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Photochemical Reduction of Vanadium(V) in Aqueous Perchloric Acid Solutions

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Synopsis. It was found that irradiation of V(V) solution gives V(IV) and an equivalent amount of oxygen. The dependence of the quantum yield on light intensity, acid concentration, wave number and the concentration of V(IV) was investigated.

It was found that reduction of vanadium(V) proceeds during irradiation of its aqueous perchloric acid solution with argon laser at 488 nm. The photochemical reduction of metal ions of a high valence state such as cerium(IV)[1–6] and iron(III)[7–11] has been studied and probable mechanisms have been discussed. However, no data have been given of vanadium(V).

Experimental

Irradiation of vanadium(V) solution was carried out with an ultra high pressure mercury lamp with solution- and glass-filters.[12] A qualtz cell for spectrophotometry (1 cm light-path length) with a suitable modification was used as a reaction vessel. The cell was thermostated at 20.0±0.1 °C in an optical bench. Stirring of the solution was carried out magnetically with a small glass-coated bar. The reactant solution was deaerated in the reaction vessel with pure nitrogen gas.

The concentration of vanadium(V) was determined photometrically at 270 nm. The value 863 $M^{-1}\cdot cm^{-1}$ was used as a molar extinction coefficient for V(V), and 143 $M^{-1}\cdot cm^{-1}$ for V(IV). The incident light intensity before and after the irradiation, and the transmitted light intensity during the irradiation were measured in an arbitrary unit with a photomultiplier. These relative intensities were converted into absolute values by means of a ferrioxalate actinometer. Inner filter effect of V(IV) is found to be negligible.

Oxygen gas generated by photolysis was identified and determined by gas-chromatography using an active carbon column and helium as a carrier gas. The equipment is shown in Fig. 1. After prolonged irradiation, the resulting gas was expelled and collected in the syringe (2 in Fig. 1) by bubbling with helium, and the gas sample was injected into a gas-chromatograph. The reaction vessel was replaced by an electrolytic cell, and the gas-chromatograph was calibrated by measuring the amount of oxygen produced by the electrolysis of 0.1 M sulfuric acid.

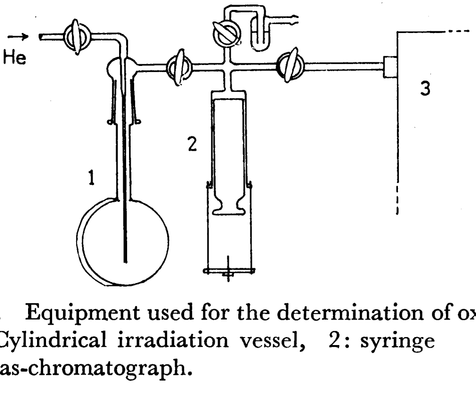

Fig. 1. Equipment used for the determination of oxygen
1: Cylindrical irradiation vessel, 2: syringe
3: gas-chromatograph.

All the solutions were prepared from analytical grade reagents. Triply distilled water obtained from an alkaline permanganate solution was used.

Results and Discussion

Stoichiometry. The EPR spectrum of the irradiated sample showed the octet signal of vanadium(IV). It was found that V(IV) is the final reduction product since no change was observed after prolonged irradiation of V(IV) solution. Under the conditions employed $VO_2(H_2O)_4^+$ was found to be the main species present in V(V) solutions and $VO(H_2O)_5^{2+}$ the main species of V(IV).[13–14]

The amount of oxygen evolved is equivalent to the amount of V(V) reduced by photolysis (Table 1). The overall reaction is thus given by the following scheme.

$$VO_2(H_2O)_4^+ + 1/2H_2O + H^+ \xrightarrow{h\nu} VO(H_2O)_5^{2+} + 1/4O_2 \qquad (1)$$

Effect of Light Intensity on the Quantum Yield of V(IV). The results show that the quantum yield of V(IV) does not depend upon the intensity of the absorbed light (Table 2). This suggests that V(IV) is formed

TABLE 1. YIELDS OF V(IV) AND OXYGEN

$HClO_4$	Yield of V(IV)	Yield of O_2
1.0 M	2.3×10^{-6} mol	5.5×10^{-7}mol
	2.2×10^{-6}	5.5×10^{-7}
	1.6×10^{-6}	4.5×10^{-7}

TABLE 2. DEPENDENCE OF THE QUANTUM YIELD OF V(IV) ON ABSORBED LIGHT INTENSITY

Absorbed light intensity	Quantum yield of V(IV)
1.15×10^{-4} Einstein$\cdot l^{-1}\cdot min^{-1}$	0.0037
1.20×10^{-4}	0.0033
1.40×10^{-4}	0.0036
2.51×10^{-4}	0.0036
3.34×10^{-4}	0.0036
3.40×10^{-4}	0.0035
3.90×10^{-4}	0.0037
4.31×10^{-4}	0.0033
4.90×10^{-4}	0.0037

$[V(V)]=1.0\times10^{-3}$ M, $[HClO_4]=1.0$ M, at 313 nm.

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by reaction of the first order with respect to the concentration of some intermediate. A similar result was obtained in the photochemical reduction of cerium(IV).

Effect of the Wave Number of Absorbed Light on the Quantum Yield of V(IV). The wave number effect was studied without any particular attention to light intensity, since the quantum yields of V(IV) and O_2 were independent of light intensity. Figure 2 shows the dependence of the quantum yield of V(IV) on the wave number and the absorption spectrum of reactant $VO_2(H_2O)_4^+$. The value 3.4 eV corresponding to the wave number 27 kK (Fig. 2) is reasonable for the formation of ·OH radical by the reaction

$$V(V) + H_2O \xrightarrow{h\nu} V(IV) + \cdot OH + H^+ \qquad (2)$$

since it is assumed in similar reactions of cerium(IV)[3-5] and iron(III).[7-11] The standard oxidation potential of the thermal reaction corresponding to the reaction (2) is $E^0 = -1.82$ V, calculated from the standard oxidation potentials $E^0(V(V) \rightarrow V(IV)) = 1.00$ V and $E^0(H_2O \rightarrow \cdot OH) = -2.82$ V. The quantum yield of V(IV) increases gradually with wave number. This might indicate that the probability of the ·OH radical escaping from the solvent cage of V(IV) increases with the photon energy.

Effect of Perchloric Acid and Vanadium(V). We see from Table 3 that the quantum yield of V(IV) does not depend upon the concentration of perchloric acid in the region 0.01—1.0 M. The quantum yields of V(IV), determined at two vanadium(V) concentrations 5×10^{-4} M and 1×10^{-3} M, were found to be $(3.5 \pm 0.3) \times 10^{-3}$ and $(3.4 \pm 0.2) \times 10^{-3}$ respectively in 0.1 M $HClO_4$ at unit ionic strength ($NaClO_4$).

The fact that neither perchloric acid nor vanadium(V) affects the quantum yield of V(IV) is in line with the fact that neither hydrolysis nor polymerization of vanadium(V) occurs under the conditions employed.

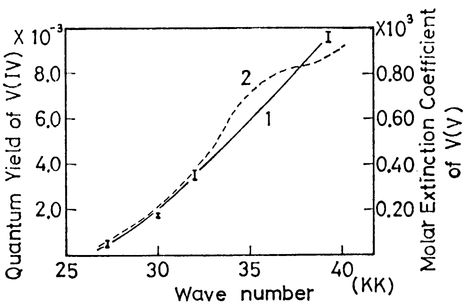

Fig. 2. The dependence of the quantum yield of V (IV) on wave number at 1.0 M $HClO_4$ and the absorption spectrum of $VO_2(H_2O)_4^+$.
1: Quantum yield of V (IV),
2: absorption spectrum of $VO_2(H_2O)_4^+$.

Table 3. Dependence of the quantum yield of V(IV) on the concentration of perchloric acid

$(HClO_4)$	Quantum yield of V(IV)
0.01 M	$(3.3 \pm 0.2) \times 10^{-3}$
0.05	$(3.2 \pm 0.1) \times 10^{-3}$
0.10	$(3.4 \pm 0.2) \times 10^{-3}$
0.50	$(3.6 \pm 0.3) \times 10^{-3}$
1.00	$(3.5 \pm 0.2) \times 10^{-3}$

$[V(V)] = 1 \times 10^{-3}$ M, (ionic strength) = 1.0 M and at 313 nm.

Retardation Effect of Vanadium(IV). It was found that the quantum yield of V(IV) decreased with an increase in the concentration of V(IV) produced by photolysis. Since the inner filter effect of V(IV) was negligible and no change was observed after prolonged irradiation of V(IV), the effect of V(IV) is attributed to the back reaction

$$\cdot OH + V(IV) \longrightarrow OH^- + V(V) \qquad (3)$$

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