction of methanol approaches unity) the rate of the recombination process (step IV) may no longer be rate-controlling if either:

(a) the radicals are immediately desorbed from the electrode surface and recombination then occurs homogeneously in the solution, or

(b) recombination at the surface is less hindered by the presence of adsorbed pinacol and is therefore no longer the rate-determining step.

In solutions containing only small amounts of water, the electrochemical discharge step* may then become rate-determining so that the value of the Tafel slope would therefore approach $\frac{RT}{\beta F}$, where $\beta = 0.5$, a situation which corresponds to an irreversible electron transfer step in the electrode process.

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* From studies of the polarographic reduction of aromatic carbonyl compounds many workers consider the electron transfer process to be reversible although, in the case of acetophenone, Mairanovskii (115) established that with increased concentration of the ketone, the electron transfer became irreversible. This effect, attributed to the formation of pinacol at the surface, was diminished by presence of alcohol in the solution (129). In the present work, although logarithmic current-potential behaviour is still observed in the high and 100% methanol-content solutions, the currents actually passing at a given potential (see Figure 20) in the region corresponding to polarographic conditions are in fact increased with increasing methanol content and the behaviour, in this respect, is hence consistent with Mairanovskii's observations and Elving and Suzuki's experiments (120) with benzophenone.

The logarithmic current-potential behaviour and the fairly large values of b obtained in the present work, particularly when the electro-reduction is carried out in nominally anhydrous methanol, certainly indicates that the electrode process is to be regarded as completely irreversible (see section 7 of this chapter). However, Elving and Suzuki (120) have pointed out that a succeeding, very fast and irreversible chemical step (such as the dimerisation envisaged here) may make the overall reaction appear irreversible although the process of electron transfer itself is reversible. The specific rate constants for the dimerisation of certain ketyl radicals have been measured in fast cyclic voltammetry (145) and are shown below:

Xanthone$^{\bullet}$ $k_d^{*} = 1 \times 10^7$

Fluorenone$^{\bullet}$ $k_d = 3 \times 10^6$

Benzophenone$^{\bullet}$ $k_d = 6 \times 10^7$

It seems reasonable to suppose approximately that the lifetime of the ketyl radical decreases and the rate of recombination to the pinacol increases with decreasing delocalisation of the odd electron in the free radical.

The rate of recombination of the ketyl radical formed in the electro-reduction of acetophenone under the conditions of fast cycling will also be very

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* The values measured are for the dimerisation reaction

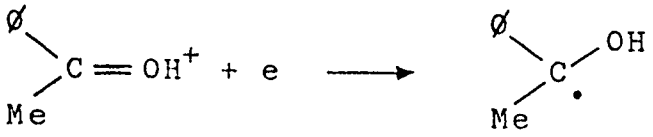
$$.RH + .RH \xrightarrow{k_d} HR{-}{-}RH$$

occurring in acidic solutions (pH $\simeq$ 1). k_d is accordingly expressed in the units litre. mole^{-1} sec^{-1}. The values for k_d recorded above may not, however, refer to the steady-state kinetics considered in 10 b since in fast cyclic voltammetry, the inhibiting effect of adsorbed product pinacol may be much diminished.

fast (say $k_d \simeq 10^8$) and, as has been suggested (Chapter III, p. 91), this may account for the failure to detect the re-oxidation process in anodic potentiodynamic sweeps even at high sweep-rates. In a recent study of the electro-reduction of acetone, Brown and Lister (93) showed that at very high voltage sweep rates ($\frac{dE}{dt}$ = 150 and 960 V. sec^{-1}) re-oxidation of the carbinol free radical could be detected and that the electrode process was reversible under these conditions (see later section 12).

(c) "Barrierless" Discharge and Tafel Slopes

An alternative possibility which can provide an explanation of the change of Tafel slope with solvent composition may be examined in terms of the condition of so-called "barrierless discharge", a type of process which has been theoretically discussed by Krishtalik (172) for the hydrogen evolution reaction. In the present case, the principle may be examined in relation to the step



in which the reverse of this process is barrierless, i.e., reoxidation of the radical could be a very rapid process. The "barrierless" situation arises in a discharge step when the potential energy profile "cuts" that of the product at

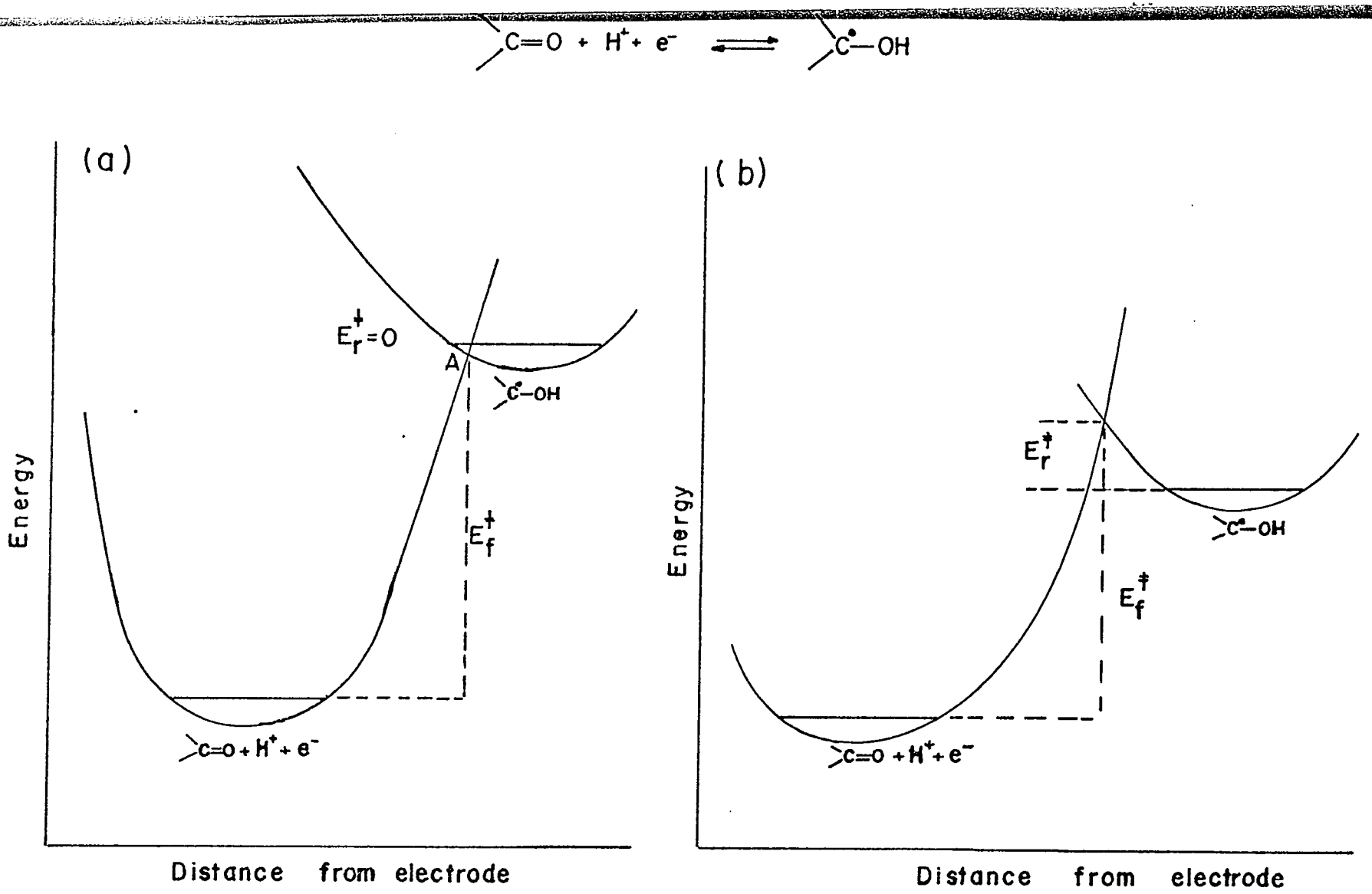
the transition state within the zero-point energy region (point A) as shown schematically in Fig. 39(a). An activation energy $E^{\ddagger}$ is then involved in the forward discharge process and is equal to the endothermicity of the reaction; zero activation energy is associated with the reverse process. Similar behaviour is related to several radical reactions in the gas phase. Changes of the energy of the initial state on account of changes of electrode potential EF then change the activation energy by βEF where β the electrochemical Brønsted or symmetry factor is now unity (Figure 39a) so that the Tafel slope is $\frac{RT}{F}$ instead of approximately RT/0.5 F. When the crossing region at the transition state falls outside the zero point region of the product state (Figure 39b), there will be a change of activation energy with changing electrode potential in the usual way but β will still be smaller than 0.5 until the transition state occurs well away from the zero point level of the product. This type of situation therefore allows

(a) the unusual Tafel slope value of ca. $\frac{RT}{F}$ to be explained and

(b) its variation towards larger values as the condition shown in Figure 39(b) applies.

In regard to the case of acetophenone reduction this type of condition could apply as follows. If the radical produced as a result of discharge is not chemisorbed, a situation

Figure 39. Schematic representation of the potential energy profiles of an electrochemical reaction involving a "Barrierless" discharge step.


C=O + H⁺ + e⁻
C•—OH
(a)
Energy
$E_r^{\ddagger}=0$
A
C•—OH
$E_f^{\ddagger}$
C=O + H⁺ + e⁻
Distance from electrode
(b)
Energy
$E_r^{\ddagger}$
C•—OH
$E_f^{\ddagger}$
C=O + H⁺ + e⁻
Distance from electrode

exactly like that of Fig. 39(a) should obtain and a Tafel slope of $\frac{RT}{F}$ will result, so that this situation should apply to the behaviour observed in the appreciably aqueous solutions with water content $\geqslant$ 20%. Physically, such a situation may be realised when it is recalled that it is the protonated species which is neutralised in the discharge step and the charged centre may then be expected to reside, in a hydrated or solvated condition, away from the surface in the outer Helmholtz plane. Chemisorption of the resulting radical may not then be involved so that the situation is like that shown in Fig. 39(a). Recombination may then occur in the outer Helmholtz region of the double-layer or after diffusion into the solution.

In the aqueous solution, water will preferentially populate the inner region of the double-layer and its displacement at appreciable cathodic potentials by a large organic molecule is usually energetically difficult. In more concentrated or limitingly pure methanol solutions, on the other hand, it may be easier for the radical to approach the surface by displacing the methanol and then to become temporarily chemisorbed* (cf. the case of H atoms at Hg in the discharge step of the hydrogen evolution reaction). The potential energy profile will then

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* Chemisorption of the ketyl radical has, for example, been postulated by Brown and Lister (93) in a study of the electroreduction of acetone.

approach that of Fig. 39(b) where the radical is stabilised to some extent by interaction with the mercury surface as in the case of H^+ discharge. Changes of potential EF will then cause changes of activation energy of β EF where β is now a more normal symmetry factor no longer unity (as for Fig. 39a), so that the Tafel slope will be increased above $\frac{RT}{F}$ and, limitingly, vary towards a value of RT/0.5 F as observed. The reverse process of reoxidation then also has a finite activation energy.

While the above explanation is an attractive one in relation to the nature of the radical production and the solvent effects, it is to be noted that slopes somewhat lower than 59 mV. ($\frac{RT}{F}$) are observed in the present work, a situation that might render the above explanation in terms of the condition shown in Fig. 39(a) doubtful. However, it must be recalled that with changing measured potential, double-layer ψ-potential effects render only part of the measured potential available for changing the rate, and also modify the surface concentration of cations so that small deviations from the $\frac{RT}{F}$ slope could be tolerated within the mechanism proposed.

The situation represented in Fig. 39(a), which it has been suggested applies to the more aqueous solvent mixtures, must correspond to the case where re-oxidation can be a very rapid process. This is consistent with the view put forward

by Elving and Pullman (56) that a "slow" electron transfer actually involves orientation of the electro-active species at the electrode. Here the species is already oriented so that re-oxidation could occur rapidly. It is also not inconsistent with the observations made in the present work that no re-oxidation could be detected in anodic sweep measurements. If the recombination under these conditions (since the radical species is not chemisorbed) also occurs very rapidly, an extremely fast sweep might be necessary in order to re-oxidize the discharged radicals before they recombine. particularly since the discharge is irreversible so that appreciably cathodic potentials would have to be reached in the reverse (anodic) sweep to cause the re-oxidation.

In conclusion, therefore, this approach leads to the expectation that in solutions containing only small amounts of water the mechanism of the electrode reaction will be an irreversible electron discharge step. The presence of significant concentrations of water in the surface layer leads to a "barrierless" condition for the discharge step due to the absence of significant chemisorption of the resulting radical so that the Tafel slope approaches a value of 59 mV.

(d) Summary of Conclusions on Mechanism and Tafel Slopes

In Table X below are summarised the various mechanistic possibilities for the Tafel slope, reaction order and H/D solvent isotope effect. Experimentally, under all conditions

Table X

Summary of Kinetic and Mechanistic Possibilities

for Acetophenone Reduction

Step	Reaction order R	Tafel slope (limiting values)	Isotope effect etc.
III	1, $f(\theta)$ n=1	$RT/\beta F$ or less depending on potential-dependent reactant adsorption; latter effect could depend on solvent	no primary isotope effect
III	0, $\theta \longrightarrow 1$ n=1	$RT/\beta F$	
III	1, n=1	$RT/F \longrightarrow \frac{RT}{\beta F}$ (Barrierless Discharge)	no isotope effect if discharge is to previously protonated ketone
IV	2, $f(\theta)$ n=2	RT/2F; Langmuir conditions; III in quasi-equilibrium	no primary isotope effect
IV	1, $f(\theta)$ n=2	RT/F; "Temkin" conditions; III in quasi-equilibrium	no primary isotope effect
IV	0; $\theta \longrightarrow 1$ n=2	limiting current	-

investigated, the apparent and true reaction orders in ketone are near to unity and the Tafel slope varies from approximately $\frac{RT}{F}$ towards a value RT/0.5 F corresponding to rate controlling discharge of a species already protonated in a prior equilibrium step.

11. RELATION OF THE PRESENT WORK TO THE THEORETICAL EQUATIONS DERIVED BY KOUTECKY AND HANUS

The electro-reduction of acetophenone has been studied by Brown (173)*, using concentrations of the ketone, pH and a solvent system which were identical with those used in the present work. The reaction order with respect to both the ketone and the hydrogen ion was found, however, to be 1.5 and a Tafel slope of 40-42 mV. was obtained. It was further pointed out by Brown that these results agreed with the theoretical equations derived by Koutecky and Hanus (119) for the current-potential relationship for a reversible electrode process followed by a rapid, irreversible dimerisation process.

The polarographic waves obtained in the reduction of aromatic carbonyl compounds at low pH illustrate the effect of a succeeding dimerisation reaction upon an electrode process. The electron transfer process may be regarded as reversible (102,112,115,124,129,133,134,166) and the primary product must be a free radical (i.e., with prior or subsequent proton

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* Here reference is made to the unpublished work of Brown reported as a discussion contribution in a Faraday Society Discussion.

transfer from the solution). The subsequent dimerisation of these radicals yields the pinacol. Koutecky and Hanus (119) have given both an exact and an approximate solution for the current passing under polarographic conditions for an overall reaction of this type. The equation of the polarographic wave is expressed as

$$\frac{\left\{\frac{i}{i_d}\right\}^3}{\left\{1-\frac{i}{i_d}\right\}^2} = \frac{k'(C_R)_b \lambda^3 t}{1.51} \qquad \text{(IV, 27)}$$

where i is the average current at the potential E along the wave, i_d is the average diffusion current, $(C_R)_b$ is the bulk concentration of reducible species, t is the drop time and k' is the specific rate constant for the dimerisation reaction. λ is a potential-dependent function given by

$$\lambda = \exp\left[\frac{zF}{RT}(E_r^o - E)\right] \qquad \text{(IV, 28)}$$

where E_r^o is the standard redox potential for the reversible electrode process. The current-potential equation is then

$$E = E_r^o + \frac{2.303RT}{3zF}\log\frac{k't}{1.51} + \frac{2.303RT}{3zF}\log(C_R)_b - \frac{2.303RT}{3zF}\log\frac{i^3}{i_d(i_d-i)^2} \qquad \text{(IV, 29)}$$

and with R, T and F having their usual values and z = 1, the equation is simplified to the form

$$E-E_r^o = 0.02 \log \frac{k't}{1.51} + 0.02 \log (C_R)_b - 0.06 \log i + 0.02 \log i_d + 0.04 \log (i_d - i) \qquad \text{(IV, 30)}$$

The specific rate constant for the dimerisation of the ketyl radical in the reduction of acetophenone is given a value 10^8 litre. mole^{-1} sec^{-1}, which is based upon the results of a study of the rates of dimerisation of ketyl radicals of fluorenone and xanthone which have recently been reported by Grabowski *et al.* (145). In a typical polarographic experiment the drop time t is 3 seconds. Since the limiting current (i_d) can be calculated from the Ilkovic equation (see Chapter I, p.25) for a chosen concentration of the ketone, then corresponding current-potential curves can be constructed*. In this way "polarographic" waves for the depolarisation scheme envisaged by Koutecky and Hanus (119) have been derived for bulk concentrations of acetophenone of (a) 10^{-2} mole. litre^{-1} and (b) 5×10^{-1} mole. litre^{-1}.

The log[current]-potential curves corresponding to the calculated values of current and potential at both concentrations are shown in Figure 40. A linear (Tafel) region is obtained over perhaps two current decades [at $(C_R)_b = 5 \times 10^{-1}$ mole.

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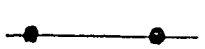
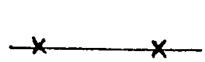
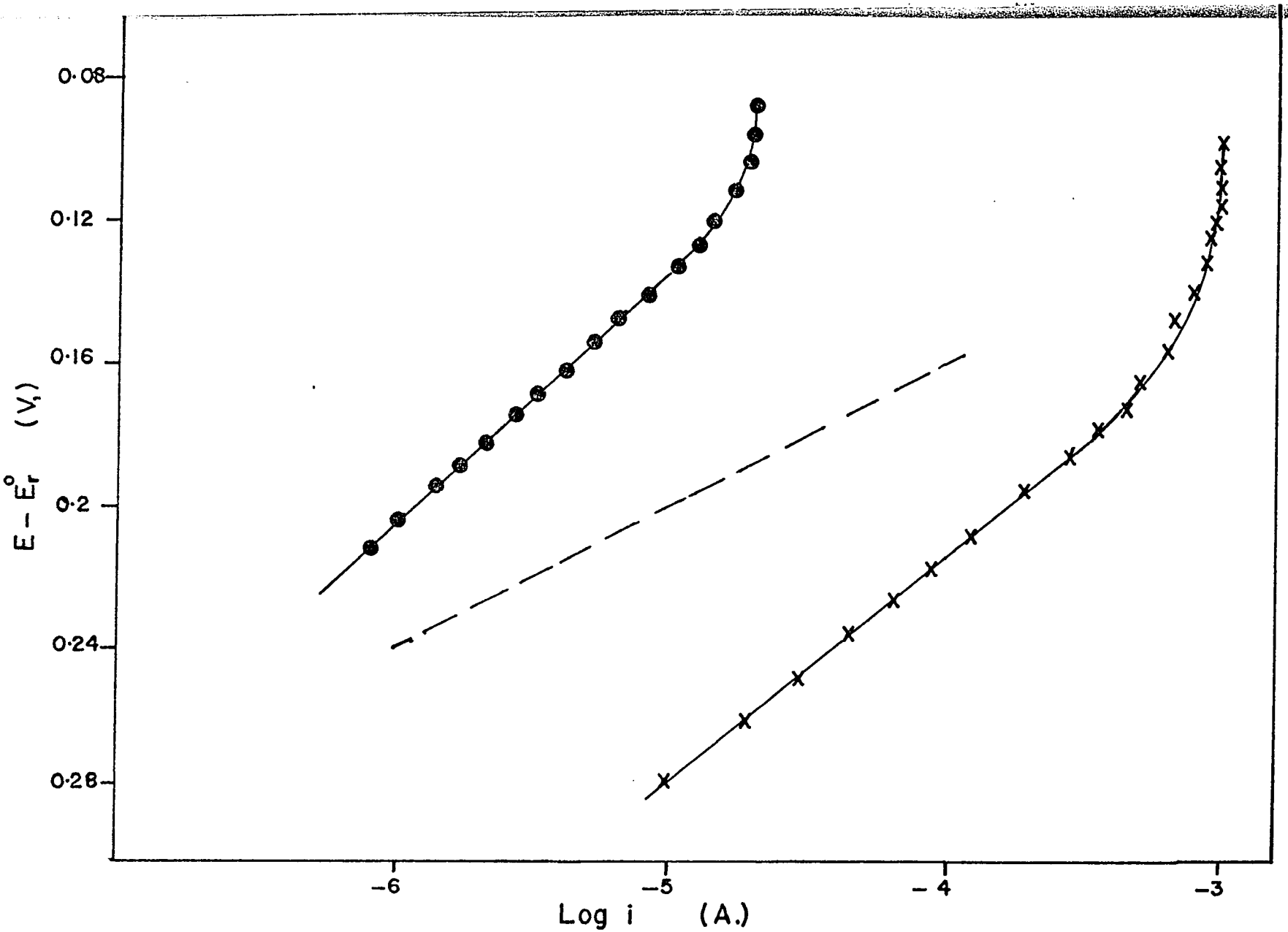
* In this calculation, the diffusion coefficient of acetophenone was taken as 8×10^{-6} cm.^{2} sec.$^{-1}$ a value which has been reported by Elving and Leone (112).

Figure 40. Log[current]-potential curves corresponding to current-potential relations predicted by the theoretical equation derived by Koutecky and Hanus (119).


10^{-2} mole. litre^{-1} acetophenone


5×10^{-1} mole. litre^{-1} acetophenone

Tafel slope of 42 mV.


0·08
0·12
0·16
0·2
0·24
0·28
E - E°r (V.)
-6
-5
-4
-3
Log i (A.)

litre^{-1}] but the Tafel slopes for the two concentrations are 70 mV. at the lower and 64 mV at the higher concentration and certainly not the value of 42 mV. discussed by Brown (shown by broken line in the Figure 40).

A reaction order $\left\{\frac{d\log i}{d\log(C_R)_b}\right\}_E$ can be obtained from equation (IV, 30). Under the condition that $i_d \gg i$ then $(i_d - i) \longrightarrow i_d$ and the equation can be simplified. Therefore

$$E-E^o = K' + 0.02 \log (C_R)_b - 0.06 \log i + 0.06 \log i_d$$

From the Ilkovic equation

$$i_d = k''(C_R)_b$$

and hence

$$E-E^o = K' + 0.08 \log (C_R)_b - 0.06 \log i$$

and

$$\left\{\frac{d\log i}{d\log(C_R)_b}\right\}_E = 1.33.$$

It can be seen from the constructed log[i]-E curves (Figure 40) that at low currents the reaction order is 1.3 and decreases to unity in the potential region of the limiting current.

At the chosen concentrations, which are several times larger than those normally used in polarography, the existence of a diffusion-limited current may be questioned. The diffusion layer thickness in an unstirred solution is probably

10^{-4} cm. in thickness (174). The surface area of a polarographic drop can be easily calculated (144) and is 0.17 cm^2 for t = 3 seconds when m (the drop weight) = 1 mg. $sec.^{-1}$ Then it can be shown that initially 8.5×10^{-9} moles of ketone are present in the diffusion layer. The electrical charge required to reduce this amount of ketone is 8.5×10^{-4} coulombs. Hence at $i = 10^{-3}$ A. the surface concentration of ketone will become zero within a "transition time" of approximately 900 m.secs. The current then becomes diffusion limited well before the drop is fully formed (t=3 seconds).

In the original paper by Koutecky and Hanus (119) it is stated that the equations for the polarographic waves obtained for the "depolarisation" scheme shown below (scheme A)

Scheme A

$$O + ze^- \rightleftharpoons R$$

$$2R \xrightarrow{k_d} D$$

are limited to the case in which the following conditions apply:

(i) that the electrode reaction is sufficiently fast to allow the ratio of the concentration of the electroactive forms at the electrode to be determined only by the electrode potential;

(ii) that the velocity of the dimerisation step is relatively large and therefore $k_d\ t \gg 1$;

(iii) that the equilibrium concentration of the dimer is far greater than that of the monomer, and

(iv) that the dimerisation reaction occurs in the solution rather than at the electrode surface.

The conditions (ii) and (iii) are most probably realised in the electro-reduction of aromatic ketones, as is supported by the magnitude of the rate constants for recombination of the ketyl radicals (see p.140). However, unless this reaction is retarded, perhaps by the surface film of pinacol as the electrode process occurs, then it is unlikely that an appreciable concentration of the radicals will diffuse away from the surface, (condition iv), even to a distance of only 10 Å at which they may be considered to be desorbed. It has already been pointed out (p. 137) that there is evidence to suggest that in the electro-reduction of benzaldehyde the dimerisation occurs at the surface in the presence of specifically adsorbed molecules (171). This viewpoint is further supported by the absence of an anodic peak in the i-E profiles obtained from potentiodynamic studies in some cases, e.g., as indicated from the experiments reported in this thesis (p.91-92) and also noted by Suzuki (126) in studies upon the reduction of benzophenone.

That the electrochemical step is probably reversible at low ketone concentrations but becomes rapidly irreversible as $(C_R)_b$ increases, has been shown by Mairanovskii (115) on the basis of a logarithmic analysis of the polarographic waves for acetophenone reduction using a modification of the

treatment of Koutecky and Hanus. In the polarographic reduction of benzophenone, Elving and Suzuki (120) concluded, however, that the assumptions involved in the theory of Koutecky and Hanus are not valid for the first polarographic wave obtained in acid solutions for this particular aromatic ketone.

Koutecky and Hanus conclude their paper (119) with the following comment:

"From the polarographic literature to the time of writing (1954), no case of dimerisation succeeding the electrode process is yet known which would not be complicated by other factors, e.g., irreversibility of the electrode process, in the reduction of aromatic carbonyl compounds or adsorption effects, or occasionally chemical reaction with the mercury surface as in the anodic oxidation of thiols".

It is perhaps surprising that the results can be correlated with a theoretical equation based on a diffusion controlled process yet a limiting current was not experimentally observed in Brown's work (173). The anomaly may be resolved, however, if it is noted that measurements were made* under conditions

---

* In this experiment, currents were recorded as i-t profiles on an oscilloscope after the application of a potential step. A new mercury surface was used for each successive current and potential determintation [cf. the study of the electro-reduction of acetone also carried out by Brown (93)]. The time intervals involved may well have been of the order of 50-100 μsecs. and it has been clearly shown (p.151) that indeed diffusion control could not be significant in solutions of such high concentration of ketone until some 800-900 m.sec. after the potential had been established.

where mass transfer was not rate limiting at any electrode potential and where the formation of the product at the surface was insignificant. However, it has been shown in Figure 40 that the polarographic wave "constructed" from the theoretical equation (IV, 29) does not give a Tafel slope of 40-42 mV. or a reaction order of 1.5 with respect to the concentration of ketone.

The potential step measurements carried out as part of the present experimental study gave
(a) a Tafel slope which was independent of $(C_R)_b$, and
(b) a reaction order of 1.1 over a fairly wide range of concentrations of ketone. The slope (65 mV.) was higher, rather than lower, than the value obtained in the steady-state measurements. Because of the oscillations which arise during the first 500-1000 μ.secs (Figure 25), measurements could not be made at time intervals as short as those probably used by Brown (93,173). Hence under the conditions involved in the present potential-step measurements, the electrode surface may have been significantly covered with pinacol and the current limited partially by diffusion control at the more cathodic potentials.

In the potential step measurements the experimental conditions may be considered in one sense to be approximately "polarographic" in nature in so far as the mercury surface is renewed for successive current-potential measurements.

One of the current-potential curves obtained by this method was analysed, for exploratory purposes, in terms of an equation given by Mairanovskii (129), which is in fact a simplified form of the relation derived by Koutecky and Hanus, and still based on the assumption of a reversible electron transfer step. The current at any potential E along the wave is given by the expression of Mairanovskii as

$$E = \varepsilon_o - \frac{RT}{zF} \ln \frac{i^{2/3}}{(i_d - i)} \qquad \text{(IV, 31)}$$

where ε_o is a characteristic potential which is independent of the concentration of ketone. With R, T and F having their usual values, and for z = 1, the linear relation between $\log \frac{i^{2/3}}{i_d - i}$ and E should have a slope of 59 mV. The analysis of the "polarographic wave" obtained at $(C_R)_b$ = 0.13 mole. litre^{-1}* gave a slope of 80 mV. (Figure 41) which is higher than the expected slope and is consistent with some degree of irreversibility in the electrode process (115) as indicated by other aspects of the present work.

12. POTENTIODYNAMIC STUDIES: INTERPRETATION OF THE EXPERIMENTAL RESULTS AND CORRELATION WITH THE STEADY-STATE KINETIC STUDIES

Current-potential profiles were also obtained from potentiodynamic studies on the electro-reduction of acetophenone

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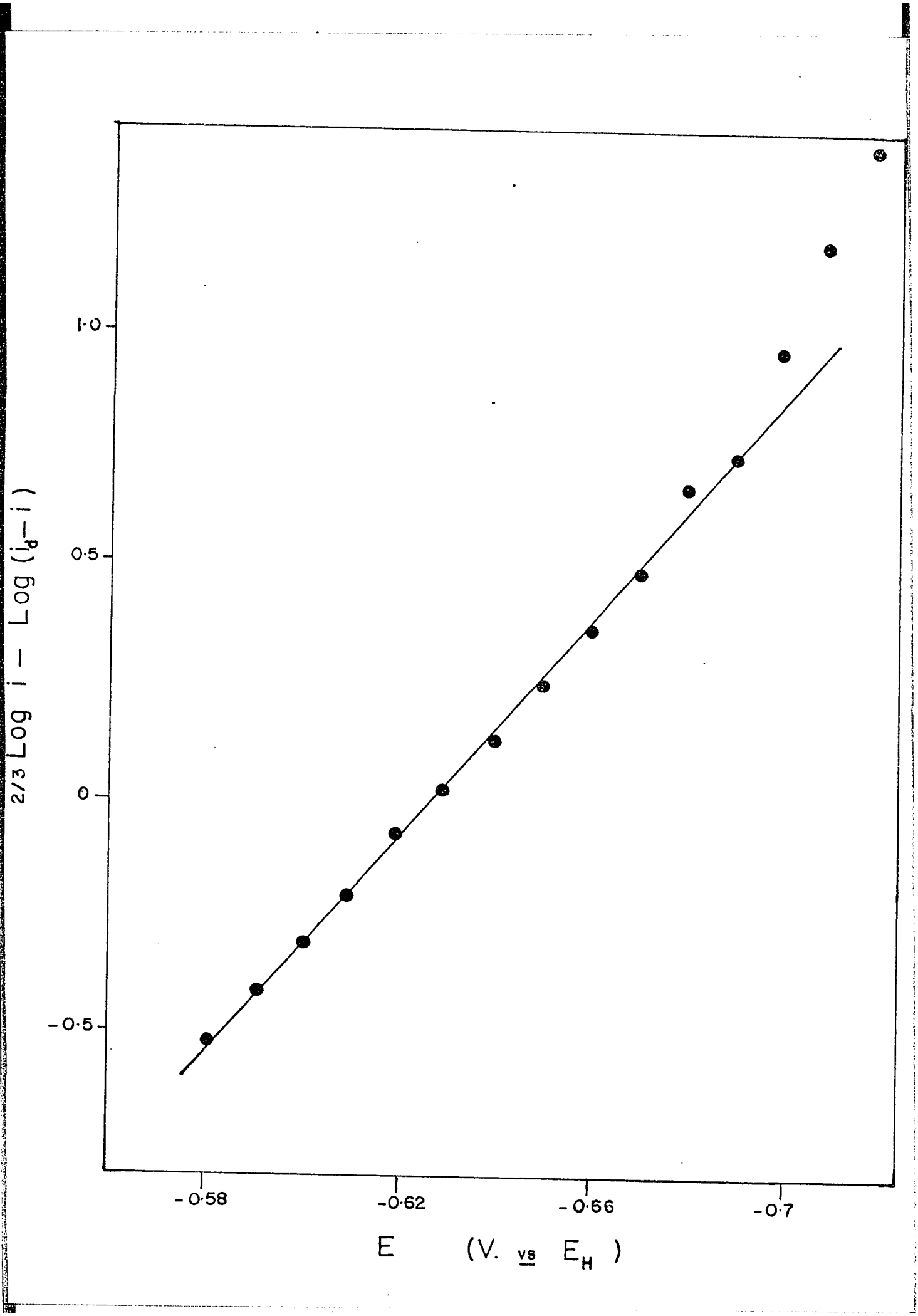
* The limiting current is indicated by the curvature of the log[i]-E relation of Figure 26 and was taken as 1.4×10^{-3} A.

Figure 41. Analysis of a log[current]-potential curve obtained from potential-step measurements in terms of a theoretical equation derived by Mairanovskii (115,129).


1·0
0·5
0
-0·5
2/3 Log i — Log (i_d — i)
-0·58
-0·62
-0·66
-0·7
E (V. vs E_H)

(i) partially aqueous and

(ii) nominally anhydrous methanol solutions.

In both cases the analysis of the results led to a linear dependence of the peak current (i_p) upon $\sqrt{\frac{dE}{dt}}$ and of the peak potential upon $\log \left\{\frac{dE}{dt}\right\}$.

Qualitatively, this behaviour is characteristic of a diffusion-controlled, irreversible process. Theoretical equations for the peak current and peak potential for such an electrode process have been derived by Delahay (144) and also presented in a recent review of the theory of stationary electrode polarography (74). It is shown that the peak current is linearly dependent upon such parameters as the diffusion coefficient, D, the bulk concentration, $(C_R)_b$, and the square root of the sweep-rate. However, this dependence is also found for a reversible electrode process (144) but the peak potential is then independent of the applied rate of change of potential.

Alternative forms of the theoretical equations for a totally irreversible process have been derived, e.g., by Gokhshtein (175), where peak current and peak potential are related as follows:

$$\ln i_p = \ln \left\{0.227zFA(C_R)_s k_s\right\} - \frac{\alpha Z_a F}{RT} (E_p - E_r^o) \qquad \text{(IV, 32)}$$

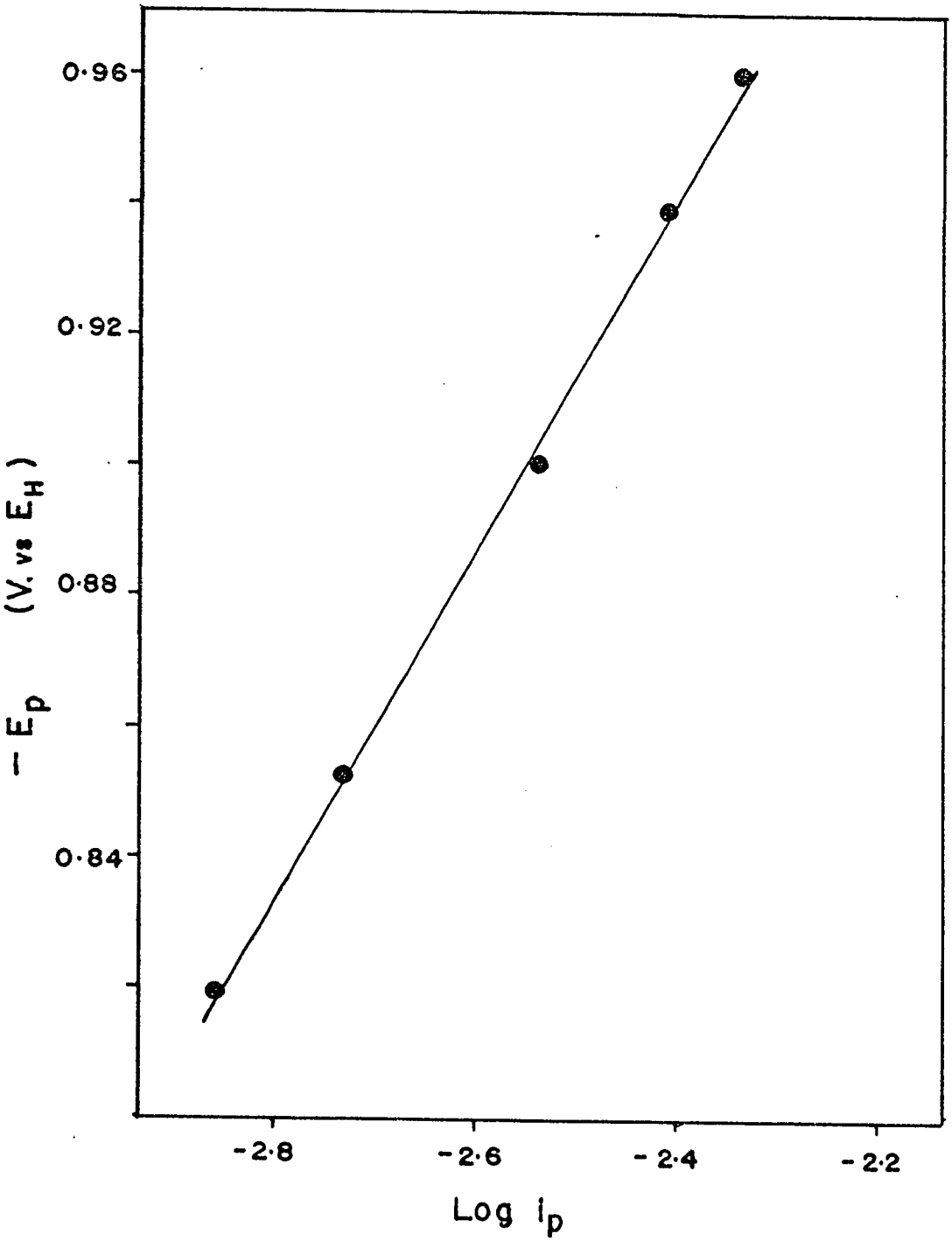
where $(C_R)_s$ is the surface concentration of the reducible species and k_s is the heterogeneous rate constant for the

electrode process. The results obtained in the present work were also analysed in terms of the form of this equation (Figure 42). A fairly linear relation was obtained from results obtained in the two solvent systems, although the narrow range of potential-scan may obscure any noticeable departure from linearity.

A further approach to obtaining kinetic information from potentiodynamic studies has been described by Reinmuth (176), who showed that for an irreversible electrochemical reaction the current flowing at the foot of the i-E curve is <u>independent</u> of scan-rate since diffusion control is then minimal. This behaviour is observed in the present work (Figure 23) and may constitute further evidence suggesting that an irreversible electrode process is involved in the electro-reduction of acetophenone. However, Nicholson and Shain (74) have shown that this criterion of irreversibility can only apply to currents which are some 10% of the peak value and its validity does not extend as high along the wave as was implied by Reinmuth.

A comparison of anodic and cathodic peak potentials is also used as a criterion for the reversibility of an electrode process, since for a reversible reaction $(E_p)_{cathodic}$ and $(E_p)_{anodic}$ are virtually superimposable (144). In the experimental studies reported in this thesis, an anodic peak corresponding to the re-oxidation of the primary product of

Figure 42. Potentiodynamic studies: Dependence of $(E_p)_{cathodic}$ upon the peak current according to an equation derived by Gokhshtein (175).


0·96
0·92
0·88
0·84
- Ep (V. vs EH)
-2·8
-2·6
-2·4
-2·2
Log ip

the electrode reaction, i.e., the ketyl radical, was not observed even at relatively high sweep-rates. The absence of an anodic peak was also reported in the cyclic voltammetric studies of the electro-reduction of benzophenone (126). However, in the case of fluorenone, a peak corresponding to oxidation of fluorenone ketyl was obtained at frequencies of approximately 100 Hz. (145). This result could not, however, be reproduced in studies of the electro-reduction of fluorenone carried out as part of the present work (see Chapter III, p.101). It is felt that this situation may be partly attributed to the added difficulties associated with working in a mixed aqueous-organic solvent which led to resistance effects as well as to the onset of sudden desorption (probably of methanol from the electrode surface), and a resulting distortion of the i-E profile at high frequencies.

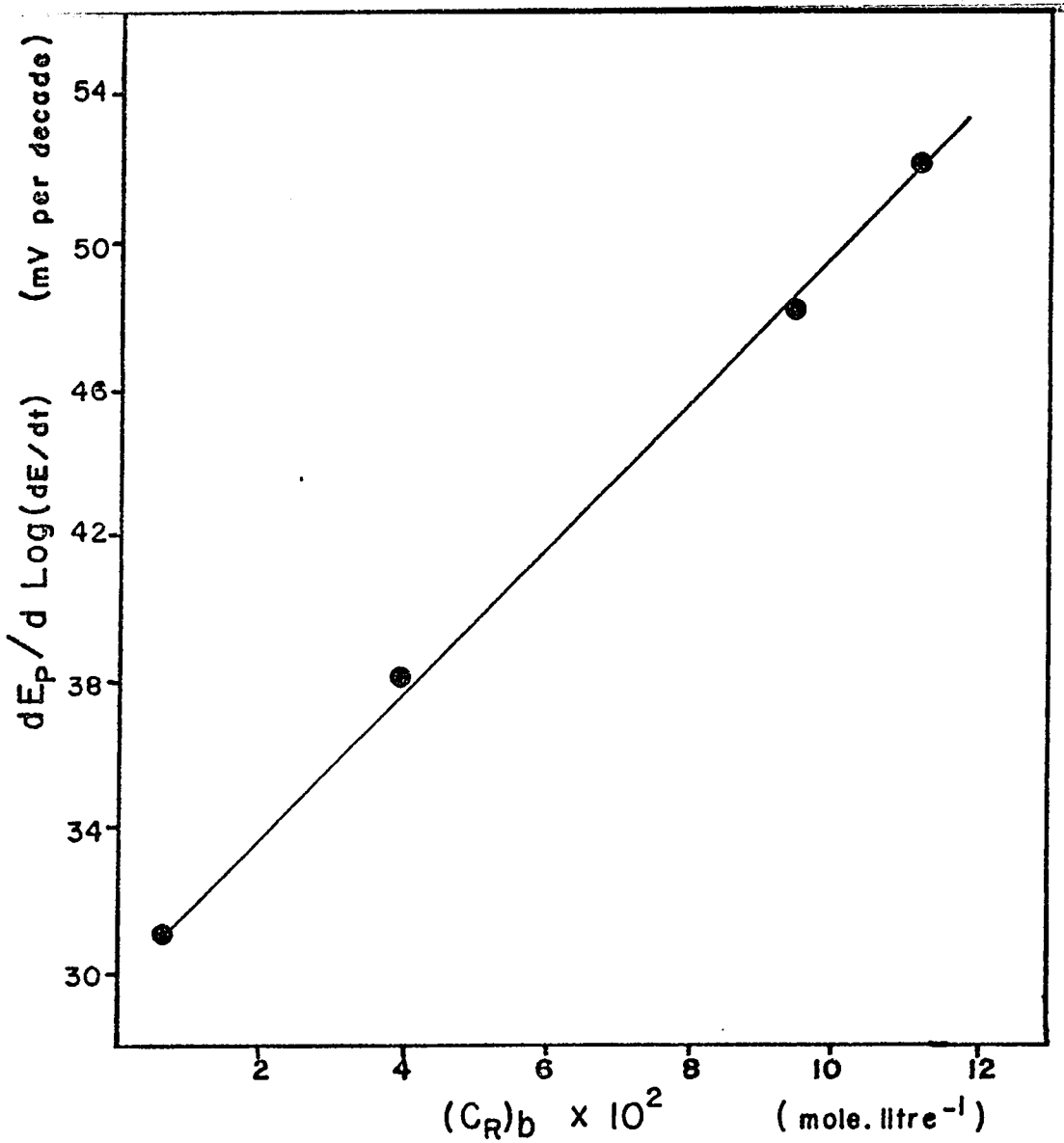
An initial conclusion regarding the nature of the electro-reduction of acetophenone under cyclic voltammetric conditions might be that it is essentially an irreversible, diffusion-controlled process. However, the peak potential was found to be markedly dependent upon the concentration of the ketone. Such behaviour is not characteristic of a totally irreversible process. The mechanism proposed to account for the results of the steady-state kinetic studies, we have shown, involves a succeeding dimerisation reaction. Furthermore, in previous work, the polarographic reduction of the aromatic carbonyl

compounds has been largely described in terms of a mechanism involving a reversible electrode process and a succeeding dimerisation step. The theory of stationary electrode polarography for such a process (scheme A. p.151) has been presented by Nicholson and Shain (74). The electro-reduction of benzaldehyde has also been studied by Saveant and Vianello (177,178) using potentiodynamic techniques and the results expressed in terms of theoretical equations for the peak current and peak potential. The peak current was shown to be linearly dependent upon $\sqrt{\frac{dE}{dt}}$. The equation for the peak potential developed by these workers (177,178) for the conditions mentioned above is given as follows:

$$E_p = E_r^o - \frac{0.059}{Z} - \frac{0.02}{Z} \log Z + \frac{0.02}{Z} \log k - \frac{0.02}{Z} \log \left\{\frac{dE}{dt}\right\} + \frac{0.02}{Z} \log (C_R)_b \qquad \text{(IV, 33)}$$

It can be seen that with increasing sweep rate, the peak potential will become more <u>cathodic</u> and the linear relation between E_p and $\log \left\{\frac{dE}{dt}\right\}$ will have a slope of 20 mV. per tenfold change in the sweep-rate. A cathodic shift of the peak potential is observed in the electro-reduction of acetophenone (Figure 23, or see Table IV) but the slope of the E <u>vs</u> $\log\left\{\frac{dE}{dt}\right\}$ relation (Figure 24) is much higher than 20 mV. In fact the slope of this relation appears to be concentration dependent (Figure 43) and increases with increasing concentration of the ketone.

Figure 43. Dependence of the slope of the relation between $(E_p)_{cathodic}$ and $\log\left\{\frac{dE}{dt}\right\}$ upon the bulk concentration of acetophenone.


dEp / d Log (dE/dt) (mV per decade)
54
50
46
42
38
34
30
2
4
6
8
10
12
(CR)b x 10^2 (mole. litre^-1)

From equation (IV, 33), it follows that with increasing bulk concentration of the reducible species the peak potential should become more anodic and the slope of the relation E_p vs log $(C_R)_b$ will again be 20 mV. for a tenfold increase in $(C_R)_b$. It was found that an increase in the concentration of acetophenone brought about a marked cathodic shift in the peak potential, i.e., the opposite to that theoretically predicted. This anomalous behaviour has been observed in the relation between $E_{\frac{1}{2}}$ and log $(C_R)_b$ in the polarographic reduction of certain aromatic aldehydes (166). In a detailed study of these reactions, it was found that at very low concentrations $E_{\frac{1}{2}}$ was dependent upon log $(C_R)_b$ according to the equation (IV, 33) but with continued increase of concentration $E_{\frac{1}{2}}$ became independent of the concentration and then began to change in the cathodic direction. At low pH, the so-called "critical concentration" was dependent upon the particular aldehyde undergoing reduction, e.g., for benzaldehyde the critical concentration was 2×10^{-3} mole. litre^{-1} but for m-toluic aldehyde it was 3×10^{-4} mole. litre^{-1}. This behaviour was attributed to the presence of a significant amount (probably almost a monolayer) of the pinacol at the electrode surface which had been formed within the life-time of the drop (see p. 121).

In the derivation of equation (IV, 33) by Saveant and Vianello (177), the molecularity of the dimerisation step was

introduced. It is considered that the reaction probably occurs homogeneously and is therefore bimolecular (i.e., the intermediate radicals are desorbed or diffuse away from the surface before recombination occurs). In the equation for the peak potential, the concentration term is written as

$$\left\{\frac{m-1}{m+1}\right\}\left\{\frac{RT}{zF}\right\} \ln (C_R)_b$$

where m is the molecularity of the homogeneous dimerisation step and therefore at 25°C, and with z = 1, this expression reduces to 0.02 log $(C_R)_b$.

It has been shown, however, that the dimerisation of the ketyl radicals may well occur at the electrode surface (120, 171), in which case the surface reaction order may not correspond to the bimolecular condition used above. Calculations from the results of the adsorption studies upon acetophenone have indicated (Table IX) that the apparent surface reaction order (R_s) can be larger than the experimentally observed reaction order (see p. 56) and is dependent upon the surface concentration of the ketone, and therefore the bulk concentration. It is therefore possible that values of m different from two may apply and that the value of m may be dependent upon the concentration of ketone if the recombination were heterogeneous. In this event, the slope of the relation between E_p and $\log(C_R)_b$ would also be dependent upon concentration and probably

different from the predicted value of 20 mV.

In the extreme case when m=1 (this corresponds to a surface excess of zero and the absence of interactions in the adsorbed layer), the peak potential would be independent of the concentration. Under such conditions, the electroreduction would correspond to an irreversible diffusion-controlled process. The observed values of the slope (Figure 43) are all larger than the predicted value of 20 mV., which may be explained if the <u>apparent</u> surface reaction order increases, i.e., as m increases, the expression $\frac{m-1}{m+2}$ approaches unity and the slope of the relation between E_p and $\log(C_R)_b$ approaches 59 mV.

CLAIMS TO ORIGINAL RESEARCH

The electro-reduction of acetophenone at a stationary mercury pool electrode and in an acidic medium (pH < 1) yielded 2,3-diphenylbutane-2,3-diol (acetophenone pinacol) with high coulombic efficiency. In the present work the kinetics of this electrochemical reaction and the adsorption behaviour of both ketone and pinacol have been studied at the same electrode and in the same solvent. The following original contributions have been made:

(a) Tafel slopes and reaction orders have been obtained for the reaction carried out in

(i) a solution of methanol (80 mole %)-water and sulphuric acid (1M), and in

(ii) nominally anhydrous methanol containing sulphuric acid (1 M).

and for the first time in an electro-organic mechanism study, the kinetics have been related to direct thermodynamic studies of reactant and product adsorption [see (f) below].

(b) The reaction kinetics were shown to be sensitive to both the pH of the solution and to the solvent composition, i.e., the concentration of water in the solution.

(c) Kinetic evidence is given that the protonated form of the ketone is the electroactive species at the electrode surface.

(d) The results of a primary H/D isotope study clearly established that the proton was <u>not</u> critically involved in the rate-determining step.

(e) The effect of change of the bulk concentration of water in the solution is reflected in a marked decrease in the

Tafel slope as the mole % water increases, and this change is particularly sharp between 0 and 5% water. The observed effect has been discussed in terms of the surface concentration of methanol. A change in the composition of the solvent mixture at the surface may lead to a change in the amount of pinacol adsorbed at the surface or possibly to a change in the rate of the protonation reaction which is believed to occur in the interfacial region.

(f) The adsorption behaviour of acetophenone and acetophenone pinacol has been studied by electrocapillary measurements, using the solvent systems described above. It was found that (i) both the reactant and the product were strongly adsorbed over a fairly wide range of cathodic potentials, and more significantly,
(ii) the presence of acetophenone pinacol at the electrode surface diminished the adsorption of the ketone itself,
(iii) the adsorption behaviour may be described by a Frumkin-type adsorption isotherm, which includes a parameter for dipole-dipole interaction effects in the adsorbed layer, and
(iv) the linear dependence of the surface concentration (Γ) of the ketone upon the logarithm of the bulk concentration indicated that Temkin-type adsorption was involved.

(g) The reaction order $\frac{R}{n}$ has been derived from several typical isotherms used to describe adsorption behaviour of neutral organic molecules at a mercury surface. The dependence of the derivative $\frac{R}{n}$ upon the surface coverage θ has

also been examined. In this way the apparent surface reaction order has been evaluated together with the true molecularity of the reaction which involved Temkin-type adsorption.

(h) The results of potentiodynamic studies do not unambiguously agree with the theoretical equations derived for (i) a totally irreversible electrode process or

(ii) a reversible electron transfer followed by a rapid, irreversible dimerisation step,

but show characteristics of each mechanism.

(i) The results of both steady-state kinetic measurements and "potential-step" relaxation methods have been examined in terms of a theoretical equation derived by Koutecky and Hanus (119) for mechanism h(ii) above.

(j) Two mechanistic interpretations of the results of the kinetic and adsorption studies have been proposed:

(i) The rate-determining step in the reaction is dependent upon the solvent composition. In partially aqueous solutions, the rate of recombination is limiting and may be hindered by the presence of a surface layer of pinacol. In nominally anhydrous solutions, the rate-determining step is an electrochemical discharge of the protonated species.

(ii) An alternative mechanism involves a "barrierless" discharge step. The sensitivity of the Tafel slope to

the solvent composition is explained in this treatment in terms of adsorption of the ketyl radical <u>after</u> electron transfer to the protonated form of the ketone, which is envisaged as located in the outer Helmholtz region of the double-layer. When the ketyl radical is not adsorbed, the "barrierless" condition does not arise and the reaction then tends to behave as a normal electron transfer process with a slope $b = RT/0.5\ F$, these conditions being applicable to the nominally anhydrous solvent.

(k) The acetophenone pinacol was found to facilitate hydrogen evolution at the mercury electrode, an effect which is similar to that observed upon the addition of certain alkaloids.

(l) A brief study of the electrochemical kinetic behaviour of benzophenone and fluorenone was also carried out for comparative purposes.

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