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Photochemical Reductive Elimination of Tetrachloroiodate(III)

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In analogy to transition metal complexes, coordination compounds of the main group metals can be also classified according to the electron configuration at the metal. Generally, the main group metals occur in oxidation states with s^0, s^2, s^2p^2 and s^2p^4 ground states. Recently, we studied the photolysis of s^0 and s^2 systems [1–4]. We now report the first results on the photochemistry of an s^2p^2 complex. The ion $[I^{III}Cl_4]^-$ was selected for this investigation. Although iodine may not be considered as a metal, its coordination compounds have much in common with those of any other main group metal. The light-sensitivity of $[ICl_4]^-$ had been noticed already in 1954 [5]. The aim of the present study was to establish the nature of the reactive excited state of $[ICl_4]^-$.

The absorption spectrum of $[ICl_4]^-$ [5] (Fig. 1) displays bands at $\lambda_{max} = 335$ ($\epsilon = 1300$), 283 (11400), 259 (18200) and 211 (49000). Upon irradiation of $[ICl_4]^-$ in acetonitrile, a smooth photoreaction took place which was independent of the exciting wavelength ($\lambda_{irr} > 250$ nm).

According to the spectral changes which were observed during the photolysis (Fig. 1) $[ICl_4]^-$ was converted to $[ICl_2]^-$. At the isosbestic points at 220 and 244 nm, both complexes have the same extinction coefficients. The photoreaction can be driven almost to completion. The final spectrum is very similar to that of an authentic sample of $[ICl_2]^-$ [6]. The progress of the photolysis was followed by measuring the extinction at 259 nm. At this wavelength $[ICl_2]^-$ absorbs much less ($\epsilon = 3500$) than $[ICl_4]^-$. The quantum yields for the conversion from $[ICl_4]^-$ to $[ICl_2]^-$ were $\phi = 0.4$ at $\lambda_{irr} = 254$ nm and $\phi = 0.25$ at $\lambda_{irr} = 333$ nm. In addition to $[ICl_2]^-$, chlorine was formed as another photoproduct. In the product spectrum Cl_2 does not show up since it absorbs only weakly ($\lambda_{max} = 320$ nm, $\epsilon = 80$) [7]. Chlorine was identified by qualitative analysis (Chlorine Test Merckoquant 10043). It follows from these observations that the photolysis takes place according to the stoichiometry

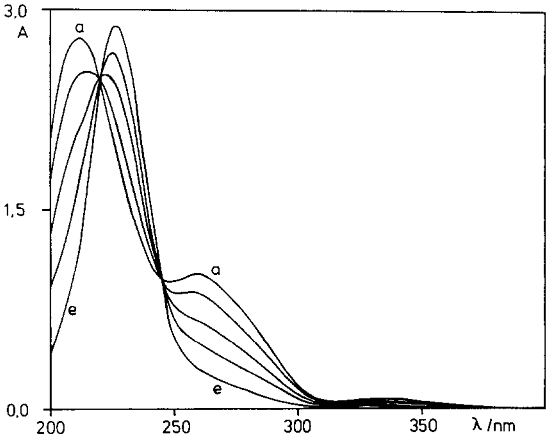

Fig. 1. Spectral changes during the photolysis of 5.64×10^{-5} M $[N(C_4H_9)_4][ICl_4]$ in CH_3CN at (a) 0, 1, 2.5, 5 and (e) 10 min irradiation time, with $\lambda_{irr} = 254$ nm and a 1-cm cell.

$$[I^{III}Cl_4]^- \longrightarrow [I^{I}Cl_2]^- + Cl_2$$

Chlorine, as one of the products, may undergo secondary reactions [5]. The reductive elimination of $[ICl_4]^-$ in CH_3CN also took place as a slow thermal reaction [5].

The anion $[ICl_4]^-$ has a square-planar structure [8, 9] (D_{4h}). The 5p orbitals of the central iodine are then split into $2a_{2u}$ and $3e_u$ orbitals [7]. With the chloride ligands located on the x and y axes, the $2a_{2u}$ orbital is derived from the p_z orbital which is nonbonding with regard to σ interaction. This is the nondegenerate HOMO of the complex and is occupied by the p^2 lone pair. As Jørgensen pointed out, it is quite interesting that the electronic structures of quadratic p^2 and d^8 complexes are rather similar, having a lone pair perpendicular to the plane of the four ligands [10]. The doubly degenerate $3e_u$ orbitals of $[ICl_4]^-$ are composed of the p_x and p_y orbitals. They are strongly σ antibonding and represent the LUMO of $[ICl_4]^-$. The lowest-energy electronic transition is a Laporte forbidden pp transition. It is assigned to the weak longest-wavelength band at $\lambda_{max} = 335$ nm [7]. The more intense bands of $[ICl_4]^-$ at shorter wavelength (<300 nm) belong certainly to ligand-to-metal charge-transfer (LMCT) transitions from the chloride ligands to the empty p_z ($3e_u$) orbital at the iodine.

The shorter-wavelength (<300 nm) LMCT excitation of $[ICl_4]^-$ initiates a very efficient reductive elimination of Cl_2. The nature of this LMCT excited state correlates well with the observed photoreaction. LMCT excitation is associated with the shift of electron density from the chloride ligands to the central iodine(III). In addition, the population of the degenerate $p_{x,y}$ orbitals leads to a Jahn–Teller distortion which could involve a contraction on the x (or y) and elongation on the y (or x) axis. In other

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words, the electron distribution and structure of the LMCT excited state of $[\mathrm{I^{III}Cl_4}]^-$ already reflects the product formation ($[\mathrm{I^{I}Cl_2}]^- + \mathrm{Cl_2}$). The reaction may proceed in a concerted fashion without any intermediates according to the stoichiometric equation.

As an alternative, product formation may occur by two subsequent one-electron transfer steps:

$$[\mathrm{I^{III}Cl_4}]^- \longrightarrow [\mathrm{I^{II}Cl_3}]^- + \mathrm{Cl}$$

$$[\mathrm{I^{II}Cl_3}]^- \longrightarrow [\mathrm{I^{I}Cl_2}]^- + \mathrm{Cl}$$

$$2\mathrm{Cl} \longrightarrow \mathrm{Cl_2}$$

While the first step would be light-induced, the second could take place as a fast thermal reaction. No attempt has yet been made to detect intermediates in order to distinguish between both mechanisms.

Upon longer-wavelength irradiation (>300 nm) into the pp band, the reductive elimination still occurs but with a lower quantum yield. It seems feasible that the pp excited state is partially deactivated to the reactive LMCT state. While the direct population of the LMCT state by Franck–Condon transitions requires higher energies, a radiationless transition from the pp state to the LMCT state may take place without a large activation barrier if the potential surface of the LMCT state extends to energies well below that of the pp state. Similar interpretations have been used to explain the photoredox chemistry of $[\mathrm{TeBr_6}]^{2-}$ [3] and certain Co(III) ammine complexes [11, 12].

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