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Preliminary communication

Diversity in photoredox chemistry of oxo or hydroxo complexes of s^2 metal ions

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Abstract

The electronic spectra of hydroxo or oxo complexes of the s² metal ions $T1^+$, Sn^{2+} , Sb^{3+} , Bi^{3+} and Te^{4+} in alkaline solutions display absorption bands in the UV region which are assigned to metal-centered sp transitions. In the case of $T1^+$ and Sn^{2+} these sp-excited states are also luminescent. TIOH is photooxidized to Tl_2O_3 by molecular oxygen while the photooxidation of $Sn(OH)_3^{-1}$ to $Sn(OH)_6^{2-}$ is even achieved by water which is reduced to hydrogen. Both complexes produce hydrated electrons upon 266 nm laser excitation. No electron ejection can be observed for the hydroxo or oxo metalates of Sb^{3+} , Bi^{3+} and Te^{4+} , which undergo a photoreduction to the metallic state with a concomitant oxidation of hydroxide to hydrogen peroxide and/or oxygen.

Keywords: Photoredox chemistry; Main group metal complexes; Oxo complexes; Hydroxo complexes

1. Introduction

Main group metal cations with an s² electronic configuration are well known to form a variety of hydroxo or oxometalates in alkaline solutions [1]. Relatively little attention has been paid to excited state properties of these complexes although initial observations on the electronic spectra and photochemistry of TIOH [2,3], Sn(OH)3⁻ [4] and $Pb(OH)_3^{-1}$ [5] have been reported. The present work was based on our previous experience with halide complexes of s^2 metals [6-11] in general and Pb(OH)₃⁻ [5] in particular. We have now extended these investigations to hydroxo or oxo metalates of Tl(I), Sn(II), Sb(III), Bi(III) and Te(IV). These complexes are accessible by simply dissolving the corresponding halide or oxide in alkaline solution. Unfortunately, their exact composition is not always clear. Accordingly, some conclusions are tentative. However, the general diversity in the photochemical behavior of this important family of coordination compounds is well documented and justifies this preliminary communication.

2. Electronic spectra

In alkaline solution T1⁺ ion exists as TIOH which shows an absorption at $\lambda_{max} = 236$ nm ($\epsilon = 1550$ M⁻¹ cm⁻¹) [2] and an emission at $\lambda_{max} = 450 \text{ nm} (\lambda_{exc} = 240 \text{ nm})$ [3]. In air-saturated solution the relative quantum yield of this emission was about 10% lower than in a deaerated system. SnCl₂ dissolves in alkaline solutions with the formation of $Sn(OH)_3^{-}$ [12]. The absorption spectrum of $Sn(OH)_3^{-}$ displays a band at $\lambda_{max} = 231$ nm ($\epsilon = 7270$ M⁻¹ cm⁻¹) and shoulders at $\lambda_{max} = 260 \text{ nm}$ ($\epsilon = 160 \text{ M}^{-1} \text{ cm}^{-1}$) and $\lambda_{\text{max}} = 278 \text{ nm} (\epsilon = 60 \text{ M}^{-1} \text{ cm}^{-1}) \cdot \text{Sn}(\text{OH})_3^{-1} \text{ emits a green}$ luminescence at $\lambda_{max} = 470$ nm ($\lambda_{exc} = 250$ nm). Alkaline solution of Sb₂O₃ contains presumably Sb(OH)₄ or SbO₂ [13]. The absorption spectrum of this solution shows a band which starts to absorb at approximately 280 nm. The absorption maximum is located around or below 200 nm. (At $\lambda = 240$ nm the molar absorbance is $\epsilon = 820 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$.) The solubility of Bi2O3 even at relatively high concentration of NaOH was very low. Such solutions which contain apparently Bi(OH)₄⁻ [14] show an absorption band at $\lambda_{max} = 247$ nm ($\epsilon = 8100 \,\mathrm{M^{-1} \, cm^{-1}}$) and a shoulder at 295 nm ($\epsilon = 210$ M^{-1} cm⁻¹). The molar absorbance was determined by converting bismutate(III) to BiCl₄⁻ (λ_{max} = 319 nm, ϵ = 5100 M⁻¹ cm⁻¹) [8] with concentrated hydrochloric acid. Alkaline solutions of TeO2 do not contain a hydroxo complex such as $Te(OH)_6^{2-}$ but tellurate(IV) as the oxometalate TeO_3^{2-} [1a, p. 1011; 1b, p. 526; 1c, p. 532]. These solutions show a shoulder at $\lambda_{\text{max}} = 247 \text{ nm} (\epsilon = 530 \text{ M}^{-1} \text{ cm}^{-1})$. The absorption maximum is apparently located under the absorption of

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the solvent. Irrespective of the composition of these metalates, their electronic spectra display a long-wavelength absorption in the UV which is assigned to the spin-forbidden metal centered sp transition ${}^{1}S_{0} \rightarrow {}^{3}P_{1}$. This assignment is based on our previous studies of the electronic spectra of halide complexes of s² metal ions [6–11,15] and Pb(OH)₃⁻ [5].

3. Photochemistry

Continuous irradiation of TIOH (10^{-3} M) does not cause any permanent chemical change, while photolysis in the presence of air was accompanied by the formation of a red-brown suspension which gave rise to a very broad absorption band at $\lambda_{max} = 593$ mm. The suspended material was apparently Tl₂O₃ [16]. Upon addition of HCl it was converted to TICl₄⁻⁻ ($\lambda_{max} = 247$ nm, $\epsilon = 15$ 850 M⁻¹ cm⁻¹) [17]. The quantum yield for the photooxidation of TIOH to Tl₂O₃ was $\Phi = 0.02$ at $\lambda_{ir} = 254$ nm. Hydrogen peroxide was qualitatively identified as a further photolysis product.

In the absence of air the photolysis of $Sn(OH)_3^-$ led to the disappearance of the absorption band at $\lambda_{max} = 231$ nm. The complex apparently underwent photooxidation to $Sn(OH)_6^{2-}$ which absorbs only below 200 nm. $Sn(OH)_3^$ disappeared with $\Phi = 1.1 \times 10^{-2}$ at $\lambda_{ir} = 254$ nm (pH 12.5; see Ref. [4]). In accordance with observations by Tennakone et al. [4], molecular hydrogen was identified as a photoreduction product by gas chrom-atography.

Laser flash photolyses of TiOH (10^{-3} M) and Sn(OH)₃⁻ (1.25×10^{-3} M) led to the formation of different intermediates as a function of time elapsed after the pulse¹. In both cases the 680 nm band in the transient spectra taken right (5 or 10 ns) after the pulse, on the basis of its position and broadness, was assigned to the hydrated electron [19]. This assignment has been confirmed by scavenging with N₂O and NO₃⁻. The quantum yields for the formation of $e_{hyd}^-(\phi_e)$ were determined from the peak absorbance at 680 nm⁻¹; $\phi_e = 0.17 \pm 0.02$ and 0.24 ± 0.04 were obtained for the TI(1) and Sn(II) complexes, respectively.

While the hydrated electron disappeared within several hundreds of ns in both systems, at the same time build-up of much longer-lived intermediates was detected, which absorbed below 550 nm, with apparent maxima at 280–300 nm. Kinetic measurements indicated that these species may be the products of the reactions between e_{nyd} and Tl(1) or Sn(II), possibly Tl(0) or Sn(I), respectively.

These results suggest that excitation of both TIOH and $Sn(OH)_3^-$ leads to the formation of a hydrated electron-oxidized complex pair (Eq. (1).

$$M^{n+} \rightarrow M^{(n+1)+} + e_{hyd}^{-}$$
(1)

If the products of the primary photoreaction (Eq. (1)) do not undergo a back reaction the hydrated electron can react with the ground-state complex being the only efficient scavenger in this system (Eq. (2)) and the $M^{(n+1)+}$ species can dismutate (Eq. (3)). The latter species can also recombine (synproportionate) with the reduced complex ($M^{(n-1)-}$) formed in reaction (2) to give the original compound (Eq. (4)).

$$e_{hyd}^{-} + M^{n+} \to M^{(n-1)+}$$
 (2)

$$2M^{(n+1)+} \to M^{n+} + M^{(n+2)+}$$
(3)

$$M^{(n-1)+} + M^{(n+1)+} \to 2M^{n+}$$
(4)

While in argon-saturated solution of TIOH reaction (4) closes the photoinduced cycle, resulting in no permanent chemical change, the Sn(1) species may reduce water, according to the overall reaction (Eq. (5)).

$$\operatorname{Sn}(OH)_{3}^{-} + 2H_{2}O + OH^{-} \rightarrow \operatorname{Sn}(OH)_{6}^{2-} + H_{2}$$
 (5)

In an air-saturated system, oxygen can react with both e_{hvd}^- and Tl(0) formed.

$$\mathbf{e}_{\mathsf{hvd}}^{-} + \mathbf{O}_2 \to \mathbf{O}_2^{-} \tag{6}$$

$$TI(0) + O_2 \rightarrow TI(I) + O_2^{-}$$
⁽⁷⁾

The subsequent dark reactions of O_2^- generate peroxide, while Tl_2O_3 (the other final product) is produced from Tl(III) formed via dismutation (Eq. (3)), according to the overall reaction (Eq. (8)).

$$2\text{TIOH} + 2\text{O}_2 \div 2\text{H}_2\text{O} \xrightarrow{\mu\nu} \text{Tl}_2\text{O}_3 + 2\text{H}_2\text{O}_2 \tag{8}$$

The photolysis of Sb(OH)₄⁻, Bi(OH)₄⁻ and TeO₃²⁻ in argon-saturated 1 M NaOH solution led to the formation of elemental metal, which increased the apparent optical density (due to opacity) over the entire long-wavelength region². Simultaneously, a decrease of the absorbance was observed at shorter wavelengths (below 230–240 nm) due to the disappearance of the original complexes. These two changes were proportional to each other (and, thus, to the turnover). The approximate quantum yields for the reduction were 0.05 for Sb(OH)₄⁻ at λ_{ir} =240 nm, 3×10^{-4} and 0.11 for Bi(OH)₄⁻ and TeO₃²⁻, respectively, at λ_{ir} =254 nm. As further product H₂O₂ was qualitatively detected in all three sys-

¹ Transient absorption spectra were determined by laser flash photolysis system of ns time resolution. Pulse energy of 12 mJ at 266 nm with a width of about 15 ns was used. Samples ware irradiated in 1 cm quartz cells with right angle monitoring of the transient absorbance. For determination of the quantum yield for the formation of hydrated electron, hexacyanoferrate(II) was utilized as a standard reference having a $\Phi_e = 0.52$ at 265 nm excitation [18].

² Since under our experimental conditions this increase of absorption was nearly proportional to the degree of photochemical conversion, quantum yield determinations were based on absorption measurements. A calibration yielded the following apparent extinction coefficients of the colloidal elements at $\lambda = 350 \text{ mm} \cdot \epsilon = 520 \text{ M}^{-1} \text{ cm}^{-1}$ for Sb, $\epsilon = 7250 \text{ M}^{-1} \text{ cm}^{-1}$ for Bi, $\epsilon = 2660 \text{ M}^{-1} \text{ cm}^{-1}$ for Te. In the case of antimony the degree of photochemical conversion was also determined by a different procedure. The colloidal antimony was first removed by centrifuging the photolograd solution. The loss of Sb³⁺ was then determined by measuring the decrease of the optical density of the remaining solution at 240 nm ($\epsilon = 820 \text{ M}^{-1}$ cm⁻¹ for Sb³⁺).

tems. Upon stirring overnight, the suspensions of metallic bismuth and tellurium redissolved in the photolyzed solutions. This reoxidation was prevented when the irradiated solutions were flushed with argon or nitrogen. No intermediates were detected by flash-photolysis experiments with the oxo or hydroxo metalates of Sb^{3+} , Bi^{3+} and Te^{4+} .

The overall stoichiometry of these photoredox reactions can be described by the following general equation:

$$\mathbf{M}^{n+} + n\mathbf{HO}^{-} \xrightarrow{n} \mathbf{M}^{0} + n/2\mathbf{H}_{2}\mathbf{O}_{2}$$
(9)

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Although the electronic spectra of the metalates of s^2 ions do not contain LMCT absorptions, Pb(II), Sb(III), Bi(III) and Te(IV) in alkaline solution are reduced to Pb(I), Sb(II), Bi(II) and Te(III), while hydroxide is oxidized to its radical in the primary photochemical step. The formation of the metallic state must then take place by subsequent thermal processes such as disproportionation or intramolecular redox reactions of the metalates generated by the initial electron transfer reaction. In the case of bismuthate(III) and tellurate(IV), the reoxidation of the free metals as photoproducts by O_2 or H_2O_2 in a dark reaction seems to be facilitated by the small size of the metal particles.

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