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Photochemical behaviour of metal complexes. Pressure effect versus mechanism

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Abstract

The purpose of this contribution is to demonstrate the usefulness of high pressure methods in mechanistic studies of photochemical and photoinduced reactions of metal complexes in solution. Examples of photosubstitution, photoisomerization and photoredox reactions of transition metal complexes have been selected for presentation. A critical evaluation as well as perspectives for the future are given. © 1997 Elsevier Science S.A.

Keywords: Photosubstitution; Photoisomerization; Photoredox reaction; Transition metal complexes

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1. Introduction

Pressure as a variable parameter in photochemical studies is a relatively new venture in contrast to its long-standing successful application in the study of thermal reactions. The fundamental principles involved in high pressure kinetics, the determination of activation and reaction volumes, the construction of reaction volume

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profiles and the interpretation of such data have been presented in many reviews and original papers [1–5]. The overall photochemical process is the result of a sequence of events, any of which can be influenced by pressure. These events include initial electronic excitation, vibrational relaxation, internal conversion, intersystem crossing, reactive, radiative and non-radiative deactivation, and further reactions of transient intermediates to the final products. To understand the effect of pressure on a photochemical reaction, it is of fundamental importance to have sufficient information on all the deactivation processes that affect the overall quantum yield. If we consider a sequence of events in which excitation of a single ground state is followed by internal conversion and intersystem crossing to the lowest excited triplet state, it can be followed by the photoreaction (k_p), nonradiative (k_n), and radiative (k_r) deactivation. The Jabłoński diagram for such a series of events is given in Fig. 1.

The photochemical quantum yield can then be expressed by Eq. (1), where τ is the lifetime of the lowest excited triplet state.

$$\phi_p = \phi_{isc} k_p/(k_p + k_n + k_r) = \phi_{isc} k_p \tau \qquad (1)$$

A similar expression can be written for the quantum yield for phosphorescence ϕ_r. The apparent activation volume based on quantum yield only is calculated according to:

$$\Delta V^{\#}_{\phi_i} = -RT \frac{\partial \ln \phi_i}{\partial p} \qquad (2)$$

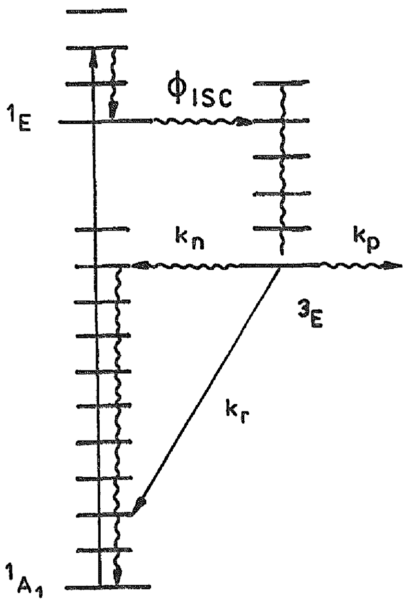


Fig. 1. Jabłoński diagram for the ligand field photolysis of Rh(III) ammine complexes [8].

However, the activation volume for the rate of a specific excited state process (k_i) is equal to

$$\Delta V^{\#}(k_i) = \Delta V^{\#}(\phi_i) - \Delta V^{\#}(\phi_{isc}) - \Delta V^{\#}(\tau) \qquad (3)$$

The non-radiative deactivation rate constant k_n and its pressure dependence can be calculated from the equation:

$$k_n = \tau^{-1} - k_p - k_r \qquad (4)$$

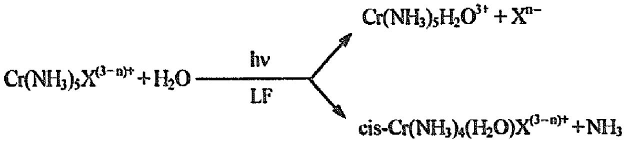
Eqs. (3) and (4) clearly demonstrate that $\Delta V^{\#}(k_i)$ can be evaluated as an independent entity only if the pressure dependencies of ϕ_i and τ are measured and if ϕ_{isc} is pressure independent.

2. Photosubstitution reactions

The most widely studied photoreaction of metal complexes is ligand photosubstitution

$$ML + L' \xrightarrow{h\nu} ML' + L \qquad (5)$$

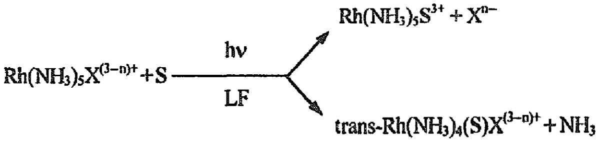
The first quantitative studies of pressure effects on such reactions were reported for a series of Cr(III) complexes [6], for which the two ligand exchange processes are thought to occur *via* different electronic excited states.



(6)

where: $X^{n-} = Cl^-$, Br^-, SCN^-, NH_3. The pressure dependence of ϕ_p resulted in significantly negative apparent $\Delta V^{\#}$ values, viz., an average value of $-6\ cm^3\ mol^{-1}$ for aquation of NH_3 and of -10 to $-13\ cm^3\ mol^{-1}$ for aquation of X^{n-}. Since little was known about the pressure dependence of the other deactivation processes, it was assumed that these apparent values represent those for the primary photoreactions. Accordingly, the data were interpreted in terms of an associative (most probably I_a) substitution process. The more negative values found for the aquation of X^{n-} as compared to NH_3 can be ascribed to solvational contributions originating from charge creation (i.e., electrostriction) in the transition state. A recent detailed reanalysis of the data [7] also supports the associative nature of the substitution process. However, it must be kept in mind that the doublet emission lifetimes of Cr(III) ammine complexes exhibit no negligible pressure dependencies, which could affect the above given interpretation.

Significantly more progress has been made in the study of photosovolysis reactions of Rh(III) ammine complexes [8–10]. For complexes of the type $Rh(NH_3)_5X^{(3-n)+}$, the photosolvolysis reactions can be summarized by Eq. (7), where S = solvent.



$$\mathrm{Rh(NH_3)_5X^{(3-n)+} + S \xrightarrow[\text{LF}]{h\nu} \begin{cases} \mathrm{Rh(NH_3)_5S^{3+} + X^{n-}} \\ \mathrm{\textit{trans}\text{-}Rh(NH_3)_4(S)X^{(3-n)+} + NH_3} \end{cases}$$

(7)

These reactions are generally accepted to follow the sequence of steps outlined in Fig. 1. Since $\phi_{\mathrm{ISC}} = 1$ for these reactions, Eq. (1) simplifies to $k_p = \phi_p/\tau$, which means that $\Delta V^{\#}(k_p)$ can be determined from $\Delta V^{\#}(\phi_p) - \Delta V^{\#}(\tau)$. It was generally found that the two photolysis reactions in (7) exhibit opposite pressure effects; a typical example for the photoaquation of $\mathrm{Rh(NH_3)_5Cl^{2+}}$ is given in Fig. 2.

Similarly, the pressure dependence of the excited-state lifetime, measured by using pulsed laser techniques, also exhibits different trends depending on the major photochemical reaction observed. Combining these data results in the $\Delta V^{\#}(k_p)$ values summarized in Table 1, from which it follows that the primary photochemical reactions exhibit the same pressure dependencies as ϕ_p.

Throughout the series of complexes, solvolysis of NH_3 is accompanied by a positive $\Delta V^{\#}(k_p)$ value, whereas the solvolysis of X^{n-} exhibits negative values. Both

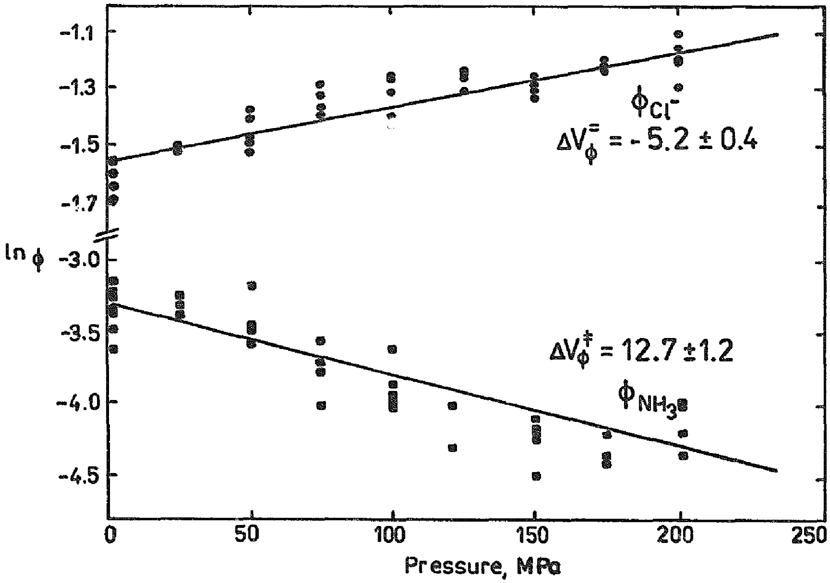
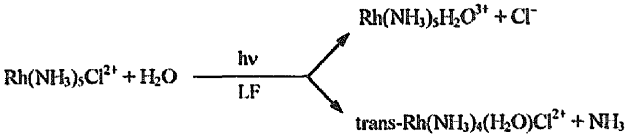
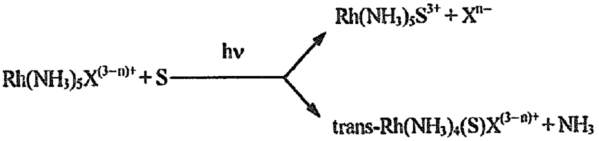


Fig. 2. Pressure dependence of the reaction [2]



$$\mathrm{Rh(NH_3)_5Cl^{2+} + H_2O \xrightarrow[\text{LF}]{h\nu} \begin{cases} \mathrm{Rh(NH_3)_5H_2O^{3+} + Cl^-} \\ \mathrm{\textit{trans}\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} + NH_3} \end{cases}$$

Table 1
Volumes of activation for the reaction [2,3]



X	S	$\Delta V^{\#}(\phi_p)$		$\Delta V^{\#}(\tau^{-1})$	$\Delta V^{\#}(k_p)$		$\Delta V^{\#}(k_n)$
		a	b		a	b	
Cl^-	H_2O	−5.2±0.4	+12.7±1.2	(−3.4)[c]	−8.6±1.6	+9.3±1.9	(−2.6)[c]
Cl^-	D_2O	−4.2±0.5	+9.5±1.6	3.5±1.1	−7.7±1.6	+6.0±2.2	−2.6±1.0
Cl^-	FMA	−4.6±0.7	+4.2±0.9	−0.3±0.4	−4.9±1.1	+3.9±1.3	0.2±0.5
Cl^-	DMF		+6.3±0.9	+1.3±0.2		+7.6±1.1	0.7±0.3
Cl^-	DMSO	−7.8±1.8	+4.4±0.9	−1±1	−8.9±2.7	+3.3±1.8	−1±1
Br^-	H_2O	−10.3±1.2	+4.6±0.6	(+3.5)[c]	−6.8±1.6	+8.1±1.2	(+2.5)[c]
Br^-	D_2O	−9.4±1.5	+3.4±0.5	+4.1±0.6	−5.3±1.8	+7.5±1.1	+2.5±1.2
NH_3	H_2O		+3.7±0.5			+3.9±0.5	0[c]
I^-	H_2O		+0.3±0.1			+1.4±0.9	0[c]
SO_4^{2-}	H_2O	−2.7±0.4			−3.9±0.6		0[c]

[c] assumed value.

these values can be interpreted in a qualitative way in terms of a D mechanism. The substantial difference in $\Delta V^{\#}(k_p)$ for the halide and ammine labilizations can be ascribed to a negative contribution from $\Delta V^{\#}_{solv}$ due to charge creation when the halide dissociates from the dipositive complex to form a tripositive cation and X^-. No appreciable charge creation is expected for the dissociation of NH_3. This difference also shows up in the overall $\Delta \bar{V}$ for the ground-state process of +3.9 and −17.8 $cm^3\ mol^{-1}$, respectively, in the case of the $Rh(NH_3)_5Cl^{2+}$ complex [8], demonstrating the important contribution of charge creation when the leaving group is anionic. A volume profile for this system is given in Fig. 3, in which it is assumed that the ligand field excited triplet state has a partial molar volume of ca. 10 $cm^3\ mol^{-1}$ larger than the ground-state molecule based on an expected increase in bond length of 0.1 A.

According to this profile it is quite possible that the excess volume of the excited state is focused along the axis of the bond cleavage process to produce a "ground-state-like" five-coordinate intermediate.

In the systems like those above 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. Therefore, in more recent studies the pressure dependence of some typical organometallic substitution reactions including low valency metal centers and neutral ligands were investigated [12–16].

$$M(CO)_6 + L \xrightarrow[313\ nm]{hv} M(CO)_5L + CO \tag{8}$$

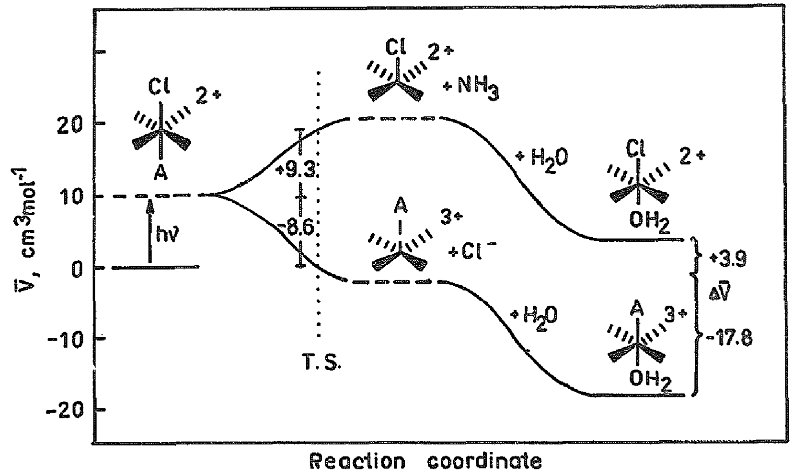
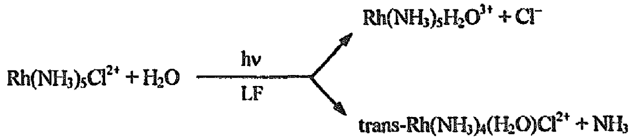


Fig. 3. Volume profile for the reaction [11]



$$Rh(NH_3)_5Cl^{2+} + H_2O \xrightarrow[LF]{h\nu} \begin{cases} Rh(NH_3)_5H_2O^{3+} + Cl^- \\ trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} + NH_3 \end{cases}$$

Photosubstitution reactions of the type outlined in (8) (M=Cr, Mo, W; L=piperidine, pyridine, acetonitrile) are all accompanied by significantly positive $\Delta V^{\#}$ values, which support the operation of a dissociative mechanism [13]. Volumes of activation for the photosubstitution of the nitrogen donor ligand by PEt_3 in $W(CO)_5(4-X-py)$ were reported to be +5.7 (X=H), +6.3 (X=NC) and +9.9 (X=acetyl) $cm^3\ mol^{-1}$ [14]. The effect of pressure on the luminescence lifetimes of the latter two complexes was found to be negligible, and the observed pressure effects were interpreted in terms of a dissociative mechanism. The larger value found for the acetyl substituted complex was ascribed to the participation of a MLCT to LF state transition prior to the dissociation of the ligand [14].

In a third system it was possible to distinguish between associative charge-transfer and dissociative ligand-field CO photosubstitution in $M(CO)_4(phen)$ (M=Cr, Mo, W) on the basis of the observed pressure dependences [15,16]. For these complexes the photoactivity of the lower lying MLCT states has been a controversial issue in the literature. On the one hand it was assumed that excitation of the MLCT state is followed by thermal back population to the higher energy LF state from which a dissociative photosubstitution reaction occurs [17]. On the other hand it was argued that the MLCT states themselves are photo-active and could undergo associative photosubstitution [18]. The pressure dependence of the quantum yield for the photosubstitution by PEt_3 was measured as a function of irradiation wavelength, and some typical results are reported in Fig. 4.

The corresponding volumes of activation are summarized in Table 2, from which

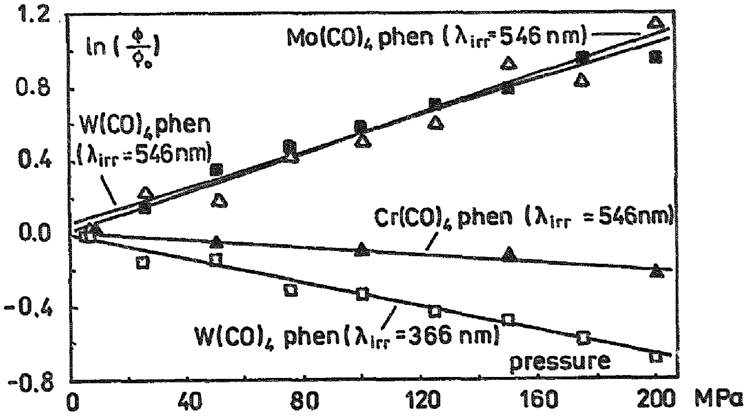


Fig. 4. Pressure dependence of the quantum yield of the reaction $M(CO)_4phen + PEt_3 \xrightarrow{hv} M(CO)_3(PEt_3)phen + CO$ in toluene [12].

Table 2

Quantum yields and volumes of activation for the reaction [16] $M(CO)_4phen + PEt_3 \xrightarrow[Toluene]{hv} M(CO)_3(PEt)_3phen + CO$

M	$[PEt_3]$ M	λ_{irr} mm	ϕ_0	$\Delta V^{\#}$ (MLCT)	$\Delta V^{\#}_{\phi/(1-\phi)}$ (LF)
Cr	0.0128	366	0.55		+9.6±1.6
	0.0135	546	0.11[a]	+2.7±0.3	
Mo	0.0128	366	0.056		+6.0±0.2
	0.135	545	0.010[b]	−13.3±1.2	
W	0.0135	366	0.018		+8.2±0.5
	0.135	546	0.006[b]	−12.0±0.7	

[a] ϕ independent of $[PEt_3]$.
[b] ϕ depends on $[PEt_3]$.

it follows that in the Mo and W complexes MLCT and LF photosubstitution occur according to associative and dissociative mechanisms, respectively.

For the smaller Cr complex the associative MLCT path does not seem to be possible and even this reaction has to follow a dissociatively activated process, presumably of the interchange type (I_d). Recently, a more systematic study of the influence of the entering ligand in such photosubstitution reactions was undertaken, and the entering ligand was changed to PMe_3, $P(Bu^n)_3$ and PPh_3 [19]. The effect of pressure on the photosubstitution quantum yield was studied over the irradiation wavelength range from 313 to 546 nm. The steric hindrance on the entering ligand controls the changeover from dissociative to associative photosubstitution on increasing the irradiation wavelength, i.e. an earlier (lower wavelength) changeover is observed for PMe_3 as compared to PPh_3. These results nicely underline the value of pressure as a key parameter to distinguish between associative and dissociative photosubstitution mechanisms. In two recent studies [20,21] the effect of pressure was employed to resolve the mechanism of the photoreactions. Photolysis of $C_pFe(CO)_2(COCH_3)$ and $P(OCH_3)_3$ in n-heptane results in competitive decarbonylation to give $C_pFe(CO)_2CH_3$ and ligand substitution to give $C_pFe(CO)(COCH_3)P(OCH_3)_3$. The quantum yields of the processes are affected by pressure and the photosubstitution process is strongly favoured at higher pressure. This is interpreted in terms of the associative ligand substitution of the solvent intermediate $C_pFe(CO)(sol)(COCH_3)$ and a competing dissociative methyl migration reaction.

MLCT photochemistry of $(CO)_5ReMn(CO)_3$(α-diimine) in CH_2Cl_2 produces $Re(CO)_5Cl$ and $Mn(CO)_3$(α-diimine)Cl, whereas the substitution product $(CO)_5ReMn(CO)_2(PPh_3)$(α-diimine) is found in the presence of PPh_3. It was suggested that both reaction paths involve the initial photodissociation of CO from the parent complex. The apparent volumes of activation found for the reaction of $(CO)_5ReMn(CO)_3$(4,4′-dimethyl-2,2′-bipyridine) with CH_2Cl_2 and PPh_3 are $+17.2 \pm 1.3$ and 15.7 ± 0.5 $cm^3\,mol^{-1}$, respectively, and underline the dissociative nature of the photochemical process [21].

3. Photoisomerization reactions

There are many ligand field photochemical reactions that result in geometrical isomerization, and especially the cis/trans photoisomerization of rhodium(III) ammine complexes has received significant attention during recent years. These systems are fairly well understood in terms of ligand dissociation from the hexacoordinate excited state prior to stereoarrangement, and several closely related theoretical models have been principally interpreted in terms of the comparative energies of the square-pyramidal, five-coordinate apical (A*) and basal (B*) intermediates shown in Fig. 5.

These intermediates were proposed to be triplet excited states capable of isomerization on a time scale competitive with deactivation, followed by trapping of a solvent molecule. An important aspect of these models is that the stronger σ-donor ligand should show a strong site preference for the basal position in the five-coordinate intermediate. In this way the stereochemistry of the isomerization reactions could be predicted.

The pressure dependence of a series of such photoisomerization reactions was investigated along with the partial molar volumes of the reactant and product species [10]. The volumes of activation for the photochemical reaction, $\Delta V^{\#}(k_p)$, were estimated from plots of $\ln(\phi/1-\phi)$ versus pressure on the basis of the ligand field excitation pattern reported for such substitution reactions of rhodium(III) complexes [8]. A summary of the values of $\Delta V^{\#}(k_p)$ and the overall reaction volume $\Delta\bar{V}$ is given in Table 3.

In most of the cases the absolute value of $\Delta V^{\#}(k_p)$ is very small and this complicates its interpretation. Similarly, $\Delta\bar{V}$ is also small and exhibits no specific correlation

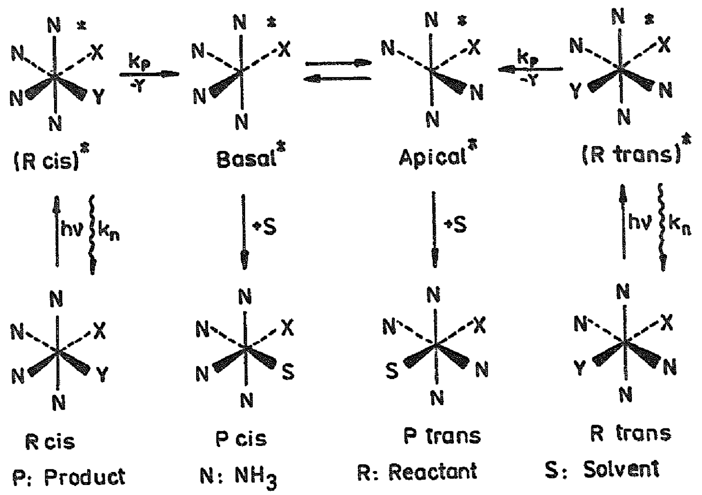


Fig. 5. General scheme for the photochemical cis/trans isomerization of Rh(III) ammine complexes [10].

Table 3
Volumes of activation for the photoisomerization reactions of a series of tetraamminerhodium(III) complexes in aqueous solution

Complex	Principal product	$\Delta V^{\#}(k_p)$ cm^3 mol^{-1}	$\Delta\bar{V}$ cm^3 mol^{-1}
cis-$Rh(NH_3)_4Cl_2^+$	trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	-3.5 ± 0.3	$+4.2\pm1.8$
cis-$Rh(NH_3)_4(H_2O)Cl^{2+}$	trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	0.0 ± 0.4	$+2.5\pm2.3$
cis-$Rh(NH_3)_4Br_2^+$	trans-$Rh(NH_3)_4(H_2O)Br^{2+}$	-2.3 ± 0.3	$+6.4\pm1.9$
cis-$Rh(NH_3)_4Br_2^+$	"$Rh(NH_3)_3(H_2O)Br_2^+$"	$+9.3\pm0.8$	$+0.7$
cis-$Rh(NH_3)_4(H_2O)Br^{2+}$	trans-$Rh(NH_3)_4(H_2O)Br^{2+}$	-1.0 ± 0.4	$+0.5\pm2.4$
trans-$Rh(NH_3)_4(OH)Cl^+$	cis-$Rh(NH_3)_4(OH)_2^+$	-8.8 ± 0.7	n.a.

n.a. — not available.

with $\Delta V^{\#}(k_p)$. A detailed discussion of the data [10] indicated that the volume data do not provide a definite description of the mechanism of the process but do underline the dissociative (I_d or D) nature of the process if a general mechanism is operative. Similar arguments to those presented before were adopted to access the partial molar volume of the LF triplet state. It follows that the interpretation of small pressure effects in photochemical reactions is subjected to much uncertainty due to the complexity of the overall reaction scheme and various processes that can account for the observed effects.

The linkage isomerization of $Co(en)_2(SO_2CH_2CH_2NH_2)^{2+}$ from an S- to an O-bonded species proceeds *via* charge transfer (CT) excitation. This is a rather unique reaction in that the O-bonded species exhibits a thermal back reaction to the S-bonded species such that a pressure dependence study of both the forward and back reaction could be done [22].

$$(en)_2Co(SOON)^{2+} \underset{\Delta}{\overset{h\nu,CT}{\rightleftharpoons}} (en)_2Co(OSON)^{2+} \quad (9)$$

The measurements demonstrate that the forward photochemical reaction exhibits a clearly positive $\Delta V^{\#}(k_p)$ value (ca. 6 cm^3 mol^{-1}), compared to that of -9.0 ± 0.7 cm^3 mol^{-1} for the thermal back reaction. Both these values are interpreted in terms of a ring-opening reaction, which can be visualized as homolysis for the ring opening of the CT state and dissociation accompanied by significant charge creation for the thermal process. A volume profile for the overall process was constructed on the assumption that the partial molar volume of the CT state is very close to that of the ground state (see Fig. 6).

The volume profile shows a difference of at least 13 cm^3 mol^{-1} between the two transition states, which is due to the increase in electrostriction and the smaller volume of the Co(III) ring-opened species.

4. Photoredox reactions

Only a few charge transfer photochemical reactions have been investigated under pressure. For bimolecular photoredox reactions, e.g. the electron transfer between a ground state quencher and an electronically excited transition metal complex, the pressure effects would be similar to those considered for the analogous ground state reactions. However, some ambiguity is again introduced by the fact that the excited

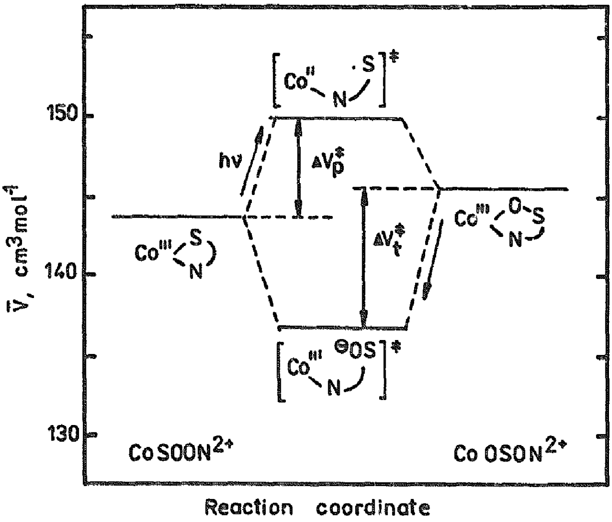


Fig. 6. Volume profile for the system [22] $(en)_2Co(SOON)^{2+} \underset{\Delta}{\overset{h\nu,CT}{\rightleftharpoons}} (en)_2Co(OSON)^{2+}$.

states very likely will have volumes different (and larger) than do the corresponding ground states.

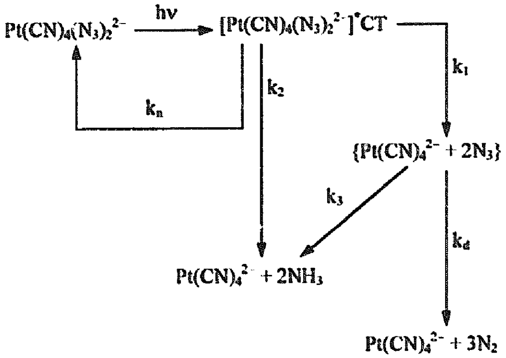
There have been several reports on pressure effects on bimolecular electronic and electron transfer quenching of the long-lived MLCT excited states of $\mathrm{Ru(bipy)_3^{2+}}$. Kirk and Porter [23] reported that quenching of aqueous $\mathrm{Ru(bpy)_3^{2+}}$ by oxygen, a diffusion controlled energy transfer process, showed a very small $\Delta V_q^{\#}$ ($+0.6\ \mathrm{cm^3\ mol^{-1}}$) and attributed that to the modest increase in the viscosity of water over the modest pressure range used (0.1 to 300 MPa).

$$[\mathrm{Ru(bpy)_3^{2+}}]^* + \mathrm{MV^{2+}} \rightarrow \mathrm{Ru(bpy)_3^{3+}} + \mathrm{MV^{+}} \qquad (10)$$

These workers reported a greater effect for the oxidative quenching by dimethyl viologen, another bimolecular process which occurs with diffusion limited rates. In this case $\Delta V_e^{\#} = -3.4\ \mathrm{cm^3\ mol^{-1}}$ for an electron transfer of this type [24]. The difference was concluded to indicate that the reaction rate is largely controlled by diffusion rather than by electron transfer.

Ito, Saito and coworkers [25] have extended the series of electronic and electron transfer quenchers. They also found that various oxidative quenchers, each of which displayed ambient $k_e \geq 1 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$, have $\Delta V_e^{\#}$ values close to $0\ \mathrm{cm^3\ mol^{-1}}$ in each case. However, a much greater range of $\Delta V_e^{\#}$ values (-11 to $24\ \mathrm{cm^3\ mol^{-1}}$) was observed with reductive quenchers.

Pressure effects on several intramolecular photoredox processes have also been investigated. The formation of a caged radical pair $\mathrm{Co^{II}(Br^{\bullet})}$ from the LMCT state was suggested to account for the pressure dependence of the CT photolysis of $\mathrm{Co(NH_3)_5Br^{2+}}$ [26]. The CT photolysis of the diazido complex trans-$\mathrm{Pt(CN)_4(N_3)_2^{2-}}$ has been shown to involve reductive elimination of azide to produce $\mathrm{Pt(CN)_4^{2-}}$ and nitrogen [27]. Irradiation at 313 nm produces LMCT excitation, and the quantum yield in water and ethanol as solvent decreased significantly with increasing pressure [28]. The resulting $\Delta V^{\#}(k_p)$ values are $+8.1 \pm 0.4$ and $14.3 \pm 0.9\ \mathrm{cm^3\ mol^{-1}}$ for water and ethanol, respectively, calculated from the slope of plots of $\ln(\phi/1-\phi)$ versus pressure on the assumption that the non-radiative deactivation rate constants are independent of pressure (see Eq (11)).



(11)

In this treatment it was assumed that the key photochemical reaction step occurs from the CT state directly populated during irradiation. The significantly positive $\Delta V^{\#}(k_p)$ values clearly underline the dissociative nature of the photochemical reaction in both solvents. The difference in the values is significant and requires a detailed interpretation. The CT excited state model as outlined in (11) was used due to the wavelength independence of the observed quantum yield, and the non-unitary yield for radical pair formation observed in the present system. The reactive state is a thermally equilibrated ligand-to-metal CT excited state that can undergo non-radiative deactivation (k_n) and simultaneous Pt–N_3 bond cleavage (k_1) to produce a caged radical species, which subsequently decomposes to $Pt(CN)_4^{2-}$ and N_2 in water and ethanol ($k_d = 7 \times 10^9\ M^{-1}\ s^{-1}$ in water) or interacts with ethanol to produce HN_3 and ethanol radicals via the abstraction of hydrogen (k_3). The additional deactivation route for the CT excited state in ethanol can account for the higher quantum yield and $\Delta V^{\#}(k_p)$ values observed in ethanol. It follows that bond breakage plays an important role in both the deactivation routes k_1 and k_2. No major solvational changes are expected since there is no overall change in charge, although the metal center is reduced from Pt(IV) to Pt(II).

The photooxidation of $Fe^{II}(CN)_5NO^{2-}$ has been studied by numerous investigators, and photooxidation of the metal center (i.e. MLCT) accompanied by solvation of the NO ligand was reported to be the major reaction mode in aqueous and non-aqueous liquid media (S = solvent in (12)). Little efforts have been made to study the intimate molecular nature of reaction (12). Arguments have been reported in favour of both associative and dissociative reaction modes [29].

$$Fe^{II}(CN)_5NO^{2-} \xrightarrow[S]{h\nu} Fe^{III}(CN)_5S^{2-} + NO \qquad (12)$$

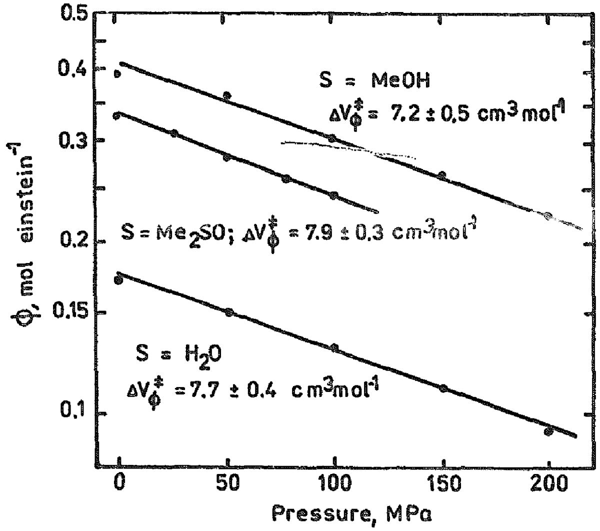
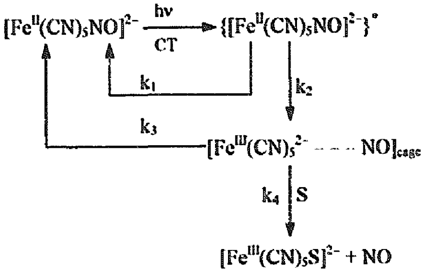


Fig. 7. Plots of lnϕ versus pressure for the reaction [30] $Fe(CN)_5NO^{2-} + S \xrightarrow{h\nu} Fe(CN)_5S^{2-} + NO$.

We found the quantum yield for the production of the $Fe^{III}(CN)_5S^{2-}$ to depend on the irradiation wavelength (i.e. energy) and the nature of the solvent (H_2O, MeOH, Me_2SO, MeCN, DMF and C_5H_5N) [30,31]. The latter dependence could be described in terms of the Gutmann donor numbers and viscosity. The quantum yield decreases with increasing donor number and viscosity of the medium. A series of measurements in water-glycerol mixtures indicated that the quantum yield parallels the fluidity of the medium, and a plot of ϕ^{-1} versus η is linear up to 50% glycerol, in the range where no observable ligand exchange involving glycerol occurred. A summary of the values of $\Delta V^{\#}(\phi)$ calculated from plots of ln ϕ versus pressure (see typical examples in Fig. 7) is given in Table 4.

These values seem to be fairly wavelength independent and only the quantum yield is significantly affected by the solvent. The latter trend correlates with the fluidity of the medium as mentioned above, and points to the participation of a cage recombination mechanism as outlined in (13). In this scheme k_2 represents the rate constant for the radical pair formation step.



(13)

The observed photooxidation yield for the mechanism outlined in (13) is given by the expression in (14), where ϕ_0 presents the primary quantum yield for radical pair formation/bond cleavage.

$$\phi=\left\{\frac{k_2}{k_1+k_2}\right\}\left\{\frac{k_4}{k_3+k_4}\right\}=\phi_0\left\{\frac{k_4}{k_3+k_4}\right\} \quad (14)$$

Values of $\Delta V^{\#}(\phi)$ and $\Delta V^{\#}(k_p)$ for the reaction [30] $Fe(CN)_5NO^{2-}+S\xrightarrow{h\nu}Fe^{III}(CN)_5S^{2-}+NO$ as a function of solvent and excitation energy

Solvent	λ_{irr} nm	ϕ^a mol einstein^{-1}	$\Delta V^{\#}(\phi)$ cm^3 mol^{-1}	$\Delta V^{\#}(k_p)$
H_2O	436	0.17	+7.7±0.4	+8.8±0.4
	313	0.37	+5.5±0.7	+7.8±1.0
MeOH	436	0.39	+7.2±0.5	+10.3±0.6
	313	0.63	+6.5±0.8	+13.0±1.9
Me_2SO	436	0.33	+7.9±0.3	+11.1±0.4
	405	0.39	+7.5±1.1	+11.4±1.6
	313	0.42	+8.4±1.3	+14.1±1.0

[a] values at ambient pressure, i.e. 0.1 MPa.

ϕ_0 and k_3 are expected to be independent of viscosity, whereas k_4 is expected to decrease with increasing viscosity. It is therefore not surprising that ϕ^{-1} depends linearly on the viscosity of the medium as reported above, with an intercept ϕ_0^{-1}. The value of ϕ_0 is such that $\phi_{H_2O}/\phi_0 = 0.82$, indicating that no significant cage effects are present in pure water. However, this ratio deviates significantly from unity for the other solvents and cage effects do play a significant role in those cases. The observed pressure effects and apparent volumes of activation, $\Delta V^{\#}(\phi)$, mainly present the contribution from k_2, i.e. the formation of the caged radical pair, and support the dissociative nature of this reaction. If we assume that k_1 for non-radiative deactivation exhibits a minor pressure dependence [1,8], then $\Delta V^{\#}(k_p)$ for the k_2 step can be estimated from a plot of $\ln(\phi/1-\phi)$ versus pressure in the usual way. The corresponding values in Table 4 show a very similar trends as $\Delta V^{\#}(\phi)$, and the larger values found in MeOH and Me_2SO are partly ascribed to the pressure dependence of the viscosity of the solvent. The expected increase in viscosity with increasing pressure, especially for Me_2SO, will result in a decrease in ϕ and a more positive $\Delta V^{\#}$ value. The results definitely rule out the possibility of an associative reaction mode and reveal the intimate nature of the dynamics of the excited state species.

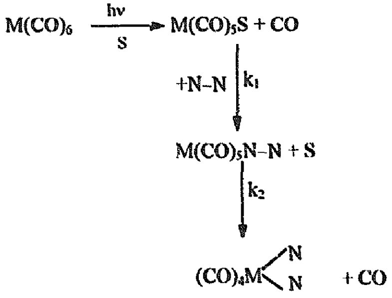
5. Photo-induced reactions

Flash photolysis techniques have in general been adopted with great success to study the substitution behaviour of reactive intermediates in organometallic chemistry. Irradiation of $M(CO)_6$ (M = Cr, Mo, W) in a coordinating solvent S produces intermediates of the type $M(CO)_5S$, which can undergo rapid subsequent ligand substitution with a nucleophile L to produce $M(CO)_5L$. The pressure dependence of such substitution reactions has been studied for a series of M, S and L, and the results once again demonstrate the crucial role played by the size of the metal center and the bulkiness of the ligand [32,33].

In one of the first studies [34] the volume of activation for the displacement of chlorobenzene by pyridine in cis-$(C_6H_5Cl)(PPh_3)W(CO)_4$ was found to be $+11.3 \pm 0.4$ cm^3 mol^{-1}, and for the ring-closure reaction in cis-$(C_6H_5Cl)(PPh_2(CH_2)_4C{=}CH_2)W(CO)_4$ $+10.5 \pm 0.3$ cm^3 mol^{-1}. Both these values are indicative of a dissociative desolvation mechanism. In a subsequent study [35], a value of $+12.3$ cm^3 mol^{-1} was reported for the dissociation of benzene from $Cr(CO)_5$(benzene). By now a series of studies have been completed on the pentacarbonyl complexes of Cr, Mo and W for a series of solvents (n-heptane, hexene, piperidine, pyridine, 2-picoline). The results enable a careful analysis of the intimate nature of these solvent displacement reactions.

When the attacking nucleophile is a bidentate species, flash photolysis of $M(CO)_6$ in the presence of N–N results in the reaction sequence outlined in Eq. (15)

for M = Cr, Mo and W.



S = solvent (15)

Detailed kinetic studies at atmospheric pressure for N−N = 1,10-phenanthroline could not resolve the nature of the $M(CO)_5N-N$ species in terms of whether it is a six or seven coordinate complex depending on the nature of M. A pressure dependence study of both the solvent displacement (k_1) and ring-closure (k_2) steps [36] clearly indicated a gradual changeover from more dissociative to more associative reactions along the series Cr, Mo, W. For instance $\Delta V^{\#}$ for the ring-closure of $Cr(CO)_5$phen is +6.2 compared to $-8.2\ cm^3\ mol^{-1}$ for $W(CO)_5$phen. Obviously the size of the central metal atom controls the nature of the substitution mechanism. Similar studies on the ring-closure reactions of photo-produced $M(CO)_5N-N$ species for N−N = bipyridine, ethylenediamine and 1,4-diisopropyl-1,4-diazabutadiene [37,38] also reveal this gradual changeover in mechanism. In the case of the sterically less hindered ethylenediamine complex, ring-closure for M = Cr also follows an associative substitution mode ($\Delta V^{\#} = -11.9 \pm 1.5\ cm^3\ mol^{-1}$). High pressure kinetic techniques have also been used to study the effect of steric hindrance on the entering ligand and the extend to which this could affect the nature of the ring-closure mechanism in complexes of the type $M(CO)_5N-N$ [37–41]. A comparison of the data in Table 5 indicates that the $\Delta V^{\#}$ values for the similar ring-closure reactions of $Mo(CO)_5L$ strongly suggest

Table 5
Activation volumes for chelate ring closure in $M(CO)_5L$ complexes in toluene (M = Mo, W) [41]

L	M	$\Delta V^{\#}$ $cm^3\ mol^{-1}$
bpy	Mo	-3.9 ± 0.6
	W	-10.9 ± 1.1
dmbpy	Mo	-5.6 ± 0.4
	W	-8.4 ± 1.0
dpbpy	Mo	5.4 ± 0.5
	W	-6.4 ± 0.6
dbubpy	Mo	6.2 ± 1.0
	W	-4.5 ± 0.2

a gradual change in mechanism from I_a to I_d on increasing the steric hindrance on the bpy ligand.

Only in the case of the most sterically hindered dpbpy and dbubpy complexes does a change in sign of $\Delta V^{\#}$ really occur; i.e., in this case the steric hindrance reaches a critical point where an associative (I_a) ring closure is no longer possible, and the reaction is forced to follow a dissociative (I_d) mechanism. In the case of the larger W metal center, the data in Table 5 indicate that the mechanism of the ring-closure reaction of substituted bpy complexes is only slightly affected by the steric hindrance on the bpy ligand, and an associative reaction mode is operative in all cases. The $\Delta V^{\#}$ data for the W complexes are between 7 and 11 $cm^3\ mol^{-1}$ more negative than those for the corresponding Mo complexes, which indicates that the larger W metal center has a greater ability to undergo bond formation with the ring-opened chelate. Clearly, these studies demonstrate the sensitivity of the ring-closure mechanism to the size of the central metal atom and to the effect of steric hindrance on the entering ligand. More recently, similar photo-induced ring-closure reactions were studied in supercritical fluids, e.g. CO_2 and ethane. A special optical cell was designed for high pressure measurements [42]. Under conditions just above the critical point, the ring-closure of $W(CO)_5phen$ (produced via flash photolysis of $W(CO)_6$ and phen in supercritical CO_2 and ethane) is tremendously decelerated by increasing pressure with activation volumes of ca. 7000 and 6000 $cm^3\ mol^{-1}$ in supercritical CO_2 and ethane, respectively [43]. These extremely large numbers are ascribed to the release of CO during the ring-closure reaction since the isothermal compressibility is very large at the critical point. Thus, the release of CO can be visualized as going from the condensed (coordinated) state to the gas phase for which the overall volume change can be as large as 22 400 $cm^3\ mol^{-1}$. In terms of this overall volume increase the observed volumes of activation are quite realistic. It should also be noted that such volumes of activation are extremely pressure dependent due to the effect of pressure on the isothermal compressibility of the medium [43].

6. Concluding remarks

The examples discussed in the previous sections demonstrate that pressure effects on the dynamics of excited state processes provide valuable new insight into the mechanistic interpretation of excited state reactions. Activation volumes do allow one to describe qualitatively the types of distortion occurring during excited state reactions. But it must be kept in mind that like other activation parameters, $\Delta V^{\#}$ data alone cannot provide a definitive description of an excited state mechanism.

Some of the difficulties lie in the unknown partial molar volumes of excited state species and some are the result of the difficulty to separate intrinsic and solvational contributions towards $\Delta V^{\#}$. Another problem is the fragmentary nature of much of the published pressure studies. Also much better understanding of the pressure influence on rates of photophysical processes is obviously needed. Despite these difficulties the use of pressure effects in the study of photochemical reaction mechanisms adds a further dimension to the available information and has a promising future.

Acknowledgements

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