Inorganica Chimica Acta, 53 (1981) L109–L110

On the Photolysis of Oxalato Vanadyl(IV) Complex in Aqueous Solution of Oxalic Acid

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Received September 9, 1980

Previously, the authors have confirmed that irradiation of oxalato titanyl(IV) complex in aqueous oxalic acid solution at 254 nm causes (i) the photoredox reaction of TiO(IV) complex to Ti(III) complex accompanied by evolution of CO_2, (ii) the hydrolysis of TiO(IV) complex into Ti(IV) hydroxide evolving equimolar amounts of CO_2 and CO with Ti(IV) hydroxide and (iii) the photodecomposition of oxalic acid sensitized by resulting Ti(III) complex with evolution of CO_2 and CO [1].

As similar reactions could be expected for oxalato vanadyl(IV) complex, the irradiation of the VO(IV) complex was carried out with UV light. On the basis of the relative amounts of the product in the solution and the gaseous products, the overall reactions occurred by the irradiation of the VO(IV) complex in aqueous oxalic acid solution at 254 nm have been studied in this paper.

Experimental

Material

Sample solutions of the VO(IV) complex were prepared by the literature method [2] and absorption spectra of them almost agreed with the literature data [3].

The composition of the complexes in the aqueous oxalic acid solution was determined by the molar ratio method: $[VO(C_2O_4)_2]^{2-}$, $VO(C_2O_4)_2$. The prominent species in the aqueous oxalic acid solution at pH 2.0 is bisoxalato vanadyl(IV) complex ion (*ca.* 99% up) in view of the stability of their constants [4]. All the chemicals of reagent grade were used without further purification.

Analyses

The VO(IV) complex ion was determined by the $KMnO_4$ titration method: (i) vanadyl ion was oxidized to V(V) ion and oxalate ion was decomposed, (ii) V(V) ion was reduced to vanadyl ion with H_2S gas in aqueous sulfuric acid solution, (iii) the excess of H_2S was removed by boiling the solution in an atmosphere of CO_2 and the hot solution was titrated with the standard $KMnO_4$ solution. The determination of V(III) ion and of gaseous products, and all the instruments for measurement were described previously [5].

Apparatus and procedure are outlined before [5].

Results and Discussion

Continuous irradiation of the VO(IV) complex in the aqueous oxalic acid solution was carried out at the molar ratio of VO(IV) to oxalic acid of 1:10 at pH 2.0. The result is shown in Fig. 1. The quantity of resulting V(III) complex increased linearly with the irradiation period in the first 30 min. and after *ca.* 50 min., reached at nearly constant value which coresponded to reductive ratio of 100%. On the other hand, the amounts of oxalic acid decomposed, of CO_2 and of CO evolved increased linearly in a further 30 minutes.

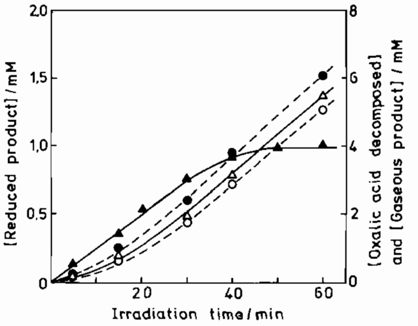

Fig. 1. The amounts of irradiation products of the VO(IV) complex in the aqueous oxalic acid solution; VO(IV): 1.02 m*M*, VO(IV): $H_2C_2O_4$ = 1:10 (molar ratio), pH 2.0. —▲—, V(III) complex produced; —△—, oxalic acid decomposed; --●--, CO_2 evolved; ---○---, CO evolved.

After irradiation, no precipitate was detected, so that the hydrolysis of VO(IV) complex did not occur in contrast to the TiO(IV) complex.

Thus, the evolution of CO would be attributable to the photosensitized decomposition of oxalic acid.

In Fig. 1, the amount of CO_2 evolved would be a sum total of two quantities: one caused by the photosensitized decomposition of oxalic acid, the other by oxidative breakdown of coordinated oxalate. Since the former produce equimolar amounts of CO_2 and CO with oxalic acid decomposed [5], the amount of CO_2 by the latter is probably derived by substracting that of CO from the total amount of CO_2. In Fig. 2, the plots are almost on line with the amount of V(III) complex produced. Therefore, the VO(IV) complex ion is photoreduced to the V(III)

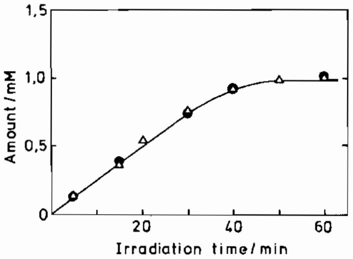

Fig. 2. Comparison of the amounts of V(III) complex produced and CO_2 evolved by oxidative decomposition of coordinated oxalate during the irradiation, △ V(III) complex produced, ● CO_2.

complex with evolution of equimolar amount of CO_2. Furthermore, the VO(IV) complex and the V(III) complex have the same molar ratio of metal to ligand, the evolution of CO_2 by oxidative decomposition of ligand corresponds to the consumption of a half mole of oxalate ion.

Then the overall reactions caused by the irradiation of VO(IV) complex in aqueous oxalic acid solution are proposed as follows:

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

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

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