Photoredox chemistry of bismuth trichloride in benzene

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Abstract

The electronic spectrum of $BiCl_3$ in benzene shows a long-wavelength absorption at $\lambda_{max} = 291$ nm which is assigned to a metal-localized sp transition. The excited state is emissive ($\lambda_{max} = 440$ nm), but only at low temperatures (in toluene glasses at 77 K). At room temperature the irradiation of $BiCl_3$ in benzene leads to a redox reaction, which yields elemental bismuth, HCl, biphenyl and chlorobenzene as final photoproducts. It is suggested that the photolysis is induced by a ligand-to-metal charge transfer (LMCT) excited state, which involves the promotion of an electron from weakly coordinated benzene to bismuth(III). This reactive LMCT state is populated from the initially excited sp state by radiationless deactivation.

Keywords: Bismuth; Arene complexes; Photochemistry

1. Introduction

Transition metal complexes with arene ligands represent an important family of organometallic compounds. Their properties, including electronic spectra and photochemistry [1,2], have been studied extensively. On the contrary, arene complexes of main group metals have attracted much less attention, although recent investigations revealed many interesting features of these compounds [3]. However, the electronic spectra and photochemistry of main group metal arene complexes have not yet been examined to our knowledge. The present work was undertaken to identify light-sensitive arene complexes of main group metals and to characterize their reactive excited states. As an initial target we selected solutions of $BiCl_3$ in benzene. Arene complexes of $BiCl_3$ have been known for a long time [4].

During recent years we have studied the optical properties of a variety of complexes of main group metals with an s^2 electron configuration [5], including $BiCl_4^-$ and $BiCl_6^{3-}$ [6]. The lowest excited states of s^2 complexes are of the metal-centered (sp), ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT) type [5]. Generally, the photolysis of s^2 complexes leads to photoredox reactions. The partici-

pation of arene ligands would be an important extension since the photochemistry of transition metal arene complexes is restricted to substitution reactions [1,2].

2. Results

Solutions of $BiCl_3$ in benzene were saturated with argon in order to avoid any complications associated with the presence of oxygen and humidity. The electronic spectrum of $BiCl_3$ in benzene (Fig. 1) shows a long-wavelength absorption at $\lambda_{max} = 291$ nm ($\varepsilon = 4000$ $1 \, mol^{-1} \, cm^{-1}$). Owing to the solvent cut-off, shorter wavelength bands could not be detected. At room tem-
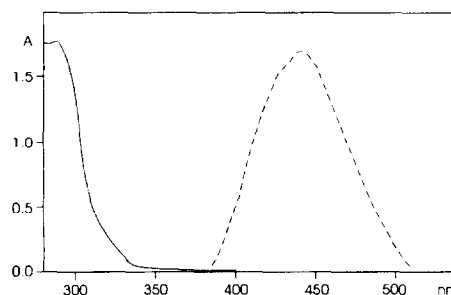

Fig. 1. Electronic spectra of 4.4×10^{-4} M $BiCl_3$ in arene solvents, 1 cm cell. Absorption (———) in benzene at room temperature; emission at $\lambda_{exc} = 300$ nm (- - - - -) in toluene at 77 K, intensity in arbitrary units.
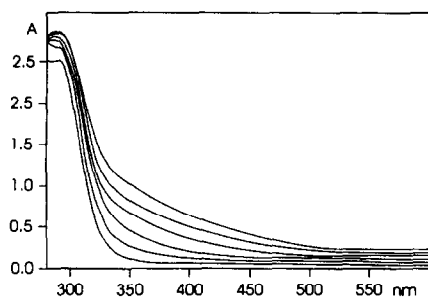
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Fig. 2. Spectral changes during the photolysis of $BiCl_3$ in benzene; $c = 6.4 \times 10^{-4}$ M, $\lambda_{irr} = 313$ nm, $t = 0, 30, 60, 90, 120, 150$ s, 1 cm cell.

perature an emission was not observed, while glasses of $BiCl_3$ in toluene showed a blue luminescence (Fig. 1) with $\lambda_{max} = 440$ nm at 77 K. The excitation maximum at 328 nm did not match the longest wavelength absorption at $\lambda_{max} = 291$ nm. However, since the solvent is still absorbing near 291 nm, the red shift of the excitation band seems to be an artifact.

Solutions of $BiCl_3$ in benzene are light sensitive. Upon irradiation ($\lambda_{irr} = 313$ nm) the colourless solution becomes yellow and dark brown at later stages of the photolysis owing to the formation of colloidal bismuth. Light scattering by the metal particles caused an increase of the optical density over the entire wavelength region (Fig. 2). After centrifuging the bismuth from the solution the remaining $BiCl_3$ could be determined spectrophotochemically. $BiCl_3$ disappeared with $\phi = 0.08$ at $\lambda_{irr} = 313$ nm. Hydrogen chloride, chlorobenzene, and biphenyl were formed as further photoproducts. As shown by gas chromatography, biphenyl was formed only in traces while chlorobenzene was a main product of the photolysis.

3. Discussion

The interaction of an arene and an s^2-metal ion can lead to different structural features ranging from a symmetrical η^6-coordination to various lower hapticities [3,4]. These geometrical variations, which have been detected in the solid state, seem to be indicative of a relatively weak bonding interaction in arene complexes of main group metals. Although the solution structure is unknown we assume, for simplicity, that in benzene $BiCl_3$ adopts a trigonal-pyramidal (C_{3v}) structure in analogy to the isoelectronic species $SnCl_3^-$ and $PbCl_3^-$ [7]. A benzene molecule may then fill the open coordination site of $BiCl_3$ in η^6 fashion. A qualitative MO scheme is presented in Fig. 3. Provided the interaction between benzene and $BiCl_3$ is indeed rather weak, slight deviations from this geometry should affect the electronic structure at Bi^{3+} only to a small extent. This assumption is supported by the observation that the

longest wavelength absorption of $BiCl_3$ in benzene at $\lambda_{max} = 291$ nm appears in the same wavelength region as those of $BiCl_4^-$ ($\lambda_{max} = 319$ nm) and $BiCl_6^{3-}$ ($\lambda_{max} = 333$ nm) [6]. Accordingly, the longest wavelength band of $BiCl_3$ in benzene is assigned to the metal-centered sp transition of the $BiCl_3$ moiety ($^1S_0 \rightarrow {}^3P_1$ for Bi^{3+} [5c,6] or $a_1 \rightarrow a_1^*$ for $BiCl_3$ in C_{3v} symmetry [5c,7]). This sp transition is apparently only slightly modified by the interaction with benzene (Fig. 3). Unfortunately, any other absorption of $BiCl_3 \times C_6H_6$ cannot be detected since benzene as the solvent cuts off the shorter wavelength region. Nevertheless, LMCT transitions from benzene to Bi(III) are expected to occur at relatively low energies in analogy to other Bi(III) complexes which contain reducing ligands [9,10]. CT absorption spectra of this type were also identified for aromatic electron donor–acceptor complexes with $TiCl_4$ as the oxidizing component [11]. According to Fig. 3, benzene to $BiCl_3$ LMCT transitions occur at higher energies than the lowest energy sp transitions.

While chloro complexes of Bi(III) show an emission at room temperature (e.g. $BiCl_6^{3-}$ with $\lambda_{max} = 475$ nm [5c,6]), the corresponding luminescence of $BiCl_3$ in toluene appears only at lower temperatures. At room temperature the emitting sp excited state is apparently deactivated to another excited state which is responsible for the photoreactivity of $BiCl_3$ in benzene. In agreement with the photoredox behaviour of $BiCl_3$ in benzene and in analogy to other Bi(III) complexes with reducing ligands [9,10], it is concluded that the reactive
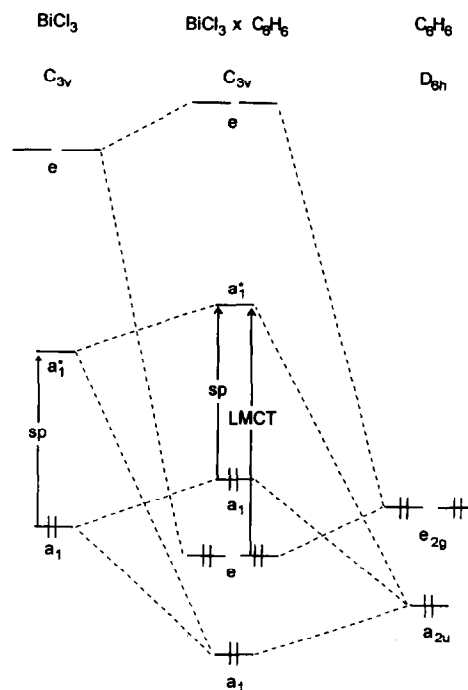

Fig. 3. Qualitative MO scheme of $BiCl_3 \times C_6H_6$ taking into account only the frontier orbitals. Adopted from Refs. [5c,7,8].
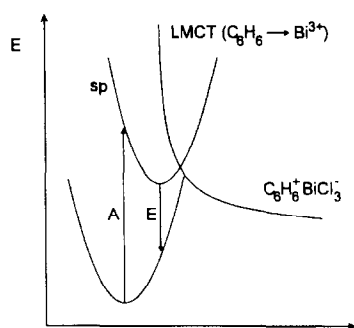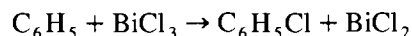
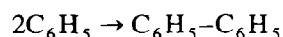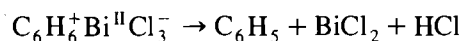Fig. 4. Potential energy surfaces for the ground and lowest energy excited states of $BiCl_3 \times C_6H_6$.

excited state of $BiCl_3 \times C_6H_6$ is of the LMCT type. The population of the reactive LMCT state following an initial sp excitation can be explained by a qualitative potential energy diagram (Fig. 4).

LMCT excitation of $BiCl_3 \times C_6H_6$ should generate the radical pair $C_6H_6^+ Bi^{II}Cl_3^-$ in the primary photochemical step. Product formation can be rationalized by the following scheme:

$$C_6H_6^+ Bi^{II}Cl_3^- \rightarrow C_6H_5 + BiCl_2 + HCl$$

$$2C_6H_5 \rightarrow C_6H_5\text{-}C_6H_5$$

$$C_6H_5 + BiCl_3 \rightarrow C_6H_5Cl + BiCl_2$$

$$3BiCl_2 \rightarrow Bi + 2BiCl_3$$

The low quantum yield of the photolysis may reflect an efficient back electron transfer within the primary radical pair. Cage escape leads to product formation. The elimination of HCl yields phenyl radicals which undergo two competing reactions. The dimerization to biphenyl is hampered by the low stationary concentration of the phenyl radicals during the photolysis. On the contrary, the facile interception of the phenyl radicals by $BiCl_3$ leads to an efficient formation of chlorobenzene in analogy to similar oxidative chlorinations by copper(II)chloride [12]. Finally, Bi(II) is not stable but undergoes a disproportionation with the generation of metallic bismuth.

4. Experimental section

4.1. Materials

$BiCl_3$ (Aldrich) was used as received. The solvents benzene and toluene were spectrograde.

4.2. Photolyses

The light source was a Hanovia Xe/Hg 977 B-1 (1000 W) lamp. Monochromatic light was obtained by

means of a Schoeffel GM 250-1 high-intensity monochromator. The photolyses were carried out at room temperature in 1 cm cells. Progress of the photolysis was monitored by UV–visible spectrophotometry. 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 photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated and equipped with an RkP-345 detector.

4.3. Instrumentation

Absorption spectra were measured with a Uvikon 860 and Uvikon 960 double-beam spectrophotometer. Emission spectra were obtained on a Hitachi 850 spectrofluorimeter which was equipped with a Hamamatsu 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency. Since benzene does not form glasses at 77 K, toluene was used for low-temperature measurements.

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