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Photosensitized Decomposition of Oxalic Acid in Aqueous Solution by Oxalato Vanadium(III) Complex

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Photodecomposition of oxalic acid in aqueous solution sensitized by oxalato vanadium(III) complex has been studied at 254 nm. The resulting products were equimolar amounts of carbon dioxide and carbon monoxide with oxalic acid decomposed. Based on the dependence of quantum yield on the concentrations of hydrogen ion and reactant, and on the redox potentials of the intermediates, the reaction scheme was proposed. In the primary process, the V(III) complex is decomposed into V(II) ion and oxalate radical through the charge-transfer-to-metal (CTTM) mechanism, followed by the redox reaction where the formic acid radical, producted from the oxalate radical through decarboxylation and subsequent protonation, is reduced by V(II) ion into carbon monoxide.

Introduction

The photolysis of oxalato tripositive transition metal complexes with UV light has been extensively investigated, and the revealed dominant reaction is the reduction of the metal center accompanied by the oxidation of coordinated oxalate [1]. The present authors confirmed that the similar redox reaction occurred in the photolysis of oxalato titanyl(IV) complex in aqueous oxalic acid solution and further that the resulting oxalato titanium(III) complex decomposed photosensitively the oxalic acid into carbon dioxide and carbon monoxide [2, 3]. It was subsequently found that the behavior in the photoreaction of oxalato vanadium(III) complex produced by the photoreduction of oxalato vanadyl(IV) complex in aqueous oxalic acid solution [4] was almost the same as that of the Ti(III) complex. The present investigation was undertaken in order to elucidate the reaction scheme for the photodecomposition of oxalic acid by the V(III) complex.

Experimental

Material

Preparation of $K_3[V(C_2O_4)_3]\cdot 3H_2O$ was carried out by an analogous method to that described elsewhere [5], which is briefly described below: Equimolar amounts (0.04 *M*) of oxalic acid and potassium oxalate were added together into aqueous solution (30 ml) of vanadium(III) chloride (0.025 *M*) with stirring on a hot plate, and the resultant solution was allowed to stand at room temperature to give a crystalline product. The precipitate was filtered, washed with aqueous 5% methanol solution until a chloride ion was not detected, and dried *in vacuo*. The product was identified by elemental analysis and IR.

Sample solutions were prepared by dissolving the product in deaerated aqueous oxalic acid solutions. All the procedure through preparing the solution was carried out in a nitrogen atmosphere. Absorption spectra of the V(III) complexes in aqueous solution were measured with a Hitachi-Perkin Elmer 139 spectrophotometer and almost agreed with the literature data [6, 7].

The composition of the complexes formed in the aqueous oxalic acid solution were determined by the molar ratio method and the stability constants were evaluated spectrophotometrically.

$$[V(C_2O_4)]^+ \ : K_1 = 6.4 \times 10^{-8}, I = 1.0, \quad \text{pH } 0.2\text{–}0.3$$

$$[V(C_2O_4)_2]^- : K_2 = 4.5 \times 10^{-6}, I = 1.0, \quad \text{pH } 1.0\text{–}1.8$$

These values are not identical with the literature values [7] because of only a difference between the referred dissociation constants of oxalic acid [8]. The prominent species in the oxalic acid solution at

TABLE I. Yields of CO_2 and CO.

	Yield of CO_2 ($\times 10^3$ *M*)	Yield of CO ($\times 10^3$ *M*)	$H_2C_2O_4$ decomposed ($\times 10^3$ *M*)	Irradiation Time (hr)
(*1*)	7.11	7.19	7.16	1.5
(*2*)	6.38	6.42	6.41	3.0

(*1*) V(III): 1.00×10^{-3} *M*, $H_2C_2O_4$: 9.81×10^{-3} *M*, pH: 2.2.
(*2*) V(III): 1.04×10^{-3} *M* $H_2C_2O_4$: 9.61×10^{-3} *M*, pH: 1.4.

pH 1.5 would be bisoxalato V(III) complex ion (*ca.* 95%) in view of the equilibrium constants. The pH values were taken on a Hitachi-Horiba F-7 pH-meter.

Apparatus and Procedures

The light source of 254 nm radiation was an 120 W low pressure mercury lamp (Eikoshia Co., Ltd) or a 500 W Xenon lamp (Ushio Co., Ltd) with use of solution- and glass-filters [9]. Light intensities were measured by the use of the potassium ferrioxalate actinometric solution. For the determination of quantum efficiency, a quartz cell (2.0 cm light path and 4.5 cm diam.) was used as an irradiation vessel. The ionic strength of the solution was kept at *I* = 1.0 with sodium perchlorate, and pH desired was controlled by addition of perchloric acid or sodium hydroxide. The solution in the quartz cell was degassed by a series of freez-pump-thaw cycle, sealed and then irradiated at 25 ± 0.5 °C for a present time period. The amount of the decomposed oxalic acid was then determined by the $KMn0_4$ titration method. As for the determination of gaseous products, a quartz tube (1.0 cm diam. X 7.0 cm length) was used and then irradiated in the same manner.

Analyses

V(III) ion was titrated with ammonium metavanadate standard solution using sodium diphenylammine-sulfonate as an indicator. Oxalate ion was titrated with $KMn0_4$ standard solution, and the amount of titrant was corrected for the quantities corresponding to oxidation of V(III) to V(V).

The volume of gaseous products was determined with a standard Toepler pump and gas buret arrangement. Carbon dioxide vaporized at −120 °C (liq N_2 and ethylene bromide cold bath) and carbon monoxide at −196 °C (liq N_2 cold bath), were transferred respectively into a capillary tube with the Toepler pump and were identified gaschromatographically (Shimazu GC-6A).

All the chemicals were of special reagent grade, used without further purification.

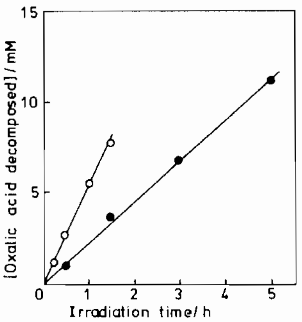


Fig. 1. The amount of oxalic acid decomposed during the irradiation. ○ V(III); 1.00×10^{-3} *M*, $H_2C_2O_4$: 9.81×10^{-3} *M*, pH: 2.2. ●V(III): 1.04×10^{-2} *M*, $H_2C_2O_4$: 9.61×10^{-2} *M*, pH: 1.4.

Results

Stoichiometry

Continuous irradiation of the V(III) complex in the aqueous oxalic acid solution was carried out at the molar ratio of V(III) to oxalic acid of 1:10. Examples at pH 1.4 and pH 2.2 are shown in Fig. 1. The quantity of decomposed oxalic acid increased linearly with the irradiation period, while the V(III) complex remained intact. As can be seen from Table I, both the yields of carbon dioxide and carbon monoxide agree with the amount of oxalic acid decomposed by the photolysis.

The overall reaction is thus given by the following equation:

$$H_2C_2O_4 \rightarrow CO_2 + CO + H_2O \qquad (1)$$

Effect of the Concentration of Oxalic Acid on the Quantum Yield of Oxalic Acid Decomposed

The quantum yield of the decomposition of oxalic acid was measured at pH 1.5 on several solutions containing V(III) of 1.1×10^{-3} *M* and oxalic acid of (4.3–34.5) X 10^{-3} *M*. The quantum yield was independent of the concentration of oxalic acid (ϕ = 0.183 ± 0.010). This value was corrected for the absorption of $V(C_2O_4)_2^-$ based on the assumption that

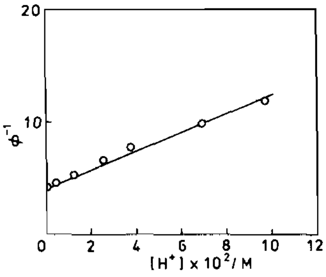


Fig. 2. Dependence of the quantum yield on the concentration of hydrogen ion. V(III): 1.1 × 10^{-3} *M*; V(III): $H_2C_2O_4$ = 1:10 (molar ratio).

the intensity of absorbed light was proportional to a ratio of the molar absorption coefficients of oxalic acid ($\epsilon = 38$) to $V(C_2O_4)_2^-$ ($\epsilon = 1100$) at 254 nm.

Effect of the Concentration of V(III) Complex

The quantum yield on the concentration of V(III) complex in region (1.0–10.0) × 10^{-3} *M* at constant molar ratio of V(III): $H_2C_2O_4$ = 1:11 (pH 2.0), is slightly increased in line from 0.225 to 0.285.

Effect of the Concentration of Hydrogen Ion

It was found that the reciprocal quantum yield of the photodecomposition of oxalic acid increased linearly with an increase in the concentration of hydrogen ion of (0.1–10.0) × 10^{-2} *M*, given in Fig. 2. According to the equilibrium constants of the two complexes, the concentration of monooxalato V(III) complex ion would be about 20–30% against to 80–70% of bisoxalato V(III) complex ion at about 10^{-1} *M* of hydrogen ion concentration. However, a molar absorption coefficient of the former ($\epsilon = 580$) is so smaller than that of the latter ($\epsilon = 1100$) at 254 nm that the existence of the former would not affect the linear relation between reciprocal quantum yield and $[H^+]$.

Discussion

In order to check up the direct photodecomposition of oxalic acid alone, the irradiation of aqueous solution of 0.05 *M* oxalic acid was carried out for 5 hours at 254 nm. Gaseous products were carbon dioxide (0.69 × 10^{-3} *M*) and carbon monoxide (0.07 × 10^{-3} *M*). Regardless of long irradiation time, the products are small in comparison with the results shown in Table I, and the relation of equimolar amounts between them can not be seen. Furthermore, because of the much difference between the molar absorption coefficients of oxalic acid and V(III) complex, it is reasonable to neglect the direct photodecomposition of oxalic acid in the solution with V(III) complex.

The overall photolysis occurring in the aqueous oxalic acid solution of V(III) complex is represented by eqn. 1. Moreover, the reaction of V(III)–oxalic acid system depends upon reactant concentration and solution pH, as is shown in Fig. 2. The decomposition of oxalic acid is significantly suppressed with the increasing of the acidity of the solution and the amounts of carbon dioxide and carbon monoxide also decrease in accordance with the increase in the acidity. Effects of the concentration of reactants on the quantum yield are not very significant. These could perhaps be ascribed to rather high concentration of reactants in the solution which caused the complications including secondary process.

By considering above results and applying the suggestion made by Heidet [10] for the uranyl oxalate system which is one of only a few metal oxalate systems to evolve carbon monoxide on irradiation, the following reaction scheme could be proposed:

$$V(C_2O_4)_2^- + h\nu \xrightarrow{Ia} V(C_2O_4)_2^{-*} \qquad (2)$$

$$V(C_2O_4)_2^{-*} \xrightarrow{K_1} V(C_2O_4)_2^- \qquad (3)$$

$$V(C_2O_4)_2^{-*} \xrightarrow{K_2} V^{2+} + C_2O_4^{2-} + C_2O_4^{\dot{-}} \qquad (4)$$

$$C_2O_4^{\dot{-}} \xrightarrow{K_3} CO_2 + \dot{C}O_2^- \qquad (5)$$

$$\dot{C}O_2^- + H^+ \xrightarrow{K_4} \dot{C}O_2H \qquad (6)$$

$$V^{2+} + \dot{C}O_2H \xrightarrow{K_5} V(OH)^{2+} + CO \qquad (7)$$

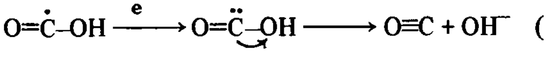
$$V(C_2O_4)_2^{-*} + H^+ \xrightarrow{K_6} V(C_2O_4)^+ + HC_2O_4^- \qquad (8)$$

$$V(OH)^{2+} + 2HC_2O_4^- \xrightarrow{K_7} V(C_2O_4)_2^- + 2H_2O \qquad (9)$$

$$V(C_2O_4)^+ + C_2O_4^{2-} \xrightarrow{K_8} V(C_2O_4)_2^- \qquad (10)$$

where Ia is the rate of light absorption in einsteins l^{-1} sec^{-1}.

The primary intermediates would probably be oxalate radical and V^{2+} ion (eqn. 4). It has been found that this V^{2+} ion is uncomplexed in its nascent state and that its V^{3+}/V^{2+} oxalate couple has a redox potential of –0.89 V *vs.* SHE [11]. The oxalate radical would be subjected to the decarboxylation (eqn. 5) into carboxyl radical which would be protonated in acidic solution [12]. The resulting formic acid radical with formal reduction potential of –0.18–-0.41 V *vs.* SHE [13] would be reduced by V^{2+} ion into carbon monoxide, and the residual OH^- ion forms a hydroxocomplex with V^{3+} ion. The formation of this complex has been found in acidic solution at pH 1.0–2.0 [14]. Thus, the plausible reaction path for a reduction of the formic acid radical is postulated as follows:



$$O{=}\dot{C}{-}OH \xrightarrow{e^-} O{=}\ddot{C}{-}OH \longrightarrow O{\equiv}C + OH^- \qquad (11)$$

The acidity dependence of the quantum yield would be explained by eqn. 8, which corresponds to the ionic dissociation reaction proposed by Murgulescu [15]. Assuming the steady state with respect to $V(C_2O_4)_2^{-*}$ and the radical species, the quantum yield of the decomposition of oxalic acid is given by:

$$\frac{1}{\phi} = \left(1 + \frac{K_1}{K_2}\right) + \frac{K_5}{K_2}[H^+] \qquad (12)$$

That is, the reciprocal quantum yield *vs.* the concentration of hydrogen ion should form a straight line. This is consistent with the experimental result and values of $K_1/K_2 = 30$ and $K_5/K_2 = 82$ are obtained from Fig. 2.

In the uranyl oxalate system, the uranyl hydrogenoxalate complex has a redox potential of –0.142 V *vs.* SHE at pH 1.7 [16] which is close to the more positive side potential of the formic acid radical. Then, the photodecomposition of oxalic acid by UO_2(VI) complex occurs in highly acidic solution accompanying evolution of equimolar amounts of carbon dioxide and carbon monoxide. Since the UO_2(VI) complex has –0.21 V *vs.* SHE at elevated pH, *e.g.* pH 4.5 and the formic acid radical is dissociated to the carboxyl radical having –0.41 V *vs.* SHE in the vicinity of pH 4.5, it seems likely that the carboxyl radical is hardly reduced by UO_2(V) complex produced in the primary process. Actually it has been reported that the rapid decrease in yield of carbon monoxide with increase in pH is seen in the pH range 1–3 [10].

In the case of Ti(III) complex, a redox potential of Ti^{3+}/Ti^{2+} oxalate couple is not known as yet, while TiO(IV) complex has 0 V *vs.* SHE at pH 0 and $[H_2C_2O_4] = 1.0$ [17]. Assuming that the Ti(III) complex has a more negative potential similar to that of the V(III) complex, the photodecomposition of oxalic acid by this complex could be explained in the same manner.

When the formic acid radical is oxidized by the following reaction [18],

$$\dot{C}O_2H \rightarrow CO_2 + H^+ + e^- \qquad (13)$$

Prominent gaseous product would be carbon dioxide. Then, it is supposed that the photoredox reaction of the M(III) complex *e.g.* $[Fe(C_2O_4)_3^{3-}]$, $[Co(C_2O_4)_3^{3-}]$ *et al.* is in accordance with this scheme.

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