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Photoreduction of Oxalato Vanadyl(IV) Complex in Aqueous Solution of Oxalic Acid

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Quantum yield of the photoreduction of oxalato vanadyl(IV) complex to oxalato vanadium(III) complex in aqueous oxalic acid solution has been determined at 254 nm. The quantum yield was almost independent of the concentrations of hydrogen ion and reactant. Then, the reaction scheme was proposed based on the stoichiometry of the photoreduction, the dependence of the quantum yield and the redox potentials of the intermediates. In the primary process, the VO(IV) complex is decomposed to oxovanadium(III) complex and oxalate radical through one-electron transfer from acid substrate to VO^{2+}. *The former intermediate is probably deoxygenated into the V(III) complex by* H^+ *ion, and the formic acid radical caused from the latter reduces the VO(IV) complex accompanied with evolution of* CO_2.

Introduction

Oxalato vanadyl(IV) complex in aqueous oxalic acid solution is photoreduced to oxalato vanadium(III) complex [1], which decomposes photosensitively the oxalic acid into CO_2 and CO [2], as are shown in eqns. 1 and 2.

$$VO(C_2O_4)_2^{2-} + 2H^+ + \tfrac{1}{2}C_2O_4^{2-} \xrightarrow{h\nu} V(C_2O_4)_2^- + CO_2 + H_2O \quad (1)$$

$$H_2C_2O_4 \xrightarrow{h\nu} H_2O + CO_2 + CO \quad (2)$$

The quantum yield of the photosensitized decomposition of the oxalic acid at 254 nm is 0.09–0.23 on several solutions containing 1.1 × 10^{-3} *M* V(III) and 11 × 10^{-3} *M* $H_2C_2O_4$ at pH 1–3. The reaction scheme of eqn. 2 has been discussed based on the redox potential of the formic acid radical produced in the primary process [2].

When the reduced form of the initial complex has less noble redox potential than that of the radical, it is reduced by this reduced-complex:

$$\dot{C}O_2H + e^- \rightarrow CO + OH^- \quad (3)$$

Accordingly, the reduced complex would be oxidized to the initial-complex and CO would be contained in the gaseous product. On the contrary, when the reduced-complex has more noble potential, the radical is oxidized by the initial-complex:

$$\dot{C}O_2H \rightarrow CO_2 + H^+ + e^- \quad (4)$$

Therefore, the initial complex would be reduced and prominent gaseous product would be CO_2.

Then, it is suggested that the reaction in the secondary process is dependent on the redox potential of the reduced-complex produced in the primary process. The present investigation has been carried out to elucidate the reaction scheme for the photoreduction of oxalato vanadyl(IV) complex in aqueous oxalic acid solution in view of the above consideration.

Experimental

The prominent species in the aqueous oxalic acid solution for the measurement of the quantum yield is bisoxalato vanadyl(IV) complex ion (*ca.* 99% up). The preparation and analyses of the sample solution, and apparatus and procedures adopted in this experiment have been outlined previously [1, 2]. The ionic strength (I = 1.0) and the temperature (25 ± 0.5 °C) of the solution are also the same. Because a molar absorption coefficient of VO(IV) complex at 254 nm (ϵ = 1170) is similar to that of V(III) complex (ϵ = 1100), the amount of oxalic acid decomposed during the irradiation was determined for taking account of the photosensitized decomposition of oxalic acid by V(III) complex produced.

Results

Effect of the Concentration of Oxalic Acid on the Quantum Yield of Photoreduction of Oxalato Vanadyl(IV) Complex

The quantum yield of the photoreduction was measured at pH 1.3 on several solutions containing 1.0 × 10^{-3} *M* VO(IV) and (3.0–30.0) × 10^{-3} *M* $H_2C_2O_4$. The quantum yield was almost independent of the concentration of oxalic acid ($\phi = 0.032 \pm 0.001$). This value was corrected for the absorption of $VO(C_2O_4)_2^{2-}$ based on the assumption that the intensity of absorbed light was proportional to a ratio of the molar absorption coefficient of oxalic acid ($\epsilon = 38$) to $VO(C_2O_4)_2^{2-}$ ($\epsilon = 1170$) at 254 nm.

Effect of the Concentration of VO(IV) Complex

The quantum yield on the concentration of VO(IV) complex in region (1.0–10.0) × 10^{-3} *M* at constant molar ratio of VO(IV): $H_2C_2O_4$ = 1:10 (pH 1.8) is slightly increased in line from 0.031 to 0.037.

Effect of the Concentration of Hydrogen Ion

The effect of the concentration of hydrogen ion on the quantum yield was examined in region (1.0–10.0) × 10^{-2} *M* at constant molar ratio or VO(IV): $H_2C_2O_4$ = 1:10 and at the VO(IV) 1.0 × 10^{-3} *M*. In this region of $[H^+]$, $VO(C_2O_4)_2^{2-}$ ion is the prominent species. Contrary to the case of V(III) complex [2], the effect was almost negligible with a constant quantum yield ($\phi = 0.032 \pm 0.002$).

Effect of the Wavelength of Irradiation

The wavelength dependence of the quantum yield is shown in Table I. The measurement was carried out at the VO(IV) 1.0 × 10^{-3} *M* and at constant molar ratio of VO(IV): $H_2C_2O_4$ = 1:10 (pH 1.8). The quantum yield decreases rapidly with the increase in the wavelength irradiated.

Discussion

Direct photodecomposition of oxalic acid in the solution with VO(IV) complex is neglected by comparing the amounts of gaseous products of oxalic acid alone [2] with that of sample solution [1].

The quantum yield of the photoreduction of the VO(IV) complex depends upon the reactant concentration and the wavelength of irradiation. The effect of the former on the quantum yield is not significant. This could perhaps be ascribed to rather high concentration of reactant in the solution which caused the complications including secondary process.

The photoreduction of the VO(IV) complex is significantly suppressed with the increasing of wavelength irradiated. Since the photoreduction in which an electron transfers from coordinated ligand to metal center, is caused by the irradiation of UV light in CT absorption band, the wavelength dependence of the quantum yield is comprehensible.

TABLE I. Wavelength Dependence of the Quantum Yield.[a]

λ/nm	ϕ
254	0.031
313	0.002
405–408	<0.001
577–579	0

[a] VO(IV): 1.0 × 10^{-3} *M*, $H_2C_2O_4$: 10.0 × 10^{-3} *M*, pH: 1.8.

According to Ligane *et al.* [3], the VO(IV) complex is irreversibly reduced *via* two-electrons transfer to V^{2+} ion at −1.066 V *vs.* SHE in region of pH 5.5–6.1. If V^{2+} ion is produced in the photoreduction of VO(IV) complex, it would reduce the formic acid radical to CO and OH^- ion according to eqn. 3. Since the evolution of CO is not, however, observed in the photoreduction, any transient species having less noble potential than that of the formic acid radical would not occur. On the other hand, the V(III) complex is oxidized to VO(IV) complex at 0.236 V *vs.* SHE in acidic oxalate solution [3]. Therefore, it is inferred that the photoreduction of VO(IV) complex proceed through one-electron transfer.

By considering above results and discussion, the following reaction scheme could be proposed:

$$VO(C_2O_4)_2^{2-} + h\nu \xrightarrow{Ia} VO(C_2O_4)_2^{2-}{}^* \quad (5)$$

$$VO(C_2O_4)_2^{2-}{}^* \xrightarrow{K_1} VO(C_2O_4)_2^{2-} \quad (6)$$

$$VO(C_2O_4)_2^{2-}{}^* \xrightarrow{K_2} VO(C_2O_4)^- + C_2O_4^- \quad (7)$$

$$VO(C_2O_4)^- + 2H^+ \xrightarrow{K_3} V(C_2O_4)^+ + H_2O \quad (8)$$

$$C_2O_4^- \xrightarrow{K_4} CO_2 + \dot{C}O_2^- \quad (9)$$

$$\dot{C}O_2^- + H^+ \xrightarrow{K_5} \dot{C}O_2H \quad (10)$$

$$VO(C_2O_4)_2^{2-} + \dot{C}O_2H + H^+ \xrightarrow{K_6} V(C_2O_4)_2^- + CO_2 + H_2O \quad (11)$$

$$V(C_2O_4)^+ + C_2O_4^{2-} \xrightarrow{K_7} V(C_2O_4)_2^- \quad (12)$$

V^{3+}/V^{2+} oxalate couple has so negative potential of −0.89 V *vs.* SHE [3] that the formic acid radical (−0.18–−0.41 V *vs.* SHE [4]) is inactive for the V(III) complex. So the radical would reduce the VO(IV) complex with evolution of CO_2, as is shown in eqn. 11. It means that the VO(IV) complex has more noble potential than that of the radical in aqueous oxalic acid solution. Since H^+ ion is, however, reduced in preference to the VO(IV) complex in acid solution, the reduction potential of the complex in acidic solution is not obtained by means of polarography [3].

Assuming the steady state with respect to $VO(C_2O_4)_2^{2-*}$ and the radical species, the quantum yield of the photoreduction of oxalato vanadyl(IV) complex is given by:

$$\phi = \frac{2K_2}{K_1 + K_2} \qquad (13)$$

That is, the quantum yield is independent of $[H^+]$, and the obtained K_1/K_2 is about 62.

The transient species of $VO(C_2O_4)^-$ ion in eqn. 7 has not been known as yet. However, VO^{2+}/VO^+ redox couple of uncomplexed ions has potential of −0.044 V *vs.* SHE [5], and the transient species of oxouranium(V) complex is proposed in view of CTTM transition in the primary process in the photoreduction of oxalato uranyl(VI) complex in aqueous oxalic acid solution [6]. Therefore, it is suggested that the $VO(C_2O_4)^-$ ion is produced as a transient species in the primary process.

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