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# Studies on Photo-polarography. I. Polarographic Behavior of Trioxalatoferrate(III) Ion under Ultraviolet Irradiation

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The polarographic behavior of trioxalatoferrate(III) ion under irradiation of ultraviolet light was studied. Trioxalatoferrate(III) was photo-chemically reduced in the bulk and the polarographic reduction current changed into the oxidation one, which showed a highly kinetic characteristic. The current-time curve during one drop growth of the dropping mercury electrode under irradiation was analyzed, and the rate constant of the photo-chemical reaction ($k_\nu$) was evaluated. The apparent value given as $k_\nu' = I_0 \varepsilon k_\nu$ was 0.35 $cm^{-1}$, where $I_0$ being the intensity of the incident light and $\varepsilon$ the extinction coefficient. The time dependence of the photopotential was elucidated on the basis of the Nernst equation. The possible photonometric determination of dissolved oxygen was suggested from the effect of dissolved oxygen on the half-life of the photo-chemical reaction.

The redox behavior of ferri- and ferro-oxalate complexes has been studied by von Stackelberg and von Freyhold,[1] Lingane,[2] and Randles and Somerton.[3] In their early work, the chemical constitution of ferrooxalate complex, which depends on the concentration of excess oxalate, was determined.

On the other hand, Rao and Aravamudan[4] have shown that iron(III) is photo-chemically reduced in the presence of excess citric acid, and that it can then be titrated with a standard solution of sodium vanadate. Thus, they proposed a photonometric determination of oxalic acid in the presence of excess ferric sulfate. Bricker and Schonberg[5] reported a new photonometric method for the separatory determination of vanadium and chromium by using the photo-chemical reduction of ferrioxalate.

Recently, Berg and his coworkers have investigated the effect of continuous or flash irradiation on the current-potential characteristics of ketyl radicals,[6] hydroquinones,[7,8] benzophenone,[6] and

1) M. von Stackelberg and H. von Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).
2) J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).
3) J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 937 (1952).
4) G. G. Rao and G. Aravamudan, *Anal. Chim. Acta*, **13**, 328, 415 (1955).
5) C. E. Bricker and S. S. Schonberg, *Anal. Chem.*, **30**, 923 (1958).
6) H. Berg and H. Schweiss, *Naturwiss.*, **47**, 513 (1960); *Nature*, **191**, 1270 (1961).
7) H. Berg, *ibid.*, **47**, 320 (1960); *Z. Chem.* (Leipzig), **2**, 237 (1962).
8) H. Berg, *Rev. of Polarog.* (Japan), **11**, 29 (1963).

other organic compounds.[6] As a result of their studies they have suggested four groups of photopolarographic reaction.

The present authors have investigated the photopolarographic behavior of trioxalatoferrate(III) ion in 0.5 M potassium oxalate with the continuous ultraviolet irradiation. The results and the apparent rate constant of the photo-chemical reaction evaluated are presented in this paper.

## Experimental

**Apparatus.** The current-voltage curves were recorded with Yanagimoto Polarograph Model PA-102 and Shimadzu Polarograph Model RP-2.

The characteristics of the dropping mercury electrode (DME) were as follows: $m=1.30$ mg/sec, $t=4.5$ sec with the open circuit in an air-free 0.5 M potassium oxalate solution. A hammer with 4.0 sec interval was used to give the constant life-time of the DME.

For recording the current-time curve during one drop of the DME under a given voltage, Iwasaki Model 5155 cathode-ray oscilloscope with a plug-in amplifier Model SP-30H-A were used. The constant applied voltage was supplied from Yokogawa Model P-1 precision potentiometer through series 1 kΩ resistor, which is used to give the current signal.

The experimental arrangement is shown in Fig. 1. The light beam was emitted from Ushio Type UXL 500 DV xenon lamp (A in Fig. 1). The light was passed through a focusing lens, B, and was focused on a side of the DME. A quartz cell, C, (a conventional 10 mm quartz cell for the UV spectrophotometer) was used and the optical path of the incident light through the solution to the DME was about 3 mm. The geometry was kept constant throughout the measurements.

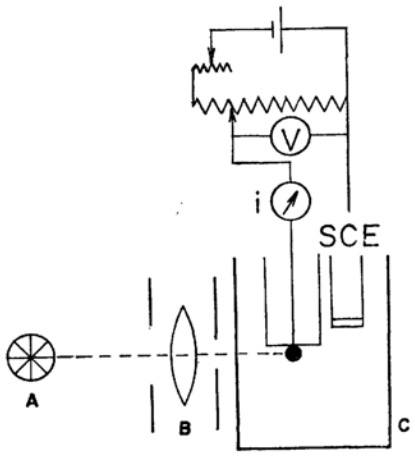


Fig. 1. The irradiation system.

The variation of the room temperature was about ±2°C. The temperature rise by the continuous irradiation is shown in Fig. 2. It is concluded that the temperature rise of the solution by the continuous irradiation during 5 min is as small as 1.8°C.

**Reagents.** The trioxalatoferrate(III) solution was prepared by dissolving metallic iron in dilute sulfuric acid, evaporating the excess acid, and then diluting to be $1.0\times10^{-2}$ M in its concentration (pH=9.5) with aqueous 0.5 M potassium oxalate solution. Purified nitrogen was used to remove dissolved oxygen in the solutions.

All other chemicals were of analytical reagent grade, and they were purified by the conventional methods.

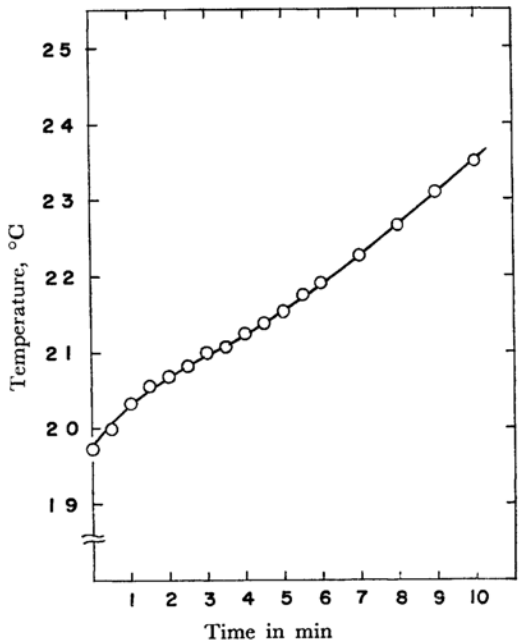


Fig. 2. Variation of temperature with the irradiation time in 0.5 M potassium oxalate solution.

## Results and Discussion

**D. C. Polarography.** Trioxalatoferrate(III) developed a well-defined polarographic reduction wave, of which the half-wave potential was −0.26

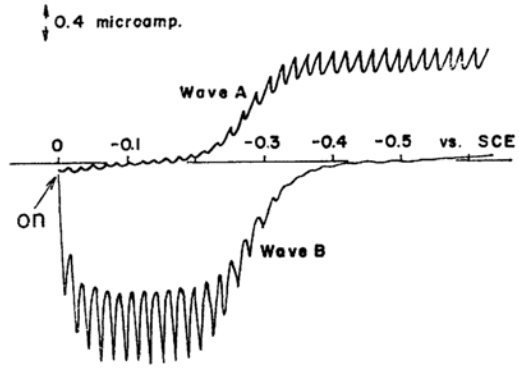


Fig. 3. D. C. polarograms of 0.4 mM trioxalatoferrate(III) ion in 0.5 M potassium oxalate solution.
Wave A: the reduction wave of trioxalatoferrate(III).
Wave B: the anodic wave appeared by the irradiation.

V *vs.* SCE (Wave A in Fig. 3). During the ultraviolet irradiation, the cathodic wave disappeared rapidly and a new anodic wave (Wave B in Fig. 3) appeared at almost the same potential as the cathodic wave. It is noteworthy that the anodic limiting current was about 1.6 times greater than the cathodic limiting current.

The dependence of the photo-polarographic limiting current at −0.15 V (the potential to give the limiting anodic current) on the height of mercury reservoir was examined. The result is shown in Fig. 4. It is seen in Fig. 4 that the photo-polarographic limiting current is actually unchanged by the mercury head, while the cathodic current without irradiation shows a trend to increase with increase of the mercury head.

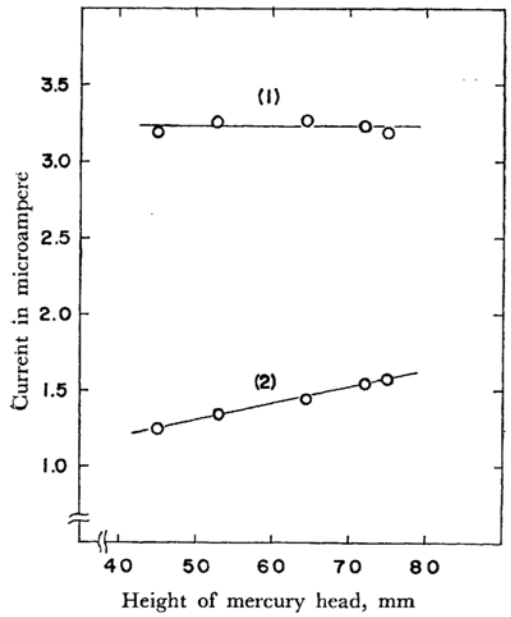


Fig. 4. Dependence of limiting current of (1) wave B and (2) wave A on the height of mercury head.

Figure 5 shows the plot of log *i versus* log *t* during one drop growth of the DME at −0.15 V after the continuous irradiation for 200 sec. From the inclination of the plot it was found that the photo-polarographic current varied with time to the power of 0.59. This result coupled with the above mentioned result in relation to the effect of the mercury head suggests the kinetically controlled feature of the photo-polarographic current. Thus, the following scheme of the parallel reactions is assumed at −0.15 V under continuous irradiation.

Electrode Reaction: $R - e = O$ (1′)

Photo-chemical Reaction: $O + h\nu = R$ (2′)

The reaction scheme shown in Eqs. (1′) and (2′) involves the regeneration of the reductant at the vicinity of the electrode surface by the photo-chemical reaction. Thus, the flux of the reductant toward the electrode surface is increased by the ultraviolet irradiation. This seems to elucidate the above-mentioned fact that the anodic limiting current under irradiation is about 1.6 times greater than the cathodic limiting current, which is observed without irradiation.

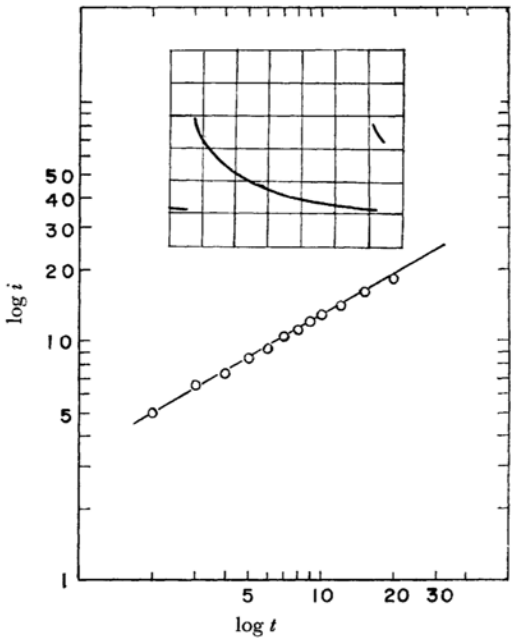


Fig. 5. log *i* - log *t* plots for the curve shown above, which was recorded during one drop growth of the DME after irradiation for 200 sec at −0.15 V.

**Polarographic Current-Time Curve during One Drop Growth of DME.** The parallel reactions occurring at −0.5 V and in the bulk are expressed as Eqs. (1) and (2), *i. e.*,

$$Fe(ox)_3^{3-} + e^- \rightleftarrows Fe(ox)_3^{4-} \quad (1)$$

$$Fe(ox)_3^{3-} + \tfrac{1}{2}C_2O_4^{2-} + h\nu \rightleftarrows Fe(ox)_3^{4-} + CO_2 \quad (2)$$

The variation of the concentration of the trioxalatoferrate(III) ion by the reaction given in Eqs. (1) and (2) is expressed by the following differential equation, *i. e.*,

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) + \left(\frac{2x}{3t}\right)\left(\frac{\partial C}{\partial x}\right) - k_\nu\left(\frac{I_0}{l}\right)\left(1 - e^{-\varepsilon lC}\right) \quad (3)$$

In the right hand side of Eq. (3) the first term represents Fick's 2nd. law, the second term represents the convection due to the growth of the mercury drop, and the third term represents the effect of the coupled photo-chemical reaction, where the absorption of the incident light is obeyed by Beer's law.

The magnitude of the photo-kinetic current for Eq. (3) can then be evaluated for the initial and boundary conditions given as follows:

$$\left.\begin{array}{lll} C=C_i^* & \text{for } x\geqq 0, & t=0 \\ C=0 & \text{for } x=0, & t>0 \\ C=C_i^*e^{-k_\nu' t} & \text{for } x\to\infty, & t\geqq 0 \\ \text{with } k_\nu'=k_\nu\varepsilon I_0 & & \end{array}\right\} \quad (4)$$

where $C_i^*$ is the initial bulk concentration of the trioxalatoferrate(III) ion, and $t$ the reaction time from the irradiation.

Reinert derived an explicit equation for this boundary value problem,[9] and Berg and Schwiess applied the Reinert's equation to a similar problem.[7,8] The explicit equation for the photo-polarographic current ($i_{rd}$) during the growth of one mercury drop is then expressed as,

$$i_{rd} = KC_i^* e^{-k_\nu' (t+t'-u\tau)\bar{\alpha}} \quad (5)$$

where $t$ is the reaction time from the irradiation, $t'$ the time difference between the start of the drop growth of the DME and the start of the reaction, $\tau$ the life-time of the DME, $u=0, 1, 2, \cdots$ for the first, second, third, — drop, $\bar{\alpha}$ the average exponent for $i_d$-$t$ curve, $K$ the Ilkovic constant, $I_0$ the intensity of the incident light, $\varepsilon$ the extinction coefficient, and $l$ the length of the layer.

In Eq. (5) the plot of $\log(i_{rd}/(t+t'-u\tau)^{\bar{\alpha}})$ *versus* $t$ yields a straight line and the value of $k_\nu'$ can be computed from the inclination. On the other hand, Eq. (6) can be derived from Koutecky's theory,[10] *i. e.*,

$$i_{rd}/i_d = F(y_t) \quad \text{with } y_t = k_\nu \varepsilon I_0 t = k_\nu' t \quad (6)$$

where $F(y_t)$ is an exponential function of $y_t$.[9] From Eq. (6) the plot of $\log(i_{rd}/i_d)$ *versus* $t$ also yields a straight line, of which the inclination gives the value of $k_\nu'$. These two plots are shown in Fig. 6, and the value of $k_\nu'$ is computed to be 0.35 $cm^{-1}$ from the slopes of two plots, the slopes being agreed well with each other as is seen in Fig. 6. This value of $k_\nu'$ is the apparent rate constant of the photo-chemical reaction, and it involves the terms, the intensity of the incident light ($I_0$), the extinction coefficient ($\varepsilon$), and the net rate constant of the photo-chemical reaction ($k_\nu$). Among these terms the absolute intensity of the incident light was difficult to measure at this stage, so that only the total dosage of light was determined under the same geometry. The experiment was carried out for 0.6 mM trioxalatoferrate(III) solution by irradiation during 150—200 sec, followed by stirring of the solution and polarographic determination of the concentration of trioxalatoferrate(III) remaining unreduced in the solution. The total dosage evaluated was $1.8\times10^{15}$ molecules/sec. Only this rather relative datum is available at this stage. Since the photo-chemical reaction proceeds in the bulk of the solution, but only the reaction proceeded in the reaction zone at the vicinity of the electrode surface pertains to the electrode reaction, it seems to be very complicated to confer an absolute physical significance on the apparent value of $k_\nu'$, and further investigation is required before the physical meaning of $k_\nu'$ will be embodied.

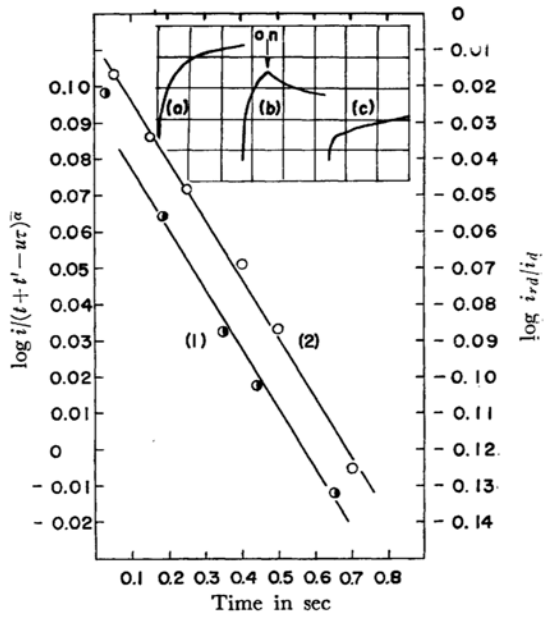


Fig. 6. log-plots plotted from the current-time curve (b) which shows the current during the drop growth of the DME. In curve (b) the continuous irradiation was started on the way of the second drop and the time of irradiation is denoted by ↓.

**Photopotential.** A typical photopotential-time curve for ferri-oxalate/ferro-oxalate system is shown in Fig. 7. It is evident that the potential rapidly shifts toward more negative potentials during irradiation and finally it attains to a plateau. When the irradiation was extinguished, the electrode potential slowly returned to the value near the initial potential. Similar trend has been observed for a variety of organic compounds,[11-13] and this trend can be attributed to the mixing of the irradiated part and unirradiated part of the solutions. The shift of the electrode potential by irradiation can simply by elucidated by the Nernst equation, *i. e.*,

$$E = E^\circ + \left(\frac{RT}{nF}\right)\ln\frac{[Fe(ox)_3^{3-}]}{[Fe(ox)_3^{4-}]} \quad (7)$$

9) K. E. Reinert, *Z. Electrochem.*, **66**, 379 (1962).
10) J. Koutecky, *Collection Czechoslov. Chem. Commun.*, **18**, 311 (1953).
11) I. Levin and C. E. White, *J. Chem. Phys.*, **18**, 417 (1950); **19**, 1079 (1951).
12) I. Levin, J. R. Wiebush, M. B. Bush and C. E. White, *ibid.*, **21**, 1654 (1953).
13) J. J. Surash and D. M. Hercules, *Z. Electrochem.*, **66**, 1602 (1962).

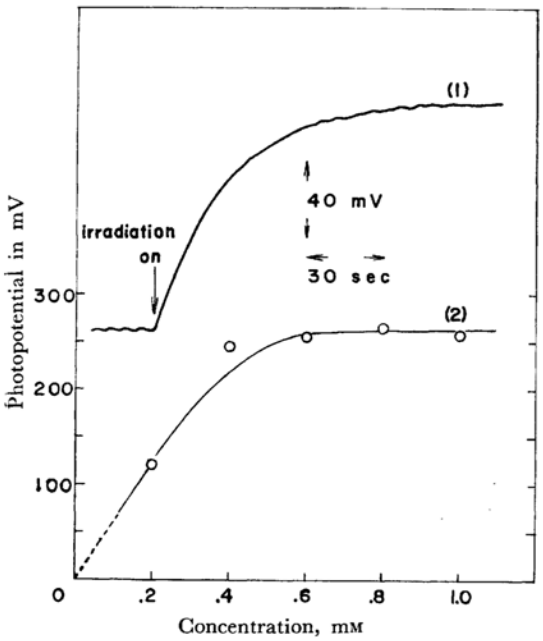


Fig. 7. (1) Photopotential-time curve of 0.2 mM trioxalatoferrate(III) in 0.5 M potassium oxalate solution.
(2) Dependence of photopotential on the concentration of trioxalatoferrate(III).

During the course of irradiation $Fe(ox)_3^{3-}$ is gradually converted into $Fe(ox)_3^{4-}$, and then the ratio of $Fe(ox)_3^{3-}/Fe(ox)_3^{4-}$ becomes smaller as a function of time. Such a behavior will tend to produce a negative-going potential according to Eq. (7). After the sufficient irradiation a steady state of the ferro-oxalate concentration is reached at the electrode surface, and a plateau is observed as is seen in curve (1) of Fig. 7. The photo-potential at the concentrations higher than 0.6 mM trioxalatoferrate (III) was evaluated as great as 258 mV.

**Effect of Oxygen.** Figure 8 shows the dependence of half-life time, which means the time required to attain the half-wave height of the anodic wave since the time of irradiation, on the concentration of dissolved oxygen. The measurement was carried out at the constant applied voltage of +0.05 V *vs.* SCE, where trioxalatoferrate(III) and oxygen are not electrolytically reduced.

When oxygen is present in the solution containing trioxalatoferrate(III), the decay time of trioxalatoferrate(III) by irradiation is elongated by the regeneration of the oxidant due to the chemical reaction of oxygen with the reductant formed during the course of irradiation. The reaction scheme will be expressed as follows;

$$\left.\begin{aligned} &Fe(ox)_3^{3-} + (1/2)C_2O_4^{2-} + h\nu \rightleftarrows Fe(ox)_3^{4-} + CO_2 \\ &Fe(ox)_3^{4-} + O_2 \rightleftarrows Fe(ox)_3^{3-} + O_2^- \\ &Fe(ox)_3^{4-} \rightleftarrows Fe(ox)_3^{3-} + e^- \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \end{aligned}\right\} \quad (8)$$

In Fig. 8 an induction period is seen at the very low concentration of dissolved oxygen. This effect can often be seen in the usual redox reactions. Then, the variation of the half-life is apparently linear with increase of the oxygen concentrations covered in this experiment. This effect can be used for the photonometrical determination of dissolved oxygen.[14]

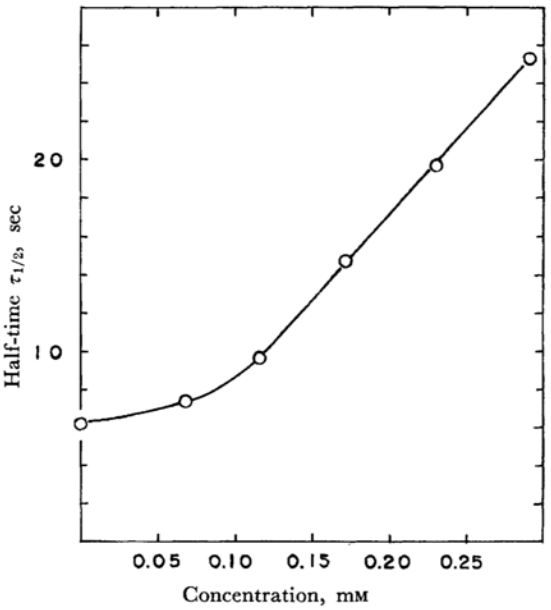


Fig. 8. Dependence of half-life of the photochemical reaction on the concentration of dissolved oxygen in 0.5 M potassium oxalate solution containing 0.6 mM trioxalatoferrate(III) ion.

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14) T. Kuwana, *Anal. Chem.*, **35**, 1398 (1963).