

A KINETIC STUDY OF THE THERMAL AND PHOTOSUBSTITUTION REACTION
 $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}(\text{NCC}_6\text{H}_5)][\text{PF}_6] + \text{CH}_3\text{CN} \rightleftharpoons$
 $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}(\text{NCCH}_3)][\text{PF}_6] + \text{C}_6\text{H}_5\text{CN}$

SÍLVIA M.B. COSTA, ALBERTO R. DIAS and FERNANDO J.S. PINA

Centro de Química Estutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex (Portugal)

(Received February 26th, 1981)

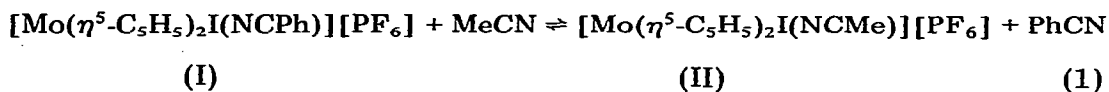
Summary

The kinetic study of the thermal and photochemical reaction $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}(\text{NCPH})][\text{PF}_6] + \text{MeCN} \rightleftharpoons [\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}(\text{NCMe})][\text{PF}_6] + \text{PhCN}$ in 1,2-dimethoxyethane, using excess MeCN and PhCN is described. The inverse of the pseudo first order constants for the forward and reverse reactions varies linearly with $[\text{PhCN}]/[\text{MeCN}]$ and $[\text{MeCN}]/[\text{PhCN}]$, respectively, while the inverse of the quantum yield for the disappearance of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}(\text{NCPH})][\text{PF}_6]$ varies linearly with $[\text{PhCN}]/[\text{MeCN}]$. The results indicate a dissociative mechanism for both the thermal and photosubstitution reactions.

Introduction

Our previous studies [1] on the photochemistry of complexes of the type $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{X}(\text{L})][\text{PF}_6]$, X = halide, L = PPh₃, py, CH₃CN, CO, have shown that monosubstitution is associated with ligand field excited states, in agreement with the general pattern observed in photosubstitution reactions [2]. In particular, these states are very efficient in the photosubstitution of mononuclear metal carbonyls [3], and in such cases a dissociative mechanism was proposed. However, other studies on the thermal and photochemical behaviour of complexes containing the $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2$ (M = Mo, W) moiety [4] have shown the need for kinetics studies in order to gain further insight into the mechanisms involved, and in particular to distinguish between an associative mechanism (probably occurring through a $\eta^5\text{-}\eta^3$ haptotropic shift [5]) and a dissociative one.

To initiate such studies we examined the reaction represented by eq. 1;



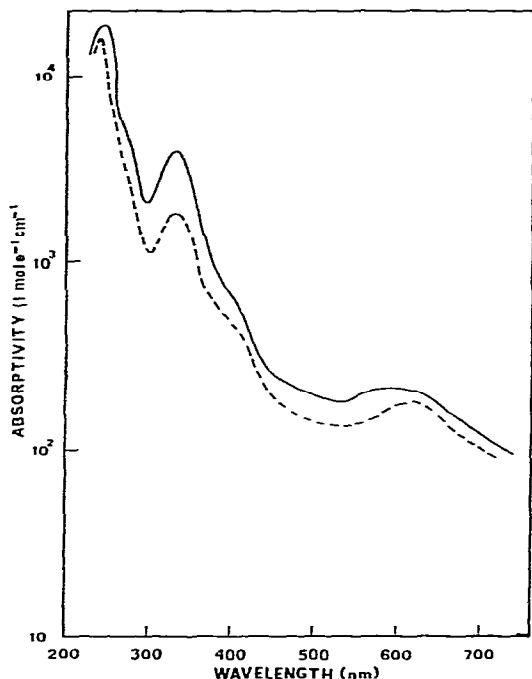


Fig. 1. Electronic spectra in 1,2-dimethoxyethane: ———— $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MoI}(\text{NCPh})][\text{PF}_6]$, - - - - $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MoI}(\text{NCMe})][\text{PF}_6]$.

we chose this reaction because of the thermal and photochemical lability of complexes I and II, and also because the electronic spectra of these complexes (Fig. 1) are such that the reaction can be monitored spectrophotometrically.

Experimental

All preparation and further manipulations were carried out under dry nitrogen unless otherwise stated. Solvents were dried over molecular sieves and distilled. Compounds $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}(\text{L})][\text{PF}_6]$, $\text{L} = \text{MeCN}, \text{PhCN}$, were prepared and purified according to the reported methods [6]. Spectrophotometric measurements were carried out using a 1 cm cell with a degassing bulb attached. The samples were degassed using three cycles (freeze-pump-thaw) to 10^{-4} Torr. The cell was then brought to atmospheric pressure by introducing nitrogen. The cell was maintained at constant temperature in a thermostated bath and then transferred rapidly to a Perkin-Elmer 124 spectrophotometer for determination of the absorption at a suitable wavelength. The concentration of species I and II were determined (at 330 nm and confirmed at 530 nm) using the system of equations $A_t = a_1c_1 + a_2c_2$ and $c_0 = c_1 + c_2$ where A_t is the absorption at the moment t (at 330 nm or 530 nm), a and c represent the molar absorbance, and the concentration (at the moment t) of species I and II, and c_0 represents the initial concentration of I.

For the photochemical experiments the samples were irradiated with a 250 W mercury discharge lamp and the $\lambda = 435.8$ nm band was selected using the

appropriate glass filters. Quantum yield measurements were made using a ferrioxalate actinometer [7].

Equations

Thermal reactions. The sequence for a dissociative mechanism is represented by eqs. 2–5 and that for an associative mechanism by eqs. 6–9.



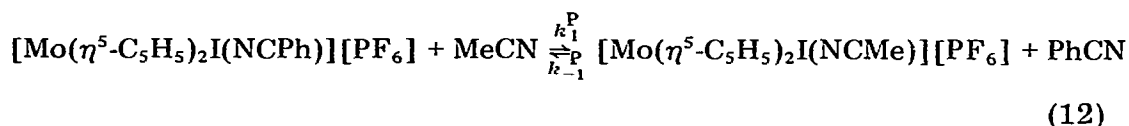
where $A = [\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}(\text{NCPh})][\text{PF}_6]$, $B = \text{MeCN}$, $C = \text{PhCN}$, $D = [\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}(\text{NCMe})][\text{PF}_6]$, $X = [\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}]^+$ and $Y = [\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{I}(\text{NCMe})(\text{NCPh})][\text{PF}_6]^*$. Using the steady-state approximation for species X and Y we obtain, eqs. 10 and 11, respectively. Dissociative:

$$-\frac{dA}{dt} = \frac{k_1 k_3 [B]}{k_2 [C] + k_3 [B]} [A] - \frac{k_2 k_4 [C]}{k_3 [B] + k_2 [C]} [D] \quad (10)$$

Associative:

$$-\frac{dA}{dt} = \frac{k'_1 k'_4 [A][B]}{k'_2 + k'_3} - \frac{k'_2 k'_3 [C][D]}{k'_2 + k'_3} \quad (11)$$

When a large excess of B and C are present, reaction 1 will become a pseudo first order reversible reaction (eq. 12).



* In Y, $(\eta\text{-C}_5\text{H}_5)_2$ implies no specific ligand bonding scheme, but most probably is best represented as $(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)$.

Under these conditions, and using eqs. 10 and 11, we obtain eqs. 13 and 14 and eqs. 15 and 16, respectively.

$$\frac{1}{k_1^P} = \frac{k_2}{k_1 k_3} \frac{[C]}{[B]} + \frac{1}{k_1} \quad (13)$$

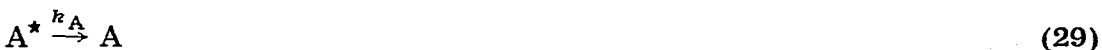
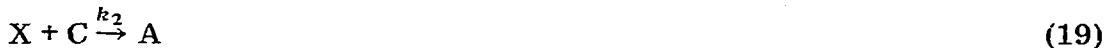
$$\frac{1}{k_{-1}^P} = \frac{k_3}{k_2 k_4} \frac{[B]}{[C]} + \frac{1}{k_4} \quad (14)$$

$$k_1^P = \frac{k'_1 k'_4}{k'_2 + k'_3} [B] \quad (15)$$

$$k_{-1}^P = \frac{k'_2 k'_3}{k'_2 + k'_3} [C] \quad (16)$$

Fitting of the experimental results to eqs. 13 and 14 or eqs. 15 and 16 will enable us to distinguish between the two possible mechanisms.

Photochemical reactions. The steps of the dissociative mechanism are represented by eqs. 17–24 and those of the associative mechanism by eqs. 25–32.





where I_1 and I_2 are the radiation absorbed by A and D, respectively, k_1^f and k_4^f are the rate constants of the primary photochemical processes, and k_A and k_D are the constants of non-radiative processes, other symbols having the same meaning as before.

Using the steady-state approximation for X, A* and D*, eq. 33 can be derived for the dissociative process, and making the same assumption for Y, A* and D*, eq. 34 is obtained for the associative mechanism.

Dissociative:

$$-\frac{dA}{dt} = \frac{k_3[B]}{k_2[C] + k_3[B]} \frac{k_1^f}{k_1^f + k_A} I_1 - \frac{k_2 k_4^f [C]}{(k_4^f + k_D)(k_2[C] + k_3[B])} I_2 \quad (33)$$

Associative:

$$-\frac{dA}{dt} = \frac{k'_3 k_1^f [B]}{(k'_2 + k'_3)(k_A + k_1^f [B])} I_1 - \frac{k'_2 k_4^f}{(k'_2 + k'_3)(k_D + k_4^f [C])} I_2 \quad (34)$$

Eqs. 33 and 34 enable us to calculate I_1/I_2 in the equilibrium and $1/\phi_A$ (where ϕ_A is the quantum yield for the disappearance of A at the beginning of the reaction); we obtain eqs. 35, 36 for the dissociative mechanism and eqs. 37, 38 for the associative mechanism.

$$\frac{I_1}{I_2} = \frac{k_2 k_4^f}{k_1^f k_3} \times \frac{k_1^f + k_A [C]}{k_4^f + k_D [B]} \quad (35)$$

$$\frac{1}{\phi_A} = \frac{k_1^f + k_A}{k_1^f} \times \frac{k_2 [C]}{k_3 [B]} + \frac{k_1^f + k_A}{k_1^f} \quad (36)$$

Associative:

$$\frac{I_1}{I_2} = \frac{k_1^f [B] + k_A}{k_4^f [C] + k_D} \times \frac{k'_2 k_4^f [C]}{k'_3 k_1^f [B]} \quad (37)$$

$$\frac{1}{\phi_A} = \frac{k'_2 + k'_3}{k'_3} + \frac{k_A}{k_1^f} \left(\frac{k'_2 + k'_3}{k'_3} \right) \frac{1}{[B]} \quad (38)$$

Again, fitting of the experimental results to eqs. 35 and 36 or 37 and 38 will enable us to decide on the mechanism.

Results and discussion

The results for the thermal reaction (30°C) are shown in Figs. 2 and 3. It can easily be seen that they fit eqs. 13 and 14 derived for the dissociative mecha-

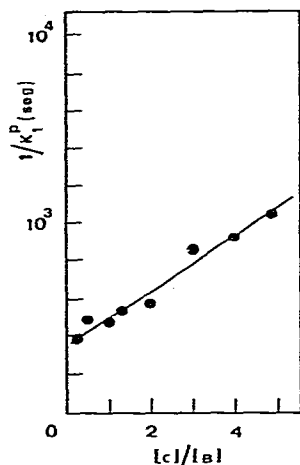


Fig. 2. Plot of the inverse of the forward pseudo first order constant versus the ratio of concentrations $[\text{PhCN}]/[\text{MeCN}]$ ($[\text{C}]/[\text{B}]$).

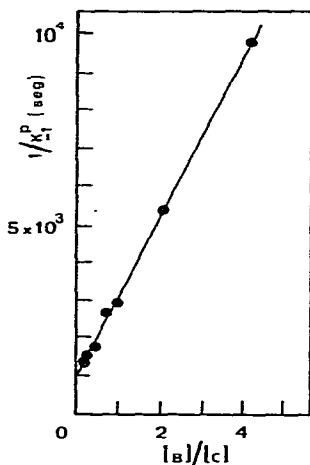


Fig. 3. Plot of the inverse of the reverse pseudo first order constant versus the ratio of concentrations $[\text{MeCN}]/[\text{PhCN}]$ ($[\text{B}]/[\text{C}]$).

nisms. Using the experimental results and eqs. 13 and 14 we have calculated the values of constants k_1 and k_4 and the ratio k_2/k_3 ; these values are given in Table 1 for temperatures varying between 25 and 45°C.

The results for the photochemical reaction (at 0°C, a temperature for which the thermal reaction is very slow) are shown in Figs. 4 and 5. It is clear that they fit eqs. 35 and 36, derived for the dissociative mechanism. Using equations 35 and 36 and the experimental results, we were able to calculate the following ratios:

$$\frac{k_1^f}{k_A} = 4.2, \frac{k_4^f}{k_D} = 0.35 \text{ and } \frac{k_2}{k_3} = 1.0$$

Although at 0°C the thermal reaction is negligible, the value of k_2/k_3 can be calculated by extrapolation ($\ln k_2/k_3 = \alpha + \beta/T$) from values at other temperatures; the value obtained: k_2/k_3 (0°C, thermal) = 1.1, is in good agreement with the photochemical value.

Assuming as a rough approximation that k_A and k_D are of the order of 10^3 sec^{-1} [8], then k_1^f and k_4^f are seven or six orders of magnitude larger than k_1

TABLE 1
VALUES OF THE CONSTANTS FOR THE THERMAL REACTION

T (°C)	k_1 (s^{-1})	k_4 (s^{-1})	k_2/k_3
25	2.0×10^{-4}	9.5×10^{-4}	0.46
30	5.5×10^{-4}	1.1×10^{-3}	0.38
35	9.6×10^{-4}	1.6×10^{-3}	0.37
40	1.8×10^{-3}	3.2×10^{-3}	0.30
45	4.6×10^{-3}	7.4×10^{-3}	0.25

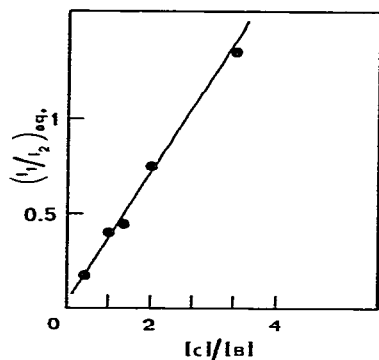


Fig. 4. Plot of the ratio of radiation intensities adsorbed in the equilibrium by $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}(\text{NCPh})]\text{-}[\text{PF}_6]$ and by $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)\text{I}(\text{NCMe})]\text{-}[\text{PF}_6]$ (I_1/I_2) versus the ratio of concentrations $[\text{PhCN}]/[\text{MeCN}]$ ($[\text{C}]/[\text{B}]$).

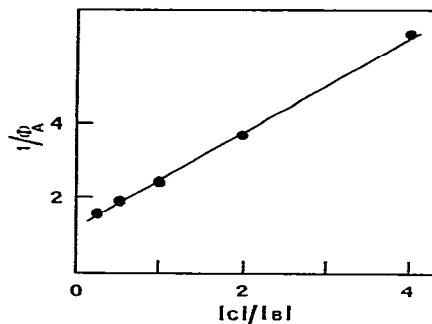


Fig. 5. Plot of the inverse of the quantum yield for the disappearance of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{I}(\text{NCPh})]\text{-}[\text{PF}_6]$ versus the ratio of concentrations $[\text{PhCN}]/[\text{MeCN}]$ ($[\text{C}]/[\text{B}]$).

and k_4 , which is in agreement with the well-known fact that $d-d$ excitation leads to an increase in ligand dissociation [9]. This result confirms our previous observation that LF excited states are σ -antibonding to the $[\text{M}]-\text{LL}'$ bond [1]. The energy of activation for the ground state substitution is 21 kcal mol^{-1} , which accounts for the lability in the ground state. The energy of the LF excited state lies (by ca. 65 kcal mol^{-1}) above the ground state, and once formed probably decays to the same intermediate giving identical reaction products.

From the results presented we conclude that reaction 1 proceeds via a dissociative mechanism.

References

- 1 S.M.B. Costa, A.R. Dias and F.J.S. Pina, *J. Organometal. Chem.*, **175** (1979) 193.
- 2 G.L. Goeffrey and M.S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979, Chapter 1.
- 3 M.S. Wrighton and D.L. Morse, *J. Organometal. Chem.*, **97** (1975) 405.
- 4 S.M.B. Costa, A.R. Dias and F.J.S. Pina, *J. Chem. Soc. Dalton*, (1981) 314.
- 5 M.L.H. Green, *Pure Appl. Chem.*, **50** (1978) 27.
- 6 M.J. Calhorda, Doctoral Thesis, Lisbon, 1980.
- 7 C.A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968, p. 208.
- 8 Gerald B. Porter in A.W. Adamson and P.D. Gleishauer (Eds.), *Concepts of Inorganic Photochemistry*, John Wiley & Sons, New York 1975, Chapter 2.
- 9 V. Balzani and V. Carassiti, *Photochemistry of Coordination Compounds*, Academic Press, New York, 1970.