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Production of Sb(IV) Chloro Complex by Flash Photolysis of the Corresponding Sb(III) and Sb(V) Complexes in CH_3CN and $CHCl_3$

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$[SbCl_6]^{2-}$ was formed in the flash photolysis of $[SbCl_6]^{3-}$ or $[SbCl_6]^{-}$ in both solutions of CH_3CN and $CHCl_3$ in the presence of an excess of chloride. $[SbCl_6]^{2-}$ had absorption maxima at 293, 328, and 390 nm in CH_3CN. A similar absorption spectrum of $[SbCl_6]^{2-}$ was also obtained in $CHCl_3$. The lifetime of $[SbCl_6]^{2-}$ was much shorter in $CHCl_3$ than in CH_3CN. $[SbCl_6]^{-}$ was easily reduced to $[SbCl_6]^{3-}$ upon continuous UV-irradiation in CH_3CN as well as in $CHCl_3$. On the other hand, $[SbCl_6]^{3-}$ was oxidized to $[SbCl_6]^{-}$ in $CHCl_3$ in the presence of oxygen, but was not in CH_3CN. The spectrum and the decay rate of $[SbCl_6]^{2-}$ were not essentially affected by oxygen in both solutions of CH_3CN and $CHCl_3$.

Generally, main-group metals exist in stable oxidation states in which the ground state of the electron configuration is either s^2 or s^0. The absorption spectra of the complexes of s^2 metal ions were characterized by sp bands at longer wavelength and MLCT absorption at shorter wavelength, and those of s^0 metal ions were characterized by LMCT bands.[1] The photoredox reactions of the main-group metal complexes with the electron configuration s^2 (Tl(I),[2,3] Sn(II),[4—7] Pb(II),[7] Sb(III),[2,7,8] Bi(III),[7,9] Te(IV),[2,10] etc.) and s^0 (Tl(III),[2] Sn(IV),[5,6,11] Pb(IV),[2,11] Sb(V)[8] etc.) were studied. The redox reactions of such complexes involve either a two-electron transfer with the direct formation of a stable oxidation state, or successive one-electron transfer steps. In the latter case, an unstable intermediate with an s^1 electron configuration can be expected to be produced. However, little is known about the chemical species of the s^1 configuration. Flash photolysis is very useful in the generation and characterization of metal ions in unusual valency states. Transient species, such as Pb(III),[12] Sn(III),[5,6] and Pt(III),[13] were detected by using a flash photolysis technique.

Vogler and Paukner[8] reported that $[SbCl_6]^{3-}$ was oxidized to $[SbCl_6]^{-}$ with the production of peroxide in air-saturated $CHCl_3$ solutions, and that $[SbCl_6]^{-}$ was reduced to $[SbCl_6]^{3-}$ with the production of chlorine in deaerated $CHCl_3$ solutions. However, it is not yet known whether the photoredox occurs by two subsequent one-electron transfer processes or by a two-electron transfer in a concerted fashion. Our principal objective in this study was to clarify the formation and its characteristics of Sb(IV) in the photoredox reactions of Sb(III) and Sb(V) in $CHCl_3$ and CH_3CN.

Experimental

Materials. The compounds $[N(C_2H_5)_4][SbCl_4]$ and $[N(C_2H_5)_4][SbCl_6]$ were prepared according to published procedures.[14,15] $CHCl_3$ and CH_3CN were of spectro grade, and all other chemicals used were of chemically pure grade. Deaeration of solutions was carried out by bubbling with pure nitrogen. Flash photolysis studies of Sb(III) and Sb(V) were carried out in CH_3Cl and CH_3CN (hereafter coordinated chloride ions are neglected, except for the case in which the number of the coordinated chloride ions is changed by reaction). When $[N(C_2H_5)_4][SbCl_4]$ and $[N(C_2H_5)_4]$-$[SbCl_6]$ are dissolved in $CHCl_3$ and CH_3CN in the presence of a large excess of chloride ($[Cl^-] > 5\times10^{-2}$ M) (M = mol dm^{-3}), the anions exist as $[SbCl_6]^{3-}$ and $[SbCl_6]^{-}$, respectively.[8] All experiments were carried out in solutions containing 0.1 M $N(C_2H_5)_4Cl$.

Methods. The absorption spectra were recorded with a Shimadzu UV-2100 spectorophotometer. Transient absorption spectra were measured by using the flash photolysis apparatus described previously.[5] The main Xe flash lamps dissipated 450 J max. at 15 kV with a flash duration of 10 μs. A nanosecond laser flash photolysis apparatus was also used, which was equipped with Hoya Continuum Nd : YAG laser (1064 nm, 10 Hz, 450 mJ) with a width of about 15 ns. 266 nm light was used in the excitation of laser photolysis. The detection system utilized a 150 W Xe lamp, a monochromator, a photomultiplier, and associated optical components. The flash photolysis apparatuses were equipped with a multichannelanalyzer (UNISOKU USP-500) of which the limit of time resolution was 10 μs. The signals were digitized with a Tektronix TDS 320 oscilloscope and analyzed with a computer. A 500 W Xe lamp was used for continuous irradiation with filters. Peroxide was determined by the peroxide test of Merck (merckoquant 10081-1M), which was used in a similar reaction system.[8]

Results and Discussion

$[SbCl_6]^{3-}$ in CH_3CN. Halide complexes of s^2 metal ions are characterized by metal-centered sp and MLCT transitions.[16,17] The absorption spectrum of $[SbCl_6]^{3-}$ in CH_3CN containing 0.1 M $N(C_2H_5)_4Cl$ has absorption maxima at 308 nm ($^1S_0 \rightarrow {}^3P_1$, $\varepsilon = 1.58\times10^3$ M^{-1} cm^{-1}), 267 nm ($^1S_0 \rightarrow {}^3P_2$, $\varepsilon = 5.10\times10^3$ M^{-1} cm^{-1}), and 234 nm ($^1S_0 \rightarrow {}^1P_1$, $\varepsilon = 2.88\times10^4$ M^{-1} cm^{-1}) (Fig. 1).

It is known that in deaerated $CHCl_3$ solutions Sb(III) is not oxidized to Sb(V) upon continuous irradiation at 263 nm.[8] In our study of CH_3CN, Sb(III) was found not to also be

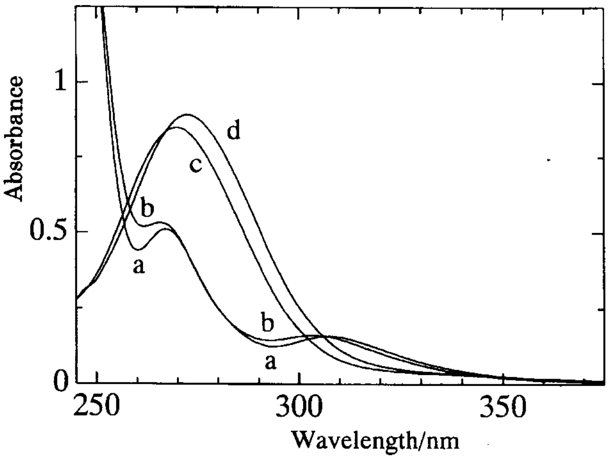

Fig. 1. Electronic absorption spectra of $[SbCl_6]^{3-}$ and $[SbCl_6]^-$ complexes in CH_3CN and $CHCl_3$ in the presence of 0.1 M $N(C_2H_5)_4Cl$. a: 1.00×10^{-4} M $[SbCl_6]^{3-}$ in CH_3CN, b: 1.00×10^{-4} M $[SbCl_6]^{3-}$ in $CHCl_3$, c: 1.00×10^{-4} M $[SbCl_6]^-$ in CH_3CN, and d: 1.00×10^{-4} M $[SbCl_6]^-$ in $CHCl_3$.

oxidized to Sb(V) upon irradiation at $\lambda > 250$ nm. However, a transient absorption spectrum was obtained in the flash photolysis of Sb(III) in deaerated CH_3CN solutions (Fig. 2A). The spectra displayed intense bands at 293, 328, and 390. The shape and ratio of the optical densities are the same during disappearance at the absorption. Hence, this spectrum is caused by one species. The following reaction scheme may be used for interpretating the experimental results, where Sb(III)* denotes excited state:

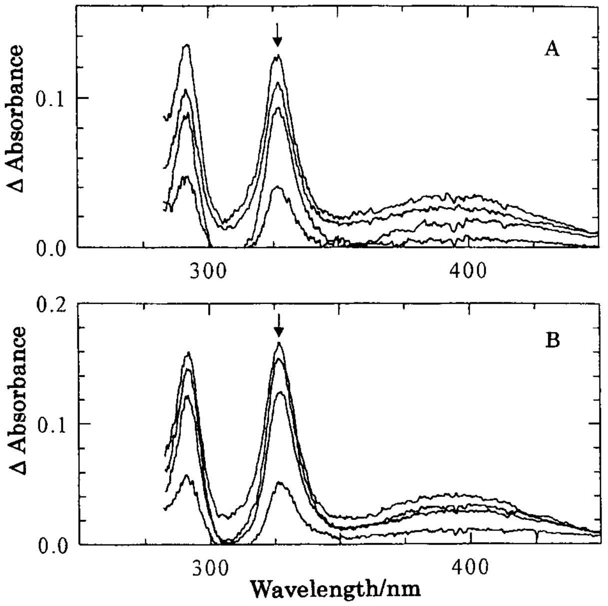

Fig. 2. Transient absorption spectra obtained in the flash photolysis of 5.0×10^{-5} M $[SbCl_6]^{3-}$ CH_3CN solutions containing 0.1 M chloride. (A) measured at 500 μs, 5 ms, 50 ms, and 500 ms after the flash in a deaerated solution, (B) measured at 500 μs, 5 ms, 50 ms, and 500 ms after the flash in an O_2-saturated solution.

$$\mathrm{Sb(III)} \xrightarrow{h\nu} \mathrm{Sb(III)}^*, \tag{1}$$

$$\mathrm{Sb(III)}^* + \mathrm{CH_3CN} \longrightarrow \mathrm{Sb(IV)} + \cdot\mathrm{CH_3CN}^-, \tag{2}$$

$$2\mathrm{Sb(IV)} \longrightarrow \mathrm{Sb(III)} + \mathrm{Sb(V)}, \tag{3}$$

$$\cdot\mathrm{CH_3CN}^- \longrightarrow \text{decomposition product.} \tag{4}$$

The Sb(III)* formed by light absorption (Eq. 1) undergoes electron transfer to give Sb(IV) and $\cdot CH_3CN^-$ (Eq. 2). The obtained transient absorption spectrum was attributed to Sb(IV) and its decay obeyed a second-order kinetics with a k_3/ε value of 6.8×10^2 cm s^{-1}. Sb(V) was not detected upon continuous irradiation of Sb(III), as stated above. This observation may be interpreted in terms of consecutive reactions, in which the oxidation of Sb(III) to Sb(V) (Eqs. 2 and 3) and its subsequent photochemical reduction to Sb(III) take place. This explanation is supported by the fact that Sb(V) is easily photoreduced to Sb(III) (Fig. 3). The continuous irradiation of Sb(V) at > 250 nm in a deaerated CH_3CN solution was accompanied by spectral changes with isobestic points at 350 and 256 nm, except at the beginning of photolysis. The absorption maxima at 307 and 267 nm, which are attributed to Sb(III), appeared after prolonged irradiation. The mechanism for the reduction of Sb(V) will be discussed later. $\cdot CH_3CN^-$ will generate together with Sb(IV) (Eq. 2). Such a $\cdot CH_3CN^-$ was reported in the pulse-radiolysis of CH_3CN ($e_{ag}^- + CH_3CN \rightarrow \cdot CH_3CN^-$).[18] $\cdot CH_3CN^-$ is very unstable, which decomposes according to Eq. 4 ($k_4 = 2\times10^6$ s^{-1}).[19,20]

Complexes of s^2 metal ions, such as Tl(I),[3,21] Sn(II),[22,23] and Sb(III),[8,23] are well known to undergo photooxidation in the presence of oxygen,

$$\mathrm{M}^{n+} + \mathrm{O_2} \longrightarrow \mathrm{M}^{(n+2)+} + \mathrm{O_2}^{2-}. \tag{5}$$

Upon continuous irradiation, Sb(III) is oxidized to Sb(V) along with the production of peroxide in air-saturated $CHCl_3$

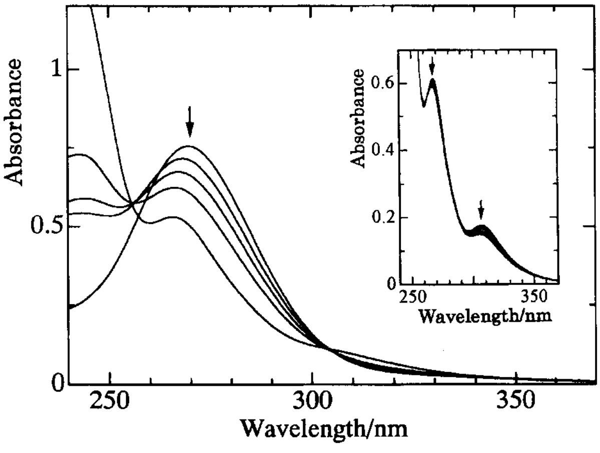

Fig. 3. Spectral changes during the photolysis of 1.0×10^{-4} M $[SbCl_6]^-$ in deaerated CH_3CN solutions in the presence of 0.1 M chloride. Irradiation time: 0, 0.5, 1.0, 6.5, and 42 min at $\lambda > 250$ nm, 1-cm cell. The inset shows the spectral changes during the photolysis of 9.0×10^{-5} M $[SbCl_6]^{3-}$ containing 1.0×10^{-5} M $[Sb(Cl)_6]^-$ in an O_2-saturated solution. Irradiation time: 0, 2, 4, 6, and 8 min at $\lambda > 250$ nm.

solutions,[8] on the other hand, it did not occur in CH_3CN, although peroxide was produced. In the flash photolysis of Sb(III) in O_2-saturated solutions, a transient spectrum, which was very similar to that obtained in deaerated solution, was observed (Fig. 2B). These results obtained in the O_2-saturated solutions can be explained by the following reactions:

$$\mathrm{Sb(III)^* + O_2 \longrightarrow Sb(IV) + O_2^-}, \qquad (6)$$

$$\mathrm{Sb(III) + O_2^- \longrightarrow Sb(IV) + O_2^{2-}}. \qquad (7)$$

It has been reported that Sb(III)* is quenched by oxygen in $CHCl_3$ with a rate constant of 2.7×10^9 $M^{-1}\,s^{-1}$.[8] Sb(III)* would be also quenched by oxygen in CH_3CN[24] as well as in $CHCl_3$; the resulting O_2^- reacts with Sb(III) to give Sb(IV) and peroxide. The decay rate constant of Sb(IV) was the same as that obtained in deaerated solutions within the experimental error. No production of Sb(V) in the photolysis of Sb(III) in O_2-saturated solutions can be attributed to the subsequent photochemical reduction of Sb(V) formed by Eqs. 6, 7, and 3 to Sb(III) as well as in the photolysis of deaerated Sb(III) solutions. This is supported by the fact that Sb(V) is easily reduced to Sb(III) in the photolysis of an O_2-saturated Sb(III) solution containing a small amount of Sb(V) (Fig. 3, see inset).

$[SbCl_6]^-$ in CH_3CN. Complexes of s^0 metal ions are characterized by low-energy LMCT states. In accordance with the nature of such an excited state, the metal ion undergoes reduction, and the ligand does an oxidation.[2,5] The absorption spectrum of Sb(V) in CH_3CN in the presence of 0.1 M $N(C_2H_5)_4Cl$ has an absorption maximum at 272 nm (LMCT transition, $\varepsilon = 8.34\times10^3$ $M^{-1}\,cm^{-1}$) (Fig. 1). In the flash photolysis of Sb(V) in deaerated CH_3CN solutions, a transient absorption spectrum, which had absorption maxima at 293 and 328 nm and a shoulder at ca. 345 nm, was obtained (Fig. 4A). The absorption band at ca. 345 nm completely disappeared within 5 ms after the flash, and the remaining spectrum was identical with that obtained in the photolysis of Sb(III) solutions. The spectrum obtained by deducting the spectrum at 50 μs from that at 5 ms displayed an absorption maximum at 345 nm, which was attributed to radical anion $\cdot Cl_2^-$. The absorption maximum of $\cdot Cl_2^-$ in CH_3CN only slightly shift to the longer wavelength side than that in aqueous solution ($\lambda_{max} = 340$ nm).[27—29] Thus, the short-lived and the longer lived intermediates were assigned to be radical anion $\cdot Cl_2^-$ and Sb(IV), respectively: These transient species will be produced by the following reactions:

$$\mathrm{[SbCl_6]^- \xrightarrow{h\nu} [SbCl_5]^- + \cdot Cl}, \qquad (8)$$

$$\mathrm{[SbCl_5]^- + Cl^- \longrightarrow [SbCl_6]^{2-}}, \qquad (9)$$

$$\mathrm{\cdot Cl + Cl^- \longrightarrow \cdot Cl_2^-}. \qquad (10)$$

The LMCT excitation of Sb(V) gives $[SbCl_5]^-$ and $\cdot Cl$ (Eq. 8). In the presence of a large excess of chloride, the resulting $[SbCl_5]^-$ and $\cdot Cl$ react with Cl^- to give $[SbCl_6]^{2-}$ (Eq. 9) and $\cdot Cl_2^-$ (Eq. 10), respectively. Typical oscillograms obtained by flashing a deaerated Sb(V) solution are given in Fig. 5. The first and second decays correspond to the disappearance of $\cdot Cl_2^-$ and Sb(IV), respectively. The decay of $\cdot Cl_2^-$ obeyed a second-order kinetics with k_{11}/ε value of 4.8×10^5 $cm\,s^{-1}$ (Fig. 5A, see inset):

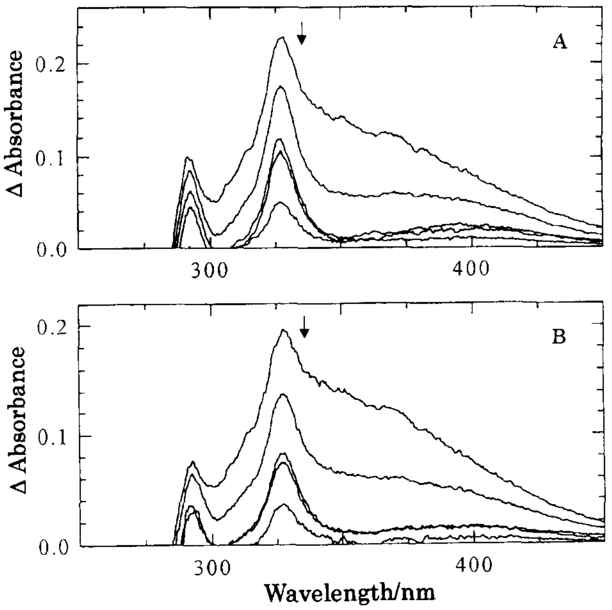

Fig. 4. Transient absorption spectra obtained in the flash photolysis of 5.0×10^{-5} M $[SbCl_6]^-$ CH_3CN solutions containing 0.1 M chloride. (A) Measured at 50 μs, 500 μs, 5 ms, 50 ms, and 500 ms after the flash in a deaerated solution, (B) Measured at 50 μs, 500 μs, 5 ms, 50 ms, and 500 ms after the flash in an O_2-saturated solution.

$$\mathrm{\cdot Cl_2^- + \cdot Cl_2^- \longrightarrow \cdot Cl_3^- + Cl^-}. \qquad (11)$$

Taking $\varepsilon = 8800$ $M^{-1}\,cm^{-1}$ as the molar absorption coefficient of $\cdot Cl_2^-$ at 340 nm,[29] although it was measured in aqueous solution, the decay rate constant was estimated to be approximately $k_{11} = 3.7\times10^9$ $M^{-1}\,s^{-1}$. This value agrees fairly well with that obtained in aqueous solution.[30] The rate constant of the disproportionation of $\cdot I_2^-$ ($k = 2.8\times10^9$ $M^{-1}\,s^{-1}$)[31] obtained in the flash photolysis of iodomercurate(II) in $CHCl_3$ also agrees fairly well with the value in aqueous solution.[30] Sb(IV) also decayed with a second-order rate constant of $k_3/\varepsilon = 6.9\times10^2$ $cm\,s^{-1}$ (Fig. 5B, see inset). This value was the same as that obtained in the Sb(III) system within the experimental error. Assuming Eqs. 8, 9, and 10, the concentration of Sb(IV) must be equal to that of $\cdot Cl_2^-$. On this basis, the molar absorption coefficient of Sb(IV) is estimated to be roughly $\varepsilon =$ ca. 6500 $M^{-1}\,cm^{-1}$ from Fig. 4, taking $\varepsilon = 8800$ $M^{-1}\,cm^{-1}$ for $\cdot Cl_2^-$.[29] Thus, the decay rate constants of Sb(IV) formed in Sb(III) and Sb(V) solutions were estimated to be roughly ca. 4.2×10^6 and ca. 4.5×10^6 $M^{-1}\,s^{-1}$, respectively. The transient absorption spectrum (Fig. 4B) and the decay rates of $\cdot Cl_2^-$ and Sb(IV) were not influenced by oxygen.

$[SbCl_6]^{3-}$ in $CHCl_3$. Sb(III) has sp transition bands at 304 nm ($\varepsilon = 1.59\times10^3$ $M^{-1}\,cm^{-1}$), 265 nm ($\varepsilon = 5.27\times10^3$ $M^{-1}\,cm^{-1}$), and 245 nm ($\varepsilon = 2.25\times10^4$ $M^{-1}\,cm^{-1}$) in $CHCl_3$ containing 0.1 M $N(C_2H_5)_4Cl$ (Fig. 1). In deaerated

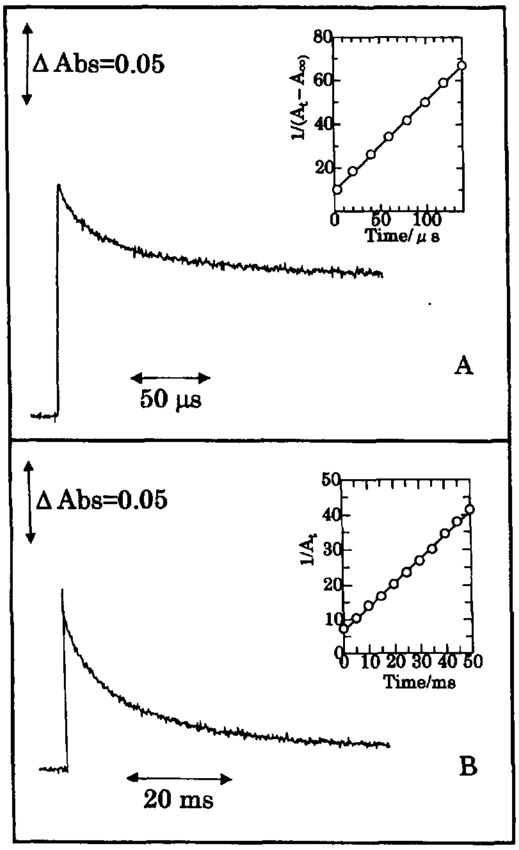

Fig. 5. Oscilloscope traces showing changes in absorbance measured at 330 nm after the flash of deaerated 1.0×10^{-4} M $[SbCl_6]^-$ CH_3CN solution in the presence of 0.1 M chloride. (A) First decay which shows the disappearance of $\cdot Cl_2^-$. Inset: second order kinetic plot for the decay of $\cdot Cl_2^-$. A_t is the total absorbance observed at a time t. A_∞ is the absorbance after $\cdot Cl_2^-$ disappeared. (B) Second decay which shows the disappearance of Sb(IV). Inset: second-order kinetic plot for the decay of Sb(IV).

$CHCl_3$ solutions Sb(III) is not oxidized to Sb(V) upon continuous irradiation.[8] On the other hand, in the flash photolysis of Sb(III) in deaerated $CHCl_3$ solutions, an absorption spectrum of transient species was obtained (Fig. 6A). The spectrum had absorption maxima at 293, 327, and 390 nm, which were similar to those of Sb(IV) obtained in CH_3CN. The decay obeyed second-order kinetics with $k_3/\varepsilon = 3.0\times10^5$ $cm\,s^{-1}$. Assuming that the molar absorption coefficient of Sb(IV) in $CHCl_3$ is the same as that in CH_3CN, the rate constant of the disproportionation of Sb(IV) is estimated to be roughly 2.0×10^9 $M^{-1}\,s^{-1}$. This assumption seems to be reasonable judging from the fact that the absorption maxima and their absorption coefficients of Sb(III) and Sb(V) in CH_3CN are approximately the same as those in $CHCl_3$, as shown in Fig. 1. The decay rate of Sb(IV) in $CHCl_3$ is about four hundred and forty times larger than that in CH_3CN. Halocarbon solvents are relatively easily reduced,[32] and are known to act as electron acceptors in the photooxidations of a great variety of transition-metal complexes.[32—35] From these facts, the following reactions are suggested to explain the experimental results:

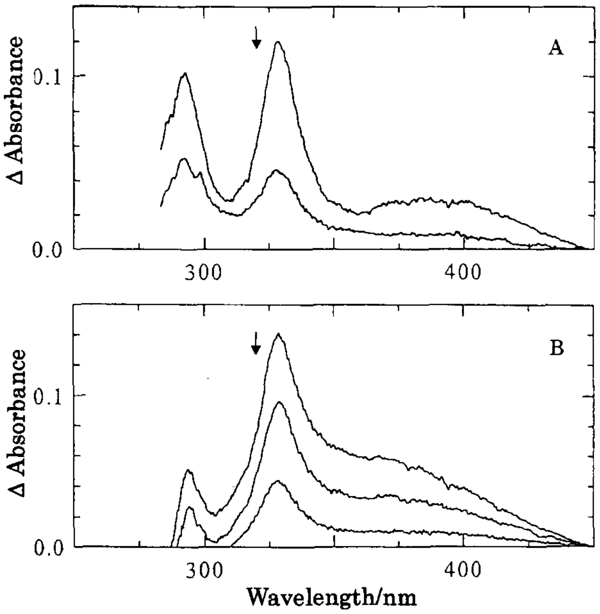

Fig. 6. Transient absorption spectra obtained in the flash photolysis of $[SbCl_6]^{3-}$ and $[SbCl_6]^-$ complexes in $CHCl_3$ solutions containing 0.1 M chloride. (A) $[SbCl_6]^{3-}$ = 2.5×10^{-5} M, measured at 50 and 500 μs after the flash in a deaerated solution. (B) $[SbCl_6]^-$ = 1.0×10^{-5} M, measured at 50, 100, and 500 μs after the flash in a deaerated solution.

$$\mathrm{Sb(III)} \longrightarrow \mathrm{Sb(III)}^*, \quad (1)$$

$$\mathrm{Sb(III)}^* + CHCl_3 \longrightarrow \mathrm{Sb(IV)} + \cdot CHCl_3^-. \quad (12)$$

The excited state of Sb(III) formed by Eq. 1 appears to be quenched by $CHCl_3$ (Eq. 12) as well as by CH_3CN, and the resulting Sb(IV) disappears by Eq. 3 with a rate constant of ca. 2.0×10^9 $M^{-1}\,s^{-1}$.[8] The $\cdot CHCl_3^-$ is very unstable, which decomposes by the following mechanism:

$$\cdot CHCl_3^- \longrightarrow \cdot CHCl_2 + Cl^-, \quad (13)$$

$$\cdot CHCl_2 + CHCl_3 \longrightarrow \cdot CCl_3 + CH_2Cl_2, \quad (14)$$

$$2\cdot CCl_3 \longrightarrow C_2Cl_6. \quad (15)$$

Reactions (13), (14), and (15) are reported to occur in the photolysis of various complexes, such as $[Ru(bpy)_2Cl_2]$, $Bu_4N_2[PtCl_6]$ etc. in $CHCl_3$.[36,37] The $\cdot CHCl_3^-$ radical eventually releases Cl^- to give a dichloromethyl radical, $\cdot CHCl_2$ (Eq. 13). Further, the dichlorometyl radical, $\cdot CHCl_2$, reacts with $CHCl_3$ to give trichloromethyl radicals (Eq. 14).[36—39] The resulting $\cdot CCl_3$ seems to disappear by Eq. 15. The rate constant of Eq. 15 is 3.7×10^8 $M^{-1}\,s^{-1}$, although this value was measured in an aqueous solution.[40]

Sb(V) and peroxide are produced upon continuous irradiation of Sb(III) in $CHCl_3$ in the presence of oxygen, and the ratio of Sb(V) and peroxide is 1.02.[8] It was found that Sb(IV) was formed in the flash photolysis of Sb(III) in $CHCl_3$ solutions in the presence of oxygen. It is suggested that the Sb(IV) and O_2^{2-} are formed according to the Eqs. 6 and 7 in $CHCl_3$ as well as in CH_3CN. The resulting Sb(IV) produced

Sb(V) by Eq. 3. The result that the ratio of Sb(V) and peroxide is 1.02 is explained by this mechanism. Oxygen also had no influence on both the spectrum and the decay constant in $CHCl_3$.

$[SbCl6]^-$ in $CHCl_3$. Sb(V) has absorption maxima at 273 nm ($\varepsilon = 8.93 \times 10^3$ M^{-1} cm^{-1}) in $CHCl_3$ in the presence of 0.1 M $N(C_2H_5)_4Cl$ (Fig. 1). The transient absorption spectrum obtained in deaerated $CHCl_3$ solutions of Sb(V) has absorption maxima at 293 and 330, and a shoulder at ca. 345 nm (Fig. 6B). The decay rates of $\cdot Cl_2^-$ and Sb(IV) were $k_{11}/\varepsilon = 5.1 \times 10^5$ $cm\,s^{-1}$ (roughly k_{11} = ca. 4.5×10^9 $M^{-1}\,s^{-1}$, assuming that the molar absorption coefficient for $\cdot Cl_2^-$ is 8800 $M^{-1}\,cm^{-1}$) and $k_3/\varepsilon = 3.2 \times 10^5$ $cm\,s^{-1}$ (roughy k_3 = ca. 2.1×10^9 $M^{-1}\,s^{-1}$, assuming that the molar extinction coefficient for Sb(IV) is 6500 $M^{-1}\,cm^{-1}$), respectively. The decay rate of $\cdot Cl_2^-$ obtained in $CHCl_3$ was close to that obtained in CH_3CN, and the spectra and the decays of $\cdot Cl_2^-$ and Sb(IV) were not affected by oxygen. The chlorine produced by Eq. 11 is consumed in a side reaction.[8] The decay rate of Sb(IV) produced from Sb(V) was similar to that from Sb(III). The reaction scheme in the flash photolysis of Sb(V) in $CHCl_3$ would be given by Eqs. 8, 9, and 10 as well as those in CH_3CN.

Mixture of Sb(III) and Sb(V) Chloro Complexes in $CHCl_3$. In the flash photolysis of the mixture of Sb(III) and Sb(V) in deaerated $CHCl_3$ solutions, only one intermediate, which was attributed to Sb(IV), was detected (Fig. 7). An absorption maximum at ca. 345 nm, which appeared in the photolysis of Sb(V) solutions, was not observed. These results can be explained by the following reaction scheme:

$$\mathrm{Sb(III)^* + CHCl_3 \xrightarrow{h\nu} Sb(IV) + \cdot CHCl_3^-,} \tag{12}$$

$$\mathrm{\cdot CHCl_3^- + Sb(V) \longrightarrow CHCl_3 + Sb(IV),} \tag{16}$$

$$\mathrm{[SbCl_6]^- \xrightarrow{h\nu} [SbCl_5]^- + \cdot Cl,} \tag{8}$$

$$\mathrm{[SbCl_5]^- + Cl^- \longrightarrow [SbCl_6]^-,} \tag{9}$$

$$\mathrm{\cdot Cl + Cl^- \longrightarrow \cdot Cl_2^-.} \tag{10}$$

$$\mathrm{\cdot Cl_2^- + Sb(III) \longrightarrow 2Cl^- + Sb(IV).} \tag{17}$$

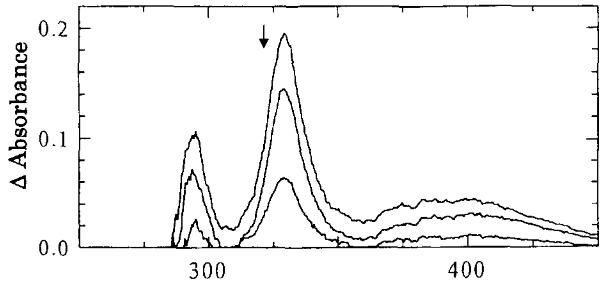

Fig. 7. Transient absorption spectra obtained in the flash photolysis of the mixture of 2.5×10^{-5} M $[SbCl_6]^{3-}$ and 1.0×10^{-5} M $[SbCl_6]^-$ $CHCl_3$ solutions containing 0.1 M chloride. Measured at 50, 100, and 500 μs after the flash in a deaerated solution.

The over-all reaction is given as

$$\mathrm{Sb(III) + Sb(V) \xrightarrow{h\nu} 2\ Sb(IV).} \tag{18}$$

Because both Sb(III) and Sb(V) initially exist in this system, the reducing radical, $\cdot CHCl_3^-$, and the oxidizing radical, $\cdot Cl_2^-$, react with Sb(V) and Sb(III), respectively, to give Sb(IV) (Eqs. 16 and 17). Reaction (17) is supported by the following fact: $\cdot Cl_2^-$ reacts with s^2 chloro complexes, such as Tl(I) ($k_{19} = 5 \times 10^9$ $M^{-1}\,s^{-1}$),[41] Pb(II) ($k_{19} = 1.9 \times 10^9$ $M^{-1}\,s^{-1}$),[42] and Bi(III) ($k_{19} = 9 \times 10^9$ $M^{-1}\,s^{-1}$),[43] to give s^1 complexes (Eq. 19), although these rate constants were measured in hydrochloric acid solutions.

$$\mathrm{\cdot Cl_2^- + M^{n+} \longrightarrow 2Cl^- + M^{(n+1)+}.} \tag{19}$$

Conclusions. Upon continuous UV-irradiation of a Sb(V) in both deaerated solutions of $CHCl_3$ and CH_3CN, Sb(V) is reduced easily to Sb(III). On the other hand, although Sb(III) is oxidized to Sb(V) in $CHCl_3$ in the presence of oxygen, it does not occur in CH_3CN. It was found that Sb(IV), which has the s^1 electron configuration, was detected as an intermediate in the flash photolysis of Sb(III) or Sb(V) in both CH_3CN and $CHCl_3$ solutions. This fact shows that successive one-electron transfer steps are involved in the photoredox reactions of these complexes. Further, from these observations it is suggested that regenerations of the starting complexes prevent an observation of photoactivity in the photolysis of Sb(III) in CH_3CN.

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24 In the case that all the Sb(III)* can not be quenched completely by oxygen, $\cdot CH_3CN^-$ radicals in Sb(III)-CH_3CN systems and $\cdot CCl_3$ in Sb(III)-$CHCl_3$ systems react with oxygen to give $O_2{}^-$ ($\cdot CH_3CN^- + O_2 \rightarrow CH_3CN + O_2 \quad k = 1.0\times10^{10}\ M^{-1}\ s^{-1}$)[20,25] and $CCl_3OO\cdot$, respectively. The resulting $O_2{}^-$ and $CCl_3OO\cdot$ radicals react with Sb(III) to give $O_2{}^{2-}$ and CCl_3OO^- respectively. The peroxide, CCl_3OO^-, is stable for weeks in $CHCl_3$.[26] The ratio of $SbCl_6{}^-$ to peroxide was reported to be 1.02,[8] which can be also explained with the reaction scheme.

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