Photochemical Generation of Tribromostannate(II) by Redox and Substitution Reactions

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Hexabromostannate(IV) in acetonitrile undergoes a photochemical reductive elimination according to the equation \([\text{SnBr}_6^{2-} \rightarrow [\text{SnBr}_3]^- + \text{Br}_3^-]\) with \(\phi = 0.06\) at \(\lambda_{\text{max}} = 313\) nm. The formation of \([\text{SnBr}_3]^-\) takes place also by irradiation of \([\text{Ru(SnBr}_3)_2\text{Br}]^{4+}\) in acetonitrile with visible light. This photosubstitution occurs with \(\phi > 0.09\) at \(\lambda_{\text{max}} = 436\) nm.

Introduction

Photocatalysis by metal complexes is a rapidly expanding branch of catalysis and photochemistry [1]. For special applications the light-induced formation of catalysts offers distinct advantages or is even required. As an example the base-catalyzed cross-linking of polymers for lithographic image formation may be mentioned [2]. Accordingly, it is of general importance to search for photochemically generated compounds which are potential catalysts. Tin(II) compounds have been applied in a variety of technical processes including catalytic reactions such as polymerizations [3, 4]. In this context our observations on the photochemical generation of \([\text{SnBr}_3^-]\) should be of some interest although an immediate application is not anticipated. As an important aspect of the present work it is demonstrated that quite different compounds, \([\text{SnBr}_6]^{2-}\) and \([\text{Ru(SnBr}_3)_2\text{Br}]^{4+}\), can be used as precursors for the light-induced generation of \([\text{SnBr}_3]^-\). However, the reaction conditions such as the photoactive wavelength region are rather different for both compounds. The appropriate choice of suitable parameters could be crucial for potential applications.

Experimental Section

Materials

The compound \((\text{NEt}_4)_2[\text{SnBr}_6]\) was prepared according to a published procedure [5]. \((\text{NEt}_4)_4[\text{Ru(SnBr}_3)_2\text{Br}]\) was synthesized (see below) in analogy to the preparation of \((\text{NEt}_4)_4[\text{Ru(SnCl}_3)_2\text{Cl}]\) [6].

Synthesis of \((\text{NEt}_4)_4[\text{Ru(SnBr}_3)_2\text{Br}]\)

To 20 ml of 3 M HBr was added dropwise \(\text{H}_2\text{PO}_3\) in order to reduce elemental bromine. The reduction was complete when \(\text{Br}_3^-\) was not anymore detected spectrophotometrically (\(\lambda_{\text{max}} = 296\) nm). To this solution which was saturated with argon was added 1.14 g \((3 \times 10^{-3}\) mol\) of \([\text{Ru(SnCl}_3)_2\text{Cl}]\). The resulting solution was stirred at 90 °C under reflux for 20 h. Afterwards the solution was cooled to r.t. and filtered. To the filtrate was added dropwise 3.2 g \((15.2 \times 10^{-3}\) mol\) of \((\text{NEt}_4)_3\)Br in 20 ml of 3 M HBr. The brick-red precipitate was collected by filtration, washed with ethanol and ether, and dried in a vacuum in the presence of KOH pellets. The product was recrystallized from \(\text{CH}_3\text{CN}\) by addition of ether, yield 6.7 g \((90\%)\).

Analysis for \(\text{C}_1\text{H}_4\text{Br}_5\text{Sn}_2\text{N}_2\text{RuSn}_3\)

Caled C 15.42 H 3.23 N 2.25%.
Found C 15.60 H 3.27 N 2.46%.

Photolyses

The light source was an Osram HBO 200 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained by means of Schott PIL/IL interference filters 313 and 436 nm or by a Schoeffel GM 250/1 high-intensity monochromator. The photolyses were carried out in solutions of acetonitrile (spectrograde) in 1 cm spectrophotometer cells at r.t. under argon. Progress of the photolyses was monitored by UV-visible spectrophotometry. The photoproducts were identified by their absorption and emission spectra. For quantum yield determinations the complex con-

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centrations 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 a RkP-345 detector.

**Instrumentation**

Absorption spectra were measured with a Hewlett-Packard 8452A diode array or a Shimadzu UV-2100 absorption spectrometer. Emission and excitation spectra were obtained on a Hitachi 850 spectrofluorimeter equipped with a Hamamatsu 928 photomultiplier for measurements up to 920 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations.

**Results**

The electronic spectrum of [SnBr₆]²⁻ in CH₃CN (Fig. 1) has absorption bands at λ₂₈₅ = 285 nm (ε = 7200 M⁻¹ cm⁻¹) and 217 nm (9500). The irradiation of [SnBr₆]²⁻ in CH₃CN led to a clean photoreaction according to the equation

\[ [\text{SnBr}_6]^{2-} \rightarrow [\text{SnBr}_3]^- + \text{Br}_3^- . \]

This stoichiometry was confirmed by the spectral variations (Fig. 1) which accompanied the photolysis. The absorption spectrum of [SnBr₆]²⁻ was converted to that of [SnBr₃]⁻ (λ₂₁₇ = 217 nm, ε = 10,580) [7] and Br₃⁻ (λ₂₹₆ = 296 nm, ε = 55,000) [8]. The photolysis could be driven to completion. The formation of [SnBr₃]⁻ led also to the appearance of its orange photoluminescence (λ₂₆₉ = 603 nm) [7]. The progress of the photoreaction was monitored by the increase of the absorption at λ = 269 nm. The quantum yields of the photolysis were \( \phi = 0.10 \) at \( \lambda_{\text{irr}} = 254 \) nm, 0.06 at 282 nm, 0.06 at 313 nm, and 0.04 at 333 nm.

The absorption spectrum of [Ru(SnBr₃)₅Br]⁴⁻ in CH₃CN (Fig. 2) shows bands at λ₂₄₉ = 495 nm (ε = 1500) and 351 nm (24,700). On the basis of the spectral changes which were observed during the photolysis of [Ru(SnBr₃)₅Br]⁴⁻ in CH₃CN the products could not be identified. However, the photochemical release of [SnBr₃]⁻ was indicated by its orange photoemission which appeared upon irradiation of [Ru(SnBr₃)₅Br]⁴⁻. Since the photolysis led to a substantial decrease of the absorption of the ruthenium complex at λ₂₉₆ = 351 nm the progress of the photoreaction was monitored at this wavelength. At \( \lambda_{\text{irr}} = 436 \) nm the quantum yield of the photolysis was estimated to be \( \phi > 0.09 \). Even upon irradiation at λ = 600 nm the formation of [SnBr₃]⁻ was still observed.

**Discussion**

The absorption bands of [SnBr₆]²⁻ are assigned to ligand-to-metal charge transfer (LMCT) transitions \( t₁ₚ(π*) \rightarrow a₁g(σ*) \) at \( λ_{\text{max}} = 285 \) nm and \( t₁ₚ(π*) \rightarrow a₁g(σ*) \) at \( 217 \) nm [9]. In analogy to other \( s⁰ \) complexes [10, 11] including [SnCl₆]²⁻ [12] LMCT excitation of [SnBr₆]²⁻ leads to a reductive elimination with the formation of [SnBr₃]⁻ and Br₃⁻.

**Fig. 1.** Spectral changes during the photolysis of 6.75×10⁻⁵ M (NEt₄)₂[SnBr₃] in acetonitrile at 0 (a) and 8 min (e) irradiation time with \( \lambda_{\text{irr}} = 313 \) nm; 1 cm cell.

**Fig. 2.** Electronic absorption spectrum of 1.5×10⁻⁵ M (NEt₄)₄[Ru(SnBr₃)₅Br] in acetonitrile at room temperature, 1 cm cell.
Reliable assignments for the absorption of \([\text{Ru(SnBr}_3\text{)}_5\text{Br}]^{4-}\) are not yet available. However, according to a recent discussion of the electronic spectra of trichlorostannyl complexes of \(\text{Ru(II)}\) \cite{13}, the long-wavelength bands of \([\text{Ru(SnBr}_3\text{)}_5\text{Br}]^{4-}\) may be tentatively assigned to intraligand (IL) transitions of the \([\text{SnBr}_3\text{]}^{-}\) ligand which are modified by coordination to the transition metal. As it was also observed for several trichlorostannyl \(\text{Ru(II)}\) complexes \cite{13}, the photolysis of \([\text{Ru(SnBr}_3\text{)}_5\text{Br}]^{4-}\) leads to a photosubstitution of the \(\text{SnX}_3^{-}\) ligand.

With regard to potential applications various aspects of the photochemical generation of \([\text{SnBr}_3\text{]}^{-}\) should be emphasized. Although both photochemical reactions, the reductive elimination of \([\text{SnBr}_6\text{]}^{2-}\) and the photosubstitution of \([\text{Ru(SnBr}_3\text{)}_5\text{Br}]^{4-}\), lead to the formation of \([\text{SnBr}_3\text{]}^{-}\), the irradiating light is limited to the UV region in the case of \([\text{SnBr}_6\text{]}^{2-}\) (see Fig. 1) while the light sensitivity of \([\text{Ru(SnBr}_3\text{)}_5\text{Br}]^{4-}\), which covers also the whole absorption spectrum of this complex (Fig. 2), extends from the UV down to wavelengths as long as 600 nm. \([\text{SnBr}_3\text{]}^{-}\) as the product of the photolysis of \([\text{SnBr}_6\text{]}^{2-}\) and \([\text{Ru(SnBr}_3\text{)}_5\text{Br}]^{4-}\) can be easily detected by luminescence spectroscopy \cite{7}. This method is a rather selective analytical tool and can be applied to solutions as well as to matrices which are not completely transparent.

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