Studies on Electrode Processes of Oxovanadium(IV). I. Polarographic Behaviors and Photochemical Reaction in Potassium Oxalate Solution

Mitsutaka KITAMURA and Hideo IMAI

Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima 730

(Received December 19, 1974)

Oxovanadium(IV) was found to develop a fairly stable oxidation wave as well as a reduction wave at the dropping mercury electrode in an aqueous solution containing M potassium oxalate. The predominant entity in the solution was $[VO(ox)_2]^{2-}$, and both the oxidation wave with one-electron transfer, and the reduction wave with two-electron transfer were irreversible. The anodic transfer coefficient evaluated from the logarithmic plot and Tafel plot was 0.60—0.63, and the exchange current density estimated tentatively from the Tafel plot was 1.8×10^{-6} A/cm^2. The effect of aerial oxidation of V(IV) to V(V) and the photochemical reduction of V(V) to V(IV) were investigated through the controlled potential electrolysis, absorption spectroscopy and ESR studies. The polarographic kinetic current of the oxidation process was observed under ultra-violet light irradiation. The apparent rate constant of the photochemical reduction evaluated from the kinetic current was $(0.02—0.04)/\varepsilon\phi I_0$ s^{-1}, where ε is the molecular extinction coefficient, ϕ the quantum yield and I_0 the intensity of the incident light.

Since vanadium shows various oxidation states from −1 to 5, numerous electrochemical investigations on its oxidation and reduction processes have been reported. However, only a limited number of papers refers to the oxidation process of oxovanadium (IV).

Lingane[1] has investigated the polarographic behaviors of vanadyl ion in various media, and has found the oxidation wave in a strongly alkaline medium. He has observed both the oxidation and reduction waves in an ammoniacal solution. However, the solution is very unstable and form a precipitate even in the presence of sodium sulfite added in order to avoid the oxidation. Bishop and Hitchcock[2] reported the oxidation of V(IV) in an acetate buffer of pH=4 at a platinum electrode, and suggested the possible chemical step coupled with the electrochemical oxidation. On the other hand, Dean and Herringshaw[3] have studied the oxidation of vanadyl ion by aerial oxygen. In relation to the photochemical reaction Setapathy *et al.*[4] have studied the photolysis of the aqueous suspension of V_2O_5 in oxalic acid. In general, the electrode processes of oxovanadium (IV) involve complications due to the aerial oxidation and coupled chemical and photochemical reactions.[5,6]

Our findings are that a stable polarographic oxidation wave as well as the reduction wave of oxovanadium (IV) can be observed in the solution containing M potassium oxalate, and that the oxidized entity is easily reduced by the irradiation of ultra-violet light. The kinetics of the polarographic oxidation process of oxovanadium (IV) and that of the photochemical reduction of V(V) are presented in this paper.

Experimental

The test solution was prepared by mixing the deaerated stock solution of vanadyl sulfate and M potassium oxalate solution unless otherwise noted. All reagents were of an analytical grade.

The electrochemical experiments were carried out by using a Shimadzu Model RP-50 polarograph and a Model PS-2 potentiostat. A quartz cell with a dropping mercury electrode (DME) and a saturated calomel electrode (SCE) were used for the measurement. The characteristics of the DME were as follows; the rate of flow of mercury=0.72 mg/s, the life-time=9.1 s under the head of mercury=40 cm at the applied potential of +0.15 V *vs.* SCE.

A xenon lamp (500 W) and Toshiba UV-D25 filter to pass 250—350 nm light were used for the photochemical study.

The spectrophotometric measurements were carried out by using a Shimadzu Model UV-200 dual beam spectrometer. For the ESR studies a Nihon Denki Model JES-ME ESR spectrometer was used under the following conditions; X-band microwave, modulation frequency of 100 kHz, modulation width of 6.3 gauss, the sample tubing of 1 mm diameter with 6 μl test solution.

The temperature was 28±1 °C.

Results and Discussion

Polarographic Behaviors of Oxovanadium(IV) in M Potassium Oxalate. The predominant entity of oxovanadium(IV) in M potassium oxalate solution (pH=8.4) is considered to be $[VO(ox)_2]^{2-}$.[6] It develops the polarographic oxidation wave as well as the reduction wave as shown in Fig. 1.

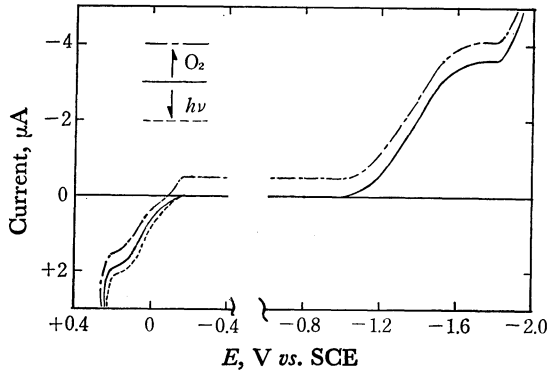

Fig. 1. Polarograms of oxovanadium(IV) in M Potassium oxalate.
—— polarogram of deaerated solution, ----- polarogram of oxidized solution, ------ polarogram of irradiated solution

The oxidation wave appeared at +0.025 V *vs.* SCE. The wave form was rather extended along with the potential axis than the well-defined reversible wave. The wave-height was approximately one half of the

reduction wave. The electrode process can be expressed as follows:

$$V(IV) - e = V(V) \quad (1)$$

Bishop and Hitchcock[2] have suggested the kinetic complication due to the coupled chemical reaction. However, no evidence could be observed so far as the effect of the mercury head on the wave-height was concerned as shown in Fig. 7.

The reduction wave of the two-electron transfer process appeared at −1.35 V *vs.* SCE. The wave form was also extended along with the potential axis, and the process was irreversible. It is noteworthy that the reduction wave showed the trend to split into two steps when the concentration of vanadyl ion was higher than 4 mM.

The dependence of the wave-height on the concentration of the vanadyl ion is illustrated in Fig. 2. Both the oxidation and reduction wave-heights showed good linear relationship with the vanadyl ion concentration. However, the linearity was no longer observed when the concentration exceeded 2 mM. The value of the diffusion coefficient estimated from the Ilkovic equation was 6.6×10^{-6} cm²/s.

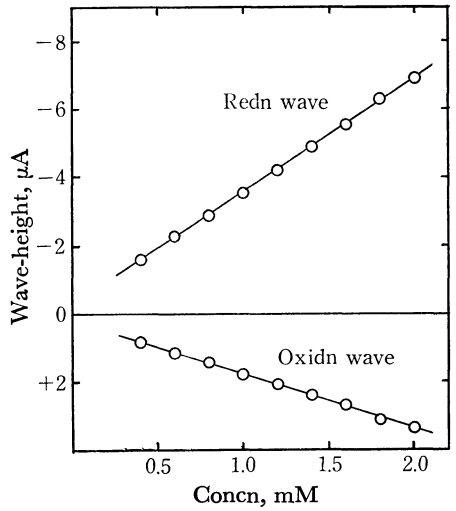

Fig. 2. Dependence of polarographic wave-height on concentration of oxovanadium(IV).

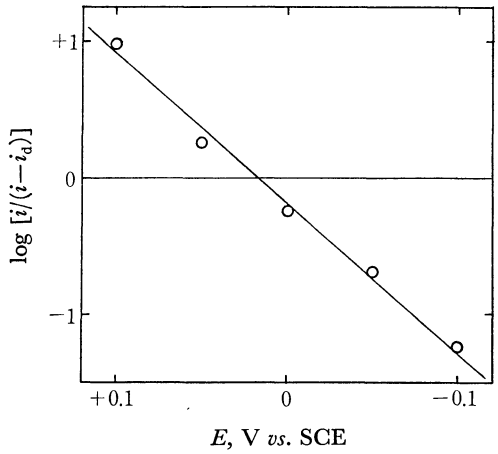

Fig. 3. Logarithmic plot of oxidation process of oxovanadium(IV).

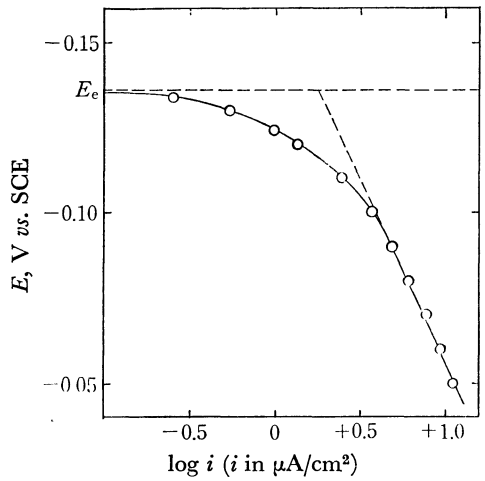

Fig. 4. Tafel plot of oxidation process of oxovanadium-(IV). E_e: equilibrium potential

Electrode Kinetics of Oxidation Process of Oxovanadium(IV). The polarographic oxidation current was recorded at each potential controlled by the potentiostat, and the $\log[i/(i_d-i)]$ *versus* the potential plot was obtained as shown in Fig. 3. From the inclination of this linear plot the anodic transfer coefficient of 0.63 was estimated.[7] On the other hand, the Tafel plot was obtained from the foot of this oxidation wave as shown in Fig. 4. The inclination of this Tafel plot gave the value of the anodic transfer coefficient as great as 0.60. Both data showed a fairly good agreement.

The value of the equilibrium potential for V(V)—V(IV) couple was tentatively evaluated assuming that the Tafel plot will be an asymptote along with the potential coordinate at the equilibrium potential as shown in Fig. 4. The exchange current density estimated from the intercept was 1.8×10^{-6} A/cm².

Oxidation of Oxovanadium(IV) by Aerial Oxygen, Electrolytic Oxidation of V(IV) and Photochemical Reduction of V(V). When dissolved oxygen was contained in the oxovanadium(IV) solution, the wave-height of the polarographic oxidation decreased and a new reduction wave appeared at −0.13 V *vs.* SCE as shown in Fig. 1. The height of the new wave was exactly equal to the decrement of the oxidation wave. The oxidation process of V(IV) by aerial oxygen in an alkaline solution was studied by Dean and Herringshaw[3] as formulated in the following;

$$O_2 + 2VO_3^{2-} + H_2O = 2VO_3^- + 2OH' + H_2O_2 \quad (2)$$

followed by

$$H_2O_2 + 2VO_3^{2-} = 2VO_3^- + 2OH' \quad (3)$$

In view of their results, the new reduction wave appeared at −0.13 V *vs.* SCE seems to be the reduction of V(V) to V(IV).

The solution color changed from light blue to light yellowish green by the aerial oxidation. A similar color change was observed by the electrolytic oxidation at the controlled potential of +0.15 V *vs.* SCE. The absorption band at λ_{max}=600 nm disappeared completely by the oxidation and the band at λ_{max}=310 nm decreased simultaneously in its intensity as shown in Fig. 5.[8,9] The ESR spectra of oxovanadium(IV) in

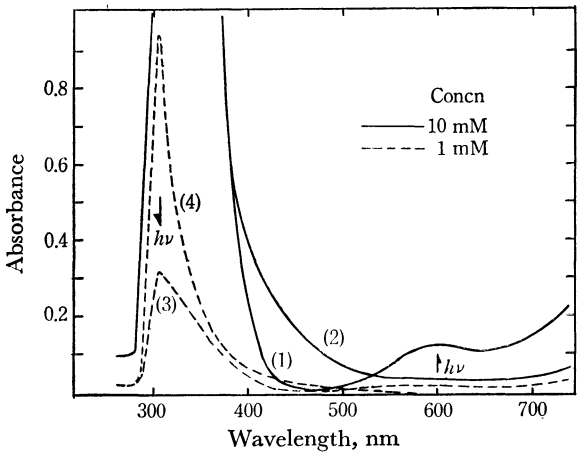

Fig. 5. Absorption spectra of oxovanadium(IV) and (V).
Curves 1 and 2: 10 mM, Curves 3 and 4: 1 mM, Curves 1 and 3: deaerated or irradiated solution, Curves 2 and and 4: oxidized solution

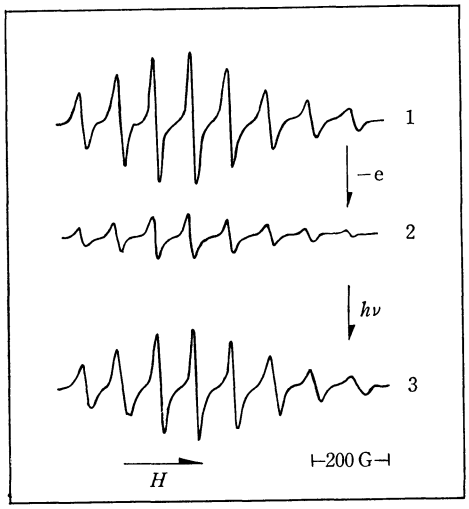

Fig. 6. ESR spectra of oxovanadium(IV).
Curve 1: deaerated solution, Curve 2: oxidized solution, Curve 3: irradiated solution

M potassium oxalate solution showed eight components corresponding to the nuclear spin of 7/2 as shown in Fig. 6.[9] The ESR spectrum also decreased and disappeared in its intensity as the oxidation proceeded. It is noteworthy that vanadium of +5 oxidation state has no more spin in its d-shell. These changes in color, electronic absorption and ESR spectra were restored to the original state by the irradiation of ultra-violet light as shown in Figs. 5 and 6. The increase of the oxidation wave-height and disappearance of the new reduction wave were observed by the ultra-violet light irradiation as shown in Fig. 1. The photochemical reaction can be expressed as follows;

$$V(V) + h\nu = V(IV) - e \qquad (4)$$

and the oxidation of oxalate to form carbon dioxide seems to be coupled with Reaction (4), *i.e.*, $1/2C_2O_4^{2-} - e = CO_2$.

Kinetics of Photochemical Reduction of V(V) in M Potassium Oxalate Solution. The effect of the mercury head of the DME on the polarographic oxidation and reduction wave-heights is illustrated in Fig. 7. Both waves showed the linear increase with the square root of the mercury head. This characteristic corresponds well to the polarographic diffusion-controlled current. However, when the solution was irradiated by the ultra-violet light in the course of the polarographic oxidation, the inclination of the plot decreased slightly as shown in Fig. 7. This reveals the characteristic of the polarographic kinetic current, namely, the oxidation process of oxovanadium(IV) is coupled with the regeneration of V(IV) by the photochemical reduction of V(V), which is the product of the electrolytic oxidation. The reaction scheme is expressed by the combination of Reactions (1) and (4).

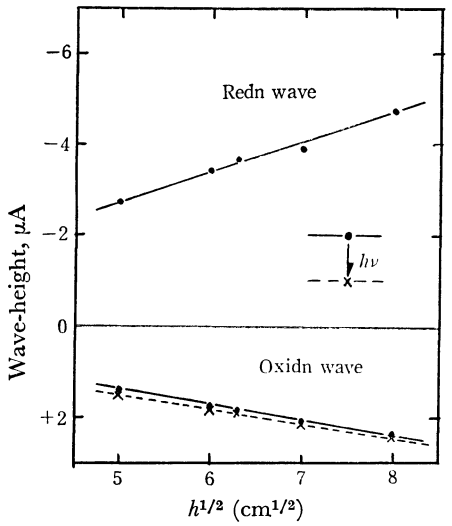

Fig. 7. Dependence of polarographic wave-height on DME mercury head.
Broken line: oxidation wave under ultra-violet light irradiation

Assuming that the Lambert-Beer's law holds for the light absorption of the V(V) species, the differential equation relating to the semi-infinite diffusion at the vicinity of the electrode-solution interface can be expressed as follows;

$$\frac{\partial C_{IV}}{\partial t} = D_{IV}\frac{\partial^2 C_{IV}}{\partial x^2} + \frac{2x}{3t}\frac{\partial C_{IV}}{\partial x} + \frac{k\phi I_0}{l}(1-e^{-\varepsilon C_V l}) \qquad (5)$$

$$\frac{\partial C_V}{\partial t} = D_V\frac{\partial^2 C_V}{\partial x^2} + \frac{2x}{3t}\frac{\partial C_V}{\partial x} - \frac{k\phi I_0}{l}(1-e^{-\varepsilon C_V l}) \qquad (6)$$

where C's are the concentration of respective species, k the rate constant of the photochemical reduction, ϕ the quantum yield, ε the molecular extinction coefficient, I_0 the intensity of the incident light, the thickness of the reaction layer and the other symbols are of the usual significance. Eqs. (5) and (6) can be simplified by the approximation that $\exp[-\varepsilon C_V l] \approx 1-\varepsilon C_V l$ and that $D_{IV} \approx D_V$.[10] The explicit equation for this case has been derived by Henke and Hans.[11] The numerical data of i_c/i_d were in the range from 1.04 to 1.10, where i_c is the mean limiting current under ultra-violet light irradiation and i_d the mean diffusion-controlled current. From the data the rate constant of the photochemical reduction, k, was evaluated as $(0.02—0.04)/\varepsilon\phi I_0\ s^{-1}$. The evaluation of the molecular extinction coefficient,

ε, the quantum yield, ϕ, and the intensity of the incident light, I_0, involves complication in this case so that it will be remained for the future.

References

1) J. J. Lingane, *J. Amer. Chem. Soc.*, **67**, 182 (1945).
2) E. Bishop and P. H. Hitchcock, *Analyst*, **98**, 553 (1973).
3) G. A. Dean and J. F. Herringshaw, *Talanta*, **10**, 797 (1963).
4) K. C. Satapathy, R. Palmer, and B. Sahoo, *Indian J. Chem.*, **1**, 402 (1963).
5) Y. Israel and L. Meites, *J. Electroanal. Chem.*, **8**, 99 (1964).
6) For a review see, J. Selbin, *Chem. Rev.*, **65**, 153 (1965).
7) H. Matsuda and Y. Ayabe, This Bulletin, **28**, 422 (1955).
8) J. Selbin and T. R. Ortolano, *J. Inorg. Nucl. Chem.*, **26**, 37 (1964).
9) R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, **33**, 1107 (1960), Y. Ujihira, Y. Suzuki, and H. Takami, *Bunseki Kagaku*, **23**, 987 (1974), T. R. Ortolano, J. Selbin, and S. P. McGlynn, *J. Chem. Phys.*, **41**, 262 (1964).
10) K. Yamashita and H. Imai, *Rev. Polarog. Kyoto*, **18**, 10 (1972).
11) Karl-Heinz Henke and W. Hans, *Z. Elektrochem.*, **59**, 676 (1955).