

Photoredox Chemistry of Chloro Complexes of Antimony(III) and (V)

A. VOGLER* and A. PAUKNER

Universität Regensburg, Institut für Anorganische Chemie, Universitätsstrasse 31, D-8400 Regensburg (F.R.G.)

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Abstract

The complex $[\text{SbCl}_6]^{3-}$ in CHCl_3 shows a phosphorescence ($\lambda_{\text{max}} = 520 \text{ nm}$, $\phi = 2.4 \times 10^{-3}$, $\tau \leq 50 \text{ ns}$) originating from the lowest sp excited state. Oxygen quenches this luminescence and participates in the photooxidation of Sb(III): $[\text{SbCl}_6]^{3-} + \text{O}_2 \rightarrow [\text{SbCl}_6]^{-} + \text{O}_2^{2-}$. At $\lambda_{\text{irr}} = 263 \text{ nm}$ the quantum yield was $\phi = 0.081$. The photoproduct $[\text{SbCl}_6]^{-}$ in CHCl_3 is light-sensitive too. Ligand to metal charge transfer excitation induces a reduction of Sb(V): $[\text{SbCl}_6]^{-} + 2\text{Cl}^{-} \rightarrow [\text{SbCl}_6]^{3-} + \text{Cl}_2$. At $\lambda_{\text{irr}} = 272 \text{ nm}$ the quantum yield was $\phi = 0.1$. The photogenerated chlorine undergoes secondary reactions.

Introduction

The photochemistry of coordination compounds of the main group metals is a rather interesting but largely neglected area of inorganic photochemistry [1]. Although a systematic concept of this subject has not yet been developed some simple considerations may be used as guidelines.

Generally, the main group metals exist in stable oxidation states in which the ground state electron configuration is either s^0 or s^2 . The absorption spectra of complexes of the s^0 metals are characterized by ligand to metal charge transfer (LMCT) bands [2]. LMCT excitation initiates a two-electron reduction of the metal as typical photoreaction [1, 3]. LMCT transitions may also occur for complexes of s^2 metals. However, metal-centered sp transitions are usually the lowest-energy transitions of s^2 complexes [2]. It is quite important that these sp excited states are frequently luminescent even at room temperature and in solution [4, 5]. It is known for many years that s^2 metals such as Tl(I) [6, 7], Sn(II) [4, 8, 9], and Sb(III) [10, 7] undergo a photooxidation in the presence of O_2 . Although this reaction is also of interest with regard to technical applications [8, 9], the nature of the reactive excited state has never been discussed. In the present study

we report relevant observations on the photooxidation of Sb(III) to Sb(V) as well as the photoreduction of Sb(V) to Sb(III).

Experimental

Materials

The compounds $[\text{NH}(\text{C}_2\text{H}_5)_3][\text{SbCl}_4]$ and $[\text{N}(\text{C}_2\text{H}_5)_4][\text{SbCl}_6]$ were prepared according to published procedures [11]. Chloroform was Spectro Grade.

Photolyses

The light source was a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic irradiations were achieved with a Schoeffel GM 250-1 monochromator. Solutions of the complexes were photolyzed in 1-cm spectrophotometer cells at room temperature. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproducts. Absorbed light intensities were determined by a Polytec pyroelectric radiometer that was calibrated and equipped with a RkP-345 detector. Progress of the photolysis was monitored by UV-Vis spectral measurements.

Spectroscopy

Absorption spectra were measured with a Varian-Techtron Super Scan 3 recording spectrophotometer and a Zeiss PMQ II spectrometer for measurements at selected wavelengths. Emission spectra were obtained on a Hitachi 850 spectrofluorimeter which was equipped with a Hamamatsu 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency. Absolute emission quantum yields were determined by comparison of integrated emission intensity of $[\text{SbCl}_6]^{3-}$ with that of quinine sulfate in 0.5 M H_2SO_4 ($\lambda_{\text{max}} = 452 \text{ nm}$; $\phi = 0.546$) [12] at identical conditions such as exciting wavelength, optical density, apparatus parameters etc.

* Author to whom correspondence should be addressed.

Analyses

Peroxide was determined by the peroxide test of Merck (Merckoquant 10011) which was calibrated with H_2O_2 in CHCl_3 in the concentration range 10^{-4} to 5×10^{-3} M. Chlorine was identified by the Cl_2 test of Merck (Merckoquant 10027 and 10043/2). The O_2 concentration of an air-saturated CHCl_3 solution was determined by measuring the fluorescence quantum yield of anthracene in CHCl_3 in the presence and absence of oxygen according to a procedure reported by Bowen and Metcalf [13, 14].

Results

$[\text{SbCl}_6]^{3-}$

When $[\text{SbCl}_4]^-$ was dissolved in CHCl_3 in the presence of excess chloride ($>5 \times 10^{-2}$ M) the anion $[\text{SbCl}_6]^{3-}$ was formed. The absorption spectrum of $[\text{SbCl}_6]^{3-}$ (Fig. 1) displays bands at $\lambda_{\text{max}} = 303$ nm ($\epsilon = 1120$), 263 nm ($\epsilon = 3965$), and 245 nm ($\epsilon = 7875$). Upon light absorption $[\text{SbCl}_6]^{3-}$ in CHCl_3 showed an emission at $\lambda_{\text{max}} = 520$ nm (Fig. 2). It was independent of the exciting wavelength ($\lambda_{\text{exc}} = 263$,

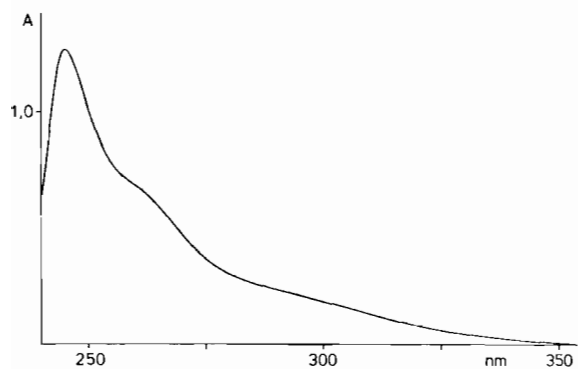


Fig. 1. Electronic absorption spectrum of 1.6×10^{-4} M $[\text{NH}(\text{C}_2\text{H}_5)_3][\text{SbCl}_4]$ in CHCl_3 in the presence of 0.25 M $[\text{NH}(\text{C}_2\text{H}_5)_3]\text{Cl}$; 1-cm cell.

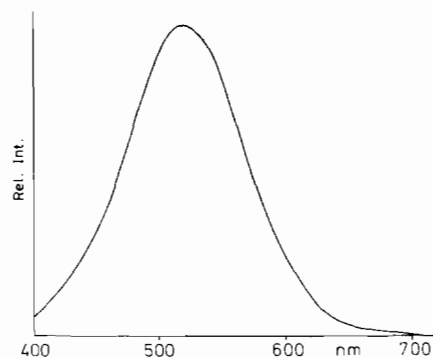


Fig. 2. Emission spectra of 1.22×10^{-3} M $[\text{NH}(\text{C}_2\text{H}_5)_3]-[\text{SbCl}_4]$ in CHCl_3 in the presence of 0.5 M $[\text{N}(\text{C}_2\text{H}_5)_4]\text{Cl}$; 298 K, 1-cm cell, $\lambda_{\text{exc}} = 300$ nm, relative intensity.

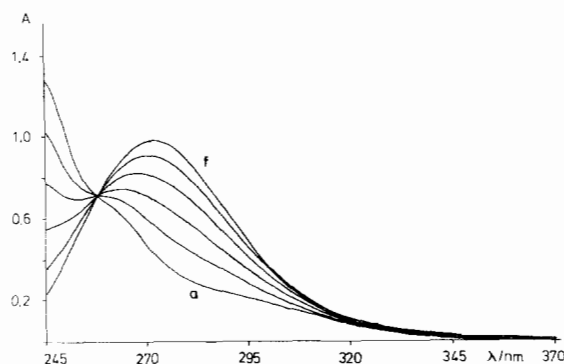


Fig. 3. Spectral changes during the photolysis of 1.6×10^{-4} M $[\text{NH}(\text{C}_2\text{H}_5)_3][\text{SbCl}_4]$ in CHCl_3 in the presence of 0.25 M $[\text{NH}(\text{C}_2\text{H}_5)_3]\text{Cl}$ and 4.5×10^{-3} M O_2 at (a) 0, 10, 20, 30, 40, and (f) 50 s irradiation time, with $\lambda_{\text{irr}} = 263$ nm and a 1-cm cell.

300 and 337 nm). In the absence of oxygen (argon-saturated solution) the absolute emission quantum yield was $\phi = 2.4 \times 10^{-3}$. The emission lifetime was $\tau \leq 50$ ns [15]. In an air-saturated solution (4.5×10^{-3} M O_2) the emission quantum yield dropped to $\phi = 1.5 \times 10^{-3}$.

Irradiation of $[\text{SbCl}_6]^{3-}$ in air-saturated solutions of CHCl_3 was accompanied by spectral changes (Fig. 3) which indicate clearly the formation of $[\text{SbCl}_6]^-$. This Sb(V) complex is characterized by an absorption at $\lambda_{\text{max}} = 272$ nm. At the isosbestic point at $\lambda = 258$ nm $[\text{SbCl}_6]^{3-}$ and $[\text{SbCl}_6]^-$ have the same extinction coefficient ($\epsilon = 4500$). The formation of $[\text{SbCl}_6]^-$ was monitored by measuring the extinction at its absorption maximum at 272 nm taking into account the optical density of $[\text{SbCl}_6]^{3-}$ at this wavelength ($\epsilon = 2966$). At $\lambda_{\text{irr}} = 263$ nm $[\text{SbCl}_6]^-$ was formed with $\phi = 0.081$. In addition to $[\text{SbCl}_6]^-$ peroxide O_2^{2-} was formed as a photo-product. The ratio of $[\text{SbCl}_6]^-$ to O_2^{2-} was found to be 1.02.

In deaerated CHCl_3 solutions $[\text{SbCl}_6]^{3-}$ was essentially not light-sensitive. After longer irradiation periods small spectral changes took place. These were identical to those observed in the presence of oxygen. It is assumed that in this case the photolysis is due to traces of oxygen which are difficult to remove by deaeration.

$[\text{SbCl}_6]^-$

The absorption spectrum of $[\text{SbCl}_6]^-$ in CHCl_3 (Fig. 4) is dominated by a band at $\lambda_{\text{max}} = 272$ nm. The complex does not show any emission. Upon irradiation ($\lambda = 272$ nm) of $[\text{SbCl}_6]^-$ in an argon-saturated CHCl_3 solution which contained an excess of chloride ($>5 \times 10^{-2}$ M) $[\text{SbCl}_6]^{3-}$ was formed as indicated by the accompanying spectral changes (Fig. 4). The conversion of $[\text{SbCl}_6]^-$ to $[\text{SbCl}_6]^{3-}$ was monitored by measuring the decrease of extinc-

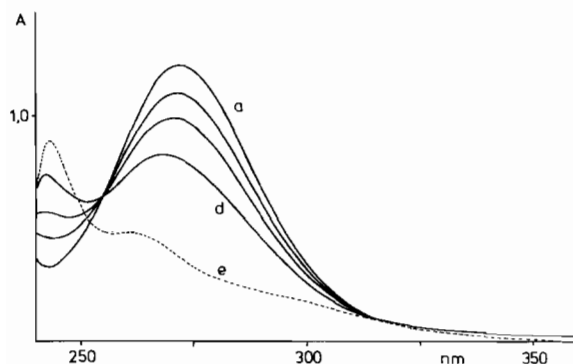


Fig. 4. Spectral changes during the photolysis of 1.8×10^{-4} M $[\text{N}(\text{C}_2\text{H}_5)_4][\text{SbCl}_6]$ in argon-saturated CHCl_3 in the presence of 0.25 M $[\text{NH}(\text{C}_2\text{H}_5)_3]\text{Cl}$ at (a) 0, 5, 10, (d) 20, and (e) 160 s irradiation time, with $\lambda_{\text{irr}} = 272$ nm and a 1-cm cell.

tion at the band maximum of $[\text{SbCl}_6]^-$ at 272 nm. The quantum yield for the disappearance of $[\text{SbCl}_6]^-$ was $\phi = 0.1$ at $\lambda_{\text{irr}} = 272$ nm.

Besides $[\text{SbCl}_6]^{3-}$ chlorine was assumed to be another photoproduct. However, the photolyzed solution contained only traces of free Cl_2 . It seems likely that chlorine ($\lambda_{\text{max}} = 330$ nm, $\epsilon = 97$) reacts thermally and/or photochemically with the alkylammonium ions which are present in the solution. Such a reaction was reported to occur during the photolysis of $[\text{N}(\text{butyl})_4][\text{ICl}_4]$ in chlorinated solvents [16]. The formation and subsequent consumption of Cl_2 may be also related to the loss of the isosbestic point at later stages of the photolysis of $[\text{SbCl}_6]^-$ (Fig. 4).

$[\text{SbCl}_6]^{3-}/[\text{SbCl}_6]^-$

When the photolysis of $[\text{SbCl}_6]^{3-}$ was carried out in a sealed cell which contained an air-saturated CHCl_3 solution containing an excess of free chloride the oxidation of $[\text{SbCl}_6]^-$ and its subsequent reduction to $[\text{SbCl}_6]^{3-}$ took place in the same system. In the beginning of the photolysis ($\lambda_{\text{irr}} = 263$ nm) the formation of $[\text{SbCl}_6]^-$ was observed as indicated by the appearance of the absorption maximum at 272 nm. At later stages the photoproduct $[\text{SbCl}_6]^-$ started to absorb light and underwent a photoreduction to $[\text{SbCl}_6]^{3-}$ which in turn was again photooxidized.

Upon prolonged photolysis the oxygen was completely consumed and the photooxidation stopped. This was indicated by the reversal of the spectral changes which took place in the beginning of the photolysis since in the absence of oxygen only the photoreduction of $[\text{SbCl}_6]^-$ can take place. Unfortunately, a side reaction during the photolysis of $[\text{SbCl}_6]^-$ (see above) interferes with a complete reversibility of this system.

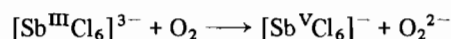
Discussion

$[\text{SbCl}_6]^{3-}$

Antimony(III) is a s^2 metal. Chloro complexes of Sb(III) exist in a variety of coordination numbers and structures in the solid state [17, 18] and presumably also in solution [19, 20]. The highest coordination number and the most regular structure was found for the octahedral $[\text{SbCl}_6]^{3-}$ ion. In coordinating solvents coordination may be complicated by the participation of solvent molecules. In non-coordinating solvents such as CHCl_3 the absorption spectra of chloro complexes of Sb(III) depend somewhat on the concentration of added chloride. However, at complex concentrations of about 10^{-4} M and chloride concentrations above 5×10^{-2} M the spectrum (Fig. 1) does not change anymore. It is then certainly reasonable to assume that octahedral $[\text{SbCl}_6]^{3-}$ is the prevailing species under these conditions.

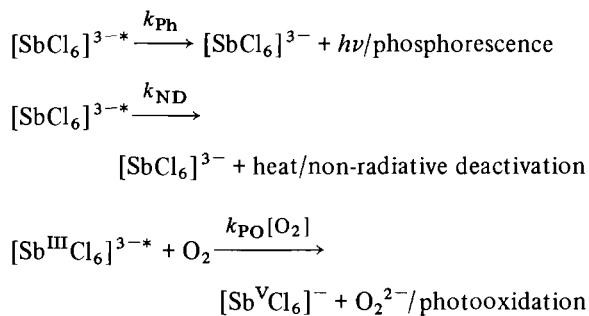
The absorption bands of $[\text{SbCl}_6]^{3-}$ [21, 22] (Fig. 1) can now be assigned quite analogous to those of the isoelectronic $[\text{TeX}_6]^{2-}$ complexes [23, 24]. All low-energy transitions are sp transitions ($s^2p^0 \rightarrow s^1p^1$). Compared to $[\text{TeX}_6]^{2-}$ these sp bands of $[\text{SbCl}_6]^{3-}$ are shifted to shorter wavelength. In agreement with previous publications [21, 22] we suggest the following assignments: $\lambda_{\text{max}} = 303$ nm, ${}^1A_{1g} \rightarrow {}^3T_{1u}$ (${}^1S_0 \rightarrow {}^3P_1$); $\lambda_{\text{max}} = 263$ nm, ${}^1A_{1g} \rightarrow {}^3T_{1u}$ (${}^1S_0 \rightarrow {}^3P_2$); $\lambda_{\text{max}} = 245$ nm, ${}^1A_{1g} \rightarrow {}^1T_{1u}$ (${}^1S_0 \rightarrow {}^1P_1$). All transitions are parity-allowed. The two lowest-energy transitions are spin-forbidden and derived from two different excited states of the Sb^{3+} ion (3P_1 and 3P_2). The emission of $[\text{SbCl}_6]^{3-}$ at $\lambda_{\text{max}} = 520$ nm (Fig. 2) is then assigned to the ${}^3T_{1u} \rightarrow {}^1A_{1g}$ transition. The large Stoke's shift is certainly associated with a strong tetragonal Jahn-Teller distortion in the excited state. Such a distortion has been also observed for $[\text{TeX}_6]^{2-}$ [25]. The phosphorescence of $[\text{SbCl}_6]^{3-}$ (Sb^{3+} in concentrated hydrochloric acid) has been detected before but only at 77 K [26]. In CHCl_3 solutions this emission is of moderate intensity even at room temperature. Some oxygen quenching occurred in air-saturated solutions.

While $[\text{SbCl}_6]^{3-}$ is quite light-stable in the absence of air it is photooxidized by oxygen according to the stoichiometry



We suggest that the sp excited state of $[\text{SbCl}_6]^{3-}$ undergoes a two-electron transfer to O_2 . This may occur in two subsequent one-electron transfer steps or in one two-electron transfer as a concerted process. The following reaction scheme may be used for the interpretation of the experimental data (* denotes the ${}^3T_{1u}$ sp excited state)





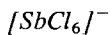
This simple scheme yields the following equations

$$\begin{aligned}
 \tau &= \frac{1}{k_{\text{Ph}} + k_{\text{ND}} + k_{\text{PO}}[\text{O}_2]} \\
 \phi_{\text{Ph}} &= \frac{k_{\text{Ph}}}{k_{\text{Ph}} + k_{\text{ND}} + k_{\text{PO}}[\text{O}_2]} \\
 \phi_{\text{PO}} &= \frac{k_{\text{PO}}[\text{O}_2]}{k_{\text{PO}}[\text{O}_2] + k_{\text{Ph}} + k_{\text{ND}}}
 \end{aligned}$$

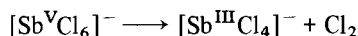
The lifetime τ in the absence of oxygen, the phosphorescence quantum yield ϕ_{Ph} in the absence and presence of oxygen, and the photooxidation quantum yield ϕ_{PO} were measured. Although the precise emission lifetime could not be determined it was found to be close to the limit of time resolution of the equipment (50 ns). From these data and equations individual rate constants were calculated: $k_{\text{Ph}} = 4.8 \times 10^4 \text{ s}^{-1}$, $k_{\text{ND}} = 2.0 \times 10^7 \text{ s}^{-1}$, and $k_{\text{PO}} = 2.7 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$. The large rate of phosphorescence emission is certainly due to the internal heavy atom effect of antimony. The phosphorescence quenching by oxygen is apparently close to the diffusion-controlled limit. From the last equation the photooxidation quantum yield was calculated to be $\phi_{\text{PO}} = 0.37$. This is the efficiency of the primary photo-reaction. However, back electron transfer may partially regenerate $[\text{SbCl}_6]^{3-}$. This process might lead to a reduction of the experimental quantum yield to the observed value of $\phi_{\text{PO}} = 0.081$.

The first observation of the photooxidation of Sb(III) was reported by Brüll and Schlägel in 1934 [10]. They carried out the photolysis in an acidic (HCl) aqueous solution. It seems that under these conditions several different chloro complexes of Sb(III) are present. Nevertheless, Brüll and Schlägel were able to identify H_2O_2 as a photolysis product. Other reducing s^2 metals such as Tl(I) [6, 7] and Sn(II) [4, 8, 9] were also found to undergo this type of photooxidation. Although very little is known about these reactions it is reasonable that all these photooxidations take place quite analogous to that of $[\text{SbCl}_6]^{3-}$. In this context it is quite interesting that these photooxidations may find technical

applications. The photolysis of Sn(II) in the presence of oxygen has been used for electroless metal deposition [8, 9, 27, 28].

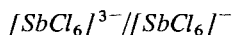


Antimony(V) is a s^0 metal. It follows that only LMCT transitions can occur. Consequently, the intense long-wavelength absorption of $[\text{SbCl}_6]^{-}$ at $\lambda_{\text{max}} = 272 \text{ nm}$ is assigned to the $t_{1u}(\pi) \rightarrow a_{1g}$ LMCT transition which is also characteristic for similar s^0 complexes [21, 29]. Upon LMCT excitation $[\text{SbCl}_6]^{-}$ in CHCl_3 undergoes an efficient reduction of the metal. It is suggested that the primary photo-reaction is a reductive elimination according to the equation

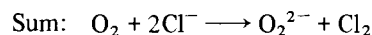
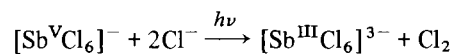
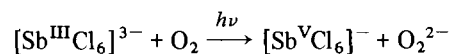


In the presence of excess chloride $[\text{SbCl}_4]^{-}$ is converted to $[\text{SbCl}_6]^{3-}$. However, chlorine as photo-product was detected only in traces. It is assumed that Cl_2 reacts in a secondary reaction with the alkylammonium counter ions. This type of reaction was observed before [16].

The reductive elimination seems to be the characteristic photoreaction of complexes of any s^0 metal. Tl(III) [3], Pb(IV) [1] and Sn(IV) [1] complexes also undergo this type of photoreaction following LMCT excitation.



The photooxidation of $[\text{SbCl}_6]^{3-}$ leads to the formation of $[\text{SbCl}_6]^{-}$ which then starts to absorb light and regenerates photochemically $[\text{SbCl}_6]^{3-}$. Finally, a photostationary concentration of Sb(III) and (V) may be established. Under suitable conditions the photolysis should then lead only to the conversion of O_2 and Cl^{-} to peroxide and chlorine



Unfortunately, the chlorine is consumed in a side reaction. This side reaction seems to be a chlorination of alkyl ammonium ions which takes place in the ion pairs $\text{NR}_4^+[\text{SbCl}_6]^{-}$. Usually, such ion pairs are only stable in solvents of low polarity. It seems feasible that this side reaction can be avoided by using polar solvents and alkali counter ions.

Acknowledgements

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