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STUDIES ON PHOTO-POLAROGRAPHY. VII.[1)] PHOTO-CURRENT OF DIMETHYLSULFOXIDE AND FORMATION OF METHYLSULFYNYLCARBONIUM ANION AT IRRADIATED DROPPING MERCURY ELECTRODE

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The photo-current produced at a dropping mercury electrode irradiated by ultra-violet light in the dimethylsulfoxide (DMSO) solution was investigated. The formation of methylsulfynylcarbonium anion by the reaction of DMSO with the solvated electron was confirmed indirectly from the influence of ethanol as the H radical scavenger on the photo-current.

In the last five years the investigation of the photo-current produced at a mercury electrode irradiated by ultra-violet light has been remarkably advanced.[2)] Brodsky and his coworkers[3-7)] have proposed the law of five halves in relation to the dependence of the photo-emission current on the electrode potential. Barker et al.,[8, 9)] Holub,[10)] Bomchil et al.,[11)] and the present authors[12)] have reported the reactions of the solvated electrons with the scavengers. They were mostly interested in accounting for the relationship between the photo-current and the scavenger concentration in solution. In the present paper the investigation of the photo-current of DMSO is reported. The experimental results suggest the formation of methylsulfynylcarbonium anions and H atoms as the intermediates, and H atoms formed enter into the successive charge transfer reaction.

Dependence of the Photo-current on the Electrode Potential: DMSO solution containing 0.1 M sodium perchlorate as the supporting electrolyte developed the appreciable photo-current at more negative potentials than about -0.5 V vs. SCE, and the photo-current increased gradually with increase of the negative potential. DMSO in the PC solution also showed the same behavior. It seems that the scavenging of electrons possibly solvated in solution by DMSO molecules results in the flow of the photo-current.

In relation to the field effect on the photo-emission current two theories have been proposed hitherto. Delahay et al.[13, 14)] have reported the experimental validity of the quadratic law, which has been originally proposed by Fowler[15)] for the photo-detached electron emission from an irradiated metal in vacuo. On the other hand, Brodsky et al.[3-7)] have proposed the 5/2 power law for the emission current in solution. Their theoretical equations are expressed as follows:

The quadratic law, $i_e = A(h\nu - h\nu_0 + e\varphi)^2$ (1)

The 5/2 power law, $i_e = B(h\nu - h\nu_0 + e\varphi)^{5/2}$ (2)

where i_e is the photo-emission current, A and B are constants which depend on the nature of metals, ν the frequency of the irradiated light, ν_0 the threshold frequency and φ the electrode potential.

Fig. 1 shows the plot of $i_p^{0.5}$ and $i_p^{0.4}$ (i_p is the observed photo-current) versus the electrode potential. The threshold potential φ_0 was determined to be -0.30 V by the extrapolation of the straight line (2) in Fig. 1. From the comparison of approximate linearities of these two plots it is difficult to conclude the difference between two theories.

Dependence of the Photo-current on DMSO Concentration: When the solvated electron is scavenged by the acceptor in solution according to Eq. (3), Eq. (4) holds for the photo-current, i.e.,[8, 9]

$$e^-_{solv} + S \xrightarrow{k_s} S^- \qquad (3)$$

$$i_p = i_d \frac{Q\delta}{1 + Q\delta}, \quad (Q\delta < 1) \qquad (4)$$

where i_p is the photo-current, i_d the rate of deposition of solvated electrons in solution, $Q = (k_s C_s / D_e)^{1/2}$, k_s the rate constant of the scavenging reaction (Eq. (3)), C_s the bulk concentration of the scavenger S, D_e the diffusion coefficient of the solvated electron and δ the real or apparent average distance from the electrode surface for the deposition of solvated electrons.

When the scavenger concentration is very low and the condition that $(k_s C_s / D_e)^{1/2}$ is much smaller than unity holds, Eq. (4) can be approx-

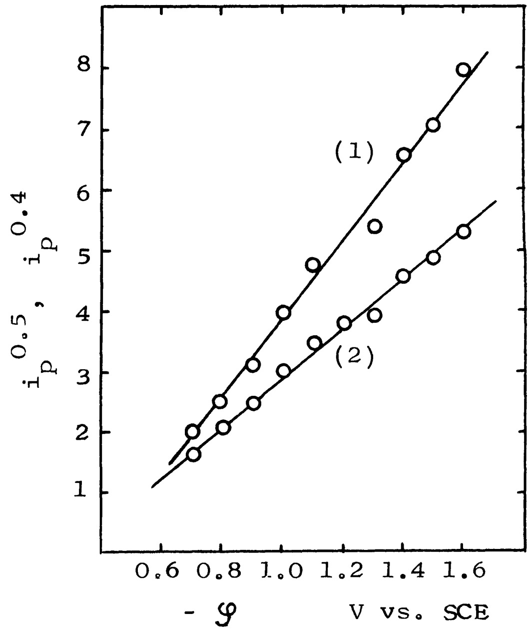

Fig. 1. Dependence of $i_p^{0.5}$ and $i_p^{0.4}$ on the electrode potential φ for DMSO solution containing 0.1 M $NaClO_4$.
(1) Plot of $i_p^{0.5}$ vs. φ.
(2) Plot of $i_p^{0.4}$ vs. φ.

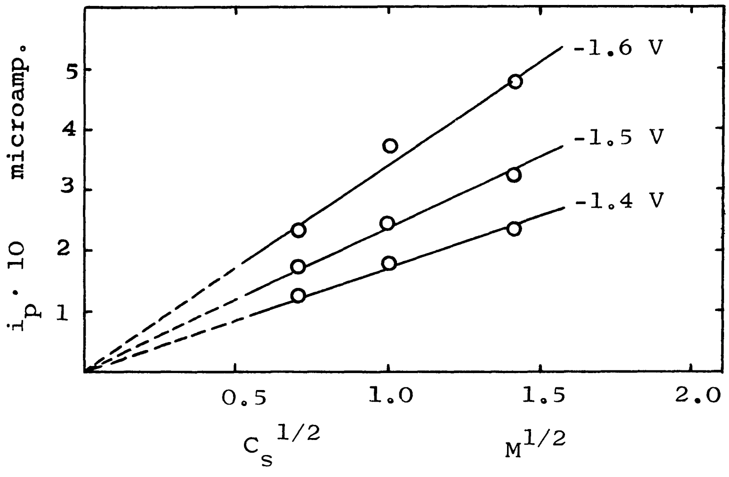

Fig. 2. Dependence of i_p on $C_s^{1/2}$ for PC solution containing DMSO and 0.1 M $NaClO_4$, where C_s is the concentration of DMSO.

imated by Eq. (5) as follows:

$$i_p = i_d \left(\frac{k_s C_s}{D_e}\right)^{1/2} \cdot \delta \qquad (5)$$

Eq. (5) indicates that the photo-current is linearly proportional to the square root of the scavenger concentration. The same relationship have been derived by the present authors[12)] by treating the semi-infinite diffusion problem of aquated electrons with scavenger ions or molecules in solution.

The experimental results shown in Fig. 2 prove the validity of the reaction scheme assumed as Eq. (3).

Influence of Ethanol on the Photo-current: From the above mentioned result the scavenging reaction of the solvated electron by DMSO is expressed by Reaction (a) and the successive oxidation reaction or reduction of H atoms formed by Reaction (a) is represented by Reaction (b) or (c).

The decrease of the photo-current was observed by the addition of ethanol to the DMSO solution in the potential range less negative than -1.45 V vs. SCE as shown in Fig. 3. Ethanol is a well-known H atom scavenger, and it is assumed that ethanol scavenges H atom formed by the homogeneous electron capture by DMSO (Reaction (d)). The α-ethanol radicals thus formed will be readily oxidized at the potentials covered in this experiment (Reaction (e)). In relation to the molecular hydrogen formation a catalytic process is more plausible than the formation of molecular hydrogen from H atoms by the homogeneous or heterogeneous combination in pair, so that H atoms enter into Reaction (c) at the electrode surface in a one-electron transfer reaction. Accordingly, the assembly of the following competitive and successive reactions can be taken into consideration as the most plausible one,

$$e^-_{solv} + (CH_3)_2SO \xrightarrow{k_s} CH_3SO\bar{C}H_2 + H \qquad (a)$$

$$H \xrightarrow{k_b} H^+_{solv} + e^- \qquad (b)$$

$$H + e^- + (CH_3)_2SO \xrightarrow{k_c} H + CH_3SO\bar{C}H_2 \qquad (c)$$

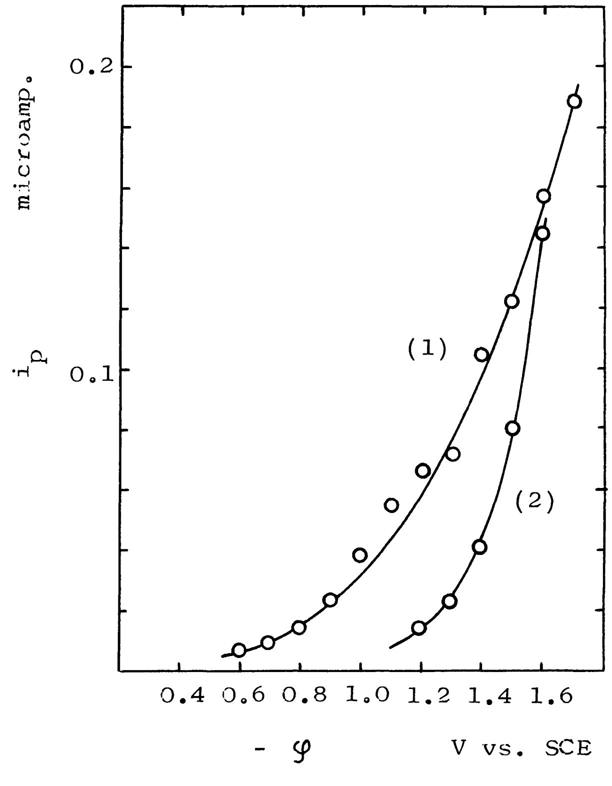

Fig. 3. Influence of ethanol on i_p for DMSO solution containing 0.1 M $NaClO_4$.

(1) i_p - φ curve in the absence of EtOH.

(2) i_p - φ curve in the presence of EtOH.

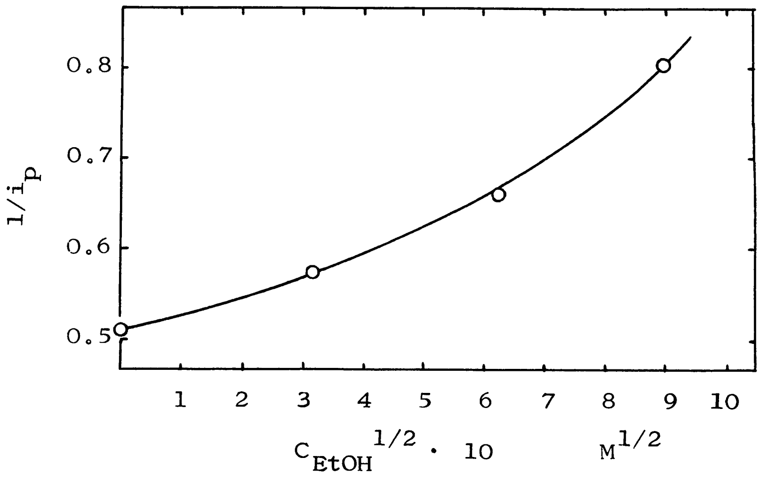

Fig. 4. Plot of $1/i_p$ versus $C_{EtOH}^{1/2}$ for PC solution containing 1 M DMSO and 0.1 M $NaClO_4$ at -1.3 V vs. SCE.

$$H + C_2H_5OH \xrightarrow{k_d} H_2 + CH_3\dot{C}HOH \qquad (d)$$

$$CH_3\dot{C}HOH \longrightarrow CH_3CHO + H^+_{solv} + e^- \qquad (e)$$

Supposing that the heterogeneous oxidation of the α-ethanol radical proceeds rapidly (Reaction (e)), the approximate steady state photo-current can be expressed as follows:[9]

$$i_p = i_d \frac{Q\delta}{1 + Q\delta} \cdot \frac{1}{1 + Q'/Q} \cdot \frac{2k_c}{k_b + k_c} \qquad (6)$$

where Q' denotes $(k_d C_{EtOH}/D_H)^{1/2}$, C_{EtOH} the concentration of ethanol and D_H the diffusion coefficient of the H radical. From Eq. (6) the plot of the reciprocal of the photo-current at the constant potential vs. the square root of the ethanol concentration should yield a straight line, provided that Q is held constant.

Fig. 4 shows the plot obtained in the DMSO solution in PC. The linear relationship expected from Eq. (6) holds approximately in Fig. 4.

Further works are in progress and will be reported elsewhere.

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