to $HCo(CO)_4$. The effect of a hidden small band on the intensity of the 2034 cm^{-1} could not be discerned. In addition, a splitting of 7 cm^{-1} is larger than what one usually expects for argon matrices. For example, bands split by the matrix of the three isomers of $Co_2(CO)_8$ are only split by approximately 4 cm^{-1} or less. The close proximity of these bands to those reported by Hanlan et al.[16] in Ar/CO matrices suggests that the bands should be assigned to the A_1 and E modes of $Co(CO)_4$. The larger separation between the bands in the matrix doped with CO can be the result of site perturbations or molecular distortion. The analysis of how much $Co(CO)_4$ deviates from tetrahedral symmetry has been based on infrared[17,25] and ESR[16] experiments. The splitting observed in these experiments between the two most intense bands is the smallest splitting yet reported for $Co(CO)_4$ in argon matrices and is the same as was reported for $Ir(CO)_4$ and $Rh(CO)_4$.[25] The hydrogen atom is not probably located in the immediate vicinity of $Co(CO)_4$ nor are there any CO molecules doped in the matrix to cause site perturbations as was the case in earlier studies. Thus, the molecule probably exists in a uniform argon environment. Although the molecule is presumably less distorted than is the case in CO matrices, it is interesting to note that the ESR spectra are nearly identical in the two matrices.

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Registry No. $HCo(CO)_4$, 16842-03-8; $Co(CO)_4$, 58207-38-8; $DCo(CO)_4$, 62342-66-9.

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Tris(2,2'-bipyridine)ruthenium(II)-Photosensitized Oxidation of Antimony(III) and Production of Hydrogen Peroxide in Dilute Hydrochloric Acid Solution

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The formation reaction of hydrogen peroxide and the oxidation reaction of antimony(III) proceed continuously with the irradiation of visible light in the oxygen-dissolved 0.5 M HCl solution containing $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) and Sb(III). The kinetic and quenching experiments have suggested a mechanism in which the electron transfer from the lowest excited state of $Ru(bpy)_3^{2+}$ to a dissolved oxygen molecule occurs.

Introduction

The irradiation of tris(2,2'-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) with visible light results in the formation of a charge-transfer excited state ($[Ru(bpy)_3^{2+}]^*$) which is commonly considered as a triplet charge-transfer excited state.[1] Reactions of $[Ru(bpy)_3^{2+}]^*$ involve energy-transfer reactions,[2] electron-transfer reactions to the luminescence quenchers,[3] and those from the luminescence quenchers.[4]

However, one serious problem in the use of photochemically generated $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{+}$ as the strong oxidant and reductant, respectively, is associated with the fast back-reactions with the products of the quenchers.[5]

We found that the oxidation of Sb(III) and the formation of H_2O_2 proceeded continuously in $Ru(bpy)_3^{2+}/Sb(III)/O_2$/dilute HCl with the irradiation of the visible light. In this paper we report a study on the mechanism of the photoinduced reactions in this system.

Experimental Section

$[Ru(bpy)_3Cl_2]\cdot 6H_2O$ was prepared by the method described elsewhere[6] and recrystallized 3 times from water. A stock solution of Sb(III) in dilute HCl was usually prepared by dissolving GR grade $SbCl_3$ (Kanto Kagaku) in 2.5 M HCl. A stock solution of Sb(III) in dilute H_2SO_4 was prepared by warming $SbCl_3$ with small amounts of concentrated H_2SO_4 until evolution of white smoke, and then the residue was dissolved in 2.5 M H_2SO_4. Hydrolysis occurs if the acidity is below 2.5 M, but the process is very slow.[7] In all cases, freshly prepared samples for the irradiation were always used to avoid hydrolysis of the Sb(III). The concentration of HCl in the irradiation samples was usually kept at 0.5 M. The concentrations of Sb(III) and Sb(V) were determined by means of a Yanagimoto P-8 polarograph.[8] A typical procedure for the determination of hydrogen peroxide was as follows: 1 aliquot of the irradiation sample was poured into a column (10-mm diameter and 30-mm length) of cation-exchange resins (Dowex 50-X8, 100-200 mesh, the hydrogen form) followed by washing with water. The concentration of hydrogen peroxide in

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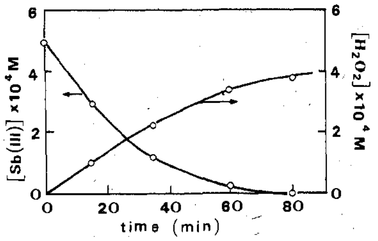

Figure 1. Plots of [Sb(III)] and $[H_2O_2]$ vs. irradiation time in O_2-saturated 0.5 M HCl solution (1.0×10^{-4} M $Ru(bpy)_3^{2+}$, 5.0×10^{-4} M Sb(III)).

the eluate was determined by the colorimetric method.[9] The absorption spectra were observed with a Hitachi 320 spectrophotometer. The light source of a 150-W tungsten lamp with a UV cutoff filter (Kenko, Skylight L-40, UV) was used for the illumination of visible light. A cylindrical glass cell (40-mm diameter and 15-mm thickness) containing the irradiation sample was kept in a thermostated cell compartment. The temperature of all the irradiation samples was kept at 25 ± 0.2 °C.

The quenching experiments were carried out by using a Shimadzu RF-500 spectrofluorometer at 25 ± 0.1 °C. Excitation was carried out at 455 nm. In the quenching studies, the concentration of $Ru(bpy)_3^{2+}$ was kept at 1.0×10^{-5} M. If necessary, dissolved oxygen in the $Ru(bpy)_3^{2+}$ solutions was removed carefully by bubbling nitrogen gas which was passed through alkaline pyrogarol solution. The concentration of the dissolved oxygen in the solution was adjusted by saturation of air, nitrogen–oxygen mixtures, and pure oxygen gas at 25 °C.

Results and Discussion

With the irradiation of the visible light, the oxidation reaction of Sb(III) to Sb(V) and the formation reaction of H_2O_2 proceeded simultaneously in air- and oxygen-saturated 0.5 M HCl solution containing $Ru(bpy)_3^{2+}$ and Sb(III), while the visible absorption spectrum of these solutions due to $Ru(bpy)_3^{2+}$ was changed little during 1-h irradiation. In a concentration region of HCl higher than 1 M, however, appreciable change of the absorption spectrum was observed with the prolonged irradiation. This suggests that the photochemical decomposition of $Ru(bpy)_3^{2+}$ occurs at higher HCl concentration. Houten and Watts[10] suggested that the irradiation of a 1.0×10^{-4} M $Ru(bpy)_3^{2+}$ in 0.1 M HCl at 25 °C for 5 h resulted in no detectable disappearance of the starting material, and, however, photolysis at 95 °C with 436-nm irradiation resulted in labilization of the bipyridine ligand. In the present studies, it was also ascertained that (i) no direct formation of H_2O_2 was observed in 0.5 M HCl solution of $Ru(bpy)_3^{2+}$ in the presence and absence of oxygen, (ii) the oxidation reaction of Sb(III) by dissolved oxygen and that by hydrogen peroxide were neglected as compared with the photoinduced reactions, (iii) decrease of the concentration of Sb(III) was equal to the increase of that of Sb(V) in the irradiated sample, (iv) the formation reaction of H_2O_2 was terminated when Sb(III) had been completely consumed, and (v) no appreciable decomposition of H_2O_2 was observed in 0.5 M HCl solution of 1.0×10^{-4} M $Ru(bpy)_3^{2+}$ and 1.0×10^{-3} M H_2O_2 with the irradiation.

Typical samples of the plots of [Sb(III)] vs. time and $[H_2O_2]$ vs. time are presented in Figure 1. The rates of the oxidation reaction of Sb(III) and formation reaction of H_2O_2 were determined from slopes of [Sb(III)] vs. time plots and $[H_2O_2]$ vs. time plots in the initial stages, respectively.

Figure 2 shows the effect of the concentration of Sb(III) on the rate. In the lower concentration region of Sb(III), e.g., $[Sb(III)]/[Ru(bpy)_3^{2+}] \lesssim 3$, the rate was almost linear with respect to the concentration of Sb(III). In the higher concentration region, however, the rate did not significantly increase with the concentration of Sb(III).

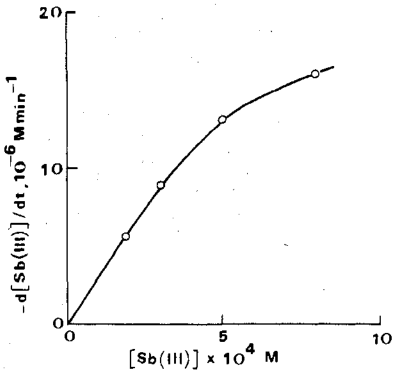

Figure 2. Dependence of the rate on the concentration of Sb(III) in O_2-saturated 0.5 M HCl solution (1.0×10^{-4} M $Ru(bpy)_3^{2+}$, 5.0×10^{-4} M Sb(III)).

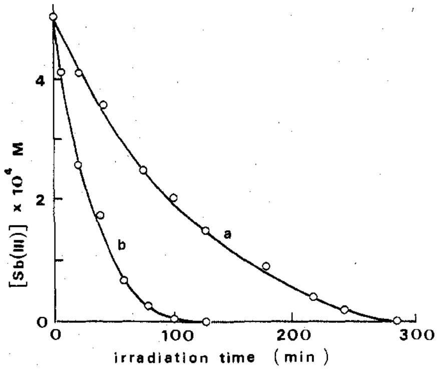

Figure 3. Variation of the concentration of Sb(III) with irradiation time (1.0×10^{-4} M $Ru(bpy)_3^{2+}$): a, air-saturated solution; b, O_2-saturated solution.

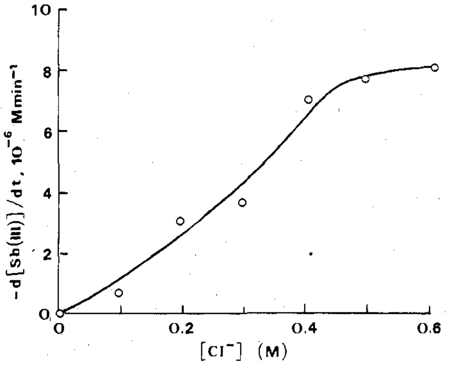

Figure 4. Effect of chloride ion concentration on the rate in O_2-saturated 0.5 M H_2SO_4/NaCl (1.0×10^{-4} M $Ru(bpy)_3^{2+}$, 5.0×10^{-4} M Sb(III)).

The effect of oxygen concentration on the rate is given in Figure 3. The rate depends on the oxygen concentration: the rate in O_2-saturated solution was about 2.5 times greater than that in air-saturated solution under the conditions employed.

The effect of chloride ion on the rate is shown in Figure 4. In these experiments the oxidation rates were determined in 0.5 M H_2SO_4 solutions containing various concentrations of sodium chloride. In 0.5 M H_2SO_4 in the absence of NaCl, no appreciable decreases in the concentration of Sb(III) and the formation of H_2O_2 were observed with 100-min irradiation. The reaction rates increased gradually with an increase in the concentration of NaCl. This suggests that chloride ion catalyzes the photoinduced reactions.

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Table I. Product Distribution in the Irradiated Solutions[a]

no.	10^4[Sb(III)], M	$[H_2O_2]/[Sb(V)]$
1[b]	2.0	0.81
2[b]	3.0	0.78
3[b]	5.0	0.79
4[b]	8.0	0.80
5[c]	5.0	0.77
6[d]	5.0	0.78
7[e]	5.0	0.76

[a] Product distributions were determined when the Sb(III) had been completely oxidized. [b] O_2 saturated 0.5 M HCl. [c] O_2 saturated 0.1 M H_2SO_4/0.5 M NaCl. [d] O_2 saturated 0.5 M H_2SO_4/0.5 M NaCl. [e] Air saturated 0.5 M HCl.

In 0.5 M H_2SO_4 in the absence of chloride ion, Sb(III) is known to exist as SbO^+.[7] So, it is clear that SbO^+ is the inactive species for the reaction. It is also known that Sb(III) can exist as $SbCl_3$ and $SbCl_4^-$ in dilute hydrochloric acid solution depending on the concentration of HCl.[7] In 0.5 M HCl the predominant species of Sb(III) is $SbCl_3$: it was suggested that $SbCl_3$ exists even in 2–4 M HCl.[7,11] The results in 0.5 M H_2SO_4/NaCl indicate that the increase in the rate on the chloride ion addition to the dilute sulfuric acid solution reflects then the increasing fraction of $SbCl_3$.

The effect of hydrogen ion concentration was found to be a minor factor in determining the rate: the rate was little affected by an increase in H_2SO_4 concentration from 0 to 2 M in aerated 0.5 M HCl solutions containing 1.0×10^{-4} M $Ru(bpy)_3^{2+}$ and 1.0×10^{-4} M Sb(III).

In the $Ru(bpy)_3^{2+}/Sb(III)/O_2$/0.5 M HCl, the photosensitized electron-transfer reactions should proceed through the reductive electron-transfer reaction (2) and/or the oxidative electron-transfer reaction (3).

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} [Ru(bpy)_3^{2+}]^* \qquad (1)$$

$$[Ru(bpy)_3^{2+}]^* + SbCl_3 \rightarrow Ru(bpy)_3^{+} + \text{product} \qquad (2)$$

$$[Ru(bpy)_3^{2+}]^* + O_2 \rightarrow Ru(bpy)_3^{3+} + O_2^- \qquad (3)$$

For clarification of the electron-transfer step of the reaction, the quenching experiments were carried out in 0.5 M HCl solutions containing 1.0×10^{-5} M $Ru(bpy)_3^{2+}$ and varing concentrations of Sb(III) and those containing 1.0×10^{-5} M $Ru(bpy)_3^{2+}$ and varing concentrations of O_2. In $Ru(bpy)_3^{2+}$/Sb(III)/0.5 M HCl, no detectable luminescence quenching of the excited state of $Ru(bpy)_3^{2+}$ by Sb(III) occurred below 1.0×10^{-3} M Sb(III). In $Ru(bpy)_3^{2+}/O_2$/0.5 M HCl, however, appreciable luminescence quenching of the $[Ru(bpy)_3^{2+}]^*$ by O_2 was observed: the Stern–Volmer plots became linear, and the value of the Stern–Volmer constant was estimated to be 1800 at 25 °C. From this, we obtain $k_q = 3.0 \times 10^9\ M^{-1}\ s^{-1}$ for the rate constant of reaction 3 by using τ_0 (excited-state lifetime in the absence of quencher) as 6.0×10^{-7} s for $[Ru(bpy)_3^{2+}]^*$.[12] This value is somewhat smaller than those obtained in neutral aqueous solutions by Meisel, Mulac, and Rabani ($k_q = 3.7 \times 10^9\ M^{-1}\ s^{-1}$)[13] and Tung and Sutin ($k_q = 3.3 \times 10^9\ M^{-1}\ s^{-1}$).[14] It is clear from the results obtained in the quenching experiments that the predominant species that reacts with $[Ru(bpy)_3^{2+}]^*$ is the dissolved oxygen molecule.

The main feature of the photo-induced reaction responsible for the experimental results is then to be considered in terms of eq 1, the quenching reaction of $[Ru(bpy)_3^{2+}]^*$ by O_2 giving the superoxide ion (eq 3), and the superoxide ion reaction with H^+ to give the HO_2 radical under the experimental conditions employed (eq 4).

$$O_2^- + H^+ \rightarrow HO_2 \quad pK = 4.8^{15} \qquad (4)$$

The scavenging reaction of $[Ru(bpy)_3^{2+}]^*$ by $SbCl_3$ competes for the nonproductive back-reaction (6). To avoid concern with the exact ionic form which antimonate may assume, we denote this simply as Sb(V), and Sb(IV) represents the intermediate species which is formed by the one-electron oxidation of $SbCl_3$. The competition between (5) and (6) would account for the rate dependence on Sb(III) (Figure 2).

$$Ru(bpy)_3^{3+} + SbCl_3 \rightarrow Ru(bpy)_3^{2+} + Sb(IV) \qquad (5)$$

$$Ru(bpy)_3^{3+} + O_2^- \text{ (or } HO_2) \rightarrow Ru(bpy)_3^{2+} + O_2 \text{ (or } O_2 + H^+) \qquad (6)$$

The HO_2 radical oxidizes $SbCl_3$ as seen in eq 7. Hydrogen

$$SbCl_3 + HO_2 + H^+ \rightarrow Sb(IV) + H_2O_2 \qquad (7)$$

peroxide is also formed by reaction 8[16] when the concentration

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (8)$$

of $SbCl_3$ is low. The intermediate species of Sb(IV) would decay mainly by the disproportionation reaction (9). Reac-

$$Sb(IV) + Sb(IV) \rightarrow Sb(III) + Sb(V) \qquad (9)$$

tions 7 and 9 were suggested on the basis of the results obtained from γ-ray irradiated oxidation of Sb(III) in dilute sulfuric acid and dilute hydrochloric acid solutions.[8]

The product distributions observed are shown in Table I. According to reactions 3–9, the stoichiometric ratio of $[H_2O_2]/[Sb(V)]$ should be about unity whereas the observed one was about 0.8. This discrepancy may be attributed to some side reactions such as chain decomposition reactions of H_2O_2 which are represented by reactions 10 and 11.[16] The chain

$$HO_2 + H_2O_2 \rightarrow H_2O + O_2 + OH \qquad (10)$$

$$H_2O_2 + OH \rightarrow H_2O + HO_2 \qquad (11)$$

decomposition presumably occurs when the concentration of H_2O_2 becomes high enough for HO_2 to react with H_2O_2 instead of with Sb(III) or itself.[16] Furthermore, the reactions of the OH radical, which is formed in reaction 10, with $Ru(bpy)_3^{2+}$ and $SbCl_3$ might be considered.

The system $Ru(bpy)_3^{2+}/Q_r/O_2$, where Q_r is a suitable reducing agent quencher, may be used as a generation system of the superoxide ion where the reaction is driven by visible light to develop photocatalytic processes for carrying out useful chemical reactions.[17]

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Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; H_2O_2, 7722-84-1; Sb(III), 23713-48-6.

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