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Preliminary communication

Photoredox reaction of cobalticinium pentacarbonylmanganate(– I) induced by outer-sphere metal to metal charge transfer excitation

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Abstract

The salts $[Co(C_5H_5)_2]^+$ $[Mn(CO)_5]^-$ and $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$ show long-wavelength absorptions at λ_{max} 740 nm and 665 nm. These bands are assigned to metal to metal charge transfer (MMCT) transitions from Mn^{-I} to Co^{III} and Cr^{I}. Upon MMCT excitation the former ion pair is converted to $Co(C_5H_5)_2$ and $Mn_2(CO)_{10}$. The latter ion pair undergoes an analogous redox reaction as a thermal process. The thermal and the light-induced electron transfer are explained on the basis of the Hush model.

Ion pairs composed of a reducing and an oxidizing metal complex are well known to display a new electronic absorption band which belongs to an intermolecular or outer-sphere (OS) charge transfer (CT) transition from the reducing to the oxidizing complex [1–3]. In many cases it has been shown that this OS CT excitation leads to stable photoproducts. Quite recently organometallic ion pairs characterized by such optical OS CT transitions have been also discovered [4–8]. The ion pairs $[Co(C_5H_5]^+$ $[Co(CO)_4]^-$ [7] and $[Co(CO)_3(PPh_3)_2]^+$ $[Co(CO)_4]^-$ [8] were found to undergo photoredox reactions upon OS metal to metal (MM) CT excitation. Since this type of light-induced electron transfer may be of general significance in organometallic photochemistry we looked for further examples. Our attention was drawn to several ion pairs which had been reported to exhibit remarkable colours: $[Co(C_5H_5)_2]^+$ $[FeH(CO)_4]^-$ (rust-brown) [9], $[Co(C_5H_5)]^+$ $[Cr(C_5H_5)(CO)_3]^-$ (violet-brown) [9], $[Cr(C_6H_6)_2]^+$ $[Cr(C_5H_5)(CO_3]^-$ (green) [9], $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$ (green) [10], and $[Co(C_5H_5)_2]^+$ $[Mn(CO)_5]^-$ (dark violet) [10]. The colours certainly do not arise from the separate complex ions but must originate from the ion pairs. We suspected that the colours are due to low-energy OS MMCT bands. In the present communication we report first results on the last two ion pair species.

The salts $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$ and $[Co(C_5H_5)_2]^+$ $[Mn(CO)_5]^-$ are soluble only in rather polar organic solvents such as acetone. In these solvents, which were deaerated by saturation with argon, the intense green and violet colors of the solid salts disappear. By analogy to findings for $[Co(C_5H_5)_2]^+$ $[Co(CO)_4]^-$ [7], it is suggested that the dissappearance of the color is due to the dissociation of the ion pairs. In the solid state the absorption spectra of the two salts were obained by scattered transmission spectroscopy of deaerated aqueous suspensions of the powdered materials. The salts are characterized by long-wavelength absorptions at λ_{max} 665 nm for $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$ and λ_{max} 740 nm for $[Co(C_5H_5)_2]^+$ $[Mn(CO)_5]^-$. These bands are apparently responsible for the green and violet colours of the solids. The components of the ion pairs are colourless ($Mn(CO)_5{}^-$) or yellow ($Co(C_5H_5)_2{}^+$ and $Cr(C_6H_6)_2{}^+$) and do not absorb above 500 nm.

As previously observed by Hieber and Schropp [10] the salt $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$ is thermally unstable, and decomposes according to eq. 1.

$$\left[Cr^{I}(C_6H_6)_2\right]^+ \left[Mn^{-I}(CO)_5\right]^- \rightarrow \left[Cr^{0}(C_6H_6)_2\right] + \tfrac{1}{2}\left[Mn^{0}_{2}(CO)_{10}\right] \qquad (1)$$

The salt $[Co(C_5H_5)_2]^+$ $[Mn(CO)_5]^-$ is thermally rather stable, but undergoes an analogous redox reaction (eq. 2) upon long-wavelength irradiation into the 740 nm band (580 nm $< \lambda_{irr} <$ 680 nm).

$$\left[Co^{III}(C_5H_5)_2\right]^+ \left[Mn^{-I}(CO)_5\right]^- \rightarrow \left[Co^{II}(C_5H_5)_2\right] + \tfrac{1}{2}\left[Mn^{0}_{2}(CO)_{10}\right] \qquad (2)$$

This reaction was driven to completion when the salt was incorporated into a transparent KBr pellet as used for IR spectroscopy. The salt in form of the ion pair was apparently preserved in the KBr matrix, as indicated by the presence of the violet colour (band at 740 nm). Upon irradiation (580 nm $< \lambda_{irr} <$ 680 nm) the violet colour disappeared. Simultaneously, the IR spectrum of $[Mn(CO)_5]^-$ ($\bar{\nu}_{max}$(CO) 1932, 1896, and 1845 cm^{-1}) [10] was completely replaced by that of $[Mn_2(CO)_{10}]$ ($\bar{\nu}_{max}$ 2060, 2014, and 1989 cm^{-1}) [10].

The long-wavelength absorptions of $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$ at λ_{max} 665 nm and $[Co(C_5H_5)_2]^+$ $[Mn(CO)_5]^-$ at λ_{max} 740 nm, which are absent from the spectra of the component complex ions, are logically assigned to OS MMCT transitions from the reducing Mn^{-I} to the oxidizing Cr^{I} and Co^{III}. This assignment is also consistent with the photoactivity of the latter ion pair. The MMCT transition generates $[Co(C_5H_5)_2]$ and the radical $Mn(CO)_5$ which yields $[Mn_2(CO)_{10}]$ upon dimerization. In the case of $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$ the same processes occur thermally.

The optical MMCT transitions as well as the thermal and photochemical redox behaviour can be understood in terms of the Hush model for thermal and optical electron transfer [1–3,11]. The starting ion pair $[Co^{III}(C_5H_5)_2]^+$ $[Mn^{-I}(CO)_5]^-$ is represented by the lefthand potential curve of Fig. 1a. When an electron is transfered from Mn^{-I} to Co^{III} the righthand curve for the radical pair $[Co^{II}(C_5H_5)_2]$ $[Mn^{0}(CO)_5]$ is obtained. Upon reduction of Co^{III} the cobalt–carbon distance undergoes a relatively large extension from 2.028 Å [12,13] to 2.096 Å [13,14] because the electron is added to an antibonding ($e_{1g}^{\star}$) *d*-orbital [13]. This accounts for the large horizontal displacement of the potential curve for the radical pair. The starting ion pair is rather stable because the thermal electron transfer requires a large activation energy E_a. However, the curve of the radical pair can be reached by the optical MMCT transition. The formation of stable products depends on the

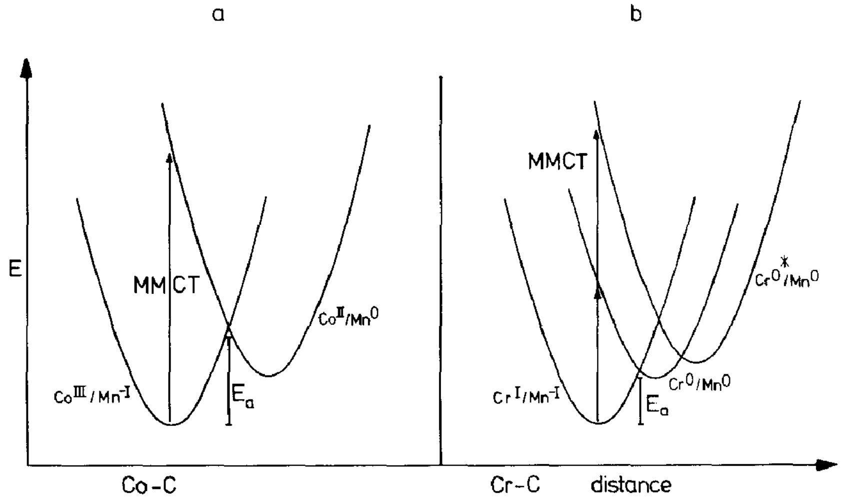

Fig. 1. Potential energy versus metal–carbon distances for the redox couples (a) $[Co^{III}(C_5H_5)_2]^+$ $[Mn(CO)_5]^-$ and $[Co^{II}(C_5H_5)_2][Mn^0(CO)_5]$ with the electron configuration e_g^{*1} at Co^{II}; (b) $[Cr^I(C_6H_6)_2]^+$ $[Mn^{-I}(CO)_5]^-$ and $[Cr^0(C_6H_6)_2][Mn^0(CO)_5]$ with the electron configuration a_{1g}^1 at Cr^I, a_{1g}^2 at Cr^0 and a_{1g}^1 e_{1g}^{*1} at Cr^0 *.

competition between back electron transfer and coupling of two $Mn(CO)_5$ radicals. This coupling is apparently fast enough. In the case of the ion pair $[Co(C_5H_5)_2]^+$ $[Co(CO)_4]^-$ the MMCT excitation generates the radical pair $[Co(C_5H_5)_2][Co(CO)_4]$ which undergoes a complete back electron transfer [7].

The thermal instability of the ion pair $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$ seems surprising since the potentials of the redox couples $[Cr(C_6H_6)_2]^{0/+}$ (−0.8 V vs. SCE) [15] and $[Co(C_5H_5)_2]^{0/+}$ (−0.9 V vs. SCE) [13] are very similar. However, for the ion pair $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$ the situation is more complicated, since Cr^I with the d^5 electron configuration provides two low-energy acceptor orbitals. The electron transfer from Mn^{-I} to Cr^I thus results in two different potential curves (Fig. 1b). The lower curve undergoes only a small horizontal displacement since the electron is accepted into the half-occupied a_{1g} orbital of Cr^I which is non-bonding. This assumption is supported by the fact that the chromium–carbon distance of $[Cr(C_6H_6)_2]$ is very similar to that of $[Cr(C_6H_6)_2]^+$ [15]. In contrast, the higher-energy curve is shifted to much larger Cr–C distances, since the acceptor orbital at Cr^I is now the same antibonding e_{1g}^* orbital as that of $[Co(C_5H_5)_2]^+$. We assign the absorption band of $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$ at λ_{max} 665 nm to the Mn^{-I} to Cr^I MMCT transition terminating at the higher-energy curve. It is assumed that a second MMCT transition to the lower curve occurs at much lower energies in the near IR region, which is not accessible with our instrumentation for solid samples. However, this curve now provides the small activation energy E_a for thermal electron transfer which is responsible for the thermal instability of the salt $[Cr(C_6H_6)_2]^+$ $[Mn(CO)_5]^-$.

Conclusion

Optical OS MMCT transitions seem to be of rather general significance in the electronic spectroscopy of organometallic compounds. MMCT excitation extends the range of organometallic photoredox processes. The observed photoactivity is also exceptional, since it occurs in the solid state.

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