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PRESSURE AS MECHANISTIC INDICATOR IN ORGANOMETALLIC PHOTOCHEMISTRY

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SUMMARY

We have recently undertaken a systematic study of the effect of pressure on photosubstitution reactions of organometallic, mostly carbonyl, complexes of the type $M(CO)_6$, $M(CO)_5L$ and $M(CO)_4L^{\frown}L$, where M = Cr, Mo and W. In some systems it was possible to measure the effect of pressure on both the photosubstitution quantum yield and the lifetime of the lowest excited state, whereas in others it was only possible to measure the former. The results are discussed in reference to data available for thermal substitution and photo-induced substitution reactions of related complexes. The results demonstrate that pressure is a key parameter, and therefore a mechanistic indicator, to distinguish between associative and dissociative photosubstitution processes of carbonyl complexes, and to discriminate between different pathways that originate from different electronic states.

INTRODUCTION

The effect of pressure on reaction rates and quantum yields, and the volume of activation estimated from these, constitute important phenomena which help to complete our comprehension of thermal and photochemical mechanisms (ref. 1-6). In the past we performed a series of detailed investigations on the mechanisms of excited-state reactions of Rh(III) ammine complexes and were able to estimate volumes of activation for photochemical reaction steps by combining quantum yield and luminescence lifetime measurements as a function of pressure (ref. 7-10). In these

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systems the interpretation of the data is sometimes complicated by solvational contributions that play a role when net charge creation or neutralization is involved during the substitution process. We have, therefore, undertaken a series of high pressure studies on the photochemical substitution reactions of metal complexes in a low oxidation state and with neutral ligands. In such reactions, electrostrictional effects are not expected to play a significant role, such that the interpretation of the volume of activation data should be fairly straightforward. The investigated systems are presented in the following subsections.

PHOTOSUBSTITUTION REACTIONS OF $M(CO)_6$

Ligand field photolysis of $M(CO)_6$ (M = Cr, Mo, W) results in the stepwise formation of $M(CO)_5L$ and $M(CO)_4L_2$, where L is a σ donor ligand. The pressure dependence of the photosubstitution quantum yield for the formation of $M(CO)_5L$ was studied for L = piperidine, pyridine and acetonitrile (ref. 11). Typical results for the reaction of $Cr(CO)_6$ with piperidine are shown for various solvents in Fig. 1 and for the reactions of $M(CO)_6$ with pyridine in Fig. 2. The overall observed results are summarized in Table 1. In all investigated reactions Φ decreases significantly with

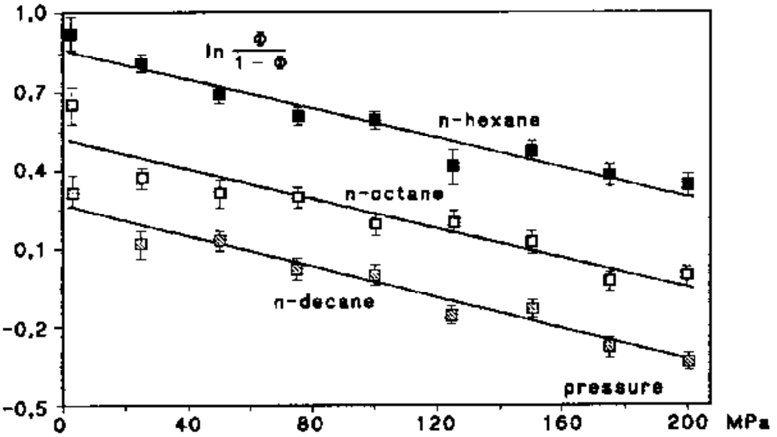


Fig. 1. Pressure dependence of the photosubstitution reaction on $Cr(CO)_6$ in various solvents, L = piperidine

$$Cr(CO)_6 + L \xrightarrow[313\ nm]{h\nu} Cr(CO)_5L + CO$$

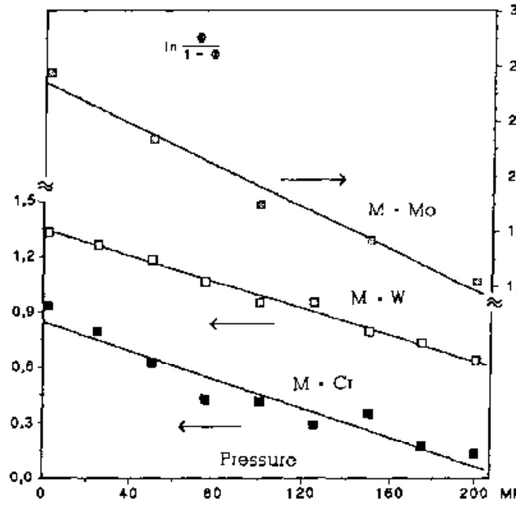


Fig. 2. Pressure dependence of the photosubstitution reaction on $M(CO)_6$ in n-heptane, L = pyridine

$$M(CO)_6 + L \xrightarrow[313\ nm]{h\nu} M(CO)_5L + CO$$

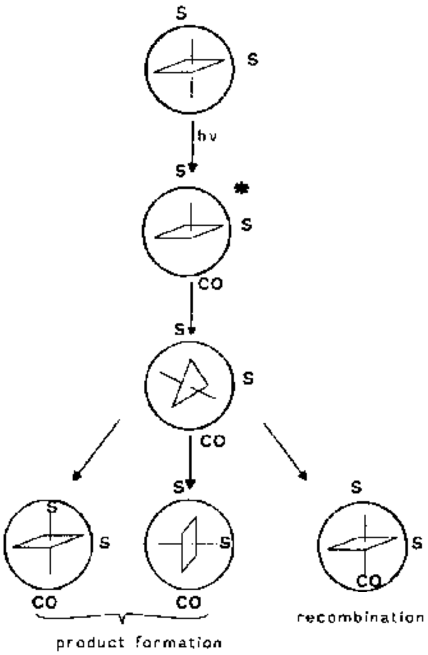
TABLE 1

Summary of the quantum yield at normal pressure and activation volumes for photosubstitution reactions on $M(CO)_6$ in various solvents

complex	ligand	solvent	Φ_0	$\Delta V^{\#}_{\Phi}$	$\Delta V^{\#}_{\Phi/(1-\Phi)}$
$Cr(CO)_6$	piperidine	n-pentane	0.72 ± 0.01	3.3 ± 0.4	9.1 ± 1.3
		n-hexane	0.72 ± 0.01	2.5 ± 0.2	7.0 ± 0.7
		n-heptane	0.73 ± 0.01	3.2 ± 0.2	9.3 ± 0.6
		n-octane	0.66 ± 0.01	3.0 ± 0.4	7.0 ± 1.0
		n-decane	0.58 ± 0.02	3.7 ± 0.3	7.3 ± 0.7
		n-dodecane	0.58 ± 0.02	3.6 ± 0.3	7.6 ± 0.5
		perfluorhexane	0.47 ± 0.02	5.6 ± 0.5	9.2 ± 0.3
$W(CO)_6$	pyridine	n-heptane	0.79 ± 0.01	2.4 ± 0.1	8.8 ± 0.4
$Mo(CO)_6$	pyridine	n-heptane	0.93 ± 0.01	1.6 ± 0.1	14.0 ± 1.2
$Cr(CO)_6$	pyridine	n-heptane	0.72 ± 0.02	3.6 ± 0.3	9.5 ± 1.0
$Cr(CO)_6$	acetonitrile	n-heptane	0.72 ± 0.02	3.5 ± 0.3	9.3 ± 1.0
		acetonitrile	0.70 ± 0.02	1.7 ± 0.2	5.0 ± 0.6

increasing pressure, which results in positive volumes of activation calculated from either the pressure dependence of Φ or $\Phi/(1-\Phi)$ (ref. 9).

These results can be interpreted in terms of the following proposed reaction scheme (ref. 11, 12):



Photolysis of $M(CO)_6$ produces $M(CO)_5$ in an excited triplet state, which can deactivate through an inverse-Berry pseudorotation and recombination with either CO or a solvent (S) molecule.[13,14] The $M(CO)_5S$ species will undergo rapid substitution in the presence of L to produce $M(CO)_5L$ with an overall quantum yield of ca. 2/3. The ratio of the rate constants for solvation (k_s) and recombination (k_{CO}) will in fact determine the quantum yield of the substitution process, i.e. $\Phi < 2/3$ when $k_s < k_{CO}$, which could be the case for weak coordinating solvents such as perfluorohexane. On the other hand, Φ can be larger than 2/3 when $k_s > k_{CO}$, which is obviously the case for the reaction of $Mo(CO)_6$. Under these conditions $\Delta V^{\#}_{\Phi/(1-\Phi)} = \Delta V^{\#}(k_s) - \Delta V^{\#}(k_{CO})$ and represents the difference in the volume of activation for the reaction of $M(CO)_5$ with S or CO. Both these quantities will be significantly negative and their absolute magnitudes should depend on the extend of bond formation in the transition state. Since the mentioned solvent molecules are all expected to bind weakly to the $M(CO)_5$ moiety, it is safe to expect that $|\Delta V^{\ddagger}(k_S)| < |\Delta V^{\ddagger}(k_{CO})|$. Thus the overall positive value of $\Delta V^{\ddagger}_{\Phi/(1-\Phi)}$ demonstrates the effective recombination of $M(CO)_5$ with CO on a volume basis.[15]

The subsequent reactions of $M(CO)_5S$ with L to produce $M(CO)_5L$ also exhibit characteristic pressure dependencies. Flash photolysis of $M(CO)_6$ in a weakly coordinating solvent produces $M(CO)_5S$ which is followed by a rate-determining substitution reaction with L. The pressure dependence of this step results in typical $\Delta V^{\ddagger}$ data of +0.8±0.5, -2.0±0.3 and -4.8±0.4 $cm^3\ mol^{-1}$ for S = chlorobenzene, L = $P(OPr^i)_3$ and M = Cr, Mo and W, respectively. Similar data for S = fluorobenzene and L = 1-hexene are +9.4±0.7, +5.8±0.8 and +2.5±0.2 $cm^3\ mol^{-1}$ for M = Cr, Mo and W, respectively (ref. 16). The results clearly demonstrate a gradual changeover from a more dissociative to a more associative reaction mode along the series of complexes, i.e. on increasing the size of the central metal atom. A similar changeover was also recently reported for the replacement of chelating ligands on complexes of the type $M(CO)_4(\overset{\frown}{S\ S})$ (ref. 17).

PHOTOSUBSTITUTION REACTIONS OF $W(CO)_5L$

Recent investigations have focused on the reactivity of complexes with a metal-to-ligand charge transfer (MLCT) state as lowest excited state, such as in $W(CO)_5L$ for L = 4-acetyl- and 4-cyano-pyridine, in contrast to L = pyridine where a LF state is the LEES. These complexes undergo photosubstitution according to the reaction in (1), where X = H, CH_3CO and CN. The effect of

$$W(CO)_5(4\text{-X-py}) + P(OEt)_3 \xrightarrow[\text{toluene}]{h\nu,\,436\ \text{nm}} W(CO)_5P(OEt)_3 + 4\text{-X-py} \qquad (1)$$

pressure on the photosubstitution quantum yield as well as on the lifetime of the MLCT state was investigated (ref. 11,18). The photoreactions of $W(CO)_5L$ have been interpreted in terms of a model such as described in Fig. 3 (ref. 19). Initial excitation is followed by rapid internal conversion/intersystem crossing to the LEES. For L = py, the LEES is a ligand field (LF) state, whereas for L = 4-X-py (X being a strong electron-withdrawing substituent) a less reactive MLCT state is the LEES. The model suggests that most of the observed photochemistry in the latter state occurs via back population from the MLCT to the more labile LF state.

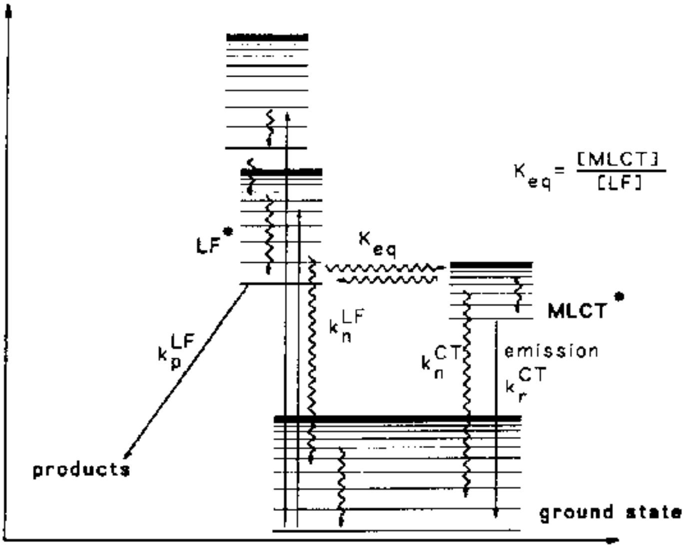


Fig.3. Schematic diagramme representing the various reaction routes of $W(CO)_5L$ complexes

The pressure dependence of the total decay rate (τ^{-1}) of MLCT emission from the 4-acetylpyridine complex resulted in a $\Delta V^{\ddagger}$ value of +0.1±0.3 cm^3 mol^{-1}, and from the 4-cyanopyridine analogue in +1.2±0.3 cm^3 mol^{-1}. The lifetime of the LF state in the pyridine complex is <10 ns, and was immeasurable using a 20 ns laser pulse. In this case $K_{eq} \ll 1$ and $\Phi_P = k_P^{LF}/(k_P^{LF} + k_n^{LF})$, such that $\Delta V^{\ddagger}(k_P^{LF})$ can be obtained from a plot of $\ln[\Phi_P/(1-\Phi_P)]$ versus pressure (see Fig. 4) and has a value of +5.7±0.3 cm^3 mol^{-1}. For the other two complexes $K_{eq} \gg 1$ and $\Phi_P = k_P^{LF}(K_{eq}^{-1})\tau$, such that $\Delta V^{\ddagger}(\Phi_P) = \Delta V^{\ddagger}(k_P^{LF}) - \Delta V(K_{eq}) - \Delta V^{\ddagger}(\tau^{-1})$. The values of $\Delta V^{\ddagger}(\Phi_P)$ were determined from a plot of $\ln \Phi_P$ versus pressure (see Fig. 4) and are +9.9 and +6.6 cm^3 mol^{-1}, respectively (ref. 18). If it is assumed that $\Delta V^{\ddagger}(k_P^{LF})$ is insen-

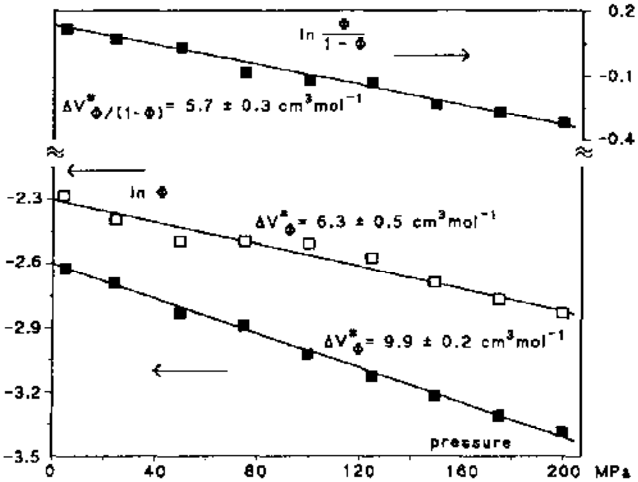


Fig. 4. Plots of ln Φ and ln[Φ/(1−Φ)] versus pressure for the photolysis of $W(CO)_5$pyridine (■, upper half), $W(CO)_5$(4-cyanopyridine) (□), and $W(CO)_5$(4-acetylpyridine) (■, lower half) at 436 nm in toluene according to eq. (1).

sitive to the substituent X (i.e. approx. +5.7 cm³ mol⁻¹ in each case), it follows that $\Delta\bar{V}(K_{eq})$ can be calculated from the values of $\Delta V^{\neq}(\Phi_P)$ and $\Delta V^{\neq}(\tau^{-1})$. The resulting values of $\Delta\bar{V}(K_{eq})$ are −4.3 and −1.8 cm³ mol⁻¹ for the 4-acetyl- and 4-cyano-pyridine complexes, respectively, and consistent with the volume difference expected between the LF and MLCT excited states (ref. 20). It follows that the larger activation volumes in the case of the substituted pyridine complexes originate from a positive $\Delta V^{\neq}(k_P^{LF})$ and a moderate volume difference $\Delta\bar{V}(K_{eq})$ between the LF and MLCT states.

PHOTOSUBSTITUTION REACTIONS OF $M(CO)_4$phen

The photochemistry and photophysics of $M(CO)_4$phen (phen = 1,10-phenanthroline, M = Cr, Mo, W) have received significant attention from various groups mainly because of the important role played by both LF and MLCT excited states in such processes. A simplified energy state diagram is given in Fig. 5 along with the possible chemical and physical deactivation routes

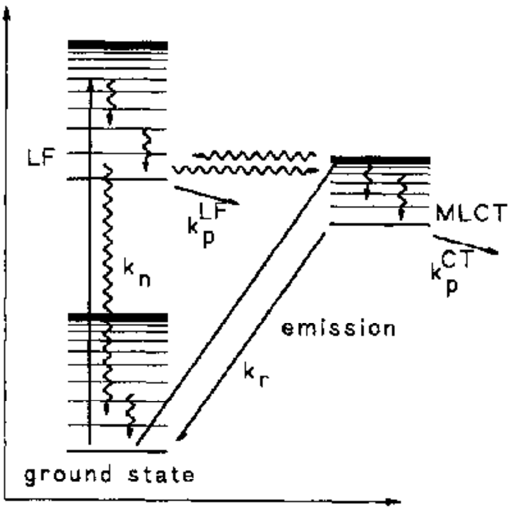


Fig. 5. Schematic diagram representing the various reaction routes of $M(CO)_4$phen complexes

(ref. 11, 21). The photosubstitution reactions of $M(CO)_4$phen follow the overall reaction (2), where L is a ligand with a P or N donor atom. The quantum yield for this reaction 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 photoactivity of the lower lying MLCT states has been a controversial issue in the literature. On the one hand it is assumed that the observed photosubstitution proceeds purely dissociatively from the LF excited state, i.e. excitation of the MLCT state is followed by thermal back population to the LF state (ref. 22). On the other hand it is argued that the MLCT states themselves are photo-active (ref. 23). We have studied the pressure dependence of these processes in order to resolve this controversy (ref. 21).

$$M(CO)_4\text{phen} + L \longrightarrow fac\text{-}M(CO)_3(L)\text{phen} + CO \qquad (2)$$

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 $\ln(\Phi/\Phi_0)$ versus pressure in Fig. 6 and the calculated volumes of activation are summarized in Table 2. Most important is our observation that MLCT excitation yields

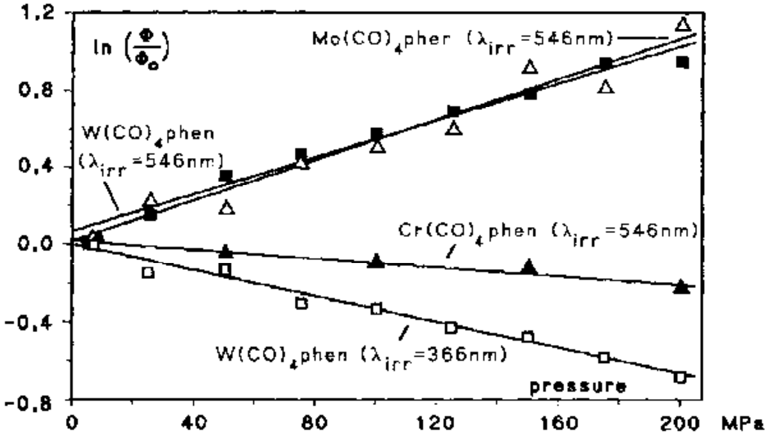


Fig. 6. Pressure dependence of the quantum yield of the reaction $M(CO)_4phen + PEt_3 \xrightarrow{h\nu} M(CO)_3(PEt_3)phen + CO$ in toluene

TABLE 2
Quantum yields and volumes of activation for the photosubstitution of CO in $M(CO)_4$phen by PEt_3 in toluene

complex	$[P(Et)_3]$ [mole/l]	λ_{irr} [nm]	Φ_0 [mole/Einstein]	$\Delta V^{\ne}_{\Phi}$ [cm^3/mole]	$\Delta V^{\ne}_{\Phi/(1-\Phi)}$ [cm^3/mole]
$Cr(CO)_4$(phen)	0.0135	546	0.11 ± 0.01	+ 2.7 ± 0.3	+ 3.0 ± 0.3
$Mo(CO)_4$(phen)	0.135	546	(1.02 ± 0.08) x 10^{-2}	-13.3 ± 1.2	-13.6 ± 1.2
$W(CO)_4$(phen)	0.135	546	(6.0 ± 0.4) x 10^{-3}	-12.0 ± 0.7	-12.0 ± 0.7
$W(CO)_4$(phen)	0.0135	366	(1.79 ± 0.02) x 10^{-2}	+ 8.1 ± 0.5	+ 8.2 ± 0.5

a significant negative volume of activation for M = Mo and W, whereas LF excitation yields a positive volume of activation for M = W. The latter value is a strong indication for a dissociative substitution mechanism as found in our earlier studies (ref. 7-10). The negative volume of activation observed on MLCT excitation underlines the validity of an associative substitution process originating from this state. The partial transfer of electron density from the metal to the ligand is presumably responsible for the associative reaction mode during this excitation. Naturally the size of the central metal atom must play a crucial role in the possibility to accommodate an additional ligand. The small positive $\Delta V^{\neq}$ value found for the Cr complex may indicate a changeover in mechanism from more associative for the larger metal centers (Mo and W) to more dissociative for the smaller center (Cr).

The results of these studies underline the value of pressure as a key parameter to distinguish between associative and dissociative photosubstitution mechanisms.

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