Pressure as the Key Parameter to distinguish between Associative Charge-transfer and Dissociative Ligand-field Photochemistry. CO Substitution in $W(CO)_4$(1,10-phenanthroline)

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The pressure dependence of the quantum yield for photosubstitution of CO in $W(CO)_4$(1,10-phenanthroline) was studied at different excitation wavelengths: volumes of activation of -12 cm^3 mol^{-1} for the reaction following irradiation into the charge-transfer band and $+8$ cm^3 mol^{-1} for the reaction following short wavelength excitation are clear evidence for an associative reaction of the charge-transfer excited state and a dissociative reaction of the energetically higher ligand-field excited state, respectively.

The photochemistry and photophysics of $W(CO)_4$(phen) (phen = 1,10-phenanthroline) have received significant attention from various groups mainly because of the important role played by both ligand-field (LF) and charge-transfer (CT) excited states in such processes. A simplified energy state diagram is presented in Figure 1 along with the possible chemical and physical deactivation routes. Detailed studies of the solvatochromism of the emission spectra, the luminescence excitation spectrum, and the resonance Raman excitation profile, led to the assignment of the observed absorption bands to specific electronic transitions.[1,2] The lowest energy absorption and emission bands were assigned to MLCT transitions.

The first systematic investigation[3] of the photochemistry of $W(CO)_4$(phen) demonstrated that the quantum yield for the reaction (1) increases substantially with increasing energy of excitation. This was interpreted in terms of the higher reactivity of the electronic excited LF states as compared to the MLCT states. The photo-activity of the lower lying MLCT states remains a controversial issue in the literature. On the one hand it is assumed that the observed photosubstitution proceeds purely dissociatively, and similarly to the case of the hexa- and penta-carbonyl complexes without the participation

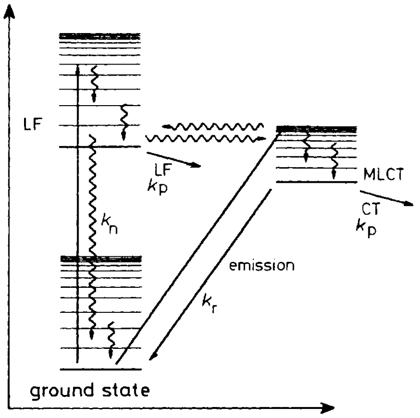

Figure 1. Electronically excited states for $W(CO)_4$(phen). LF = ligand field excited state, MLCT = metal-to-ligand-charge-transfer excited state. The rate constants for radiative, nonradiative and chemical deactivation are denoted by k_r, k_n, and k_p, respectively. The superscript LF or CT denotes whether LF or MLCT states are responsible for the given reaction pathway.

of MLCT states in the reaction step, *i.e.*, a low energy triplet LF state is populated thermally from a slightly lower lying MLCT state.[4] In this way all the observed chemistry occurs from a LF state. On the other hand it is argued that the MLCT states themselves are photoactive.[5] For a series of complexes of the type $W(CO)_4NN$ (NN = substituted 1,4-diazabutadiene, phen, and substituted phen) it was shown that the observed quantum yield depends strongly on the concentration and basicity of the entering ligand, the Tolman cone angle for L = phosphine, and the steric hindrance on NN.[5] This also accounts for the discrepancy between reported quantum yields, where different entering ligands were used.[3,4,6] These trends all point towards the possible operation of an associative photosubstitution mechanism.

$$W(CO)_4(phen) + L \longrightarrow \textit{cis}\text{-}W(CO)_3(L)(phen) + CO \qquad (1)$$

(L = ligand with P or N donor atom)

On excitation in the u.v. region, photosubstitution occurs from an energetically higher lying LF excited state, which also accounts for the higher quantum yields at shorter wavelengths. Excitation at longer wavelengths is accompanied by a drastic decrease in quantum yield which could be due to a thermal back-population of the LF state from the lower lying MLCT state.[4] However, variation of the excitation wavelength within the MLCT absorption band does not affect the observed quantum yield[5] although lower lying MLCT states are populated at longer wavelengths so that the energy gap to the lowest excited LF state increases and thermal back-population becomes less important. The residual quantum yield observed at longer wavelengths can therefore be interpreted in terms of direct photo-activity of the MLCT states. A correlation between the photosubstitution quantum yield and the resonance Raman spectra suggested that in the MLCT states the energy density is delocalized over the *cis* carbonyl ligands of $W(CO)_4(phen)$.[6,7] This reduces the π-back bonding ability to *cis*-CO and destabilizes the W–CO bond, such that both dissociative and associative substitution reactions from the MLCT state are possible. We have studied the pressure dependence of these processes in order to resolve the controversy.

Spectral changes observed during reaction (1) for L = PEt_3 in toluene are presented in Figure 2, from which it follows that the photosubstitution process can be studied without any difficulty. The pressure dependence of the quantum yield was studied for MLCT excitation at 546 nm and for LF excitation at 366 nm. The observed data are plotted as ln (ϕ/ϕ_0) *vs.* p in Figure 3, where ϕ_0 is the quantum yield at ambient pressure. A higher ligand concentration was selected for the irradiation at 546 nm owing to the low quantum yield in this region. The quoted volumes of activation were calculated in the usual way from the slope $(-\Delta V_{\Phi}^{\ddagger}/RT)$ of the line in Figure 3. Most important, we find that MLCT excitation yields a significant negative volume of activation whereas LF excitation yields a positive volume of activation. Before we interpret these numbers it is important to refer to the underlying relationships.

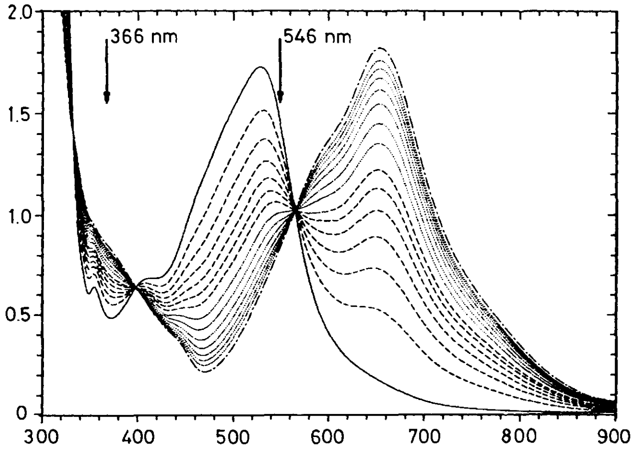

Figure 2. U.v.-visible spectral changes observed during the photochemical reaction $W(CO)_4(phen) + PEt_3 \longrightarrow W(CO)_3(PEt_3)(phen) + CO$. —— = $W(CO)_4(phen)$; – · – · – = $W(CO)_3(PEt_3)(phen)$. The arrows denote the irradiation wavelengths, leading to LF (366 nm) and MLCT (546 nm) photochemistry.

For the energy diagram given in Figure 1, the total observed quantum yield is given by equation (2), which reduces to the expression in equation (3) for LF excitation (at low wavelength) since $\phi_p^{LF} \gg \phi_p^{CT}$ and $k_p^{LF} + k_r^{LF} \ll k_n^{LF}$. For the situation in which the reaction occurs from the MLCT state, equation (4) represents the corresponding expression which can be simplified since $k_p^{CT}[L] + k_r^{CT} \ll k_n^{CT}$. On the assumption that non-radiative deactivation is not very pressure sensitive, which is usually the case,[8] the corresponding volumes of activation can be expressed as in equations (5) and (6) for equations (3) and (4), respectively. It follows that the determined $\Delta V_{\Phi}^{\ddagger}$ represent the volumes of activation for the photochemical reaction steps with rate constants k_p^{LF} and k_p^{CT}, respectively.

$$\phi_p^{tot} = \phi_p^{LF} + \phi_p^{CT} \qquad (2)$$

$$\phi_p^{tot} \approx \phi_p^{LF} = \frac{k_p^{LF}}{k_p^{LF} + k_n^{LF} + k_r^{LF}} \approx \frac{k_p^{LF}}{k_n^{LF}} \qquad (3)$$

$$\phi_p^{tot} \approx \phi_p^{CT} = \frac{k_p^{CT} \cdot [L]}{k_p^{CT} \cdot [L] + k_n^{CT} + k_r^{CT}} \approx \frac{k_p^{CT} \cdot [L]}{k_n^{CT}} \qquad (4)$$

$$\Delta V^{\ddagger}(k_p^{LF}) \approx \Delta V^{\ddagger}(\phi^{LF}) = -RT\mathrm{d}(\ln \phi^{LF})/\mathrm{d}P \qquad (5)$$

$$\Delta V^{\ddagger}(k_p^{CT}) \approx \Delta V^{\ddagger}(\phi^{CT}) = -RT\mathrm{d}(\ln \phi^{CT})/\mathrm{d}P \qquad (6)$$

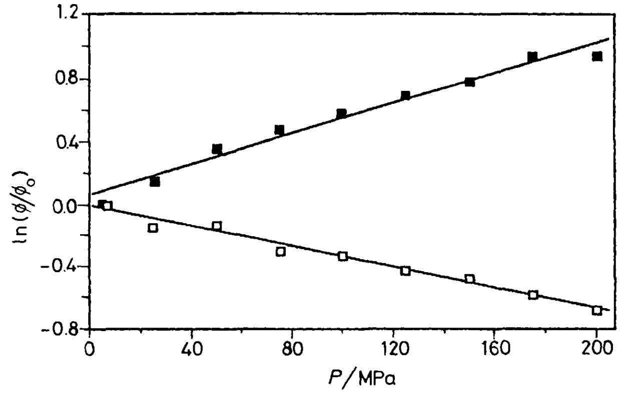

Figure 3. Pressure dependence of the quantum yield of the photochemical reaction: $W(CO)_4(phen) + PEt_3 \longrightarrow W(CO)_3(PEt_3)(phen) + CO$, as a function of irradiation wavelength at 298 K. ■, λ_{irr} = 546 nm, $[PEt_3]$ = 0.135 M, $\phi_0 = 6.0 \times 10^{-3}$, $\Delta V_{\phi}^{\ddagger} = -12.0$ cm^3 mol^{-1}; □, $\lambda_{irr.}$ = 366 nm, $[PEt_3]$ = 0.0135 M, $\phi_0 = 1.8 \times 10^{-2}$, $\Delta V_{\phi}^{\ddagger} = +8.1$ cm^3 mol^{-1}.

On excitation in the u.v. region we only expect to observe LF photolysis, such that the value of $\Delta V_{\Phi}^{\ddagger}$ of $+8.1 \pm 0.5$ cm^3 mol^{-1} is a strong indication for a dissociative substitution mechanism. A number of thermal substitution reactions of metal carbonyl complexes have revealed typical $\Delta V^{\ddagger}$ values of around +20 cm^3 mol^{-1} for the dissociation of CO.[9] The significantly smaller value observed here for the photochemical reaction can be ascribed to the increase in volume of *ca.* 10 cm^3 mol^{-1} on LF excitation due to bond lengthening. A similar trend was observed for the photo-dissociation of NH_3 in Rh^{III} ammine complexes[8,12,13] with typical $\Delta V_{\Phi}^{\ddagger}$ values ranging from 1 to 9 cm^3 mol^{-1}. Our present number of +8 cm^3 mol^{-1} for the dissociation of CO fits nicely into this range of data especially since the partial molar volumes of CO and NH_3 are not too different (*ca.* 35 and 25 cm^3 mol^{-1}, respectively, where the value for CO was estimated from the density of liquid CO at its boiling point). The negative volume of activation (-12.0 ± 0.7 cm^3 mol^{-1}) observed on CT excitation underlines the validity of an associative substitution process originating from the MLCT excited state. This volume decrease should depend on the size of the entering ligand, an aspect presently under investigation. For MLCT excitation there is no complication as discussed above for LF excitation since the partial molar volume of the CT excited state is generally known to be significantly smaller than that of the LF excited state and close to that of the ground state.[8] The interpretation of the volume of activation data for reaction (1) is simplified by the fact that we are dealing mainly with intrinsic volume changes since no major contribution from changes in electrostriction are expected during such reactions of neutral complexes and ligands.

We therefore conclude that CT excitation of $W(CO)_4(phen)$ definitely results in an associative substitution process, the partial oxidation of the central metal atom on MLCT excitation presumably being responsible for the activation of this reaction route. The significant difference in $\Delta V_{\Phi}^{\ddagger}$ for LF and MLCT excitation clearly underlines the different substitution modes operating from these states and supports earlier arguments in favour of the photoactivity of the MLCT states in such complexes.[5—7] Gray and co-workers[14] also suggested an associative mechanism for the photosubstitution of isonitriles in $W(CNR)_6$ (R = various organic residues) by pyridine. It is also noteworthy that the pressure dependence of the emission lifetime of $Cu(2,9\text{-}Me_2phen)_2^+$ suggests an associative reaction mode for radiationless deactivation from a MLCT excited state.[15] Finally, the results of the present study underline the value of pressure as a key parameter to distinguish between associative and dissociative photosubstitution mechanisms.

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