Inorganica Chimica Acta, *77* (1983) L11–L12

Photocatalytic Systems.
LVIII.* Electron Transfer in Copper(I)/Octacyanomolybdate(V) Ion Pairs Generated by IT Excitation

H. HENNIG**, A. REHOREK, D. REHOREK, Ph. THOMAS

Sektion Chemie der Karl-Marx-Universität Leipzig, DDR - 7010 Leipzig, Liebigstr. 18, G.D.R.

and D. BÄZOLD

Sektion Chemie der Friedrich-Schiller-Universität Jena, DDR - 6900 Jena, Am Staiger 3, G.D.R.

Received February 15, 1983

Introduction

Due to their unusual spectral behaviour, mixed-valence compounds have attracted considerable interest [1, 2]. However, little is known about their photochemical reactivity, although Vogler *et al.* [3, 4] have shown that mixed-valence compounds undergo electron transfer between different redox sites upon irradiation into intervalence charge-transfer (IT) bands. Since mixed-valence compounds under certain circumstances exhibit IT bands in the long-wavelength spectral region [2], they could provide a reliable route for spectral sensitization of coordination compounds [5].

However, any permanent chemical changes connected with IT excitation will be restricted by fast back electron transfer. Recently we have been able to show that long-wavelength absorption bands observed by mixing of aqueous solutions of octacyanomolybdate(IV) and higher-valent transition metal ions and cationic metal complexes, respectively, are related to IT transitions of mixed-valence ion pair associates [6]. In this paper we report preliminary results of the direct estimation of the electron transfer rate of $Cu^+/Mo(CN)_8^{3-}$ ion pairs generated by IT excitation of $Cu^{2+}/Mo(CN)_8^{4-}$ associates.

Experimental

$Cu(NO_3)_2 \cdot 3H_2O$ (Merck) and $K_4[Mo(CN)_8] \cdot 2H_2O$ [6] (5×10^{-4} *M*) were dissolved in a glycerol/water mixture (1:1 v/v). Frozen solutions were irradiated at 93 K within an ESR cavity (ERS 200, ZWG Berlin) using a high-pressure mercury lamp (HBO 200, VEB Narva Berlin) equipped with a cut-off glass filter ($\lambda > 450$ nm). Under these conditions a strong ESR signal of $[Mo(CN)_8]^{3-}$ was observed. The signal intensity P_t *vs.* time t after switching off the light-source was followed by ESR.

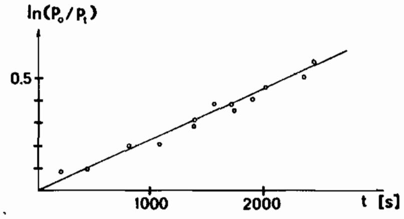

Fig. 1. ESR signal intensity $[\ln(P_o/P_t)]$ of $[Mo(CN)_8]^{3-}$ as a function of time (t) after irradiation of the mixed-valence associate $Cu^{2+}/[Mo(CN)_8]^{4-}$. ($T = 93$ K; $\lambda^{irr} = h \cdot \nu_{IT} = 436$ nm).

Results and Discussion

The IT band of $Cu^{2+}/Mo(CN)_8^{4-}$ ion pairs was found to appear at 20.2×10^3 cm^{-1} ($\Delta\bar{\nu}_{1/2} = 6.4 \times 10^3$ cm^{-1}; $\epsilon = 750 \pm 50$) [6]. Under the conditions mentioned above, irradiation leads to IT excitation exclusively. Thus, growth of the Mo(V) signal intensity corresponds to a photochemically induced electron transfer (1).

$$Cu^{2+}, [Mo^{IV}(CN)_8]^{4-} \underset{k_{-1}}{\overset{h \cdot \nu_{IT}}{\rightleftharpoons}} Cu^+, [Mo^{V}(CN)_8]^{3-} \qquad (1)$$

The lifetime of the Cu(I)/Mo(V) valence isomer essentially depends on the rate of back electron transfer (k_{-1}). In our experiments back electron transfer was indicated by a decrease of Mo(V) ESR signal intensity. At room temperature back electron transfer is expected to be very fast, and therefore cannot be followed by use of conventional ESR spectroscopy. Only traces of Mo(V) were detectable after switching off the light source. However, at lower temperatures detection of back-electron transfer can be readily achieved by ESR spectroscopy.

Measuring signal intensity P_o and P_t at time $t = 0$ and $t = t$ after switching off the light-source, respectively, a plot of (P_o/P_t) *vs.* time t gave a straight line (see Fig. 1) and using the slope k_{-1} has been estimated to be $(2.74 \pm 1.2) \cdot 10^{-4}$ s^{-1} ($T = 93$ K).

According to the theory [1], there is a close relationship between the energy E_{op} of the optical IT transition and the barrier of the thermal electron transfer E_{th} (*cf.* Fig. 2, eqn. (2)).

$$E_{th} = \frac{E_{op}^2}{4(E_{op} + E_o)} - H \qquad (2)$$

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*Part LVII, see Ref. [9].

**Author to whom correspondence should be addressed.

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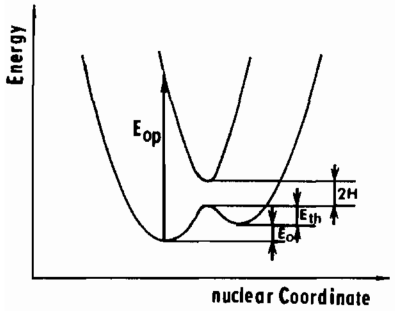

Fig. 2. Potential energy diagram as illustration of the relationship between optical IT transition (E_{op}) and the rate of thermal back electron transfer (*cf.* eqns. (2), (3), and (4), respectively.

The electronic interaction matrix element H is related to the extent of electron delocalization α^2 as given in eqn. (3).

$$H \simeq E_o \cdot \alpha^2 \qquad (3)$$

Both E_{op} and α are available from optical absorption spectra [6]. α^2 was shown to be 0.004 for $Cu^{2+}[Mo(CN)_8]^{4-}$ ion pairs, thus leading to H = 15.3 kJ·mole^{-1}. Neglecting entropy changes, the overall energy change E_o may be evaluated from standard redox potentials of $[MoCN)_8]^{4-}$ ($E^\theta(Mo^V/Mo^{IV})$ = 0.84 V) and Cu^{2+} ($E^\theta(Cu^{2+}/Cu^+)$ = 0.17 V), respectively.

Hence, for the thermal barrier of back electron transfer, E_{th}, one obtains E_{th} = 32.4 kJ·mole^{-1}.

The experimentally determined rate constant k_{-1} is in a reasonable agreement with the theoretically predicted value. The latter is given by eqn. (4) [7].

$$k_{-1} = \frac{2H^2}{h} \cdot \left(\frac{\pi^3}{E_{th} \cdot RT}\right)^{1/2} \cdot \exp[-E_{th}/RT] \qquad (4)$$

Using the data given above k_{-1} will be found to be 8.2×10^{-4} s^{-1} at 93 K. For room temperature (T = 295 K) eqn. (4) leads to $k_{-1} = 1.3 \times 10^9$ s^{-1}.

Hence, at room temperature the lifetime of photogenerated Mo(V) will be about 1 ns in $Cu^+/Mo(CN)_8^{3-}$ ion pairs. Any Mo(V) detectable in solution even shortly after irradiation at room temperature, therefore, is due to diffusional escape from Cu(I)/Mo(V) ion pairs. The recently reported [8, 9] sequential two-photon redox processes of $Cu^{II}/Mo^{IV}(CN)_8^{4-}$ ion pairs very likely involve liberation of Mo(V) as well. More quantitative measurements are planned in order to understand photoreactions of mixed-valence ion pairs.

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