

Luminescence Quenching and Photooxidation of Trichlorostannate(II) by Oxygen

Alexander Becht, Arnd Vogler*

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg

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The luminescence of $[\text{SnCl}_3]^-$ in acetonitrile ($\tau = 1.6 \mu\text{s}$) is quenched by oxygen with $k = 3.8 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. This quenching is associated with an electron transfer from $[\text{SnCl}_3]^-$ in its $^3\text{P}_1$ sp-excited state to O_2 . Secondary processes lead to the formation of $\text{SnOCl}_2(\text{CH}_3\text{CN})_n$ with an overall quantum yield of $\varphi = 1.5$ at $\lambda_{\text{irr}} = 254 \text{ nm}$. While this Sn(IV) complex is not light sensitive, $[\text{SnCl}_6]^{2-}$ in CH_3CN undergoes a photochemical reductive elimination with the generation of $[\text{SnCl}_3]^-$ with $\varphi = 0.015$ at $\lambda_{\text{irr}} = 254 \text{ nm}$.

Introduction

It has been known for sixty years that tin(II) chloro complexes in aqueous solution undergo a photooxidation in the presence of oxygen [1]. These studies have revealed some of the details of the reaction mechanism. The photooxidation of tin(II) has found interesting applications. It is utilized for the generation of metallic images in the electronics industry [2]. Nevertheless, some basic features of this photooxidation are not yet understood. The reactive excited state and the primary photochemical step were not characterized in previous studies. Relevant observations are now reported and discussed. The present investigation was facilitated by our related work on the photooxidation of other s^2 metal ions [3] such as Sb^{3+} [4], Tl^+ [5], and Pb^{2+} [6]. These studies did not only reveal the initial events in the photooxidation, but it was also shown that these photooxidations can be reversed by a subsequent reductive photoelimination of the photooxidized products. The photolysis of complexes of s^0 ions such as Sb^{5+} , Tl^{3+} , and Pb^{4+} may thus lead to the regeneration of the corresponding s^2 ions. In the present work this possibility was also explored for Sn^{4+} .

Experimental

Materials. The compounds $(\text{NEt}_4)[\text{SnCl}_3]$ [7] and $(\text{NEt}_4)_2[\text{SnCl}_6]$ [8] were prepared according

to published procedures. Acetonitrile was spectrograde.

Spectroscopy. Absorption spectra were recorded with a Uvikon 860 double-beam spectrophotometer. 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 variations. Absolute emission quantum yields were determined by comparison of integrated emission intensities of $[\text{SnCl}_3]^-$ with that of quinine sulphate in 0.5 M H_2SO_4 ($\lambda_{\text{max}} = 452 \text{ nm}$; $\varphi = 0.546$) [9] under identical conditions of excitation wavelength, optical density, and apparatus parameters.

Photolyses. The photolyses were carried out at room temperature in 1-cm spectrophotometer cells. The light source was a Hanovia Xe/Hg 977 B-1 (1000 W) lamp. Monochromatic light ($\lambda_{\text{irr}} = 254 \text{ nm}$) was obtained by means of a Schoeffel GM 250-1 high-intensity monochromator. 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 photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated and equipped with an RkP-345 detector.

Analyses. Peroxide was identified using the peroxide test of Merck (Merckoquant 10011). Chlorine was detected following a published procedure [10].

Results

All experiments were carried out in acetonitrile solutions. Owing to complicated equilibria of various tin(II) chloro complexes in aqueous solutions [11] water is less suitable as a solvent. The salt

* Reprint requests to Prof. Dr. A. Vogler.

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D-72072 Tübingen

$(\text{NEt}_4)[\text{SnCl}_3]$ was dissolved in acetonitrile without decomposition. The complex ion $[\text{SnCl}_3]^-$ in argon-saturated CH_3CN showed a green luminescence with $\lambda_{\text{max}} = 510 \text{ nm}$ ($\lambda_{\text{exc}} = 250 \text{ nm}$), $\varphi = 0.07$ [12] and $\tau = 1.6 \mu\text{s}$. In air-saturated acetonitrile ($[\text{O}_2] = 2.2 \times 10^{-3} \text{ M}$) [13] the emission quantum yield dropped to $\varphi = 0.03$.

While in argon-saturated acetonitrile $[\text{SnCl}_3]^-$ was not light-sensitive, an efficient photolysis took place in the presence of oxygen. The irradiation was accompanied by the disappearance of the green luminescence and by changes in the absorption spectrum (Fig. 1). The decrease of the concentration of $[\text{SnCl}_3]^-$ was determined by measuring the absorbance decrease at $\lambda = 292 \text{ nm}$. The anion $[\text{SnCl}_3]^-$ disappeared with a quantum yield of $\varphi = 1.5$ at $\lambda_{\text{irr}} = 254 \text{ nm}$. Small amounts of peroxide ($\sim 10^{-5} \text{ M}$) were detected in the photolyzed solution of $[\text{SnCl}_3]^-$ ($1.68 \times 10^{-4} \text{ M}$). The same spectral changes which took place during the photolysis of $[\text{SnCl}_3]^-$ in acetonitrile (Fig. 1) were also observed when these solutions were exposed to air in the dark. However, the thermal reaction was much slower.

Messin *et al.* identified the tin(IV) complex $\text{SnOCl}_2(\text{CH}_3\text{CN})_n$ with $n = 1-2$ as the product of the thermal autoxidation of SnCl_2 in CH_3CN [14]. It is concluded that $\text{SnOCl}_2(\text{CH}_3\text{CN})_n$ was also produced in the photolysis of $[\text{SnCl}_3]^-$ in acetonitrile in the presence of air.

The spectral changes which took place during the photolysis of $[\text{SnCl}_3]^-$ in CH_3CN (Fig. 1) did

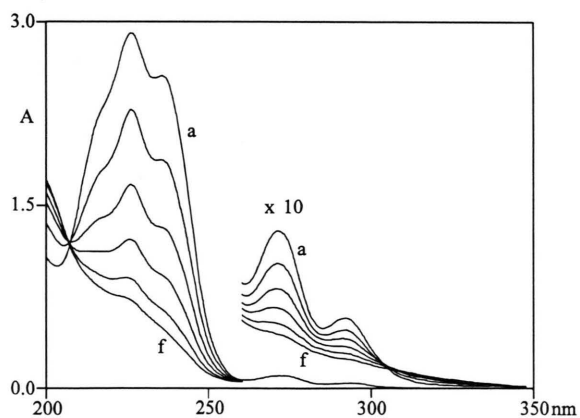


Fig. 1. Spectral changes during the photolysis of $1.68 \times 10^{-4} \text{ M}$ $(\text{NEt}_4)[\text{SnCl}_3]$ in CH_3CN at (a) 0, 5, 10, 15, 20 and (f) 25 sec irradiation time ($\lambda_{\text{irr}} = 254 \text{ nm}$).

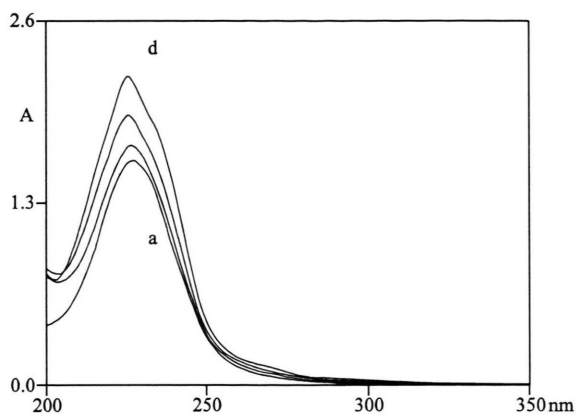


Fig. 2. Spectral changes during the photolysis of $1.37 \times 10^{-4} \text{ M}$ $(\text{NEt}_4)_2[\text{SnCl}_6]$ in CH_3CN at (a) 0, 10, 20 and (d) 30 min irradiation time ($\lambda_{\text{irr}} = 254 \text{ nm}$).

not depend on the presence of additional chloride ($\sim 10^{-2} \text{ M}$). Accordingly, under these conditions the irradiation of $[\text{SnCl}_3]^-$ did not yield $[\text{SnCl}_6]^{2-}$, which has an absorption spectrum somewhat different from that of the photooxidation product.

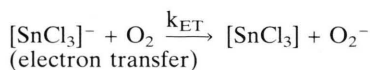
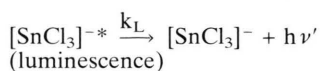
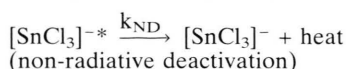
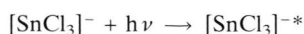
While $\text{SnOCl}_2(\text{CH}_3\text{CN})_n$ in CH_3CN was hardly light-sensitive, the complex ion $[\text{SnCl}_6]^{2-}$ underwent a clean photoconversion to $[\text{SnCl}_3]^-$ in the absence of air as indicated by the concomitant spectral variations (Fig. 2). The formation of $[\text{SnCl}_3]^-$ was also confirmed by the appearance of its green luminescence. Chlorine was detected as a further photoproduct by qualitative analysis. The reductive elimination of $[\text{SnCl}_6]^{2-}$ to form $[\text{SnCl}_3]^-$ took place with a quantum yield of $\varphi = 0.015$ at $\lambda_{\text{irr}} = 254 \text{ nm}$.

In the presence of air the photolysis of $[\text{SnCl}_6]^{2-}$ in CH_3CN initially led to the formation of $[\text{SnCl}_3]^-$, but at later stages $[\text{SnCl}_3]^-$ underwent a secondary photolysis with the formation of $\text{SnOCl}_2(\text{CH}_3\text{CN})_n$ (see above).

Discussion

The longest-wavelength absorption bands ($\lambda_{\text{max}} = 272$ and 292 nm) and the emission ($\lambda_{\text{max}} = 510 \text{ nm}$) of $[\text{SnCl}_3]^-$ are assigned to a metal-centered sp transition between the $^1\text{S}_0$ ground and $^3\text{P}_1$ excited state [12]. The emission of $[\text{SnCl}_3]^-$ is quenched by oxygen. Simultaneously, $[\text{SnCl}_3]^-$ undergoes a photooxidation. According to these observations and in analogy to other s^2 complexes [3]

the primary events of this photooxidation can be described by the following scheme:



This scheme yields some simple equations:

$$\tau = \frac{1}{k_{\text{ND}} + k_{\text{L}} + k_{\text{ET}}[\text{O}_2]}$$

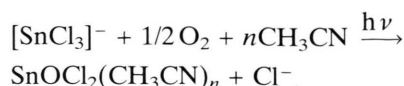
$$\varphi_{\text{L}} = \frac{k_{\text{L}}}{k_{\text{ND}} + k_{\text{L}} + k_{\text{ET}}[\text{O}_2]}$$

$$\varphi_{\text{ET}} = \frac{k_{\text{ET}}[\text{O}_2]}{k_{\text{ND}} + k_{\text{L}} + k_{\text{ET}}[\text{O}_2]}$$

From the luminescence data the second-order rate constant ($k_{\text{ET}} = 3.8 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$) and the quantum yield ($\varphi_{\text{ET}} = 0.57$) for excited state electron transfer from $[\text{SnCl}_3]^-$ to O_2 were obtained.

The quantum yield for the disappearance of $[\text{SnCl}_3]^-$ is much higher ($\varphi = 1.5$) than that of the primary electron transfer. This discrepancy is caused by secondary processes. Tin(III) [15] and O_2^- which are initially generated may participate in a variety of subsequent reactions. Furthermore, peroxide, which was identified as a main product in similar photooxidations, appears only in traces in the photolysis of $[\text{SnCl}_3]^-$. It is assumed that peroxide does not accumulate because it is consumed in a thermal oxidation of $[\text{SnCl}_3]^-$. This re-

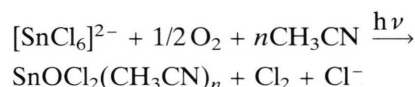
action would also account for the observation that the photooxidation quantum yield exceeds unity. The final product formation takes place according to the overall stoichiometry:



This photooxidation product is not light-sensitive while the related tin(IV) complex $[\text{SnCl}_6]^{2-}$ undergoes an efficient reductive elimination:



In analogy to many other s^0 complexes this photoreaction is induced by LMCT excitation. The corresponding LMCT absorption appears at $\lambda_{\text{max}} = 228 \text{ nm}$ ($\epsilon = 13500 \text{ L mol}^{-1} \text{ cm}^{-1}$) [16]. The primary step of this photolysis probably consists of a homolytic Sn–Cl bond cleavage which generates a tin(III) intermediate [15]. Subsequent reactions lead to the formation of $[\text{SnCl}_3]^-$ as the final product which undergoes an irreversible photooxidation to tin(IV) in the presence of O_2 (see above). The overall photolysis of $[\text{SnCl}_6]^{2-}$ in the presence of oxygen then takes place according to the stoichiometry:



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