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Some Aspects of the Photoelectrochemical Effect at the Mercury — Aqueous Solution Interphase*

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The emissive properties of a polarized mercury surface in contact with aqueous solutions of electron acceptors is discussed. The proportionality between photocurrent and light intensity is experimentally verified; the origin of the residual current is discussed, and the potentialities of a photoelectrochemical method of study of the properties of intermediates and radicals is illustrated for carbon dioxide.

INTRODUCTION

There appears to be agreement at present with regards to the nature of the currents observed on irradiation with U. V. light of a polarized metal electrode in contact with solution containing suitable electron scavengers, such as N_2O . The mechanism of photoemission involves¹⁻³: photoexcitation, emission, thermalization and finally, reaction and diffusion of the hydrated electrons (e_{aq}^-).

A basic feature of any photoelectrochemical experiment involving the generation of hydrated electrons, is that the current actually measured is that due only to radicals which have decayed to stable species in the solution. The decay mechanism may involve a homogeneous process (such as $e_{aq}^- + e_{aq}^- \longrightarrow H_2 + 2 OH^-$)⁴, or a heterogeneous charge transfer reaction (such as $H + H^+ + e_m \rightarrow H_2$)⁵.

There are two further difficulties in the interpretation of the photocurrents:

- 1) The deposition function of the photoelectrons is not known, and
- 2) The scavenging reaction, and diffusion region (both of e_{hv}^- and of its decay products) occur partially or totally, depending on the base electrolyte concentration, within the diffuse double layer. Under these conditions, the potential dependence of the photocurrent contains information not only on the emissive properties of the metal surface, but also on the diffusion and reaction of e_{aq}^- in an electric field⁶.

The choice of the kind of deposition function that must be used in solving the diffusional problem is to some extent arbitrary. The problem

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is in deciding whether a non-thermalized electron can still react with scavengers, prior to the hydration step; pulse radiolysis experiments appear to give some evidence for the reactivity of the precursor of e_{aq}^- (Ref. 7, 8), a situation which might be greatly favoured in the photoelectrochemical case by the low energy of the emitted electrons.

In spite of this difficulty, it has been found that simple deposition functions, such as a delta function¹ or a step function⁶, give a correct description of the scavenger concentration (C_s) dependence of the photocurrents (J_p) and both models predict a limiting behaviour of the form

$$J_p = \delta k_{II} C_s J_E \quad (1)$$

where δ is a distance parameter and k_{II} is the homogeneous scavenger reaction rate constant and J_E is the total photoemitted current.

One of the interests of the photoelectrochemical effect is the possibility of studying the electrochemical properties of the products of the scavenging reaction. Table I summarizes some of the radicals which have been generated in this way.

TABLE I
*Radicals Generated by Photoelectrochemical Effect at the
Mercury—Aqueous Solution Interface*

Radical	Parent Compound	Reference
OH \cdot	N ₂ O	1
OH \cdot	H ₂ O ₂	this work
H \cdot	H ₃ O ⁺	1
CH ₃ CHOH \cdot	CH ₃ CH ₂ OH	5
CO ₂ \cdot	CO ₂	H \cdot
CH ₃ \cdot	CH ₃ Cl, CH ₃ I	9

The purpose of the present work was: a) to test the proportionality between measured photocurrents and incident radiation, predicted by the proposed diffusional models^{1,6}; b) to elucidate the relevance of O₂, a common impurity present in electrochemical systems, to the measured photocurrents and c) to study the electrochemical properties of radicals generated as products of the scavenging reaction and compare them with what is known about the electrochemistry of the parent compound.

EXPERIMENTAL

The experimental arrangement was similar to that described by de Levie and Kreuser² (Fig. 1), but the 100 c/s modulation of the light output of the lamp was employed instead of a mechanical chopper to obtain a modulated photocurrent.

A 200 W medium pressure Mazda Hg arc lamp was used. The image of the arc was formed on the mercury drop after passing through a 360 nm filter, having an 80 nm bandwidth (Fig. 2) and most of the active lamp output was in the 366 nm band. The lamp output was continuously monitored with a RCA 935 phototube.

The frequency doubling facility of the reference unit was used to provide the reference channels of the phase sensitive detector, using the 50 Hz line signal as input signal, and the phototube output was employed to phase the PSD with respect to the exciting radiation. The photocurrent was recorded at an electronically controlled pre-specified time after the birth of the drop, and after a short delay it was dislodged by means of a small hammer operated by the same timing circuit.⁹

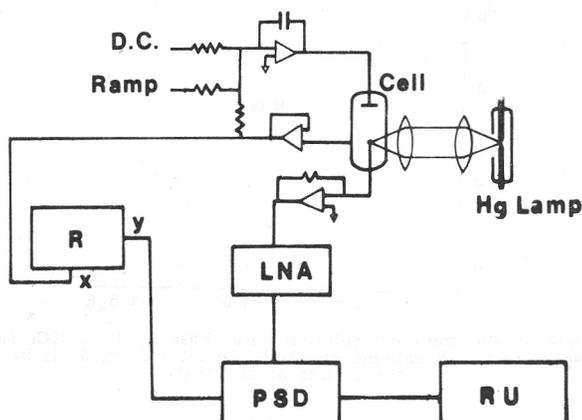


Fig. 1. Block diagram of the potentiostat and synchronous rectification system employed for the measurements of photocurrents R = X - Y recorder (Bryans, 26000); L.N.A. = Low Noise Amplifier (Brookdeal 450); R.U. = Reference Unit (Brookdeal 422); P.S.D. = Phase Sensitive Detector (Brookdeal 411). Current Follower feedback resistance = 200 Ω ; feedback capacitance = 100 pF. All operational amplifiers type Texas Instruments, SN72741.

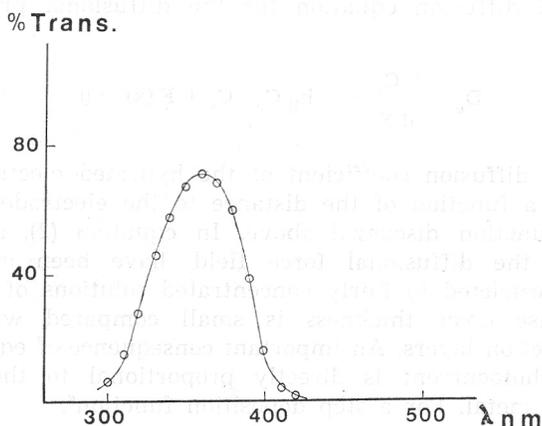


Fig. 2. Transmission of the 360 nm filter used in all the measurements.

In this way, each drop provided a data point, and the results presented below, are direct recordings from the instrument. In de Levie's arrangement, some positive feedback was included; this is certainly a convenient facility when studying photocurrents in very dilute solutions. Since the present work was restricted to concentrated solutions, no positive feedback was found to be necessary. In any case with the operational amplifiers used, it would not have been practical to attempt work in dilute solutions. The instrument was phased by connecting the phototube to the current follower and the quadrature component of the current brought to zero by shifting the phase of the reference unit channels with respect to the modulated light output of the lamp. In this way, the photocurrent measured in an actual experiment, was always in phase with the U.V. radiation; this point was also experimentally verified. A typical photocurrent - potential plot is shown in Fig. 3 for N_2O , in good agreement with previously published results on this system². Before each run, the N_2O solution photocurrent was measured and used for calibration purposes (i. e., to account for changes in drop area, positioning of the cell, etc, from run to run).

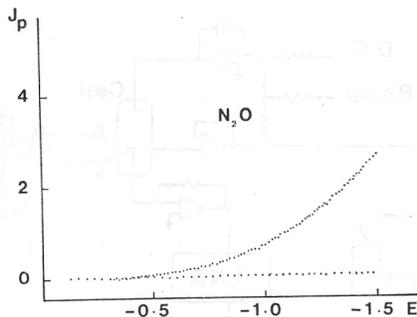


Fig. 3. Photocurrents at the mercury solution interphase — 1 M KCl saturated with N_2O . Potentials with respect to a 1 N calomel electrode. In all graphs, J_p is in arbitrary units. All the results at $23 \pm 1^\circ C$.

The general experimental precautions described¹⁰ were observed in the purification of mercury and water, and in the preparation of the dropping mercury electrodes employed.

The Radiation Intensity Dependence of the Photocurrent

Fick's second diffusion equation for the diffusional processes occurring after emission is⁶

$$D_{e^-} \frac{\partial^2 C_{e^-}}{\partial x^2} - k_H C_{e^-} - C_s + F(x) = 0 \quad (2)$$

where D_{e^-} is the diffusion coefficient of the hydrated electrons, C_{e^-} is their concentration as a function of the distance to the electrode, x , and $F(x)$ is the deposition function discussed above. In equation (2), all diffuse layer contributions to the diffusional force field, have been excluded and its applicability is restricted to fairly concentrated solutions of base electrolyte, where the diffuse layer thickness is small compared with that of the diffusion and reaction layers. An important consequence of equation (2) is that the calculated photocurrent is directly proportional to the total emission current from the metal. For a step deposition function⁶,

$$J_p = J_E \left\{ 1 - \frac{1}{\delta Q} [1 - \exp(-\delta Q)] \right\} \quad (3)$$

where

$$Q = \left[\frac{k_H C_s}{D_{e^-}} \right]^{1/2}$$

This proportionality is due to the linear character of equation (2) and would be expected to break down if a second order recombination reaction (such as $e_{aq}^- + e_{aq}^-$) is important, or if the scavenger concentration is itself a function of distance. Also, diffuse layers effects should lead to non-linear behaviour.

A direct proportionality between the photocurrent and the light intensity has been previously reported¹², although no data on this question appears to have been published. The use of A. C. modulated U. V. radiation makes

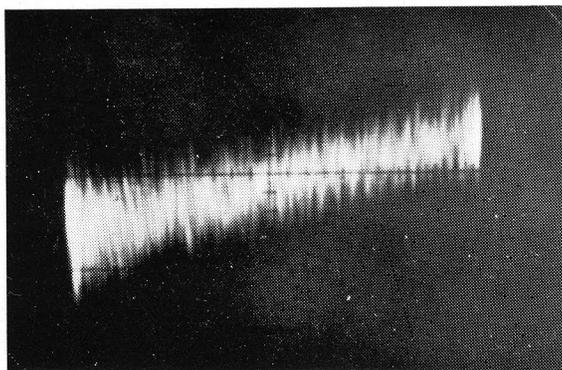


Fig. 4. 1 M HCl. Photocurrent as a function of light intensity. $E = -1.30$ Volts; sensitivity: $X = 0.2$ V/cm, $Y = 1$ mV/cm.

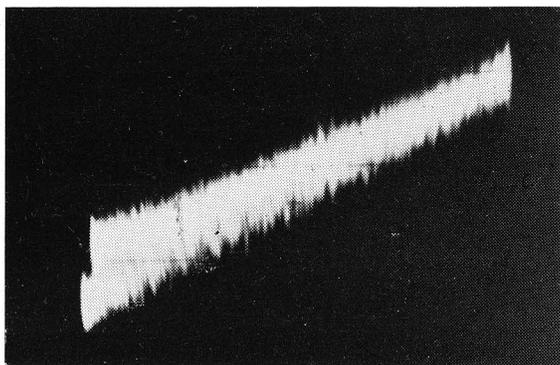


Fig. 5. 1 M HCl saturated with N_2O . Photocurrent as a function of light intensity. Full lamp output. $E = -1.65$ Volts, sensitivity $X = 0.2$ V/cm, $Y = 2$ mV/cm.

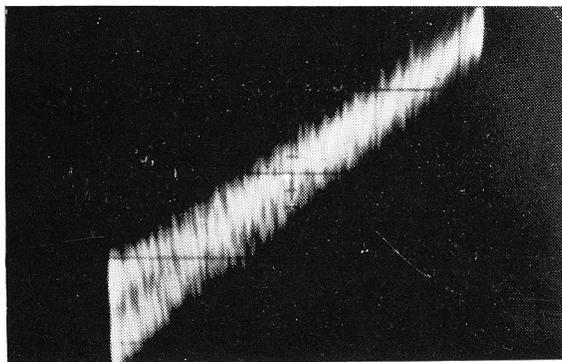


Fig. 6. 1 M KCl saturated with CO_2 . Photocurrent as a function of light intensity. Full lamp output. $E = -1.60$ Volts; sensitivity: $X = 0.2$ V/cm; $Y = 1$ mV/cm.

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the experimental verification of the proportionality between photocurrent and light intensity very easy, by displaying the photocurrent on the Y axis of an oscilloscope screen, and the light intensity as measured by the phototube response, on the X axis. Figs. 4, 5 and 6 show this for HCl, N_2O and CO_2 solutions. The unfiltered photocurrent signal was taken directly from the output of the current follower and the photographs were taken 8.0 seconds after drop birth. The presence of high frequency noise is inevitable in the current flow arrangement employed, since it behaves as a differentiating circuit due to the capacitative input impedance represented by the double layer capacitance of the mercury surface. Another feature of Figs. 4, 5 and 6, is the presence of 50 and 150 Hz noise in the photocurrent. This can be seen in the splitting of the signal at one end of the trace, and could be directly observed in the shape of the photocurrent signal. Although many precautions were taken to isolate the cell and potentiostat from mains noise (both cell and potentiostat were enclosed in a Faraday cage) its complete removal is very difficult. However, this mains noise does not introduce any errors in the rectified signal, since the P.S.D. effectively rejects these components. From Figs. 7, 5 and 6 it can be seen that the mean value of the photocurrent is proportional to the light intensity for the three systems analysed, showing the validity (at least in this aspect) of the approach described by equation (2).

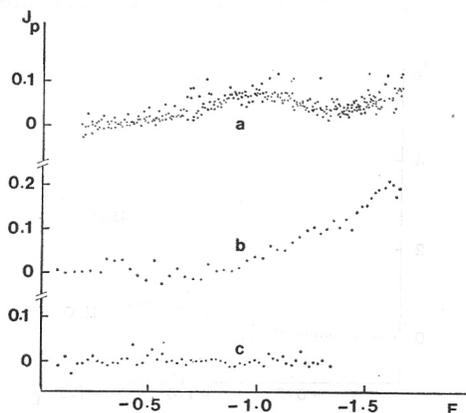


Fig. 7. Photocurrents at a Hg — 1 M KCl oxygen saturated solution interface. a) = O_2 saturated solution; b) = deaerated solution (residual photocurrent); c) = instrumental noise (no illumination) at different potentials. The sensitivity employed here is 10 times that of the results shown in Fig. 3.

The Photoelectrochemical Reduction of O_2 and H_2O_2

In the absence of electron acceptors in the solution, a residual photocurrent is still observed at potential cathodic to -1 volt^{1,15}. This residual photocurrent may be attributed to several causes^{1,15}, such as the inevitable presence of trace impurities *e.g.*, O_2 , the reaction of e_{aq}^- with the solvent, and the second order electron decay. In order to test the influence of O_2 on the residual photocurrent, the latter was measured for oxygen-free and oxygen saturated KCl solutions. These results are shown in Fig. 7. Due to

the high sensitivity employed in these measurements, a considerable degree of scatter is evident. The results for the O_2 saturated solution were obtained by multiple potential scannings, so as to reveal the average potential dependence of the photocurrent. Curve (a) shows the instrumental noise, as a function of potential in the absence of illumination indicating that this is independent of the value of the double layer capacitance. Curves (b) and (c) show a comparison between the residual photocurrent and that due to the presence of O_2 . There are three features to notice: 1) at a sufficiently cathodic potential, the potential dependence of J_p for the O_2 -saturated solution appears to become similar to that of the residual photocurrent; 2) a broad maximum in the photocurrent can be observed at a potential of ~ -1.0 V; 3) the value of the photocurrent is very low, some 10 times that observed for a saturated N_2O solution.

Oxygen is known to be a very efficient electron scavenger (rate constant $k_{O_2+e^-} = 1.9 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$)^{13,14}. However, due to its electrochemical reactivity, it is doubtful whether it can act as an electron scavenger at potentials cathodic to -0.2 V., the primary product of the reduction being H_2O_2 .

It is suggested then, that the photocurrent observed in the presence of oxygen, is that due only to the electrochemically generated H_2O_2 acting as electron acceptor. At potentials more negative than -1 V, the reduction of H_2O_2 approaches diffusion control, and the photocurrent due to the scavenging process should decrease. This effect is illustrated in Fig. 8, where

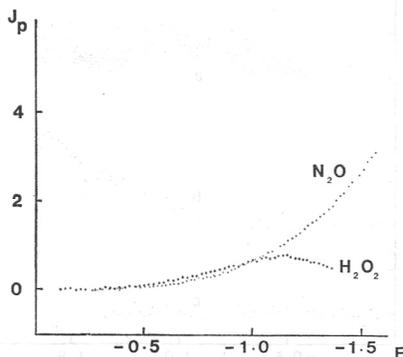


Fig. 8. Photocurrents at a dropping mercury electrode in contact with a 0.02 M N_2O and a 0.03 M H_2O_2 solution in 1 M KCl. Potentials vs. the N.C.E.

the photocurrents for an H_2O_2 solution, are compared with those observed with N_2O . The product of the scavenging reaction by H_2O_2 is the OH^\cdot radical¹³



In all the accessible potential range, the OH^\cdot radical is further reduced to OH^-



and the stoichiometric number (*i.e.* the number of electrons permanently lost by the electrode for each successful scavenging act) for the photoelectrochemical reduction of H_2O_2 is 2.

The corresponding photoelectrochemical reduction mechanism for N_2O is:¹



At the concentrations of N_2O and H_2O_2 studied, equation (1) is reasonably correct⁶. If the stoichiometric number, for both processes is the same,

$$\frac{J_p(N_2O)}{J_p(H_2O_2)} = \left[\frac{C_{N_2O} \cdot k_{(N_2O + e^-)}}{C_{H_2O_2} \cdot k_{(H_2O_2 + e^-)}} \right]^{1/2} \quad (5)$$

and taking $k_{(N_2O + e^-)} = 8.7 \times 10^9$ (Ref. 4) and $K_{(H_2O_2 + e^-)} = 1.3 \times 10^{10} M^{-1} sec^{-1}$ (Ref. 14, 16), we calculate $\frac{J_p(N_2O)}{J_p(H_2O_2)} = 0.7$ in reasonable agreement with the results presented in Fig. 8 up to a potential of ~ -0.9 V.

The decrease noted at more negative potentials is due to the onset of diffusion control in the reductions on H_2O_2 , with the corresponding decrease in the surface concentration of scavenger, but the similarity of the stoichiometric numbers for the H_2O_2 and N_2O photoelectroreduction at potentials anodic to this, can be taken as evidence for the correctness of the mechanism described by equations (1) and (2). It is then not surprising to find a maximum in the J_p -potential relationship in the photoelectrochemical reduction of O_2 , where H_2O_2 is the photoelectrochemical active species. The very low value of J_p observed in the case of O_2 related both to its significantly lower solubility in a 1 M KCl solution, than that of N_2O ($8.9 \times 10^{-7} M$ and $1.92 \times 10^{-2} M^{-1} sec^{-1}$ respectively¹⁷), and to its concentration in the reaction and diffusion region being determined by a preceding electrochemical step. It is interesting to note the similarity in the increase in the photocurrent at potentials cathodic to -1.3 V, which would suggest a similar mechanism for the photocurrent in this potential range both in the presence and absence of O_2 .

It can be concluded then, that the origin of the residual photocurrent is not related to the presence of trace amounts of oxygen as an impurity.

The Photoelectrochemical Reduction of Carbon Dioxide

The photoelectrochemical activity of CO_2 was first reported by Heyrovský¹², but no data corresponding to this system has been published. Fig. 9 shows the photocurrents as a function of potential for a saturated CO_2 solution in 1 M KCl, measured with the phase detection technique described above. No photocurrent is observed for potentials anodic to -1.2 V. This was also verified experimentally by performing measurements with increased sensitivity. The absence of a photocurrent in this case, contrasts markedly with that of the N_2O case (Fig. 9), and the sudden onset of the photocurrent at potentials cathodic to -1.2 , -1.3 V, indicates the formation of an oxidizable radical as the primary product of the scavenging process. A similar explanation was advanced by Barker¹ to account for the decrease in the value of the stoichiometric number in the photoelectrochemical reduction of H_3O^+

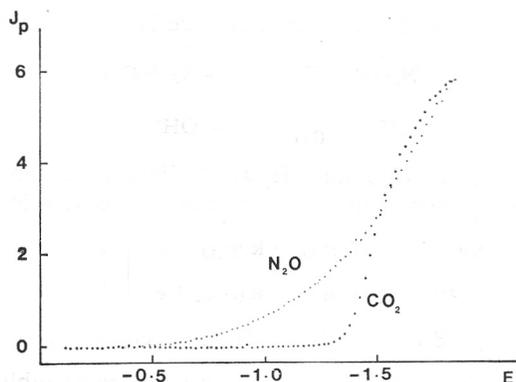
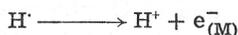


Fig. 9. Photocurrents at a dropping mercury electrode in contact with a 1 M KCl solution saturated with N_2O and CO_2 . Potentials vs. the N.C.E.

at potentials anodic to -0.8 V (vs S. C. E.). In that case, the decrease was attributed to the reaction



the H^+ atom being the primary product of the scavenging reaction of H_3O^+ .

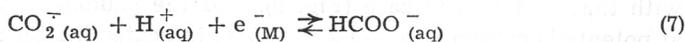
A similar explanation can be offered in the present case. CO_2^- is known from radiation chemistry studies, to be formed as the primary product, *i. e.*,



$$k(\text{CO}_2 + e_{\text{aq}}^-) = 7.7 \cdot 10^9$$

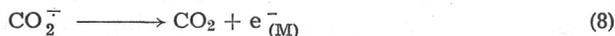
As it was stressed above, current will only flow across the interphase, if the decay products of the scavenging reaction are stable in solution with respect to reoxidation at the electrode. It should be pointed out also, that due to the small value of the thickness of the diffusion and reaction layer (of the order of 100 – 200 Å), it is very unlikely that an oxidizable species formed in it, can diffuse away into the solution¹. The appearance of a photocurrent is then related to the electrochemical properties of the radical CO_2^- , either as an adsorbed species on the electrode, or as a radical in solution.

From the comparison of the photocurrents due to N_2O and CO_2 (Fig. 9), the photoelectrochemical stoichiometric number was found to increase from 0 up to a value of 2 at a potential of -1.7 V. It has been proposed that the *electrochemically* generated CO_2^- radical is further reduced to the formate ion¹⁸. In the photoelectrochemical situation, the radical stabilizing mechanism is very likely to be



and this would account for the observed value of 2 for the stoichiometric number *i. e.*, for each electron captured by a CO_2 molecule, a further electron is lost by the metal to form a formate ion. Also, reaction (7) determines

whether a photocurrent would flow across the interphase, or the oxidation process



would occur. That is to say, the photocurrent appearance potential has a significant physical meaning in terms of the electrochemical properties of the radicals generated in solution. Equation (7) predicts that the appearance potential would be related to the strength of the proton donor present in solution. This is indeed the case as it can be seen, when the CO_2 photocurrents in a 1 M KCl solution, are compared with those in 1 M KHCO_3 (Fig. 10).

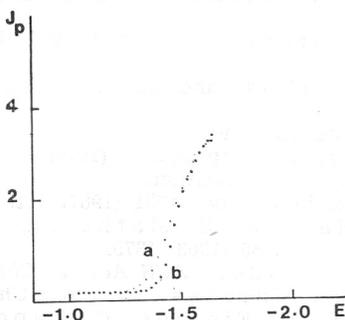


Fig. 10. Photocurrent at a dropping mercury electrode in contact with CO_2 saturated solutions of a) 1 M KCl and b) 1 M KHCO_3 . Potentials vs. the N.C.E.

In the former case, the proton donors are H_3O^+ and H_2CO_3 , whereas in the latter, the weaker acid HCO_3^- acts as the main proton donating species. (The pH of a CO_2 saturated KHCO_3 solution is close to 7). The results presented in Fig. 10, show that the appearance potential is shifted to more negative potentials for weaker proton donors, in accordance with the proposed mechanism. An alternative reaction sequence can be envisaged, involving the formation of the carboxylate radical, *i. e.*,



The COOH^- radical has been observed in aqueous solutions, and the pK_a of reaction (10) found to be 3.8¹⁹. Undoubtedly, in sufficiently acid solutions, the protonation step is bound to occur to a significant extent, resulting in a mixed mechanism; further work is in progress to distinguish between these two possibilities.

The photoelectrochemical effect offers some very interesting possibilities to gain insight both on the physical aspects of the photoemission process and in the electrochemistry of radicals and intermediates occurring in an electrochemical process. The difference between an electrochemical reduction process and a photoelectrochemical one, is in the possibility of observing *only*

the effects brought about by the generation of radicals by independent means. This is particularly interesting when phase detection techniques are employed to extract the information of these effects brought about only by the incident radiation from an overall current flowing across the interphase.

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IZVOD

Neki aspekti fotoelektrokemijskog efekta na granici faza živa — vodena otopina

D. J. Schiffrin

Opisani su eksperimenti fotoemisije s površine živine kapajuće elektrode u vodenu otopinu stimulirane moduliranim ultravioletnim svjetlom. Proučavana je redukcija O_2 i H_2O_2 u 1 M KCl i HCl kod katodičkih potencijala. Fotoelektrična struja, koja se mjeri uzrokovana je elektrokemijski generiranim H_2O_2 , koji dalje djeluje kao akceptor elektrona. Kod potencijala negativnijih od -1.0 V prema ZKE, redukcija H_2O_2 približava se uvjetima kontrole procesa difuzijom. Usporedbom utjecaja N_2O i H_2O_2 vidi se da je uz pretpostavku jednakih stehiometrijskih brojeva kvocijent fotostruja $J_p(N_2O)/J_p(H_2O_2) = 0.7$. Usporedbom uvjeta redukcije N_2O i CO_2 u 1 M KCl i $KHCO_3$ otopinama vidi se, da stehiometrijski broj za redukciju CO_2 raste do 2 kod potencijala od -1.7 V. To se tumači time što se elektrokemijski stvoreni radikal Co_2^- reducira fotoelektronima u prisustvu H^+ -donora u $HCOO^-$. Utvrđen je i proporcionalitet između fotostruje i intenziteta svjetla. Također se diskutira o mogućim uzrocima postojanja rezidualnih fotostruja.

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