

GENERAL DISCUSSION

INTERMEDIATES IN ELECTROCHEMICAL REACTIONS

Dr. R. Parsons (*Bristol*) said: I should like to add to Professor Gerischer's list a new method which may have some prospect of success. This is the application of photoelectron spectroscopy (ESCA) to material adsorbed on electrode surfaces. It is well established¹ that the strongly bound intermediate in the formic acid oxidation,

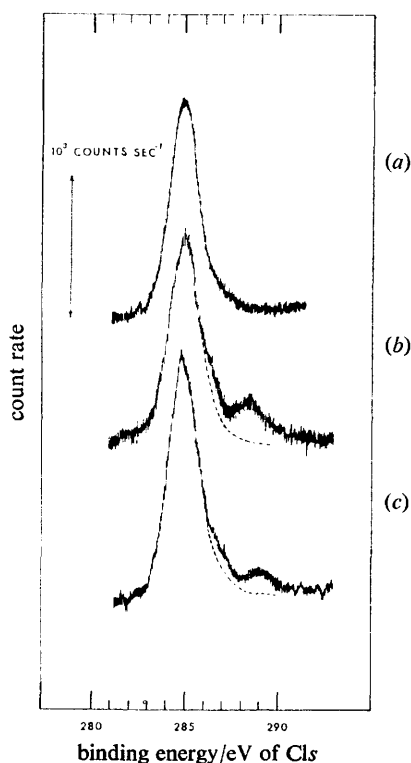


FIG. 1.—Photoelectron spectra of carbon $1s$ line of platinised platinum electrode dipped in (a) 0.5 M aqueous sulphuric acid, (b) formic acid, (c) methanol. The electrode was then washed and introduced into the spectrometer which was evacuated without heating the specimen.

and the similar intermediate in methanol oxidation on Pt, is retained on an electrode which is removed from the reagent solution, washed and transferred to another solution. Dr. A. Capon and I, together with Drs. G. Allen and P. M. Tucker of C.E.G.B., Berkeley Nuclear Laboratories, have attempted to detect this species using ESCA. The strongly bound intermediate was formed on a platinized Pt electrode which was then washed in de-oxygenated water and then introduced into a Vacuum Generators ESCA spectrometer which was then evacuated without heating

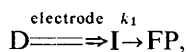
¹ A. Capon and R. Parsons, *J. Electroanal. Chem.*, 1973, **44**, 1, 239; 1973, **45**, 205.

the electrode. The resulting spectra for the carbon 1s line are shown in fig. 1. The large peak at ~ 285 eV appears on all spectra and is attributed to hydrocarbon material from pump oil. The small peak at ~ 289 eV appears only on electrodes which have been dipped in (a) HCOOH or (c) CH₃OH; when they were dipped in 0.5 M H₂SO₄ (curve (b)) it did not appear. Since the shift in the energy of this peak is comparable to that of carbon attached to oxygen, it seems reasonable to attribute this peak to an intermediate such as the postulated COH adsorbed with three bonds to Pt although the effect of the bonding to Pt is unknown.

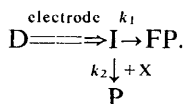
Although the peak is small these results do suggest that ESCA provides a useful addition to the repertoire of methods for studying intermediates in electrode reactions as well as oxide layers.¹ However, it must be noted that the species studied is probably not an intermediate in the main oxidation reaction of formic acid although it is in the oxidation of methanol.

Prof. A. A. Vlček (Prague) said: Prof. Gerischer mentioned in his talk several methods used for the detection and characterization of unstable intermediates of electrode reactions. All methods mentioned are based on the application of physico-chemical techniques for the *direct* detection of the intermediate. There is, however, an *indirect* method, usually requiring no special instrumentation but quite a lot of chemical skill and intuition.

This method is based, in principle, upon the addition of a suitable substance which reacts very rapidly with the intermediate (I) in a specific and characteristic way, giving a product (P) from the nature of which the nature of the intermediate can be deduced. If the original reaction is described by the scheme



the new reaction sequence is then



The effectiveness of the method depends upon the specificity of the $\text{I} + \text{X} \rightarrow \text{P}$ process and upon its rate. The induced reaction has, obviously, to compete with the $\text{I} \rightarrow \text{FP}$ reaction. This can be achieved only if the rates of both processes are at least comparable. On the other hand, this method can be used in cases where the $\text{I} \rightarrow \text{FP}$ process is so rapid that the steady state concentration of I is very low to be detected by available physicochemical methods. Provided a suitable reaction can be found, this extends the possible range of detection of short lived intermediates to those with life-times of the order $10^{-8} - 10^{-9}$ s. Experimentally not the unstable intermediates but the, more or less, stable product of the induced reaction (P) is being followed. The detection of this product can be achieved by electrochemical methods or by any other method used to follow the products of electrode reaction. Thus, for example, long term electrolysis in the presence of X is carried out and the reaction mixture is analyzed for the product P. In suitable cases, the product P can be isolated and characterized in more detail. Another means of detecting the induced reaction $\text{I} + \text{X}$ is, in cases where X is electroactive itself, to follow the changes of the electrochemical behaviour of X. This approach has been used, for example, for the detection of CH₃-anions formed in the course of the reduction of some organo-

¹ K. S. Kim, N. Winograd and R. E. Davis, *J. Amer. Chem. Soc.*, 1971, **93**, 6296.

metallics in tetrahydrofuran.¹ In this case, magnesium bromide (reduced with two electrons) was added to the solution and polarographic curve was recorded. The CH_3^- -anions (or *Cryptoanions*— $\text{CH}_3^- \cdot \text{M}$) are formed at the electrode surface and diffuse from the electrode. Magnesium bromide, diffusing to the electrode, is consumed by the reaction forming MgCH_3Br , which is reduced by one electron only. The reaction is thus manifested by the decrease of the wave of magnesium bromide.

Several other reactions were followed by this method especially in combination with the preparative electrolysis and separation and identification of the product of the induced reaction.

Prof. Sir George Porter (*Royal Institution*) said : Kuwana has described the use of signal averaging for the improvement of signal/noise ratio. Equally effective is to increase the monitoring light intensity which again produces an improvement in signal/noise proportional to the square root of the intensity. Pulsed light sources, which can temporarily increase intensity by a factor of several hundred, are useful for this purpose.

Prof. T. Kuwana (*Ohio*) said : We have used 75-100 W tungsten-iodine lamps in the visible region of the spectrum. For the u.v., we have employed 100 W xenon arc lamps with highly stabilized power supplied. Although signal-to-noise can be improved by the use of higher intensity, there are two mitigating features. The first is that one must be careful that the light does not initiate any photochemical processes at or near the electrode surface. The second is that a higher lamp wattage does not necessarily produce a corresponding increase in the light intensity through the optical system, since what is important is the energy-density of the image through the entrance and exit slits of the dispersion system. A higher energy lamp may have a greater total radiant energy, but the energy density per surface area of the arc or filament may not increase significantly. We have used lamps with small area filaments or arcs and have operated them near their maximum rated wattages.

For measuring small changes in our light intensity (usually less than 1 part in 100) due to some electrochemical perturbation on the cell, we have used a Princeton Applied Research Corp. Model TDH-9 signal averager, or more recently a mini-computer which is locked-in phase with the repetitive waveform driving the potentiostat.

Dr. A. Bewick (*University of Southampton*) said : In the paper by Kuwana *et al.* emphasis is placed upon making measurements at very short times in order to evaluate high kinetic rate constants in the decay reactions of intermediates. I wish to point out that in many cases very high rate constants can be obtained from simple steady state measurements if all of the available information is utilised. For example, a rate constant of $7.5 \times 10^3 \text{ l. mol}^{-1} \text{ s}^{-1}$ is evaluated in our paper at this Discussion from steady state measurements of both the current density and the amount of intermediate present and it illustrates the advantage of combining both electrochemical and optical data. This particular rate constant is well below the limiting value set by the sensitivity of the optical technique in determining the steady state amount of material and diffusion controlled rate constants should be accessible.

I wish to ask Kuwana about the details of the absorption spectrum he observed for the thianthrene cation radical. The spectrum is not given in his paper and it would be interesting to know if he observed additional peaks due to the formation of

¹ A. A. Vlček and S. Vozka, to be published (Thesis of S. Vozka, (Prague, 1972)).

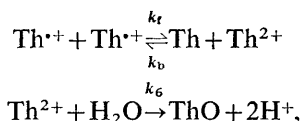
aggregate species similar to those shown on our spectra. This complication needs to be considered when interpreting the kinetic data.

Dr. T. Kuwana (*Ohio, U.S.A.*) said: In general, the larger the rate constant of the homogeneous chemical reaction involving an electrogenerated intermediate, the shorter is the time gate available for optically observing this intermediate following a chronoamperometric step experiment. It is true that for certain mechanisms, a steady state concentration of a reactant may allow the observation time to be moderately long even though the rate is fast. For mechanism studies when one does not know the mechanism *a priori*, it is best to monitor the optical absorbance over a wide a time duration as possible. The shape of the (absorbance, time) curve can serve then as a diagnostic for a particular mechanism.

Dr. B. Kastening (*Jülich*) said: The disproportionation mechanism II (eqn (14), (18) and (19) of the paper by Broman *et al.*) has not been discussed in terms of a rate-determining electron transfer (eqn (18)), which is frequently observed with anion radicals in the presence of water. While this possibility may not be operative for purely aprotic solvents in which the equilibrium constant is strongly in favour of the cation radicals, the presence of water would cause a considerable shift of the equilibrium towards the right and would affect the rate constant k_f of the electron transfer. It would be interesting whether this mechanism would result in a working curve (fig. 6) different from curve A and could they account for the experimental results.

Dr. T. Kuwana (*Ohio, U.S.A.*) said: We did not perform any computer simulations of the absorbance-time behaviour during pulse or relaxation using explicit values of k_f or k_b for reaction (18). We assumed a pre-equilibrium condition and assumed a value of K_{eq} for reaction (18).^{1, 2} A more detailed spectroelectrochemical study coupled with product analysis is being conducted presently by Dr. Henry Blount³ of the University of Delaware. At the moment, our experimental data appear to support the working curves (absorbance, time) of either mechanism I or III, and not mechanism II (see fig. 7 of our paper).

Dr. W. J. Albery (*Oxford*) said: For the reaction scheme of eqn (18) and (19) in Kuwana's paper,



the position of the transition state will be determined by the relative values of $k_b[\text{Th}]$ and $k_6[\text{H}_2\text{O}]$. The position of the transition state does not depend on the value of k_f . However, in deducing the position of the transition state from the observed data an estimate of the value of k_f is useful. If $k_{\text{obs}} = k_f$ then the first step is rate determining, while if $k_{\text{obs}} \ll k_f$ the first step must be a pre-equilibrium and the second step the rate determining one. Kuwana's data show that k_{obs} is indeed much smaller than k_f ; hence the first step must be a pre-equilibrium.

¹ H. J. Shine and Y. Murata, *J. Amer. Chem. Soc.*, 1969, **91**, 1872; *J. Org. Chem.*, 1969, **34**, 3368.

² V. D. Parker and L. Ebersson, *J. Amer. Chem. Soc.*, 1970, **92**, 7488.

³ H. Blount, University of Delaware, private communication, Aug. 1973.

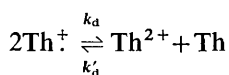
Dr. T. Kuwana (*Ohio, U.S.A.*) said: In re-examining the computer simulation employed for mechanism II, the disproportionation, we had indeed assumed instantaneous attainment of equilibrium for reaction (18). The value of $K_{eq} = k_f/k_b$ was assumed to be small as indicated by ref. (20) and (22) in our paper.

Dr. A. Bewick (*University of Southampton*) said: In reply to Kastening's comment that the disproportionation rate of the thianthrene cation radical might be low, I wish to point out that there are now sufficient data available to set a lower limit to this rate and also to show that the disproportionation mechanism is not tenable.

The disproportionation rate must be at least as large as the observed rate of decay of the cation radical which has been attributed to direct reaction with water ($k \approx 5 \text{ l. mol}^{-1} \text{ s}^{-1}$, in our paper and in Broman's paper). Therefore, the lowest value for the disproportionation rate constant, k_d , is given by

$$k_d C_{Th}^{2+} = k C_{Th}^+ C_{H_2O}. \quad (1)$$

Putting $C_{Th}^+ = 10^{-3} \text{ M}$ and $C_{H_2O} = 10 \text{ M}$ gives $k_d = 5 \times 10^4 \text{ l. mol}^{-1} \text{ s}^{-1}$. A value of 2.3×10^{-9} for the equilibrium constant, K , of the disproportionation



has been reported by Hammerich and Parker¹ from a measurement of the *reversible* half wave potential for the oxidation of Th^+ to Th^{2+} . Although in conjunction with eqn (1) this demands a reasonable value, $10^{10} \text{ l. mol}^{-1} \text{ s}^{-1}$, for the rate constant describing reaction between Th^{2+} and water, it also shows that the disproportionation route is untenable because of the value required for k'_d . From

$$k'_d = k_d/K$$

we get the impossible value, $k'_d \approx 2 \times 10^{13} \text{ l. mol}^{-1} \text{ s}^{-1}$.

Dr. B. R. Eggins (*Ulster*) said: In view of my comments on the derivation of the $dE^*/d(pH)$ relationship, are Albery *et al.* fully justified in basing their mechanistic conclusions for the order of proton and electron transfers essentially on this relationship? Have they fully considered the possible alternative mechanism of disproportionation of $BH\cdot$ radicals which, as they have clearly shown, occurs in the photochemical reaction?

The occurrence of this reaction would depend on (a) a favourable thermodynamic situation and (b) a favourable kinetic situation. (a) clearly exists because of the disproportionation following the photochemical reaction. However, the equilibrium for the disproportionation would also need to be favoured over the second electrochemical transfer in the case of the proposed ECEC mechanism or over the protonation equilibrium for the ECCE and CECE mechanisms. Probably not enough E° and K -values are known to make such comparisons. The case of (b) is even more difficult to resolve. For the ECEC mechanisms the rate of the disproportionation would need to be faster than the heterogeneous rate of the second electron transfer. For the CECE and ECCE mechanisms, one needs to compare homogeneous rates, i.e., between disproportionation and protonation of $BH\cdot$ to BH_2^+ .

While I am not suggesting that the disproportionation necessarily does occur, there are so many variables that the possibility of its occurrence cannot easily be ruled out.

¹ Ole Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537.

Dr. W. J. Albery (*Oxford*) (*partly communicated*). Even though BH^\bullet is disproportionating in the solution, it may not be disproportionating on the electrode, where it can be converted by direct electron and proton transfer to A or CH_2 . These faster first order processes are possible on the electrode, but not in the solution. The low concentration of BH^\bullet makes second order processes, such as disproportionation, less likely than the first order ones on the electrode. In the greater volume of the solution the second order process, being the only one, does destroy the BH^\bullet . The experimental results in fig. 3, 4 and 11 of our paper¹ show that BH^\bullet is indeed being either reduced or oxidised with single electron transfers. If the disproportionation mechanism was operative then we might observe no photo current at all and certainly not one with a cathodic and an anodic branch.

Dr. R. M. Reeves (*Bristol*) (*communicated*): The lowering of ΔE_s below the calculated diffusion controlled limit for the hydrogen reduction seems similar both qualitatively and semi-quantitatively to results we obtained recently for the inhibition of the potassium ion reduction by the hydrogen evolution reaction at the dropping mercury electrode.² Although there was considerable uncertainty in the absolute magnitude of the fractional reduction of current, the effect is significant in terms of the measurement technique employed. The results are similar to those of Smith and Heintz³ but do not suffer from the problems associated with the use of a pool electrode.³

Dr. G. C. Barker (*A.E.R.E. Harwell*) (*communicated*): In connection with the comment of Reeves it has to be noted that the data in table 1 of our paper refer to a reaction involving hydrogen ions as well as adsorbed hydrogen atoms. The experiments provide no certain information about the kinetics of the corresponding reaction involving water molecules, but if it is assumed (improbably) that the transfer coefficient (in contrast to that for the reaction involving hydrogen ions) is virtually zero, the average life of an adsorbed hydrogen atom under the conditions prevailing in the experiments of Reeves *et al.*⁴ at very negative potentials might be as long as 10-100 μs . Such a life would not be long enough to produce appreciable surface coverage when hydrogen ion reduction at the DME is entirely diffusion-controlled. An average life for adsorbed H of 100 μs leads to an H atom surface excess of the order of 0.5 $\mu\text{C cm}^{-2}$ if $[\text{H}_3\text{O}^+] = 5 \times 10^{-3} \text{ M}$ in the bulk of the solution. However, HLFV studies of the hydrogen evolution reaction at mercury have not thus far revealed the gradual decline in the apparent transfer coefficient to be expected if the average life of adsorbed H atoms were to be long at negative potentials when the surface concentration of H_3O^+ is small, but relatively short when the reaction is not entirely diffusion-controlled and H atoms are consumed rapidly by the reaction considered in our paper. On the evidence currently available it seems probable that for mercury the surface coverage is slight in the potential range in which the hydrogen evolution reaction usually is studied. I believe, however, that slight steady state coverage, which probably falls progressively as the potential becomes more negative, may well be the cause of some anomalous transfer coefficient values found for the hydrogen evolution reaction at mercury by the faradaic rectification method many years ago.⁵

¹ W. J. Albery, M. D. Archer, N. J. Field and A. D. Turner, this Discussion.

² R. M. Reeves, M. Sluyters-Rehbach and J. H. Sluyters, *J. Electroanal. Chem.*, 1972, **36**, 287.

³ F. R. Smith and H. Heintze, *Canad. J. Chem.*, 1970, **48**, 203.

⁴ R. M. Reeves, M. Sluyters-Rehbach and J. H. Sluyters, *J. Electroanal. Chem.*, 1972, **36**, 287.

⁵ G. C. Barker in *Transactions of the Symposium on Electrode Processes*, ed. E. Yeager (J. Wiley, New York, 1961), p. 325.

Dr. Frank R. Smith (*Newfoundland, Canada*) said: Concerning the possible slowness of electrochemical desorption of adsorbed hydrogen atoms from mercury cathodes (Barker's reaction (*h*), Pleskov's reaction B'), there is some evidence that desorption may not be faster than $\text{H}_3\text{O}_{\text{aq}}^+$ discharge from the recent studies of Heintze and Smith¹ and of Reeves, Sluyters-Rehbach and Sluyters.²

In our work we sought to measure the yield of H_2 , for comparison with the electrical measurements by measuring the over-all volume change of the mercury, the aqueous solution and any gas phase developed. Good precision was possible using the cell shown in fig. 1 which enabled increments of $1\ \mu\text{l}$ to be observed for a total catholyte volume of *ca.* 8 ml and a leak rate measured as $0.1\ \text{nl s}^{-1}$. In experiments with this cell at current densities from $40\ \mu\text{A cm}^{-2}$ to $5\ \text{mA cm}^{-2}$, the yield of H_2 ranged from 50 to 79 % of expectation, with a mean of 66.75 % and standard deviation of only 3 %. As fig. 2 and 3 indicate, the rate of volume change and hence of H_2 evolution was similarly less than expected on the basis of Faraday's Law. Hydrogen saturated 0.1 M HCl was used, the reaction and volume change at the anode eliminated from the observations by a closed solution-sealed tap and the apparatus thermostatted at $25.0 \pm 0.1^\circ\text{C}$. Observations were continued long after the current had been interrupted, the invariable result being that there was a H_2 deficit of at least 19 % even after $8 \times 10^4\ \text{s}$.

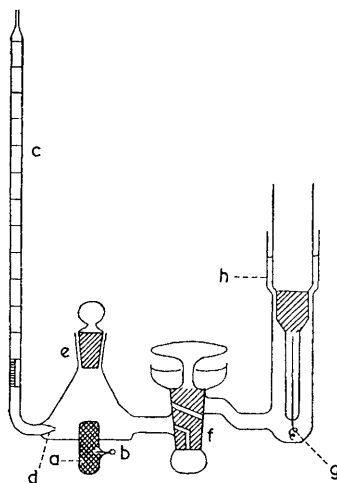


FIG. 1.—Two-compartment cell: *a*, mercury cathode; *b*, platinum contact; *c*, 0.2 ml pipette, 0.001 ml graduations; *d*, gas inlet for saturation with H_2 ; *e*, Teflon-sleeved B10 stopper; *f*, solution-sealed stopcock; *g*, platinum wire anode; *h*, C14 cone in grooved socket.

Many years ago Baars and Kayser³ measured volume changes in hydrogen evolution at several metals, principally Pt, Pb, Hg and Cu. With a simple apparatus, deficits from expectation were found, while using a so-called "improved" apparatus which, however, contained *well-greased taps*,⁴ the volumes measured agreed closely with Faraday's laws. The only other similar investigations appear to be Jofa's

¹ H-U. Heintze and F. R. Smith, *Canad. J. Chem.*, 1970, **48**, 203.

² R. M. Reeves, M. Sluyters-Rehbach and J. H. Sluyters, *J. Electroanal. Chem.*, 1972, **36**, 101.

³ E. Baars, *Marburger Sitzungsber.*, 1928, **63**, 212; E. Baars and C. Kayser, *Z. Elektrochem.*, 1930, **36**, 428.

⁴ We (Ref. (1) above) also observed fair agreement with expectations when a greased cell was used: normally a Teflon sleeve was used to seal the B10 stopper.

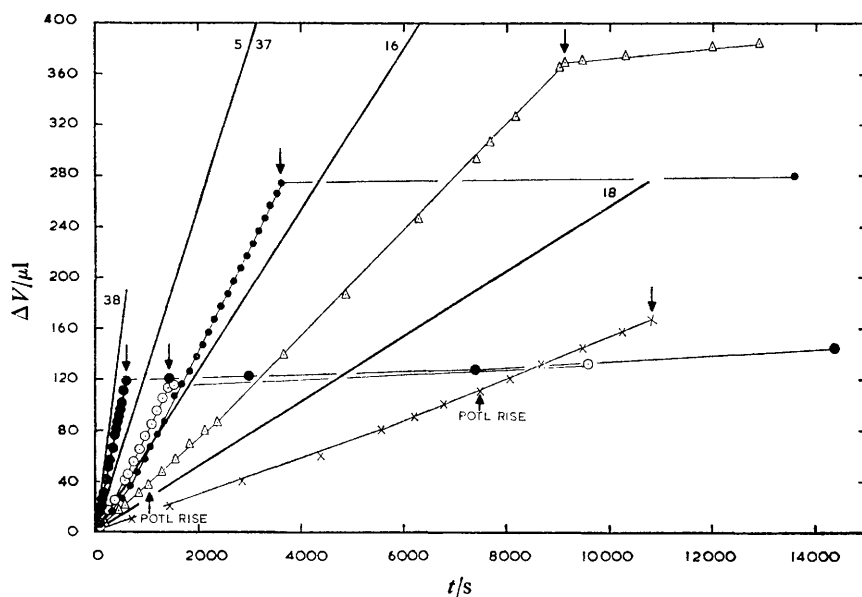


FIG. 2.—Volume changes during and after electrolysis at $200\ \mu\text{A}$ (crosses, expt. 18), $500\ \mu\text{A}$ (triangles, expt. 16), $1.00\ \text{mA}$ (open circles, expt. 37; dots, expt. 5), and $2.50\ \text{mA}$ (shaded circles, expt. 38). Arrows denote time of cessation of current, or time of potential rise where indicated. Numbered lines indicate theoretical volume changes. Electrode area $0.6\ \text{cm}^2$ (expt. 5, 16, 18), $0.5\ \text{cm}^2$ (expt. 37, 38).

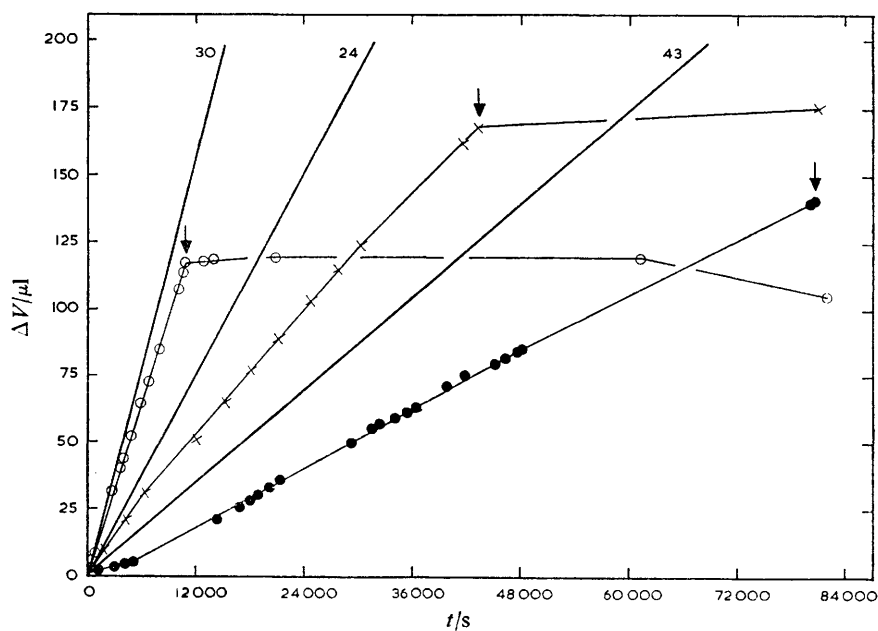


FIG. 3.—Volume changes during and after electrolysis at $22.5\ \mu\text{A}$ (shaded circles, expt. 43), $50\ \mu\text{A}$ (crosses, expt. 24) and $100\ \mu\text{A}$ (open circles, expt. 30). Arrows denote time of cessation of current. Numbered lines indicate theoretical volume changes. Electrode area $0.6\ \text{cm}^2$ (expt. 24), $0.5\ \text{cm}^2$ (expt. 30, 43).

unpublished work on Hg, cited by Frumkin,¹ Kolotyrkin's experiments with porous lead² and Müller's work³ with a dropping mercury electrode. The Russian work^{1, 2} apparently involved very low rates of H₂ generation and prolonged observations: it is not clear whether the rate of H₂ production kept pace with the current but, at sufficiently long times, agreement was obtained.

While not regarding our own work⁴ as definitive, we do believe that there is an element of doubt that hydrogen evolution at mercury (and at lead) is completed in the manner usually assumed, i.e., that electrochemical desorption is much more rapid than H₃O_{aq}⁺ discharge. We suggest that some of the adsorbed hydrogen generated in discharge leaves the mercury surface by diffusion into the bulk metal, later to reappear as H₂ gas after the current has been cut off. In experiments with Das,⁵ using highly purified mercury and solution, the slow growth and rapid decay of hydrogen overpotential has been linked to the growth and release of a single H₂ bubble from the Hg surface with a period of *ca.* 3 h at 50 $\mu\text{A cm}^{-2}$. Other evidence that slow processes, such as diffusion in the bulk metal, affect the overpotential is the observation⁵ of a prolonged rise of overpotential at current densities up to 100 $\mu\text{A cm}^{-2}$. That all is not as simple as generally assumed is indicated by the inhibition of potassium ion reduction by a product of H₃O_{aq}⁺ discharge in aqueous KCl + HCl, deduced⁶ from impedance measurements on dropping mercury electrodes.

My second point concerns the possibility, referred to by Pleskov, that the ionisation of adsorbed hydrogen is an activationless process in some potential region. I would like to suggest a possible means of observing the behaviour of this process directly over a useful potential range. We have demonstrated⁷ that a potential of +0.2 V against a hydrogen electrode in 0.2 M KOH suffices to ensure rapid ionisation of H atoms permeating through a thin lead foil after cathodic generation on the opposite face. If a sufficiently thin foil of lead, or some other high overpotential metal, were used in such a permeation experiment and sufficiently large cathodic H atom generation currents were applied, possibly from a pulsed source, it appears that the question of the activationless nature of H_{ads} ionisation could be settled. If the permeation currents proved to be independent of the potential of the diffusion side of the membrane up to -0.4 or -0.5 V this would be even more convincing than the report of Pleskov *et al.*

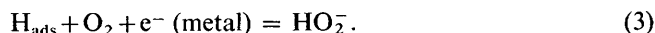
Finally, I should like to ask Barker and Pleskov whether they consider that they have satisfactorily reduced the oxygen concentration in their solutions to the point where their results are unaffected by its possible presence. Reactions such as



or



are possible processes competing with the adsorption of H_{aq} and with electrochemical desorption, respectively. The first (1) is diffusion-controlled with a rate constant of $2 \times 10^{10} \text{ l. mol}^{-1} \text{ s}^{-1}$. Nothing is known about the second process which might also occur coupled with electron-transfer:



¹ A. N. Frumkin, *Acta Physicochim. U.R.S.S.*, 1943, **18**, 23.

² Ya. M. Kolotyrkin and A. N. Frumkin, *Zhur. fiz. Khim.*, 1941, **15**, 346.

³ O. H. Müller, in *Polarography 1964*, ed. G. J. Hills (Interscience—Wiley, N.Y., 1966), Vol. I, p. 319.

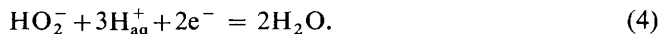
⁴ H-U. Heintz and F. R. Smith, *Canad. J. Chem.*, 1970, **48**, 203.

⁵ S. N. Das and F. R. Smith, unpublished results.

⁶ R. M. Reeves, M. Sluyters-Rehbach and J. H. Sluyters, *J. Electroanal. Chem.*, 1972, **36**, 101.

⁷ I. Čaderský, B. L. Muju and F. R. Smith, *Canad. J. Chem.*, 1970, **48**, 1789.

Reduction of the HO_2^- ion or of H_2O_2 at mercury at potentials negative to -0.5 V against S.C.E. is well known¹ with an over-all reaction:

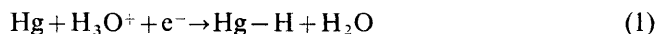


It is to be noted that the total electron consumption per photo-electron could be 2 if only reaction (3) is involved (the HO_2^- product diffusing away after its formation) but rises to 4 if both (3) and (4) participate. In conclusion, it is sometimes the practice in aqueous solution radiation chemistry to repeatedly pulse the solution before the actual experiment. This procedure, it is claimed,² lowers $[\text{O}_2]$ to a level of $< 10^{-10}$ M. Is there any future for a comparable approach in electron photo-emission studies with electrodes?

Dr. G. C. Barker (*A.E.R.E., Harwell*) said: Small traces of oxygen usually are unimportant in photocurrent studies because oxygen is reduced by the electrode throughout most of the accessible potential range and, as a result, the oxygen concentration tends to be vanishingly small in the region where hydrated electrons are captured by hydrogen ions. The reduction product, H_2O_2 , is an efficient electron scavenger but usually is not present at a sufficiently large concentration to compete effectively for hydrated electrons. Also H_2O_2 is unlikely to react more readily with adsorbed H atoms than with free H atoms and, in the case of a deoxygenated solution, thus is not likely to affect significantly the average life of adsorbed H. In practice, in photocurrent work the electron scavenger concentration usually exceeds by several orders of magnitude the concentrations of trace impurities and only in exceptional circumstances do impurities noticeably affect the photocurrent. There might be a case for pre-irradiation of the solutions in work on the residual photocurrent observed in the absence of added electron scavengers.

Dr. Yu. V. Pleskov, Dr. Z. A. Rotenberg, Dr. V. V. Eletsky and Dr. V. I. Lakomov (*Moscow*) said: The presence of oxygen traces in solution cannot affect significantly the results of photoemission measurements for the following reasons. These measurements are mainly carried out in the potential range in which oxygen is reduced under the limiting current conditions. Since the formation of atomic hydrogen and its diffusion occur at distances comparable with the thermalization length of electrons (20-30 Å), i.e., by 3 orders of magnitude less than the mean thickness of the diffusion layer, the oxygen concentration in the "hydrogen" layer is negligible compared with its concentration (a very low one) in the solution bulk.

Prof. J. W. Schultze (*Germany*) said: The evaluation of the experimental data of the hydrogen desorption includes the assumption that Faraday's law with $z = 1$ can be applied for the reaction



and, correspondingly, reaction



can proceed without current.

¹ I. M. Kolthoff and J. J. Lingane, *Polarography* (Interscience, N.Y. 2nd Edn., 1952), Vol. 2, p. 553.

² E. J. Hart and E. M. Fielden, in *Solvated Electron*, Advances in Chemistry Series No. 50, 1965, p. 253.

However, at constant potential ε the charge flow of electrosorption reactions is given by the derivative¹

$$-(\partial q_m / \partial \Gamma)_\varepsilon = \gamma F$$

where γ is the electrosorption valency which may be any broken value, in the case of reaction (1) between 0 and 1. An analysis of different systems has shown, that $\gamma \approx 1$ in the system Pt/H, but $|\gamma| \ll |z|$ for all cations and anions adsorbed on mercury, e.g., $\gamma \approx 0.15$ for the adsorption of alkali ions. Hence, in the case of reaction (1) the assumption $\gamma = z$ is a very rough one. One wonders if it can be proved by the experiments described by Barker or Pleskov.

Dr. G. C. Barker (*A.E.R.E., Harwell*) (*communicated*): The argument of Schultze is quite valid in the context of our non-steady state measurements but it seems unlikely that γ for the adsorption of H atoms on mercury will differ appreciably from unity. Even for the adsorption of relatively large alcohol radicals on mercury there is no evidence that radical adsorption at constant potential appreciably disturbs the structure of the double layer. In principle, non-steady state photopotential experiments of the type described in our paper should shed light on the parameter mentioned by Schultze but there are many practical considerations which make improbable any such clarification. Steady state photocurrent measurements, of course, tend to be unaffected by the influence of adsorbed intermediates on double layer charge density.

Dr. Yu. V. Pleskov, Dr. Z. A. Rotenberg, Dr. V. V. Eletsky and Dr. I. V. Lakomov (*Moscow*) said: A partial charge transfer during adsorption of atomic hydrogen on mercury or other metals is likely to affect the results of the photoemission measurements under non steady-state conditions, when the reactions of electrochemical desorption and ionization occur at a much slower rate than the adsorption rate of atomic hydrogen. To observe this, it is necessary to use pulsed illumination of the electrode with pulse lengths of the order of 10^{-9} - 10^{-10} s. In the case of steady-state measurements, the rates of H adsorption and electrochemical removal are the same and apparently a partial charge transfer cannot be detected.

Prof. I. E. Epelboin (*Paris*) said: Does Dr. Pleskov think that a photoelectrochemical method could be applied to the study of oxide layers, and particularly to the determination of stoichiometry?

Dr. G. C. Barker (*A.E.R.E., Harwell*) (*communicated*): Epelboin may be interested to know that we made some years ago a preliminary study of light-induced electron emission from tantalum oxide films on tantalum, using films sufficiently thick to avoid emission from the metal into the oxide film. This work proved to be a formidable task as using pulsed light of wavelength 253.7 nm there were large and somewhat irreproducible background currents connected with light-induced film growth that varied peculiarly with potential. We were, however, after much fruitless work, able to detect ² fairly reproducible changes in photocurrent at constant potential at the more negative potentials when N₂O was introduced into or removed from the solution. This current presumably was caused by the excitation of electrons in valence bands for the oxide layer, followed successively by some evaporation of hot electrons into the solution, the formation of hydrated electrons and the usual steps (except perhaps

¹ J. W. Schultze and K. J. Vetter, *J. Electroanal. Chem.*, 1973, **44**, 63.

² G. C. Barker and M. J. Williams, unpublished work.

the conversion of OH to OH⁻) that occur when N₂O is present. The quality of the results was not such as to stimulate further work along similar lines.

Dr. Yu. V. Pleskov, Dr. Z. A. Rotenberg, Dr. V. V. Eletsy and Dr. V. I. Lakomov (*Moscow*) said : The presence of an oxide layer on the electrode surface can be a source of at least two side effects superimposed on photoemission. These are: (1) the internal photoeffect in the oxide layer (which as a rule has semiconducting properties) and (2) the reduction reaction of the oxide by solvated electrons. Nevertheless, it is to be hoped that the photo-electrochemical methods in general and the photo-emission method in particular afford great possibilities for investigation of oxide layers on electrodes.

Dr. D. J. Schiffrin (*Argentina*) said : It is suggested by Barker *et al.*¹ that the oxidation of CO₂[•] is a slow process in the potential range -1.3 to -1.5 V. The observed decay of Δ*E*_s (fig. 4) at potentials anodic to -1.4 V could be equally well caused by a decrease in the value of the reduction rate constant of CO₂[•], or a combination of both effects.

Also I would like to ask why the minimum in Δ*E*_s caused by the diffusion of the OH[•] radicals (fig. 3), is not observed for the N₂O + HCO₂⁻ solution. In the latter case, one might consider that the only difference between the two experiments is the replacement on some OH[•] by CO₂[•] radicals in solution, while keeping the overall radical concentration unaltered.

Dr. G. C. Barker (*A.E.R.E., Harwell*) said: The data in fig. 4 of our paper suggest that the reduction as well as the oxidation of CO₂[•] may appear slow when studied at elapsed times smaller than 0.3 μs. As regards the absence of minima in the case of the curves in this figure it has to be noted that, with formate present at high concentration (5 × 10⁻² M), the OH radicals formed by electron capture are largely and rapidly converted homogeneously to the less reactive intermediate CO₂[•]. If at -1.6 V CO₂[•] were to be rapidly reduced by the electrode a minimum comparable with those observed in the absence of formate would be observed.

Dr. W. J. Albery (*Oxford*) said : The potential φ* in Pleskov's paper is very similar to the potential of zero photo current, *E*_{*}, in our work²; it is the potential where the photochemically generated intermediate is equally likely to be reduced or oxidised. We obtained information about the mechanism of our reaction from the variation of *E*_{*} with pH. Pleskov has similar results in his fig. 3. Has he tried to see if his results will fit on to two straight lines, one independent of pH at low values of [H₃O⁺] and one decreasing with [H₃O⁺] at higher acidities? Is there any significance in the line he has drawn in fig. 3?

Dr. D. J. Schiffrin (*Argentina*) said : There is an apparent contradiction between the experimental results presented in fig. 2 and 3 in Pleskov's paper. The differential coefficients dφ/d log (2*j*₀ - *j*/*j*) and dφ*/d log [H⁺] should have the same value if the mechanism of hydrogen removal via the adsorption stage is considered. However, the values are 120 and 60 mV respectively (the latter is the limiting value obtained from the results presented in fig. 3 at high hydrogen ion concentrations).

This discrepancy may be caused by several reasons: (a) the order with respect to

¹ G. C. Barker, D. McKeown, M. J. Williams, G. Bottura and V. Concialini, paper at this Discussion.

² W. J. Albery, M. D. Archer, N. J. Field and A. D. Turner, this Discussion.

$[H^+]$ in \vec{k}_{20} is $\frac{1}{2}$; a result which would be difficult to interpret; (b) kinetic complications introduced by the varying nature of the several proton donors present (H_2O , HSO_4^- and H_3O^+) at different H_3O^+ concentrations in the $K_2SO_4 + H_2SO_4$ mixtures, and (c) reaction (C) proceeding both through an adsorption stage and directly from solution. The use of K_2SO_4 as a base electrolyte is not recommended for the study of the properties of H^- , not only because of the uncertainties regarding the nature of the proton donors, but also due to the complications in establishing the e_{aq}^- scavenging species.

I also feel it is better not to rely heavily on theoretical photoemission expressions to calculate partial currents, i.e., when $\nu < 2$, due to the diffuse layer effects contributing to the observed photocurrent,¹ but rather use a direct comparison at the same potential with scavengers such as N_2O .

Dr. Yu. V. Pleskov, Dr. Z. A. Rotenberg, Dr. V. V. Eletsky and Dr. V. I. Lakomov (Moscow) said: The dependence of ϕ^* on pH is described by eqn (4), (5) and (7) if in these equations we put $j = j_0$ (i.e., $\vec{j}_H = \overleftarrow{j}_H$):

$$\phi^* = \frac{2.3 RT}{(\alpha + \beta)F} \log \left(\frac{\vec{K}'}{\vec{K}} + \frac{\vec{K}''}{\vec{K}} X \right).$$

As is clear from this formula, the (ϕ^*, pH) dependence cannot be represented as a simple superposition of two linear functions. In the limiting case, when $\vec{K}'/\vec{K} \ll \vec{K}''/\vec{K}X$, this dependence becomes linear and has the same slope of $2.3 RT(\alpha + \beta)F$ as the dependence of ϕ on $\log(2j_0 - j/j)$. As follows from fig. 3, at $C_{H_3O^+} < 1N$ this case is not realized as yet. The reason is not clear. It may be caused by inappropriate base electrolyte, indeed. Anyhow this question requires further experimental study.

¹ G. Bomchil, D. J. Schiffrin and J. T. D'Alessio, *J. Electroanal. Chem.*, 1970, **25**, 107.