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PRESSURE EFFECTS ON THE PHOTOCHEMICAL REACTIONS OF TRANSITION METAL COMPLEXES

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ABSTRACT

Investigations of pressure effects on the chemical and physical deactivation pathways of transition metal excited states are summarized and discussed. Particular emphasis is placed on the calculation of the activation volumes of the rate constants for the various deactivation channels and the interpretation of these in terms of reaction mechanisms.

INTRODUCTION

The interpretation of activation and reaction volumes of inorganic systems in solution has become a powerful tool for the study of inorganic reaction mechanisms. Since the 1970's several reviews have appeared which discuss the effect of pressure on thermal reaction, in particular an extensive review by Kelm and Palmer (ref. 1-4). Recently the high pressure technique has been extended to the investigation of photochemical reaction mechanisms of transition metal complexes in fluid solution. In our laboratories, the emphasis in this regard has been to elucidate the effect of pressure on the individual rate and equilibrium constants governing the primary processes which deactivate excited states (ref. 5-7). The present manuscript is an attempt to summarize our recent investigations in this field and to review briefly relevant studies from other laboratories.

In order to evaluate activation volumes of photochemical reaction mechanisms, it is important to understand the effects of pressure on all the primary processes which deactivate or communicate with the excited state responsible for the photochemistry observed. In addition to processes which involve net product formation, nonradiative and radiative deactivation, intersystem crossing/internal conversion from upper states to reactive states and equilibrium between excited states of comparable energy must all be considered. Several attempts to address pressure effects on such photophysical phenomenon of transition metal complexes are also addressed here. Pressure effects on luminescence spectra and lifetimes (largely of organic systems) have been reviewed (ref. 8).

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From transition state theory, the activation volume of a reaction rate constant is defined as:

$$\Delta V_i^{\ddagger} = - RT \frac{\delta \ln k_i}{\delta P} \tag{1}$$

where $\Delta V_i^{\ddagger}$ is the volume difference between the ground and transition states. Activation energies are nearly always positive, but activation volumes can be positive, negative or close to zero depending on the mechanism involved and on factors such as changes in solvation. There is additional data in the degree of curvature found in the $\delta \ln k_i$ vs δP plots. The second derivative $\delta^2(\ln k_i)/\delta^2 P$ represents the change in compressibility between reactants and transition state (ref. 2,3). However, the data set must be very accurate to obtain an reasonable value. For the pressure range used in most inorganic photochemical studies, such compressibility terms are too small to be obtained from experimental observations.

SOME THOUGHTS ON $\Delta V_i^{\ddagger}$ FOR PHOTOSUBSTITUTIONS OF METAL COMPLEXES

The most widely studied photoreaction of metal complexes is ligand photosubstitution.

$$ML + L' \xrightarrow{h\nu} ML' + L \tag{2}$$

If we assume that a single excited state is responsible for photosubstitution, the model illustrated in Fig. 1 can be used to define the quantum yield Φ in terms of rates of primary processes deactivating the excited state (ref. 9).

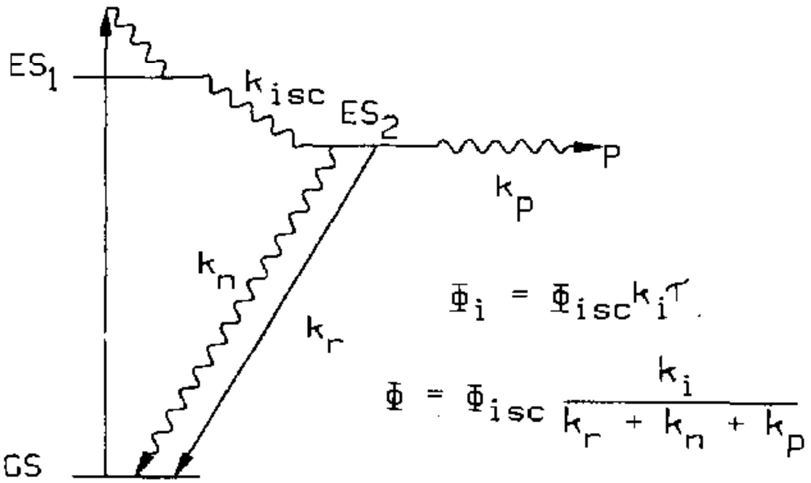


Fig. 1. Kinetic scheme for reaction from a lowest energy excited state.

The apparent activation volume based on quantum yields alone is calculated according to

$$\Delta V^{\ddagger}_{\Phi_i} = - RT \frac{\delta \ln\Phi_i}{\delta P} \qquad (3)$$

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

$$\Delta V^{\ddagger}_{i} = \Delta V^{\ddagger}_{\Phi_i} - \Delta V^{\ddagger}_{\tau} - \Delta V^{\ddagger}_{\Phi_{isc}} \qquad (4)$$

Thus $\Delta V^{\ddagger}_{i}$ can be evaluated as an independent entity if the pressure dependencies of Φ_i and τ are measured and if Φ_{isc} is pressure independent. At present this has only been done for the photoreactions of the halopentaamine rhodium(III) complexes described below.

The limiting mechanisms for ligand substitution reactions are associative (A) and dissociative (D). For an excited state ML^*, these can be illustrated thus:

$$\text{(A)} \quad [ML]^* + L' \xrightarrow{k_i} \left(M\overset{L}{\underset{L'}{<}}\right) \longrightarrow ML' + L \qquad (5)$$

$$\text{(D)} \quad [ML]^* + L' \xrightarrow{k_i} (M + L + L') \longrightarrow ML' + L \qquad (6)$$

Interchange mechanisms (I_a or I_d) involve a concerted interchange of an inner sphere ligand L and an outer sphere species L' with varying amounts of associative or dissociative character. For A, the intrinsic volume change ($\Delta V^{\ddagger}_{i}$), which is the result of changes in bond lengths between $[ML]^*$ and the reaction transition state, would be expected to be negative while that for D would be positive. However, the experimentally observed $\Delta V^{\ddagger}_{i}$ is generally more complex owing to contributions from solvation changes ($\Delta V^{\ddagger}_{solv}$) during the activation process.

$$\Delta V^{\ddagger}_{i} = \Delta V^{\ddagger}_{intr} + \Delta V^{\ddagger}_{solv} \qquad (7)$$

For reactions of high charge creation or annilation, (such as substitution reactions involving anionic ligands) $\Delta V^{\ddagger}_{solv}$ can exceed $\Delta V^{\ddagger}_{intr}$ in magnitude, and given that the former is often opposite in sign to $\Delta V^{\ddagger}_{intr}$, it may obscure the latter term. Potential contributions of $\Delta V^{\ddagger}_{solv}$ can be estimated from reaction volume profile diagrams constructed from measured partial molar volumes ($\overline{V}$) of reactants and products and estimates of partial molar volumes of proposed intermediates. Figure 2 is such a diagram for a mechanism involving the dissociation of an ionic ligand. On the diagram are indicated the volume positions of the starting species and dissociated intermediates assuming no change in solvation. Note that a positive contribution to $\Delta V_i^{\ddagger}$ would be expected ($\Delta V_{intr}^{\ddagger}$). Also indicated is the actual volume of the intermediates once solvation of the new charges is taken into account. The solvation contribution ($\Delta V_{solv}^{\ddagger}$) thus leads to an overall negative value of $\Delta V_i^{\ddagger}$ in this case. It can be seen that increased solvation leads to a negative reaction volume $\Delta \overline{V}_o$ as defined by

$$\Delta \overline{V}_o = \Sigma \overline{V}_{products} - \Sigma \overline{V}_{reactants} \qquad (8)$$

It should also be noted from Fig. 2 that the magnitude of $\Delta V_i^{\ddagger}$ relative to the volume differences estimated for the formation of intermediates is a function of the position of the transition state (T.S.) along the reaction coordinate.

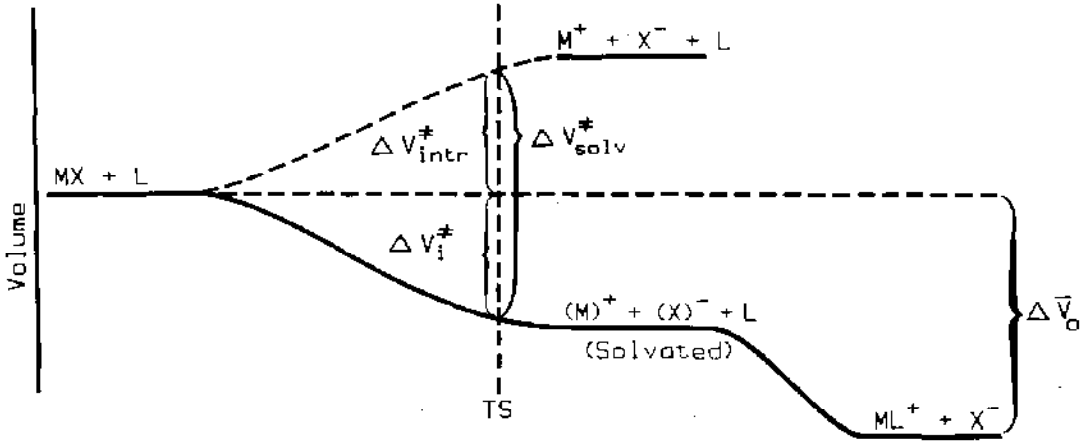


Fig. 2. Volume profile diagram showing the contributions of intrinsic and solvation activation volumes to the observed $\Delta V^{\ddagger}{}_i$ of a hypothetical ligand substitution via a D mechanism.

PHOTOPHYSICAL PROPERTIES

Since competing processes deactivate a reactive excited state (e.g., see Fig. 1) it is crucial to understand the pressure dependencies of all pathways in order to draw valid conclusions regarding the $\Delta V^{\ddagger}$'s of the reactions. Pressure effects on nonradiative pathways have often been assumed to be insignificant relative to those seen for photoreaction. This view finds support in the report by Kirk and Porter (ref. 10) that the lifetimes of

$Ru(bipy)_3^{2+}$, $Cr(bipy)_3^{3+}$ and $Cr(en)_3^{3+}$ in aqueous solution are rather insensitive to hydrostatic pressure to 2.3 kbar. However, while this may often be a valid as well as a convenient assumption, it is not universally correct. The emphasis of our photosubstitution pressure studies has been the measurement of activation volumes both for reaction quantum yields and for lifetimes under identical conditions so that $\Delta V^{\ddagger}$ values for individual rate constants can be calculated (eq. 4) with a minimum of assumptions. In the course of these investigations, we became concerned with related phenomenon, such as how electronic excitation of different orbital parentage affects the volume of the complex, and how pressure influenced rates of intersystem crossing and other nonradiative deactivation phenomenon. These concerns were the stimulus of several investigations of photophysical phenomenon described below.

Many physical properties of the medium itself may change under a high hydrostatic pressure. Physical constants such as dielectric constant, viscosity, diffusion rates and solvent structures can be perturbed due to changes in density and intermolecular forces (ref. 11). The result may be to modify the photophysical properties of a metal complex or other electronically excited chromophore. For example Drickamer and coworkers (ref. 12) have shown that the photoemission properties of $Re(phen)(CO)_3Cl$ in a number of solvents are pressure sensitive and have concluded that one of these perturbations represents a dependence of the radiative rate constant (k_r) on the pressure modified low frequency dielectric constant. The $Re(phen)(CO)_3Cl$ emission is from a metal-to-ligand charge transfer (MLCT) state and has been shown to be very sensitive to solvent effects (ref. 13). Over the pressure ranges (0-4 kbar) used to investigate metal complex photoreactions, water undergoes only small changes in viscosity or dielectric constant (ref. 14). However, such perturbations of the medium are potentially much more important in aprotic organic solvents.

PRESSURE TUNING OF EXCITED STATE EQUILIBRIA

Watts et al. (ref. 15) have shown that several Ir(III) polypyridyl complexes exhibit dual emission from equilibrated excited states in fluid solution. The lifetimes of the emission from the LF and MLCT-type states are identical at ambient temperature supporting the argument that the states are in dynamic equilibrium. We examined the pressure dependence of both the emission spectra and lifetimes of two such complexes $Ir(bpy)_2Cl_2^+$ (I) and $Ir(Mephen)_2Cl_2^+$ (II, Mephen = 5,6-dimethyl-1,10-phenanthroline) to study whether the equilibrium between states of markedly different orbital parentage could be thus perturbed (ref. 7). Figure 3 illustrates the pressure induced spectral changes noted for II in dimethylformamide (DMF) solution. At high pressure there are little or no shifts in the emission spectral maxima but there are changes in the relative

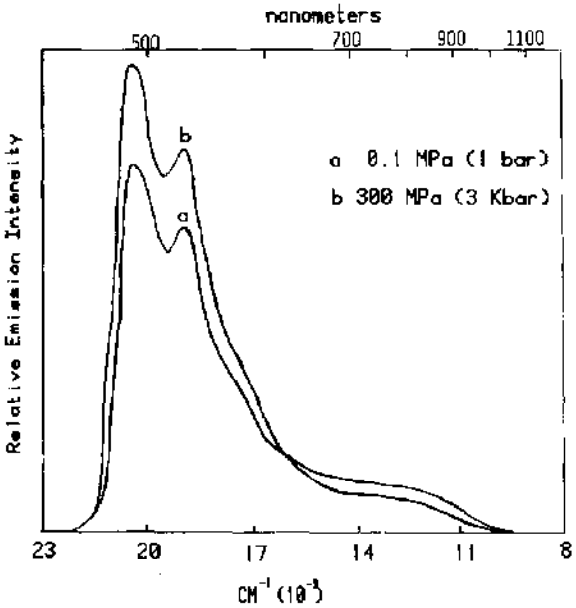


Fig. 3. Emission spectra of $Ir(Mephen)_2Cl_2^+$ in DMF at 0.1 MPa and 300 MPa.

intensities of the MLCT and LF maxima (550 and 720 nm, respectively). A plot of $\ln(I^{ct}/I^{lf})$ vs P is linear (Fig. 4a) with a slope of $-(\Delta V/RT)$ from which the $\Delta V_{apparent}$ value of -4.2 ± 0.5 cm^3/mole can be calculated. Similar behavior was seen for $Ir(bpy)_2Cl_2^+$ in DMF and the $\Delta V_{apparent}$ -4.1 ± 0.8 cm^3/mole determined. The ambient temperature emission lifetimes for both complexes remain independent of the observation wavelength indicating that the two states remain in thermal equilibrium at all pressures.

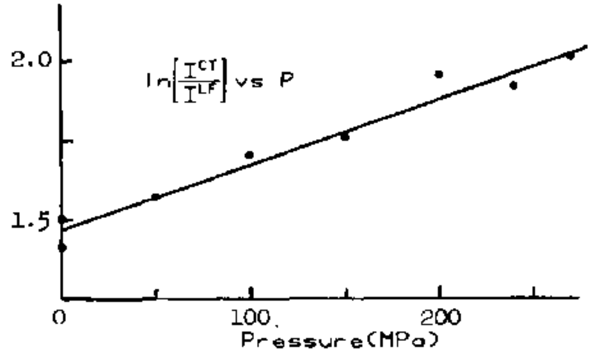
Figure 4b shows the photophysical scheme which describes the observed emissions. According to this scheme lifetimes would be described by

$$\tau^{-1} = \frac{K(k_r^{ct} + k_n^{ct}) + k_n^{lf} + k_r^{lf}}{1 + K} \tag{9}$$

Furthermore, given that I^{ct}/I^{lf} is proportional to the concentration ratio [MLCT]/[LF],

$$\Delta V_{apparent} = - RT \frac{\delta \ln(k_r^{ct}/k_r^{lf})}{\delta P} + \Delta V_{eq}^{*} \tag{10}$$

where ΔV_{eq}^{*} is the volume difference between the two excited states. If it is assumed that the k_r^{ct}/k_r^{lf} ratio is essentially pressure insensitive then $\Delta V_{apparent} \approx \Delta V^*_{eq}$ and the pressure induced changes in spectral intensity can



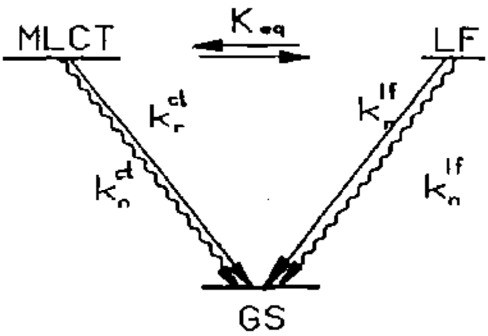


Fig. 4a. ln(I/I) vs P Plot for $Ir(Mephen)_2Cl_2^+$ in DMF.

Fig. 4b. Scheme for dual emissions from two emitting excited states of different orbital parentages.

be attributed to shifts in the relative populations of the two excited states resulting from the difference in partial molar volume between the LF and MLCT type states. That the former state is the larger by 4 cm^3/mole is consistent with the population of σ^*_{M-L} orbitals in the LF state, the result being bond length extensions and volumes estimated as much as 10 cm^3/mole larger than the ground state for some d^6 complexes (ref. 5).

For both complexes lifetime measurements show that higher pressure leads to decreased deactivation rates with $\delta(\ln\tau^{-1})/\delta P$ plots giving the $\Delta V^{\ddagger}$ values +0.3 ± 0.1 cm^3/mole and +4.0 ± 0.2 cm^3/mole for I and II, respectively (ref. 7). The differences can be explained in terms of eqn. 9. Given that emission quantum yields are small and that $k_n^{lf} >> k_n^{ct}$ (ref. 15), eqn. 9 thus simplifies to $\tau^{-1} = k_n^{lf}(1 + K)^{-1}$. For the limiting case $K << 1$, $\Delta V^{\ddagger} = -\frac{\delta}{\delta P}(RT \ln k_n^{lf})$ while for $K >> 1$, $\Delta V^{\ddagger} = \frac{\delta}{\delta P}(RT \ln K)$. For the latter, $\Delta V^{\ddagger}$ would be equal in magnitude but opposite in sign to ΔV^*_{eq}. The present cases should lie somewhere between these extremes. For $Ir(Mephen)_2Cl_2+$ the MLCT state apparently lies at the lower energy (i.e., $K > 1$) (ref. 15) thus a larger ΔV would be expected than for $Ir(bpy)_2Cl_2+$ for which the LF is the lower energy state ($K < 1$).

The assumption that the $k_r{}^{ct}/k_r{}^{lf}$ ratio is pressure insensitive must be examined given the earlier conclusion (ref. 12) that pressure effects on emission from the rhenium(I) complex $Re(phen)(CO)_3Cl$ result from changes in k_r owing to increases in solvent dielectric constant. However, examination of the emission spectra for both $Ir(Mephen)_2Cl_2^+$ and $Ir(bpy)_2Cl_2^+$ in different solvents show the I^{ct}/I^{lf} ratio to decrease in solvents of higher dielectric constant (e.g. DMSO), a change opposite from that induced by pressure (Fig. 3). Thus if the k_r^{ct}/k_r^{lf} ratio is indeed sensitive to dielectric constant perturbations, this may well serve to decrease the overall effect of pressure on the emission spectrum, so that the $\Delta V_{apparent}$ represents only the lower limit for $\Delta V^{\star}_{eq}$.

Solvation may be another factor possibly giving a different value for $\Delta V^{\star}_{eq}$ than the intrinsic volume difference between the MLCT and LF states. If, for example, the LF state were more strongly solvated than the MLCT state owing to a more ionic nature of the distorted Ir(III)-Cl bonds then this should serve to decrease $\Delta V^{\star}_{eq}$. Regardless of the magnitude of $\Delta V^{\star}_{eq}$, these studies serve to illustrate the potential pressure sensitivity of the photochemical/photophysical properties of any metal complex having low lying excited states of comparable energies but of different orbital parentages. Such effects might not only be expected for cases where dual emission is evident but might also be influential for examples where back population of a high energy state is an important pathway for nonradiative deactivation (as has been proposed for $Ru(bpy)_3^{2+}$ in ambient temperature solutions, ref. 16) or for chemical reaction (as has been proposed for chromium(III) complexes, ref. 17).

PRESSURE EFFECTS ON NONRADIATIVE RATES

<u>Spin Equilibria and Intersystem Crossing</u>: There has long been interest in the parameters that determine the equilibria and dynamics of "spin crossover" complexes for which both high spin and low spin electronic states are accessible thermally. Examples include certain d^6 iron(II) complexes which exist in ambient solution as equilibrium mixtures of the quintet high spin (HS) and singlet low spin (LS) electronic isomers (eq. 1, L is generally a polydentate nitrogen heterocycle ligand). (ref. 18)

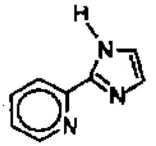
$$\underset{(LS)}{FeL_n^{2+}} \underset{k_{hs}}{\overset{k_{ls}}{\rightleftarrows}} \underset{(HS)}{FeL_n^{2+}} \qquad (11)$$

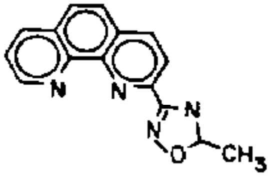
$$K = \frac{[HS]}{[LS]} = \frac{k_{ls}}{k_{hs}} \qquad (12)$$

This process serves as a model for nonradiative deactivation and provides an opportunity for examining the thermodynamic and activation parameters of the associated ligand rearrangement given that the M-L bonds in the HS isomer are about 0.1 angstroms longer than in the LS isomer (ref. 19). Thus partial molar volumes ($\Delta\bar{V}$) of the two spin states may differ by more than 10 cm^3/mole (ref. 20), a value comparable to our estimates of the volume differences between reactive

LF states and the ground state of rhodium(III) amine complexes (ref. 5, see below).

We examined (ref. 21) the pressure effects on the spin relaxation dynamics for two compounds $Fe(pyim)_3^{2+}$ (III) and $Fe(phenmethoxa)_2^{2+}$ (IV) (ligands indicated below) using a laser flash photolysis technique similar to that described by McGarvey (ref. 22) who also has recently reported some related pressure studies (ref. 23). For III and IV the two spin states are in equilibrium (eq. 11) with the K values 0.56 and 5.38 in 298 K acetone with measured partial molar volume differences $\Delta\overline{V}_0$ of 8.1 and 12.3 cm^3/mole (ref. 21), respectively. Pulse laser excitation (532 nm) of each complex leads to transient bleaching of the strong charge transfer bands of the low spin isomer followed by first order relaxation to the original spectrum with lifetimes of 45 ns for III and 110 ns for IV in 298 K acetone. Given that the electronic excited states of polypyridyl complexes of Fe(II) have been shown to have very short lifetimes (<1 ns) (ref. 24) in fluid solution, the transient bleaching can be attributed to the formation of larger than equilibrium concentrations of the HS isomer as one pathway of the excited states, and the subsequent optical changes to the spin relaxation dynamics.


III


IV

The lifetimes measured thus over the pressure range 1-3 kbar were plotted according to

$$\left(\frac{\delta \ln(\tau^{-1})}{\delta P}\right)_T = -\frac{\Delta V^{\ddagger}_{\tau-1}}{RT} \tag{13}$$

The $\Delta V^{\ddagger}_{\tau-1}$ values of 0.0 ± .5 cm^3/mole and 2.0 ± 0.5 cm^3/mole were obtained for III and IV respectively. From these and the values of $\Delta\overline{V}$ and K, the activation volumes for the forward and reverse rates, $\Delta V^{\ddagger}_{ls}$ and $\Delta V^{\ddagger}_{hs}$ were calculated from

$$\Delta V^{\ddagger}_{hs} = \Delta V^{\ddagger}_{\tau-1} - \frac{K}{1+K}\Delta\overline{V} \tag{14}$$

$$\Delta V^{\ddagger}_{ls} = \Delta V^{\ddagger}_{\tau-1} + \frac{1}{1+K}\Delta\overline{V} \tag{15}$$

where

$$\tau^{-1} = k_{hs} + k_{ls} \tag{16}$$

and

$$\Delta V_i^{\ddagger} = RT \frac{\delta}{\delta P} (\ln k_i) \tag{17}$$

The calculated values of $\Delta V_{ls}^{\ddagger}$ and $\Delta V_{hs}^{\ddagger}$ are 5.2±2.0 and -2.9±1.5 cm^3/mole for $Fe(pyim)_3^{2+}$ and 3.9±1.0 and -8.4±2.0 cm^3/mole for $Fe(phenmethoxa)_2^{2+}$. These and other parameters are summarized in Table I. Although coordinates for the transition state can only be estimated from the activation energy and volume terms, it is clear that there are significant pressure effects on the HS → LS relaxation rates. The negative $\Delta V_{hs}^{\ddagger}$ values indicate that the volume of each activated complex is indeed smaller than that of the respective high spin isomer. A qualitative two dimensional potential surface for this transformation is illustrated in Fig. 5. The results suggest that the geometric changes associated with the intersystem crossing under these conditions involve a radial compression of the metal ligand bonds consistent with several theoretical treatments (ref. 26).

TABLE I:
Activation and Thermodynamic Parameters for the Spin Relaxation of the Quintet/Singlet Equilibria of $Fe(pyim)_3^{2+}$ and $Fe(phenmethoxa)_2^{2+}$ in Acetone (Data from ref. 21 and 25).

Parameter	units	$Fe(pyim)_3^{2+}$	$Fe(phenmethoxa)_2^{2+}$
K(25°)		0.56 ± 0.18	5.4 ± 2.0
τ	ns	45 ± 5	110 ± 10
$\Delta H°$	cal/mole	3.8 ± 0.1[a]	5.7 ± 0.1
$\Delta S°$	cal/K mol	11.6 ± 0.3[a]	22.5 ± 0.5
$\Delta \overline{V}$	cm^3/mole	8.1 ± 1.3	12.3 ± 1.0
$\Delta V_{\tau^{-1}}^{\ddagger}$	cm^3/mole	0.0 ± 0.5	2.0 ± 0.3
$\Delta H_{ls}^{\ddagger}$	kcal/mole	6.7 ± 0.3	7.8 ± 0.4
$\Delta H_{hs}^{\ddagger}$	kcal/mole	2.9 ± 0.3	2.1 ± 0.2
$\Delta V_{ls}^{\ddagger}$	cm^3/mole	5.2 ± 2.0	3.9 ± 1.0
$\Delta V_{hs}^{\ddagger}$	cm^3/mole	-2.9 ± 1.5	-8.4 ± 2.0

McGarvey and coworkers have also investigated $\Delta V_i^{\ddagger}$ values for $Fe(pyim)_3^{2+}$ in acetone and several other solvents (ref. 23). Curiously, $\Delta \overline{V}$ for eq. 11 appears to be markedly solvent sensitive although the conclusion in each case is that $\Delta V^{\ddagger}_{hs}$ has a significant negative value. It is obvious that the role of solvent in these nonradiative electronic transitions needs further in depth evaluation.

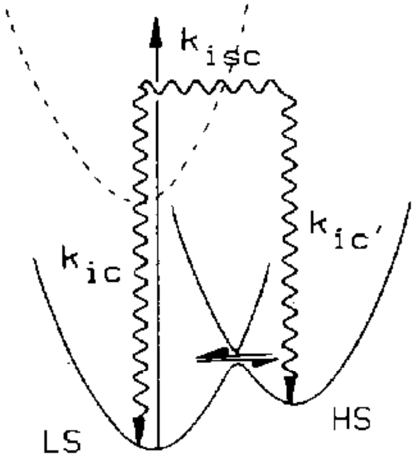


Fig. 5: Well diagram for HS/LS nonequilibrium produced by laser flash.

Nonradiative Deactivation: The analogy between the spin relaxation phenomenon in the d^6 iron(II) complexes described above and nonradiative deactivation from the reactive excited states relevant to the photochemistry of, for example, d^6 Rh(III) amine complexes is admittedly somewhat distant. In the latter case, the vertical displacements of one of the states may be as much as 15,000 cm^{-1}. However, the distortions from the ground state geometries are potentially as large or larger if excitation leads to the population of σ^*_{ML} orbitals. How nonradiative deactivation from such states responds to pressure may give some indication of the mechanism of such processes (e.g. strong and weak coupling, ref. 27).

A special case in this regard is the nonradiative deactivation of the LF excited states of several four coordinate nickel(II) complexes such as $Ni(dpe)Cl_2$(dpe = 1,2 bis(diphenylphosphino)ethane). Laser flash photolysis studies in halocarbon solvents by McGarvey and coworkers showed large negative $\Delta S^{\ddagger}$(~-70 JK^{-1} mol^{-1}) and $\Delta V^{\ddagger}$ (~-10 cm^3/mole) values (ref. 28). Given the conclusion that the lowest energy excited state is tetrahedral while the ground state has a more tightly solvated square planar configuration, these results were interpreted as indicating that the transition state for the nonradiative decay resembled the ground state in configuration.

A somewhat different situation was encountered for the deactivation of the lowest energy MLCT state of $Re(phen)(CO)_3Cl$ and related complexes in various organic solvents (ref. 12). In these cases the emission lifetimes were lengthened owing to decreased k_n values as hydrostatic pressure was applied.

Simultaneously, the emission band of this compound shifts to higher energy, a phenomenon which was correlated with pressure induced increases in the solvent dielectric constant. Thus the decreases in k_n could be attributed to larger energy gaps between ground and excited states lowering the probability of nonradiative deactivation (ref. 27).

A third situation is encountered for deactivation from metal centered LF excited states for complexes, such as the rhodium(III) amine complexes discussed below. Pressure effects on k_n values for the lowest LF states of photosubstitution active complexes are measurable (ref. 5,6). However it is notable that the magnitude and sign of the $\Delta V^{\ddagger}$'s measured for the nonradiative deactivation pathway parallel those of the predominant reactive deactivation pathway. Such an observation may indicate a substantial strong coupling component to the k_n mechanism as we proposed earlier (ref. 29). However, the emission lifetimes of the trans-Rh(cyclam)$(CN)_2^+$ ion, which is not photosubstitution active (ref. 30), is also pressure sensitive (ref. 31), k_n displaying a $\Delta V^{\ddagger}$ value of about -4 cm^3/mole. The emission maxima is blue shifted somewhat over the pressure range k_n increases, a trend opposite to that expected from energy gap law considerations. These phenomenon are currently under more quantitative scrutiny in this laboratory.

PHOTOREACTIONS OF CHROMIUM(III), COBALT(III) AND IRON(II) COMPLEXES

Cr(III) Complexes Photoaquation: The first pressure effects for photosubstitution reactions of transition metal complexes were reported by Kelm and coworkers for a series of Cr(III) complexes (ref. 32,34). These workers measured apparent activation volumes for the photoaquation reactions from pressure effects on the photosubstitution quantum yields, Φ_p. By assuming pressure independent lifetimes, they calculated activation volumes for the excited state processes from the relationship

$$\Delta V_{\Phi}^{\ddagger} = (1-\Phi_p)(\Delta V_p^{\ddagger} - \Delta V_n^{\ddagger}) \qquad (18)$$

where $\Delta V_n^{\ddagger}$ and $\Delta V_p^{\ddagger}$ are for the primary physical deactivation and photochemical reaction processes, respectively. It was also assumed that $\Delta V_n^{\ddagger} \approx 0$, given the earlier work by Kirk and Porter (ref. 10) on the pressure effects on lifetimes for $Cr(en)_3^{3+}$ and $Cr(bipy)_3^{3+}$ in aqueous solution. The $\Delta V^{\ddagger}$ values estimated in this way are summarized in Table II.

For the pentaammine complexes $Cr(NH_3)_5X^{2+}$, there are two photoaquation pathways, ammine and halide loss, respectively. The $\Delta V_{\Phi}^{\ddagger}$ values measured for these two excited state processes were both negative in each case as was $\Delta V_{\Phi}^{\ddagger}$ for ammine labilization from $Cr(NH_3)_6^{3+}$ (see Table II). The negative values for

Table II

Activation and Reaction Volumes for the Photosolvolysis of Chromium(III) Complexes

Complex	Ligand	Solvent	$\Delta V^{\ddagger}_{\Phi}$	$\Delta V^{\ddagger}_{p}$	$\Delta V^{\ddagger}_{thermal}$	Ref.
$Cr(NCS)^{3-}$	NCS^-	H_2O	2.1±0.4	2.9	-	33
CrA_5Cl^{2+}	Cl^-	"	-13.0±0.5	-13	-10.8±0.3	32
	A	"	-6.0±0.1	-9.4	-	"
CrA_5Br^{2+}	Br^-	"	-12.2±0.3	-12	-10.2±0.3	"
	A	"	-6.5±0.1	-10.2	-	"
CrA_5NCS^{2+}	NCS^-	"	-9.8±0.2	-9	-8.6±1.0	"
	A	"	-6.4±0.1	-11.4	-	"
	NCS^-	glycerol/H_2O	-9.5±0.5	-10	-	34
$CrA_6{}^{3+}$	A	"	-6.7±0.5	-12.6	-	"
$Cr(CN)_6^{3-}$	CN^-	H_2O	2.7±0.2	3.0	-	33

a-ΔV_p, ΔV_{Φ}, $\Delta V_{thermal}$ values are in cm^3/mole, A=NH_3
b-All values at ~25°C.

the ammine labilization are particularly relevant given that the overall reaction does not involve charge creation or annilation, thus the overall volume change ΔV should be small in magnitude and potential contributions of $\Delta V^{\ddagger}_{solv}$ to $\Delta V^{\ddagger}_{i}$ should also be small. In addition, the $\Delta V^{\ddagger}_{p}$ values for X^- labilization parallel the analogous thermal reactions which previously have been concluded to proceed via an associative interchange mechanism (ref. 35). Thus these observations were interpreted in terms of excited state reaction pathway with associative character, a conclusion which appears valid if both X^- and NH_3 photolabilization occur by a common mechanism from a single low energy excited state.

For the anionic complexes $Cr(CN)_6^{3-}$ and $Cr(NCS)_6^{3-}$, the measured and calculated $\Delta V^{\ddagger}_{p}$ values were found to be small but positive. These values were interpreted as indicating photosubstitution mechanisms which are much more dissociative in nature than either halide or ammine photosubstitution from the $Cr(NH_3)_5X^{2+}$ ions (ref. 32,33). This presents the interesting postulate that photosubstitution reactions of the same metal center occur by different excited state mechanisms as of result of changes in the coordination sphere (ref. 36,37). A more dissociative mechanism might indeed be expected for those complexes where monoanion is being released from a trinegative complex.

An alternative interpretation for the range of activation volumes across the Cr(III) series may lie in the perturbation of rates and equilibria illustrated in Fig. 6 and assumed unaffected by pressure in the simplified kinetic scheme. The magnitude of the energy gap between the lowest energy quartet and doublet excited states is a function of the ligands, and for many Cr(III) complexes these two excited states are relatively close in energy. Thus it is conceivable that the equilibrium constant (or rate of intersystem crossing) between the two states may be quite pressure sensitive in analogy to the $Ir(bpy)_2Cl_2^+$ complex described above (ref. 7). The reason for this would lie in the much greater distortion of the metal ligand bonds in the quartet excited state (relative to the ground state). For those cases where the doublet and quartet states are thermally accessible to each other, shifts in this equilibrium could have major affects both on lifetimes and on reaction quantum yields given the likelihood that both reaction and nonradiative deactivation occur competitively from each state.

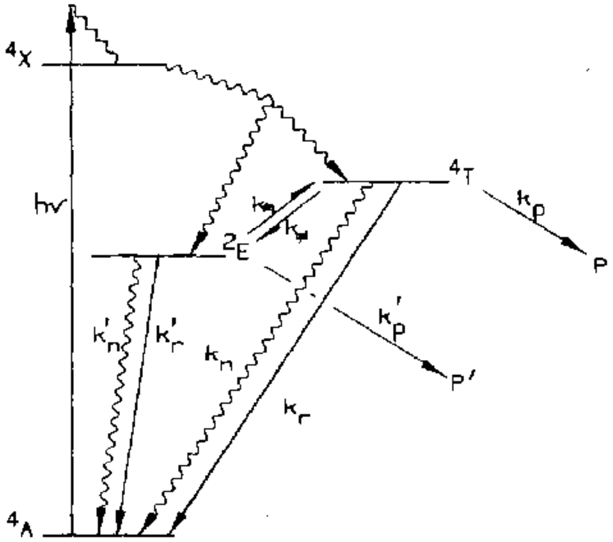


Fig. 6. A simplified generalized state diagram for the photochemistry of Cr(III) complexes (O_h symmetry assumed).

Cobalt(III): Pressure effects have also been reported for the photoreactions of $Co(CN)_6^{3-}$ and of $Co(NH_3)_5Br^{2+}$ in aqueous solution. In the former case a $\Delta V_\phi^\ddagger$ of 1.3 cm^3/mole was measured for photoaquation of CN^- (eq. 19) leading to a calculated $\Delta V_p^\ddagger$ value of 2.0 cm^3/mole based on the assumption that all other deactivation pathways are pressure insensitive (ref. 33).

$$Co(CN)_6^{3-} + H_2O \xrightarrow{h\nu} Co(CN)_5(H_2O)^{2-} + CN^- \qquad (19)$$

Previous studies have argued (ref. 38) that the reactive state is the lowest energy LF triplet $^3T_{1g}$ formed by internal conversion/intersystem crossing from the initially populated states with an efficiency near unity. A volume profile treatment has suggested that a D mechanism would have a $\Delta V^\ddagger$ as large as

+9.4 cm^3/mole (ref. 33); however, this treatment focuses on the ΔV between ground state $Co(CN)_6^{3-}$ and the fully dissociated fragments $Co(CN)_5^{2-}$ and CN^-. Franck Condon calculations have interpreted the vibrational structure of ligand field bands in the absorption and emission spectra of $Co(CN)_6^{3-}$ in terms of distortions of approximately 0.1 angstroms in the Co-CN bond between the ground state and LF excited state (ref. 39). Thus the reactive LF excited state would have a $\overline{V}$ significantly larger than that of the ground state, and the above calculation undoubtedly overestimates the probable volume change.

Kirk and Porter (ref. 40) have reported on the pressure dependencies of the photoaquation and photoredox quantum yields for aqueous $Co(NH_3)_5Br^{2+}$.

$$Co(NH_3)_5Br^{2+} + H_2O \longrightarrow Co(NH_3)_5(H_2O)^{3+} + Br^- \qquad (20)$$

$$Co(NH_3)_5Br^{2+} \longrightarrow Co^{2+} + ? \qquad (21)$$

With increasing pressure, quantum yields for both processes decrease. The latter reaction is somewhat more pressure sensitive; for 313 nm excitation, the respective $\Delta V^{\ddagger}_{\Phi}$ values are 2.5 and 4.8 cm^3/mole for eqns. 20 and 21 respectively. These results are interpreted in terms of the oft discussed mechanism (Fig. 7), in which a $Co^{II}(Br\cdot)$ caged radical pair is formed from the ligand to metal charge transfer state (CT*). This radical pair can decay by backreaction to reform $Co(NH_3)_5Br^{2+}$(k_8), diffusion apart to give redox products (k_6) or diffusion/back electron transfer to give aquation products (k_7). The positive values

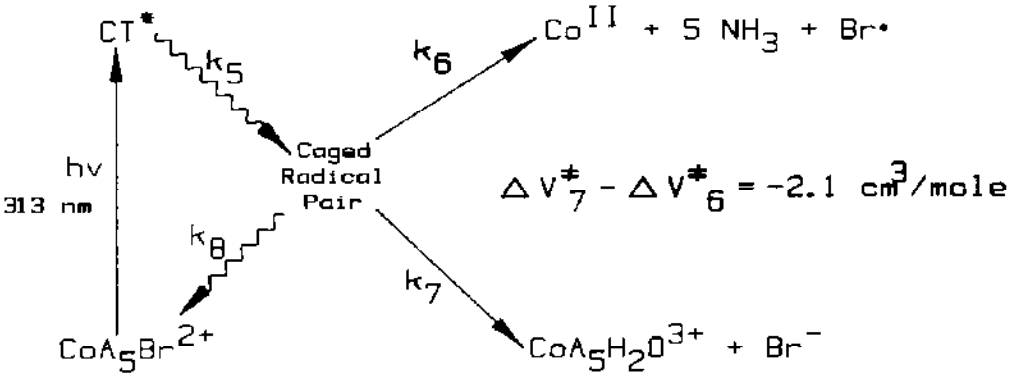


Fig. 7. Kinetic scheme for the charge transfer photochemistry of CoA_5Br^{2+} in aqueous solution assuming a caged radical pair as the precursor for both photoaquation of Br^- and photoreduction of Co(III) to Co(II).

of $\Delta V^{\ddagger}_{\Phi}$ would be consistent with the dissociative nature of both proposed processes and the smaller value for photoaquation consistent with the contribution of a negative $\Delta V^{\ddagger}_{solv}$ step owing to the creation of charge as the 2+ caged radical pair forms the separated Br⁻ and a 3+ Co(III) intermediate or product. However, as Kirk and coworkers noted (ref. 40) a definitive interpretation of the $\Delta V^{\ddagger}_{\Phi}$ values is hampered by the absence of independent information regarding those processes forming the caged radical pair and governing its decay to the starting material.

Iron(II): Drickamer and Finston (ref. 41) have investigated the pressure effects on the photoaquation of $Fe(CN)_6^{4-}$ in aqueous solution by following the photoinduced change in conductivity. The first order photocurrent risetime is related to the relative quantum efficiency of the photoreaction. The bimolecular recombination to reform $Fe(CN)_6^{4-}$ was also followed by the same technique:

$$Fe(CN)_6^{3-} \underset{k_{th}}{\overset{h\nu}{\rightleftarrows}} Fe(CN)_5(H_2O)^{2-} + CN^- \qquad (22)$$

The $\Delta V^{\ddagger}_{\Phi}$ values of 6.2 and 5.1 cm^3/mole were measured in water and 20% EtOH/water, respectively, and $\Delta V^{\ddagger}_{p}$ values of 7.7 and 8.7 cm^3/mole were calculated from eqn. 18 assuming $\Delta V^{\ddagger}_{n} = 0$. The $\Delta V^{\ddagger}_{th}$ for k_{th} in water was found to be 13.5±1.5 cm^3/mole. Comparing the $\Delta V^{\ddagger}$ values, the authors concluded that the dark reaction occurs by a limiting dissociative mechanism while the smaller positive value of $\Delta V^{\ddagger}_{p}$ indicates an interchange dissociative (I_d) mechanism for the excited state reaction. However, given that the excited state reaction is likely to occur at a much earlier transition state and that the reactive excited state (probably the $^3T_{1g}$ LF state in this case) of $Fe(CN)_6^{4-}$ would be significantly larger than the corresponding ground state, the observed $\Delta V^{\ddagger}_{p}$ may be a reasonable value for a limiting D pathway for the photoreaction as well.

RHODIUM(III) COMPLEXES: PHOTOSUBSTITUTION AND PHOTOISOMERIZATION

This section will focus on the ligand field photosubstitution reactions of the Rh(III)halopentaammine complexes.

$$Rh(NH_3)_5X^{2+} + S \xrightarrow{h\nu} \begin{cases} \longrightarrow Rh(NH_3)_5S^{3+} + X^- \\ \longrightarrow trans\text{-}Rh(NH_3)_4(S)X^{2+} + NH_3 \end{cases} \qquad (23)$$

For these systems it has been shown that LF excitation is followed by rapid intersystem crossing ($\Phi_{isc} \sim 1$) to the lowest energy excited state (LEES, see Fig. 8). From this state, reactive (k_p), radiative (k_r), and nonradiative (k_n)

deactivation occur competitively. The measurement of the luminescent lifetime and quantum yields of photoreaction under identical conditions (ref. 42,43) has allowed the calculation of the actual rate constants for the individual processes according to

$$\Phi_i = k_i\tau \tag{24}$$

These studies also demonstrated that the photoreactions of $Rh(NH_3)_5Cl^{2+}$ were dramatically solvent dependent, Cl^- labilization predominating in aqueous or formamide solutions, NH_3 labilization predominating in methanol, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) solutions. While all the excited state rate constants, as calculated according to eqn. 26, proved solvent dependent, the marked variation in photoreactivity could be largely attributed to the much greater sensitivity of the excited state Cl^- aquation rates to the solvent nature (Table III).

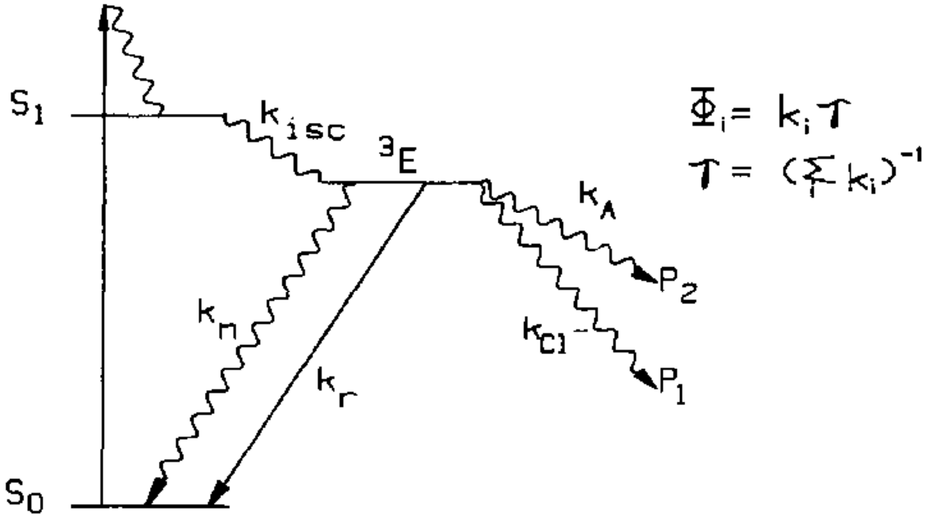


Fig. 8. Jablonski diagram for photochemistry occuring from a lowest energy ^3E state.

In collaboration with van Eldik, Kelm, Weber and Offen, we have determined the pressure dependencies of Φ_i and of τ independently (ref. 5,6). From these data the $\Delta V_i^\ddagger$ values for the key individual excited state rates were calculated according to eqns. 25-27 with considerably more confidence than in those cases described above for other metal complexes.

$$\Delta V_A^\ddagger = \Delta V_{\Phi_A}^\ddagger - \Delta V_\tau^\ddagger \tag{25}$$

$$\Delta V^{\ddagger}_{X^-} = \Delta V_{\Phi_X} - \Delta V^{\ddagger}_{\tau} \tag{26}$$

Given that $k_r << k_n, k_p$ then,

$$\Delta V^{\ddagger}_{n} = \Delta V^{\ddagger}_{\tau-1} - \frac{\Phi_X \Delta V^{\ddagger}_{\Phi_X} + \Phi_A \Delta V^{\ddagger}_{\Phi_A}}{1 - \Phi_A - \Phi_X} \tag{27}$$

The relevant $\Delta V^{\ddagger}_{\Phi}$, $\Delta V^{\ddagger}_{\tau-1}$ and $\Delta V^{\ddagger}_{l}$ values are summarized in Table IV. What is immediately apparent from these data are the large positive $\Delta V^{\ddagger}_{l}$ values for ammine photosubstitution and the large negative $\Delta V^{\ddagger}_{l}$ values for halide photolabilization in all solvents.

Table III.

Solvent effects on the deactivation rate constants from the ligand field excited state of $Rh(NH_3)_5Cl^{2+}$. (Rate constants are in the units 10^6 sec^{-1}.)

Solvent	k_{Cl}	k_A	k_n	ΔG_s [a]
H_2O	14.2	3.1	54	-2.7
FMA	4.6	1.8	30	-0.4
DMSO	0.39	0.73	15	6.0
DMF	<0.13	2.6	28	7.2

a-ΔG_s is the difference in free energy of Cl^- solvation relative to methanol. (Data from ref. 42,43.)

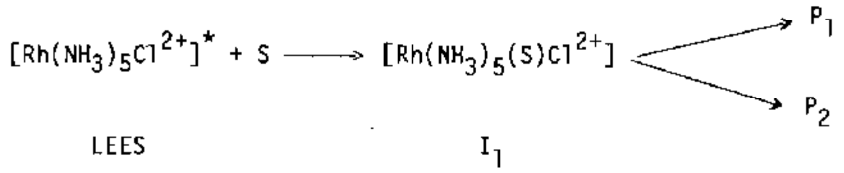
Table IV.

Volumes of Activation (in $cm^3 mol^{-1}$) calculated from pressure effects on the photoreaction/photoluminescence properties of RhA_5X^{2+} in various solvents

Solvent	$\Delta V^{\ddagger}_{\Phi_X}$	$\Delta V^{\ddagger}_{\Phi_A}$	$\Delta V^{\ddagger}_{\tau-1}$	$\Delta V^{\ddagger}_{X}$	$\Delta V^{\ddagger}_{A}$	$\Delta V^{\ddagger}_{n}$
$Rh(NH_3)_5Cl^{2+}$						
H_2O	-5.2±0.4	12.7±1.2	(-3.4)	-8.6±1.6	9.3±1.9	(-2.6)
D_2O	-4.2±0.5	9.5±1.6	-3.5±1.1	-7.7±1.6	6.2±2.2	-2.6±1.0
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
DMF	-	6.3±0.9	1.3±0.2	-	7.6±1.1	0.7±0.3
DMSO	-7.8±1.8	4.4±0.9	-1 ±1	-8.9±2.7	3.3±1.8	-1 ±1
$Rh(NH_3)_5Br^{2+}$						
H_2O	-10.3±1.2	4.6±0.6	(3.5)	-6.8±1.6	8.1±1.2	(+2.5)
D_2O	-9.4±1.5	3.5±0.5	(4.1)±0.6	-5.8±1.8	7.5±1.1	+2.5±1.2

In order to interpret ΔV_i values for the excited state deactivation pathways, it is valuable to reaction profile diagrams for proposed mechanisms. Volume profiles are constructed using the partial molar volumes of the reactants, products and intermediate species to give a relatively good positioning of the transition state with respect to volume. The problem with such models is the uncertainty of the volume of the intermediate species. For excited state reactions an additional complexity is the uncertain volume of the excited state itself (ref. 6).

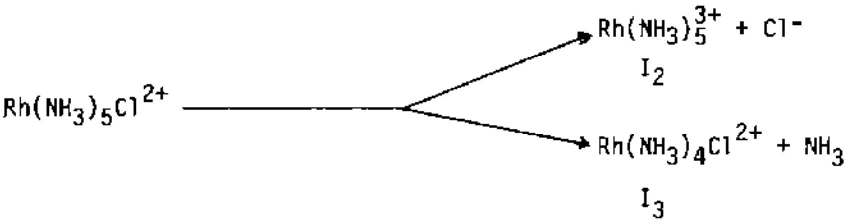
Consider the volume profile expected for a limiting A mechanism proceeding via associative attack by solvent to give a seven-coordinate intermediate, I_1, followed by ligand loss to give products:



$$\begin{tikzcd} \underset{\text{LEES}}{[Rh(NH_3)_5Cl^{2+}]^*} + S \arrow[r] & \underset{I_1}{[Rh(NH_3)_5(S)Cl^{2+}]} \arrow[r] \arrow[dr] & P_1 \\ & & P_2 \end{tikzcd} \qquad (28)$$

The volume of the transition state would lie along the volume profile between the reactants and I_1. The limiting $\Delta V^\ddagger$ for this mechanism would be the difference between the intermediate I_1 and the starting species $V(I1) - V(LEES) - V(S)$. While the values of $V(I_1)$ and $V(LEES)$ are unknown, they can be estimated from other volume data to give a $\Delta\overline{V}$ for the formation of I_1 estimated to be -15 cm^3/mole (ref. 5,6). A key point is that similar negative values would be expected for both $\Delta V_A^\ddagger$ and $\Delta V_{Cl}^\ddagger$ according to the associative mechanism. Thus the positive $\Delta V_A^\ddagger$ values experimentally found argue against the operation of a common associative photosubstitution mechanism for these Rh(III) complexes.

In contrast a limiting dissociative mechanism leads to two different intermediates



$$\begin{tikzcd} & \underset{I_2}{Rh(NH_3)_5^{3+} + Cl^-} \\ Rh(NH_3)_5Cl^{2+} \arrow[ur] \arrow[dr] & \\ & \underset{I_3}{Rh(NH_3)_4Cl^{2+} + NH_3} \end{tikzcd} \qquad (29)$$

The large and rather consistent difference between halide and amine photolabilization could be attributed to negative $\Delta V_{solv}^\ddagger$ contributions to $\Delta V_{Cl}^\ddagger$ owing to charge creation as halide dissociates from the dipositive $Rh(NH_3)_5X^{2+}$ ion to form the tripositive cation I_3 and X^-. The dissociation of ammine to give I_2 would afford no appreciable charge creation, hence a large $\Delta V_{solv}^\ddagger$ would not be expected. The volume changes calculated for the reactions to the five-coordinate intermediates I_2 and I_3 are -17.8 cm^3/mole for chloride loss and +3.9 cm^3/mole for ammine aquation. The key conclusion is that the differences in $\Delta V^{\ddagger}_{A}$ and $\Delta V^{\ddagger}_{X^-}$ are consistent with the dissociative mechanism for the substitution reactions of LF excited states. These calculations suggest that this difference could be as large as 22 cm^3/mole in aqueous solution. The observed difference ($\Delta V^{\ddagger}_{A} - \Delta V^{\ddagger}_{Cl^-}$) is 17 cm^3/mole. (The difference in FMA solution is only 9.0 cm^3/mole. It is possible that the smaller difference reflects some other pressure effect such as changes in the dielectric constant or the viscosity, but these were not investigated.)

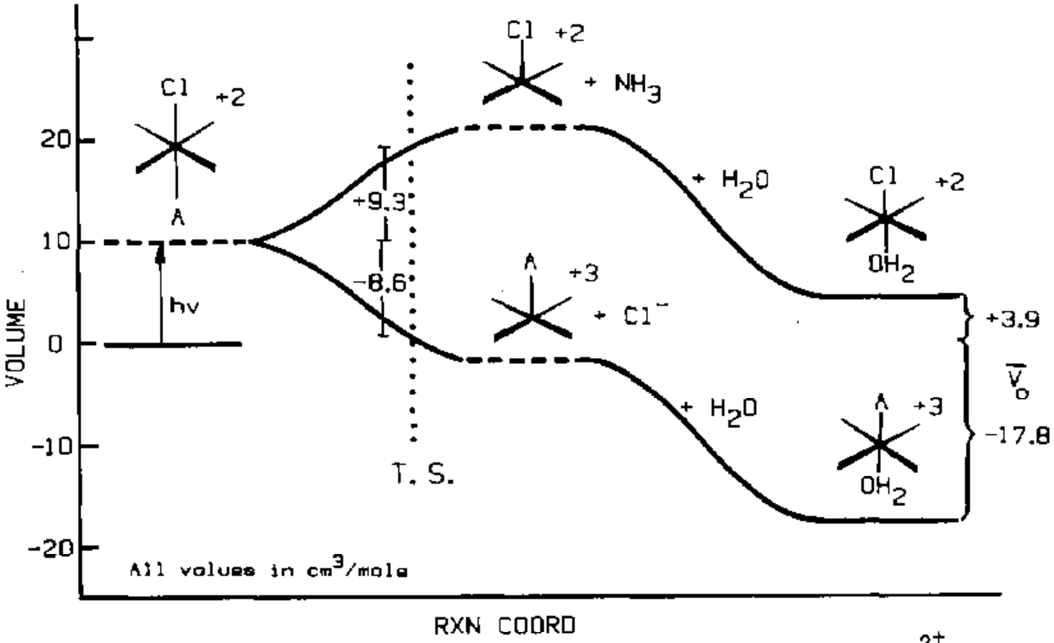


Fig. 9. Volume profile diagram for the photoaquation of $Rh(NH_3)_5Cl^{2+}$ in aqueous solution via the proposed dissociative mechanism. Volumes of activation ($\Delta V^{\ddagger}_{p}$) and reaction ($\Delta\overline{V}$) are shown for the two pathways.

Although the differences between ΔV_A and ΔV_{Cl^-} might be explained by the operation of two distinct mechanisms for these photosubstitution pathways, the data is equally well explained by the differing solvent contributions to the competitive dissociations of NH_3 or halide from the LF excited state. Alternatively an interchange mechanism showing a greater associative character for Cl^- substitution might be argued. However, the rate data of Table III show no correlation with solvent donor properties (ref. 44). Furthermore, recent investigations of product stereochemistries resulting from the LF photoaquations of tetraammine rhodium(III) complexes $Rh(NH_3)_4XY^{n+}$ provide very strong circumstantial evidence in support of a limiting D mechanism for the excited state substitution reaction (ref. 46). Apparent activation volumes $\Delta V^{\ddagger}_{\Phi}$ have also been measured for some of these tetraammine complexes (ref. 47), the absolute values of these were generally small, a result argued to imply an early transition state for the excited state dissociation pathway. An early transition state would be consistent with the observation that the excited state substitution rates of the tetraammine complexes have been determined (ref. 48) to be roughly an order of magnitude faster than those of the already very reactive ligand field excited states of the pentaammine complexes (Table III).

CONCLUDING REMARKS

It is clear from the above discussion that pressure effects on the dynamics and equilibria of excited state processes provide valuable new insight into the mechanistic interpretation of these. We have measured $\Delta V^{\ddagger}$'s for the rates of reactions and other nonradiative processes occuring on the nsec time scale and offer some models for the relevant pathways. While these allow one to envision qualitatively the types of distortion occuring along excited reaction coordinates, one should be cognizant that, like other activation parameters, there is sufficient ambiguity in the interpretation of $\Delta V^{\ddagger}$ values that such results alone are unlikely to provide a definitive description of an excited state mechanism. Some of the ambiguity lies in the unknown partial molar volumes of reactive excited states and some is the result of the difficulty of separating intrinsic $\Delta V^{\ddagger}$'s from changes in the solvation and changes in the properties of the medium. Further investigations of pressure effects on radiative and nonradiative deactivation pathways including intersystem crossing, equilibria between states of different orbital parentages and the rates of excited state reactions are in progress in this laboratory.

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