Photochemical Reactions of the Oxoperoxovanadium(V) Complex in an Acidic Aqueous Solution

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The photochemical decomposition of oxoperoxovanadium(V), $VO(O_2)^+$, was studied in perchloric acid media. It was found that the irradiation of $VO(O_2)^+$ solutions with 313, 365, and 436 nm exciting light resulted in the photoreduction of the complex, and gave VO^{2+}, with an evolution of oxygen. The overall reaction is: $4VO(O_2)^+ + 4H^+ \longrightarrow 4VO^{2+} + 3O_2 + 2H_2O$. The photochemical reaction mechanism is also discussed.

A large number of papers have been published on various aspects of the solution chemistry of peroxovanadium(V) complexes. There have been a large number of interesting kinetic studies of the formation,[1-8] decomposition,[9,10] and substrate reactions[11-15] of peroxo vanadium complexes. Further, vanadium compounds have been used as catalysts for the oxidation of olefins by H_2O_2 or ROOH.[16,17] The mechanisms of the redox reactions of peroxo vanadium compounds are generally complicated and cannot be interpreted by simple redox reactions between $VO(O_2)^+$, VO_2^+, VO^{2+}, and H_2O_2. Short-lived transients must often be assumed, particularly radical species arising from the reduction or oxidation of H_2O_2.

Information about the photochemical reactions of vanadium compounds is relatively scanty. The present study of the photolysis of the oxoperoxovanadium(V) complex in an acidic aqueous solution is an attempt to elucidate the mechanism of the photochemical reaction of the peroxo complex.

Experimental

All the chemicals used were of an analytical grade. Pure water obtained from a Millipore Super-Q system was used for the preparation of the samples. Sodium metavanadate (Soekawa Chemicals, >99% in purity) was used as the source of VO_2^+. Solutions of $VO(O_2)^+$ were prepared by adding the required amount of a standardized solution of hydrogen peroxide to a VO_2^+ solution. The equilibrium ($VO_2^+ + H_2O_2 \rightleftarrows VO(O_2)^+ + H_2O$) was thoroughly investigated.[1,9,12] The rate of the decomposition of $VO(O_2)^+$ is sufficiently slow so that photochemical reactions can be studied. The changes in the concentrations of $VO(O_2)^+$ and VO^{2+} were followed by means of absorption spectrophotometry using a Shimadzu MPS-2000 spectrophotometer. The $VO(O_2)^+$ solution was irradiated with a high- or ultrahigh-pressure mercury lamp. The monochromatic light (313, 365, and 436 nm) was obtained by the combination of solution and glass filters. The incident-light intensities were measured by the use of the tris(oxalato)ferrate(III) ion as the actinometer.[18] The oxygen evolution was measured polarographically with a Clarke-type electrode attached to a Yellow Springs Instruments Oxygen Monitor. A cell equipped with the oxygen electrode was used as the reaction vessel. The cell was thermostated at 25±0.1 °C. The reactant solution was deaerated in the reaction vessel with pure nitrogen gas in order to keep the evolved oxygen in solution as completely as possible. The oxygen dissolved initially had no influence on the photochemical reactions of $VO(O_2)^+$.

Results

Figure 1 shows the absorption spectra of oxoperoxovanadium(V), bisoxovanadium(V), and oxovanadium(IV) in 1 mol dm^{-3} perchloric acid solutions: These substances exist as $VO(O_2)^+$, VO_2^+, and VO^{2+} respectively. The absorption maxima of these vanadium compounds are as follows: $VO(O_2)^+$: absorption maxima at 285 nm (ε=486 mol^{-1} dm^3 cm^{-1}) and 456 nm (ε=281 mol^{-1} dm^3 cm^{-1}); VO_2^+: two shoulders at 260 and 330 nm; VO^{2+}: two shoulders at 240 and 640 nm and absorption maximum at 764 nm (ε=17.4 mol^{-1} dm^3 cm^{-1}).

The acidic solutions of $VO(O_2)^+$ underwent the spectral changes upon irradiation (Fig. 2). The absorbance at 456 nm decreased with an increase in the irradiation time, and a new absorption appeared at 764 nm, with an isosbestic point at about 660 nm which was due to the formation of VO^{2+}. In Fig. 3, the amounts of the decomposed $VO(O_2)^+$ and of the generated VO^{2+} upon irradiation with 366 nm light are plotted against the irradiation time. The changes in the concentration of $VO(O_2)^+$ and VO^{2+} were measured spectrophotometrically at 456 and 764 nm respectively. The amount of VO^{2+} generated increased

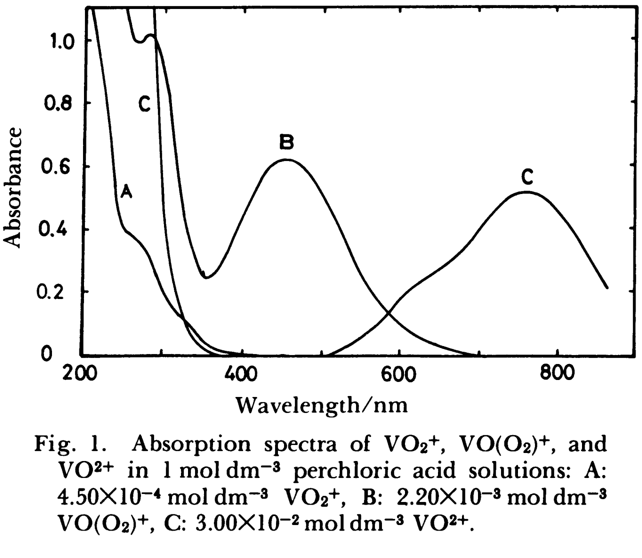

Fig. 1. Absorption spectra of VO_2^+, $VO(O_2)^+$, and VO^{2+} in 1 mol dm^{-3} perchloric acid solutions: A: 4.50×10^{-4} mol dm^{-3} VO_2^+, B: 2.20×10^{-3} mol dm^{-3} $VO(O_2)^+$, C: 3.00×10^{-2} mol dm^{-3} VO^{2+}.

Table 1. Yields of Decomposed $VO(O_2)^+$ and Produced VO^{2+} and Oxygen[a)]

	$-[VO(O_2)^+]$[b)]	$[VO^{2+}]$	$[O_2]$
	10^4/mol dm^{-3}	10^4/mol dm^{-3}	10^4/mol dm^{-3}
$VO(O_2)^+$[c)]	2.20	2.07	1.41
$VO(O_2)^+$[c)] + 2-PrOH[d)]	2.12	2.10	0.93

a) Irradiation time: 20 min, wavelength for irradiation: 366 nm. $-[VO(O_2)^+]$ and $[VO^{2+}]$ were obtained with the same irradiated solutions as were used for the determination of the evolved oxygen. A 5-cm cell was used for the spectrometrical determination of VO^{2+}, the extinction coefficient of which was small. b) Determined for the disappearance of $[VO(O_2)]^+$. c) $[VO(O_2)^+]=1.8\times10^{-3}$ mol dm^{-3}. d) $[2\text{-PrOH}]=0.25$ mol dm^{-3}.

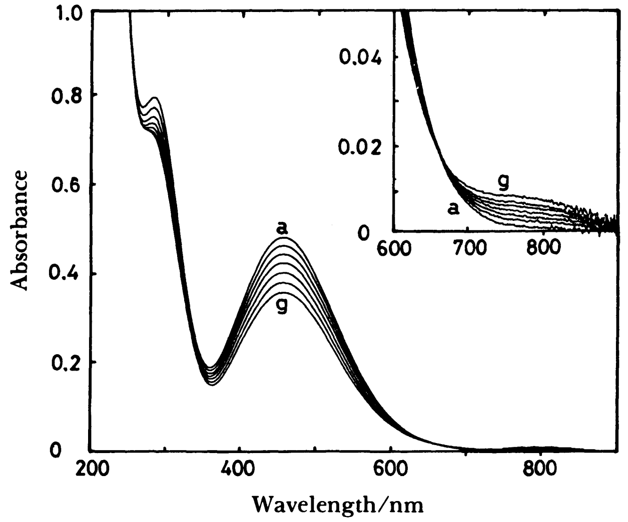

Fig. 2. Absorption spectra changes induced by 366 nm photolysis of $VO(O_2)^+$: Photolysis times for curves a—g respectively are 0, 10, 20, 30, 40, 50, and 60 min. The insert shows the enlarged spectra.

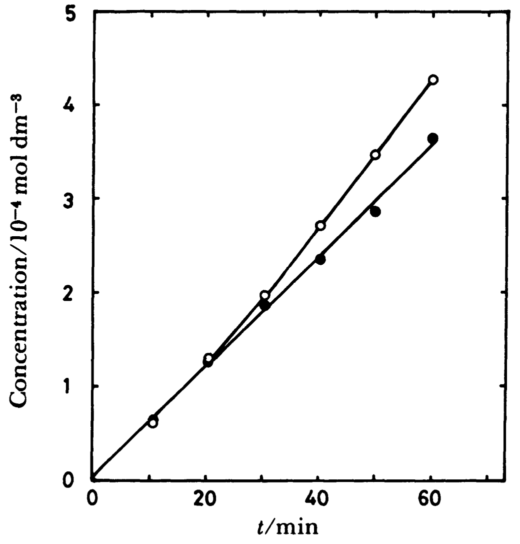

Fig. 3. Decomposition of $VO(O_2)^+$ (○) and generation of VO^{2+} (●) as a function of time upon 366 nm irradiation of 1.8×10^{-3} mol dm^{-3} $VO(O_2)^+$ in 1 mol dm^{-3} perchloric acid solution.

linearly with the increase in the irradiation time. The amount of $VO(O_2)^+$ decomposed was initially equal to that of the generated VO^{2+}. However, the former

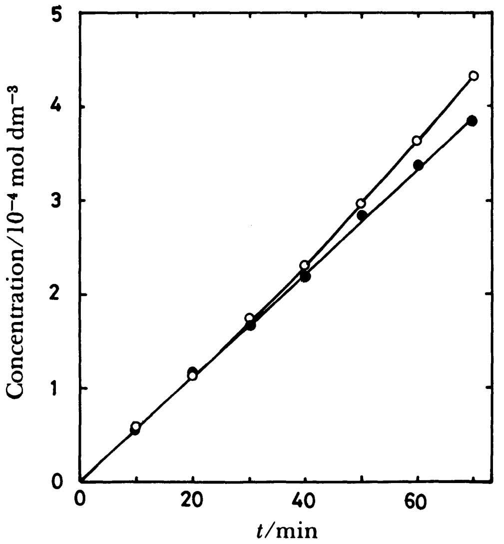

Fig. 4. Decomposed $VO(O_2)^+$ (○) and generated VO^{2+} (●) as a function of time upon 366 nm irradiation of 1.8×10^{-3} mol dm^{-3} containing 0.25 mol dm^{-3} 2-propanol in perchloric acid solution.

became larger than the latter with the increase in the irradiation time. The decomposition of $VO(O_2)^+$ was accompanied by the evolution of oxygen. The photolysis of $VO(O_2)^+$ gave 4 mol of VO^{2+} and 3 mol of O_2 per 4 mol of the complex decomposed at the initial stage. The quantum yields for the decomposition of the complex at 313, 366, and 436 nm were 0.010, 0.0038, and 0.0015 respectively.

$VO(O_2)^+$ solutions containing 2-propanol were irradiated in a 1 mol dm^{-3} percloric acid solution. The amount of $VO(O_2)^+$ decomposed by irradiation with a 366 nm light is plotted against the irradiation time in Fig. 4. The quantity of VO^{2+} resulting increased linearly with the irradiation period. The yields of VO^{2+} were the same in both the presence and absence of 2-propanol, within the limits of experimental error. The photolysis of $VO(O_2)^+$ in the presence of 2-propanol gave 2 mol of VO^{2+} and 1 mol of O_2 per 2 mol of the decomposed $VO(O_2)^+$, as is shown in Table 1.

Discussion

Photolysis of $VO(O_2)^+$. The quantum yields for the photochemical disappearance of $VO(O_2)^+$ in 1 mol dm^{-3} perchloric acid solutions increased with the increase in the energy of the exciting light; this suggests that the photodecomposition occurs into the tail of the ultraviolet band. The irradiation of an acidic solution of $\mathrm{VO(O_2)^+}$ gave rise to complicated reactions which eventually led to 4 mol of $\mathrm{VO^{2+}}$ for 4 mol of $\mathrm{VO(O_2)^+}$ decomposed, with the evolution of 3 mol of oxygen. These results suggest the following overall reaction:

$$\mathrm{4VO(O_2)^+ + 4H^+ \xrightarrow{h\nu} 4VO^{2+} + 3O_2 + 2H_2O} \tag{2}$$

We propose the following scheme to explain our results:

$$\mathrm{VO(O_2)^+ \xrightarrow{h\nu} [O{=}V^{IV}{-}O{-}O\cdot^+]^*} \tag{3}$$

$$\mathrm{[O{=}V^{IV}{-}O{-}O\cdot^+]^* + H^+ \longrightarrow VO^{2+} + HO_2} \tag{4}$$

$$\mathrm{VO(O_2)^+ + HO_2 + H^+ \longrightarrow VO^{2+} + O_2 + H_2O_2} \tag{5}$$

$$\mathrm{VO^{2+} + H_2O_2 \longrightarrow VO_2^+ + OH + H^+} \tag{6}$$

$$\mathrm{VO(O_2)^+ + OH \longrightarrow VO_2^+ + HO_2} \tag{7}$$

$$\mathrm{VO_2^+ + H_2O_2 \longrightarrow VO(O_2)^+ + H_2O} \tag{8}$$

It seems reasonable to conclude that the primary photochemistry responsible for Reaction (2) is electron transfer from $\mathrm{O_2^{2-}}$ to $\mathrm{V^V}$ (Eq. 3). This conclusion is reached for the following reasons: (1) the products of the photolysis of $\mathrm{VO(O_2)^+}$ were $\mathrm{VO^{2+}}$ and $\mathrm{O_2}$; the electron transfer from $\mathrm{O_2^{2-}}$ to $\mathrm{V^V}$ occured later to give $\mathrm{VO^{2+}}$ and $\mathrm{O_2}$; (2) vanadium(IV) compounds were obtained in the photolysis of $\mathrm{VO_2^+}$,[19] alkoxy vanadium(V) chelates,[20] and $\mathrm{VO(acac)_2Cl}$[21]; (3) vanadium(IV) is the most stable oxidation state of vanadium under ordinary conditions. This intermediate $\mathrm{O{=}V^{IV}{-}O{-}O\cdot^+}$ may be presumed to be very unstable. Thus, we assume that the first step is a cleavage of a V–O bond, affording formally the hyperoxovanadium(IV) complex (Eq. 3) in a manner similar to that previously reported in the photolysis of the diperoxo(porphyrinato)molybdenum(VI) complex.[22] The next step will be the departure of $\mathrm{HO_2}$, providing $\mathrm{VO^{2+}}$ (Eq. 4). The resulting $\mathrm{HO_2}$ will react with $\mathrm{VO(O_2)^+}$ to generate $\mathrm{H_2O_2}$, as is shown in Eq. 5. Rush and Bielki[23] have investigated the kinetics of the reaction of $\mathrm{HO_2}$ with $\mathrm{VO(O_2)^+}$ using a pulse radiolysis technique; they showed that $\mathrm{HO_2}$ reduces $\mathrm{VO(O_2)^+}$ to $\mathrm{VO^{2+}}$ according to Eq. 5 ($k_s=2.8\times10^5\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$). The resulting $\mathrm{H_2O_2}$ in Eq. 5 will react with $\mathrm{VO^{2+}}$ ($k_6=6.3\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$ [2]) as well as Fe(II) (Fenton's reagent) to give $\mathrm{VO_2^+}$ and OH radicals. Samuni et al.[2] have reported that the oxidation of $\mathrm{VO^{2+}}$ to $\mathrm{VO_2^+}$ by $\mathrm{H_2O_2}$ is accompanied by a generation of $\mathrm{VO(O_2)^+}$, even in the absence of an excess of $\mathrm{H_2O_2}$ (Eq. 8). Working at $\mathrm{[H_2O_2]<[VO^{2+}]}$ results in the appearance of $\mathrm{VO(O_2)^+}$ even before all the $\mathrm{VO^{2+}}$ has been oxidized to $\mathrm{VO_2^+}$.[1] That is, Reaction (6) is rapidly followed by Reaction (8) ($k_6=6.3\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$,[2] $k_8=2.96\times10^4\ \mathrm{mol^{-1}\,dm^3 s^{-1}}$ [10]). $\mathrm{VO(O_2)^+}$ and $\mathrm{VO^{2+}}$ compete for the OH radicals formed by Eq. 6 (Eqs. 7 and 9):

$$\mathrm{VO^{2+} + OH \longrightarrow VO_2^+ + H^+} \tag{9}$$

Since $\mathrm{VO(O_2)^+}$ is in excess relative to $\mathrm{VO^{2+}}$ under our present experimental conditions, the OH radicals react predominantly through Reaction (7) ($k_7=2.1\times10^{10}\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$, $k_9=6.4\times10^8\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$ [2]). The $\mathrm{HO_2}$ generated by Reaction (7) goes to Reaction (5). Thus, the overall reaction (2) can be explained by assuming Reactions (3)—(8).

As is shown in Fig. 3, the amount of the decomposed $\mathrm{VO(O_2)^+}$ was equal to that of the $\mathrm{VO^{2+}}$ generated at the initial stage. However, the former became larger than the latter during a prolonged irradiation time. The difference was attributed to the thermal decomposition catalyzed with $\mathrm{VO^{2+}}$. The thermal decomposition was investigated by Gardes-Alberyt et et al.[10]; they found the decomposition products to be $\mathrm{VO_2^+}$ and $\mathrm{O_2}$. At the initial stage, the thermal decomposition can be neglected. The amount of the decrease in the absorption at 285 nm in Fig. 2 became smaller with the increase in the irradiation time; this phenomenon is attributed to the generation of $\mathrm{VO_2^+}$ by the thermal decomposition for the larger extinction coefficient of $\mathrm{VO_2^+}$ ($\varepsilon=697\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$) compared to that of $\mathrm{VO(O_2)^+}$ ($\varepsilon=468\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$). However, the amount of $\mathrm{VO_2^+}$ generated at the initial stage is negligibly small.

Effect of 2-Propanol on the Photolysis of $\mathrm{VO(O_2)^+}$. The assumption stated above was checked by the addition of an excess of 2-propanol to the reaction mixture. In such a case, OH radicals will react with 2-propanol ($k_{10}=2.0\times10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$ [26]) to yield 2-propanol radicals, according to:

$$\mathrm{(CH_3)_2CHOH + OH \longrightarrow (CH_3)_2COH + H_2O} \tag{10}$$

The 2-propanol radicals react with a number of metal ions and complex ions very rapidly; their rate constants were also measured.[27] The resulting 2-propanol radicals react thus with $\mathrm{VO_2^+}$:

$$\mathrm{(CH_3)_2COH + VO_2^+ + H^+ \longrightarrow VO^{2+} + (CH_3)_2CO + H_2O} \tag{11}$$

or

$$\mathrm{(CH_3)_2COH + O_2 \longrightarrow (CH_3)_2C(OH)O_2\cdot} \tag{12}$$

$$\mathrm{VO_2^+ + (CH_3)_2C(OH)O_2\cdot + H^+ \longrightarrow VO^{2+} + (CH_3)_2CO + O_2 + H_2O} \tag{13}$$

Reaction (11) (or Reactions (12) ($k_{12}=4.5\times10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$ [28]) and (13)) can be supported by the facts that $\mathrm{VO_2^+}$ was not detected at the initial stage of the photolysis and that ketone (acetone) as an oxidation product was detected in the irradiated solutions.[29] Thus, when Reactions (3)—(6), (10), and (11) (or (12) and (13) instead of (11)) are assumed as the photochemical reaction mechanism in the presence of 2-propanol, the overall reaction can be written as follows:

$$2VO(O_2)^+ + (CH_3)_2CHOH + 2H^+ \xrightarrow{h\nu} 2VO^{2+} + (CH_3)_2CO + O_2 + 2H_2O \qquad (14)$$

The results given in Table 1 can be explained satisfactorily in terms of Reaction (14).

It may be concluded that the photochemical decomposition reactions of $VO(O_2)^+$ in acidic aqueous solution occur according to the scheme presented above.

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