Luminescence Quenching and Photooxidation of Trichlorostannate(II) by Oxygen

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The luminescence of \([\text{SnCl}_3]^–\) in acetonitrile \((\tau = 1.6 \mu s)\) is quenched by oxygen with \(k = 3.8 \times 10^9 \text{ L mol}^{-1} \text{s}^{-1}\). 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 \(\phi = 1.5\) at \(\lambda_{\text{irr}} = 254\) nm. While this Sn(IV) complex is not light sensitive, \([\text{SnCl}_3]^2+\) in CH₃CN undergoes a photochemical reductive elimination with the generation of \([\text{SnCl}_5]^{2–}\) with \(\phi = 0.015\) at \(\lambda_{\text{irr}} = 254\) 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 s² metal ions [3] such as Sb³⁺ [4], Tl⁺ [5], and Pb²⁺ [6]. These studies did not only reveal the initial events in the photooxidation process, 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 s⁰ ions such as Sb⁵⁺, Tl⁵⁺, and Pb⁴⁺ may thus lead to the regeneration of the corresponding s² ions. In the present work this possibility was also explored for Sn⁴⁺.

Experimental

Materials. The compounds \((\text{NEt}_4)_2[\text{SnCl}_3]\) [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 spectrophotometer 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 H₂SO₄ \((\lambda_{\text{max}} = 452\) nm; \(\phi = 0.546\) [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 \((\lambda_{\text{irr}} = 254\) nm) was obtained by means of a Schoeffel GM 250-I 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 photoprocess. 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
(NEt₄)[SnCl₃] was dissolved in acetonitrile without decomposition. The complex ion [SnCl₃]⁻ in argon-saturated CH₃CN showed a green luminescence with λ_max = 510 nm (λ_exc = 250 nm), φ = 0.07 [12] and τ = 1.6 μs. In air-saturated acetonitrile ([O₂] = 2.2×10⁻³ M) [13] the emission quantum yield dropped to φ = 0.03.

While in argon-saturated acetonitrile [SnCl₃]⁻ 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 [SnCl₃]⁻ was determined by measuring the absorbance decrease at λ = 292 nm. The anion [SnCl₃]⁻ disappeared with a quantum yield of φ = 1.5 at λ_ irr = 254 nm. Small amounts of peroxide (~10⁻⁵ M) were detected in the photolyzed solution of [SnCl₃]⁻ (1.68×10⁻⁴ M). The same spectral changes which took place during the photolysis of [SnCl₃]⁻ 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 SnOCl₂(CH₃CN)ₙ with n = 1–2 as the product of the thermal autoxidation of SnCl₂ in CH₃CN [14]. It is concluded that SnOCl₂(CH₃CN)ₙ was also produced in the photolysis of [SnCl₃]⁻ in acetonitrile in the presence of air.

The spectral changes which took place during the photolysis of [SnCl₃]⁻ in CH₃CN (Fig. 1) did not depend on the presence of additional chloride (~10⁻² M). Accordingly, under these conditions the irradiation of [SnCl₃]⁻ did not yield [SnCl₆]²⁻, which has an absorption spectrum somewhat different from that of the photooxidation product. While SnOCl₂(CH₃CN)ₙ in CH₃CN was hardly light-sensitive, the complex ion [SnCl₆]²⁻ underwent a clean photoconversion to [SnCl₃]⁻ in the absence of air as indicated by the concomitant spectral variations (Fig. 2). The formation of [SnCl₃]⁻ was also confirmed by the appearance of its green luminescence. Chlorine was detected as a further photoproduct by qualitative analysis. The reductive elimination of [SnCl₆]²⁻ to form [SnCl₃]⁻ took place with a quantum yield of φ = 0.015 at λ_ irr = 254 nm.

In the presence of air the photolysis of [SnCl₆]²⁻ in CH₃CN initially led to the formation of [SnCl₃]⁻, but at later stages [SnCl₃]⁻ underwent a secondary photolysis with the formation of SnOCl₂(CH₃CN)ₙ (see above).

**Discussion**

The longest-wavelength absorption bands (λ_max = 272 and 292 nm) and the emission (λ_max = 510 nm) of [SnCl₃]⁻ are assigned to a metal-centered sp transition between the ¹S₀ ground and ³P₁ excited state [12]. The emission of [SnCl₃]⁻ is quenched by oxygen. Simultaneously, [SnCl₃]⁻ undergoes a photooxidation. According to these observations and in analogy to other s² complexes [3]
the primary events of this photooxidation can be described by the following scheme:

\[
\text{[SnCl}_3\text{]}^- + h\nu \rightarrow \text{[SnCl}_3\text{]}^-* \\
\text{[SnCl}_3\text{]}^-* \xrightarrow{k_{\text{ND}}} \text{[SnCl}_3\text{]}^- + \text{heat} \quad \text{(non-radiative deactivation)} \\
\text{[SnCl}_3\text{]}^-* \rightarrow \text{[SnCl}_3\text{]}^- + h\nu' \quad \text{(luminescence)} \\
\text{[SnCl}_3\text{]}^- + O_2 \rightarrow \text{[SnCl}_3\text{]}^- + O_2^- \quad \text{(electron transfer)}
\]

This scheme yields some simple equations:

\[
\tau = \frac{1}{k_{\text{ND}} + k_L + k_{\text{ET}}[O_2]} \\
\varphi_L = \frac{k_L}{k_{\text{ND}} + k_L + k_{\text{ET}}[O_2]} \\
\varphi_{\text{ET}} = \frac{k_{\text{ET}}[O_2]}{k_{\text{ND}} + k_L + k_{\text{ET}}[O_2]}
\]

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 \([\text{SnCl}_3\text{]}^-\) to \(O_2^-\) were obtained.

The quantum yield for the disappearance of \([\text{SnCl}_3\text{]}^-\) 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, peroxyde, which was identified as a main product in similar photooxidations, appears only in traces in the photolysis of \([\text{SnCl}_3\text{]}^-\). It is assumed that peroxyde does not accumulate because it is consumed in a thermal oxidation of \([\text{SnCl}_3\text{]}^-\). This reaction would also account for the observation that the photooxidation quantum yield exceeds unity. The final product formation takes place according the overall stoichiometry:

\[
[\text{SnCl}_3\text{]}^- + 1/2O_2 + n\text{CH}_3\text{CN} \xrightarrow{h\nu} \text{SnOCl}_2(\text{CH}_3\text{CN})_n + \text{Cl}^- \\
\]

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

\[
[\text{SnCl}_6\text{]}^{2-} \xrightarrow{h\nu} [\text{SnCl}_3\text{]}^- + \text{Cl}_2 + \text{Cl}^- \\
\]

In analogy to many other \(s^0\) complexes this photoreaction is induced by LMCT excitation. The corresponding LMCT absorption appears at \(\lambda_{\text{max}} = 228 \text{ nm} \quad (\varepsilon = 13500 \text{ L mol}^{-1} \text{cm}^{-1})\) \([16]\). 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 \([\text{SnCl}_3\text{]}^-\) as the final product which undergoes an irreversible photooxidation to tin(IV) in the presence of \(O_2\) (see above). The overall photolysis of \([\text{SnCl}_6\text{]}^{2-}\) in the presence of oxygen then takes place according to the stoichiometry:

\[
[\text{SnCl}_6\text{]}^{2-} + 1/2O_2 + n\text{CH}_3\text{CN} \xrightarrow{h\nu} \text{SnOCl}_2(\text{CH}_3\text{CN})_n + \text{Cl}_2 + \text{Cl}^- \\
\]

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