

PHOTOCHEMISTRY OF COORDINATION COMPOUNDS OF MAIN GROUP METALS.  
REDUCTIVE ELIMINATION OF THALLIUM(III) COMPLEXES

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## Introduction

The photochemistry of coordination compounds of the main group metals is a rather interesting but largely neglected part of inorganic photochemistry. Within a general approach to this subject we studied recently photoredox reactions of  $[\text{Sn}(\text{N}_3)_6]^{2-}$  and  $[\text{Pb}(\text{N}_3)_6]^{2-}$  (1). These ions are examples of complexes containing a metal with an empty valence shell ( $s^0$  electron configuration). Such compounds are characterized by low-energy ligand to metal charge transfer (LMCT) bands in their absorption spectra. Reductive elimination initiated by LMCT excitation seems to be the typical photo-reaction of  $s^0$  complexes. We extended now these investigations to Tl(III) complexes in order to test the general validity of this assumption.

There is not much known about the photochemistry of Tl(III) complexes (2,3). Spectral assignments of electronic absorption bands were reported for a few tetrahalogeno complexes of Tl(III) (4,5). In the present work we studied the photochemistry of  $[\text{Tl}(\text{N}_3)_2\text{Br}_2]^-$ ,  $[\text{Tl}(\text{bipy})_2\text{I}_2]^+$  (bipy = 2,2'-bipyridyl), and  $[\text{Tl}(\text{acetate})_3]$  in some detail. Spectral assignments of absorption bands were supported by the photochemical behavior of these complexes.

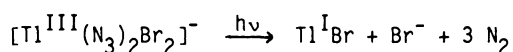
## Results and Discussion

The compounds  $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Tl}(\text{N}_3)_2\text{Br}_2]$  (6) and  $[\text{Tl}(\text{bipy})_2\text{I}_2]\text{I}$  (7), were prepared by literature procedures.  $\text{Tl}(\text{CH}_3\text{CO}_2)_3 \cdot 1.5 \text{H}_2\text{O}$  was purchased from Aldrich.

The absorption spectrum of  $[\text{Tl}(\text{N}_3)_2\text{Br}_2]^-$  in acetonitrile displays a long-wavelength band at  $\lambda_{\text{max}} = 293 \text{ nm}$  ( $\epsilon = 10200 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). This band is assigned to a LMCT transition. Since azide and bromide have comparable optical electronegativities

it is difficult to distinguish between  $\text{N}_3^- \rightarrow \text{Tl(III)}$  and  $\text{Br}^- \rightarrow \text{Tl(III)}$  CT transitions. However, the photoreaction supports the former assignment. At shorter wavelength the typical absorption features of the counterion  $[\text{As}(\text{C}_6\text{H}_5)_4]^+$  appear in the spectrum ( $\lambda_{\text{max}} = 271, 265, 259 \text{ nm}$ )<sup>6</sup>).

Upon irradiation of the LMCT band ( $\lambda_{\text{irr}} = 313 \text{ nm}$ ) of  $[\text{Tl}(\text{N}_3)_2\text{Br}_2]^-$  in  $\text{CH}_3\text{CN}$  the evolution of nitrogen was observed. Simultaneously, the intensity of the LMCT band decreased. Finally, this absorption disappeared when the photolysis went to completion. In the later stages of the photolysis the solution became cloudy due to the formation of insoluble  $\text{TlBr}$ . These observations are consistent with a reductive elimination:



The disappearance of  $[\text{Tl}(\text{N}_3)_2\text{Br}_2]^-$  was determined by the decrease of the extinction at  $\lambda_{\text{max}} = 293 \text{ nm}$ . Upon irradiation at  $313 \text{ nm}$  the reductive elimination occurred with a quantum yield of  $\phi = 0.3$ .

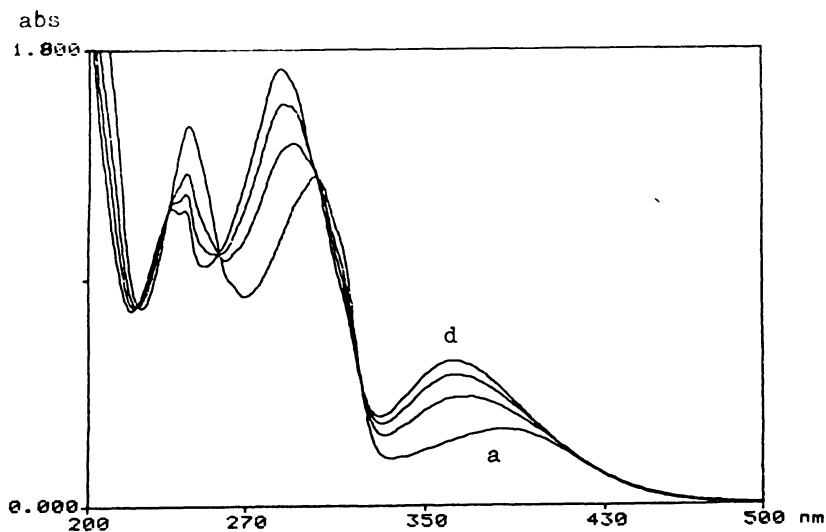
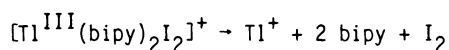


Fig. 1.

Spectral changes during the photolysis of  $5.33 \cdot 10^{-5} \text{ M}$   $[\text{Tl}(\text{bipy})_2\text{I}_2]^+$  in  $\text{CH}_3\text{CN}$  at (a) 0 and (d) 200 s irradiation time, with  $\lambda_{\text{irr}} > 200 \text{ nm}$  and a 1-cm cell.

The absorption spectrum of  $[\text{Tl}(\text{bipy})_2\text{I}_2]^+$  in  $\text{CH}_3\text{CN}$  (Fig. 1) consists of 3 bands at  $\lambda_{\text{max}} = 374 \text{ nm}$  ( $\epsilon = 4700$ ),  $302 \text{ nm}$  (23210), and  $244 \text{ nm}$  (28200). The longest wavelength band at  $374 \text{ nm}$  may be due to a  $\text{J}^- \rightarrow \text{Tl}(\text{III})$  LMCT transition since  $[\text{TlI}_4]^-$  shows such an absorption at  $\lambda_{\text{max}} = 397 \text{ nm}$ <sup>4,5</sup>). However, the photochemical behavior of  $[\text{Tl}(\text{bipy})_2\text{I}_2]^+$  (see below) is not consistent with this assignment. As a reasonable alternative the band at  $374 \text{ nm}$  may be assigned to a  $\text{J}^- \rightarrow$  bipy ligand to ligand (LL) CT transition. The complex  $[\text{Be}(\text{bipy})\text{I}_2]$  shows such a LLCT band at  $368 \text{ nm}$  ( $\epsilon = 7000$ )<sup>8</sup>). The second band of  $[\text{Tl}(\text{bipy})_2\text{I}_2]^+$  at  $302 \text{ nm}$  should be assigned to the  $\pi\pi^*$  intraligand (IL) transition of the bipy ligand which absorbs in this region. An  $\text{I}^- \rightarrow \text{Tl}(\text{III})$  LMCT transition could also contribute to this band since low-energy absorptions of this type are expected to appear near this wavelength<sup>4,5</sup>). The third absorption at  $244 \text{ nm}$  is certainly a  $\text{I}^- \rightarrow \text{Tl}(\text{III})$  LMCT band in agreement with the photochemical behavior of  $[\text{Tl}(\text{bipy})_2\text{I}_2]^+$ .

Irradiation ( $\lambda_{\text{max}} > 200 \text{ nm}$ ) of  $[\text{Tl}(\text{bipy})_2\text{I}_2]^+$  in  $\text{CH}_3\text{CN}$  was accompanied by spectral changes (Fig. 1) which are consistent with a reductive elimination according to:

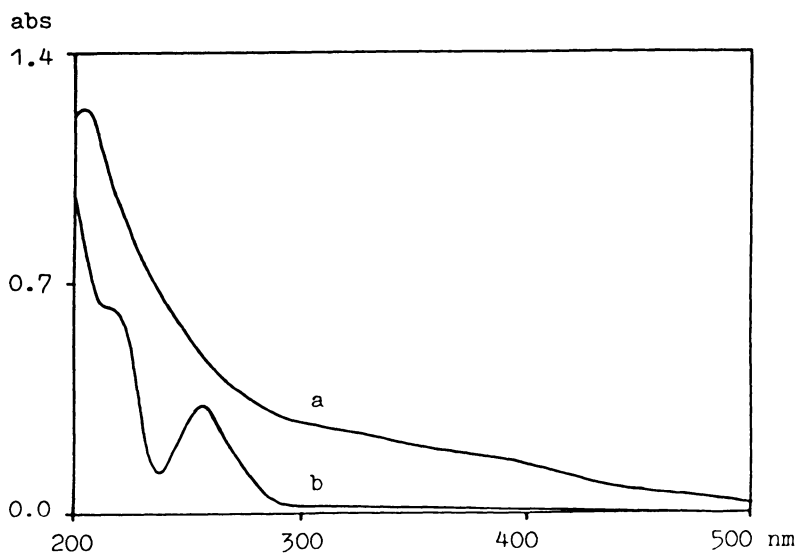


In the photolyzed solution the absorption maximum at  $360 \text{ nm}$  is caused by  $\text{I}_2$ . The new band at  $286 \text{ nm}$  is apparently a superimposition of absorption maxima of  $\text{I}_2$  ( $\lambda_{\text{max}} = 289 \text{ nm}$ ) and free bipy ( $\lambda_{\text{max}} = 280 \text{ nm}$ ). The presence of released bipy is also indicated by bands at  $\lambda_{\text{max}} = 235$  and  $243 \text{ nm}$ .

In accordance with the assignments of the absorption bands of  $[\text{Tl}(\text{bipy})_2\text{I}_2]^+$  the quantum yields of the reductive elimination ( $\Phi = 0.54$  at  $\lambda_{\text{irr}} = 254 \text{ nm}$ ,  $0.03$  at  $302 \text{ nm}$ , and  $2.9 \times 10^{-3}$  at  $366 \text{ nm}$ ) decreased with increasing wavelength of irradiation.

The photochemistry of some thallium(III) carboxylates of the type  $\text{Tl}(\text{RCOO})_3$  where R is a larger aliphatic group was studied by Kochi and Bethea<sup>2</sup>). The photolysis of these compounds in benzene solution led to the formation of Tl(I) and oxidation of carboxylate ( $\text{RCOO}^- - \text{e}^- \rightarrow \text{R}\cdot + \text{CO}_2$ ).

In the present work we investigated the photolysis of  $\text{Tl}(\text{CH}_3\text{COO})_3$  which does not dissolve in benzene. In the solid state Tl(III) is essentially hexacoordinated by three chelating acetate ligands <sup>9</sup>). In aqueous solution the acetate ligands are partially substituted <sup>10</sup>). Since in acetonitrile such ligand substitutions are generally less efficient it is assumed that  $\text{Tl}(\text{CH}_3\text{COO})_3$  dissolves in  $\text{CH}_3\text{CN}$  without dissociation. The absorption spectrum of  $\text{Tl}(\text{CH}_3\text{COO})_3$  in acetonitrile (Fig. 2)

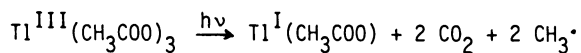


**Fig. 2**

Absorption spectra of  $9.9 \times 10^{-5}$  M  $[\text{Tl}(\text{CH}_3\text{COO})_3]$  (a) and its photolysis product (b) in  $\text{CH}_3\text{CN}$ ,  $\lambda_{\text{irr}} > 200$  nm, 1-cm cell

is rather featureless. The complex starts to absorb in the visible region. The absorption increases towards shorter wavelength. A maximum appears at 203 nm ( $\epsilon = 12430$ ) while shoulders occur at 240 nm ( $\epsilon = 6440$ ) and 395 nm ( $\epsilon = 1660$ ). These absorptions can certainly be assigned to acetate  $\rightarrow$  Tl(III) LMCT transitions.

The spectral changes which accompanied the irradiation (white light from a high-pressure mercury arc) of  $\text{Tl}(\text{CH}_3\text{COO})_3$  in  $\text{CH}_3\text{CN}$  indicated the formation of Tl(I) acetate (Fig. 2) which shows absorption bands at  $\lambda_{\text{max}} = 256$  nm and 214 nm. Although the oxidation products were not identified it is assumed that the reductive elimination takes place according to the equation:



The methyl radicals may undergo dimerization or other secondary reactions. At  $\lambda_{\text{irr}} = 254 \text{ nm}$  the quantum yield for the disappearance of  $\text{Tl}(\text{CH}_3\text{COO})_3$  was  $\Phi = 0.14$ . It dropped to  $\Phi = 0.01$  at  $\lambda_{\text{irr}} = 395 \text{ nm}$ .

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