Preliminary communication

Photoredox reaction of [Cr(CO)₅I] induced by ligand to metal charge transfer excitation

Horst Kunkely and Arnd Vogler *

*Institut für Anorganische Chemie der Universität Regensburg, Universitätsstrasse 41,
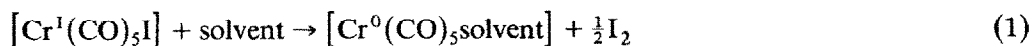D-8400 Regensburg (F.R.G.)*

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Abstract

The complex $[Cr^I(CO)_5I]$ is characterized by a long-wavelength absorption at λ_{max} 638 nm. This band is assigned to a ligand to metal charge transfer (LMCT) transition from iodide (π) to Cr^I (t_{2g}). Upon LMCT excitation the complex undergoes a photoredox reaction with a quantum yield $\phi \sim 0.01$ according to the equation: $[Cr^I(CO)_5I] + CH_3CN \rightarrow [Cr^0(CO)_5CH_3CN] + \frac{1}{2}I_2$. This reaction takes place also thermally.

Ligand to metal charge transfer (LMCT) excited states play an important role in the electronic spectroscopy [1–3] and photochemistry of transition metal complexes [2,3]. However, optical LMCT transitions have been rarely identified in the spectra of metal carbonyl complexes [1,4]. Since the central metal is generally not very oxidizing, LMCT absorption bands are expected to occur at rather short wavelength. Owing to interference by absorptions of a different origin an unambiguous detection of LMCT bands of carbonyl complexes seems to be rather difficult. Moreover, reactive LMCT states of metal carbonyl complexes are virtually unknown as far as we are aware. This is in contrast to the rich photochemistry of these compounds, which in most cases is initiated by ligand field (LF) and metal to ligand charge transfer (MLCT) excited states [4]. We report here the exceptional behavior of [Cr(CO)₅I], which is characterized by a reactive low-energy LMCT state.

The electronic absorption spectrum of [Cr(CO)₅I] (Fig. 1) displays absorption maxima at λ_{max} 638 nm ($\epsilon = 620$), ~ 450 nm (shoulder, $\epsilon = 400$), 361 nm ($\epsilon = 2800$), 286 nm ($\epsilon = 9800$, 234 nm ($\epsilon = 23000$), 220 nm (shoulder, $\epsilon = 19600$), and 200 nm ($\epsilon = 16600$). The green-blue color of this complex essentially arises from the longest-wavelength band at 638 nm. The compound is thermally unstable [5–8]. Behrends and Herrmann observed even in 1967 [6] that in many solvents a redox reaction takes place according eq. 1.
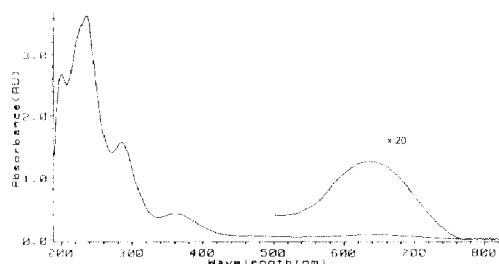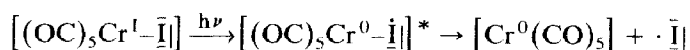
$$[Cr^I(CO)_5I] + solvent \rightarrow [Cr^0(CO)_5solvent] + \tfrac{1}{2}I_2 \qquad (1)$$

Fig. 1. Electronic absorption spectrum of 1.04×10^{-4} M [Cr(CO)$_5$I] in acetonitrile under argon (273 K, 1-cm cell).

We confirmed this observation. The conversion was accompanied by characteristic spectral changes. The absorption spectrum of [Cr(CO)$_5$I] in CH$_3$CN disappeared and was replaced by that of [Cr(CO)$_5$CH$_3$CN] (λ_{max} 388 nm, $\epsilon = 3500$). The progress of this reaction was monitored by measuring the decrease of extinction at 638 nm. The half-life of [Cr(CO)$_5$I] in acetonitrile was $t_{1/2}$ 10 min at 0°C and $t_{1/2}$ 2 min at 20°C.

This redox reaction does not only occur thermally but also photochemically. Upon irradiation into the long-wavelength band of [Cr(CO)$_5$I] (λ_{irr} 577 nm) the reaction was considerably accelerated, to an extent depending on the light intensity. Owing to the thermal instability of [Cr(CO)$_5$I] precise determination of the quantum yield was not possible but it was estimated to be $\phi = 10^{-2} \pm 50\%$. This estimate was made by comparing the extents of reaction amount for an irradiated solution and one kept in the dark. The photolysis was limited to less than 10% conversion at complete light absorption (absorbance ~ 2). The temperature of the solution was kept constant at 0°C to minimize the thermal reaction and to avoid any heating by the absorbed light. The absorbed light intensity (1.62×10^{-8} E s^{-1} at 577 nm) was determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with an RkP-345 detector.

The compound [Cr^I(CO)$_5$I] is a paramagnetic low-spin d^5 complex [5] with an electron hole in the d_π orbitals (t_{2g} in O_h symmetry). Owing to this hole the complex is rather oxidizing. It is reversibly reduced to [Cr^0(CO)$_5$I]$^-$ at $E_{1/2}$ 0.70 V vs. Ag/AgCl [8]. The combination of the oxidizing metal and reducing iodide ligand results in the thermal instability of [Cr(CO)$_5$I]. In addition an optical low-energy LMCT (I$^-$ to Cr^I) transition should be present. The long-wavelength band at λ_{max} 638 nm is thus logically assigned to this transition, which involves the promotion of an electron from a p_π (I) orbital to the t_{2g} (Cr) orbitals. This assignment is supported by the photochemical behavior of the complex and by comparison of its spectrum with those of related complexes. Other oxidizing low-spin d^5 complexes, such as [Fe^{III}(CN)$_5$X]$^{3-}$ [9] and [Ru^{III}(NH$_3$)$_5$X]$^{2+}$ [10] with X$^-$ = NCS$^-$, are also characterized by long-wavelength LMCT bands. In contrast, the reduced d^6 complex [Cr^0(CO)$_5$I]$^-$ shows no such low-energy absorption [11].

The photochemical redox reaction of [Cr(CO)$_5$I] reflects simply the electron distribution in the LMCT excited state*:

$$\left[(OC)_5Cr^I\!-\!\bar{I}|\right] \xrightarrow{h\nu} \left[(OC)_5Cr^0\!-\!\underline{I}|\right]^* \rightarrow \left[Cr^0(CO)_5\right] + \cdot\underline{I}|$$

The low quantum yield of product formation may arise from a competing deactivation of the LMCT state back to the ground state of $[Cr(CO)_5I]$. The primary product $[Cr(CO)_5]$ is coordinatively unsaturated, and scavenged by a solvent molecule to generate the stable complex $[Cr(CO)_5CH_3CN]$. In this context it is of interest that the well-known photoreactions of Co^{III} [3,12] and Ru^{III} ammine [13] complexes, which are also induced by LMCT excitation, seem to be much more complicated.

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