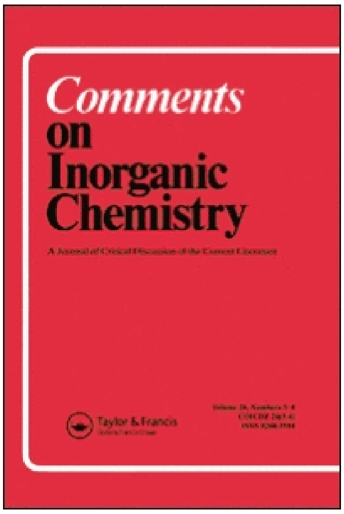

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Mechanistic Implications of Pressure-Dependent Photochemical and Photophysical Parameters of Chromium(III) Complexes

John F. Endicott[a]; Chong Kul Ryu[a]
[a] Department of Chemistry, Wayne State University, Detroit, Michigan

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Mechanistic Implications of Pressure-Dependent Photochemical and Photophysical Parameters of Chromium(III) Complexes

Mechanistic interpretation of observed pressure-dependent photochemical $\phi(X)$ and photophysical (τ) parameters can be very complicated when more than one photoactive electronic state must be considered. The $^4T_{2g}$ and ^2E_g states of $Cr(NH_3)_6^{3+}$ differ by (4–5) × 10^3 cm^{-1} and are both photoactive. Proposed models either postulate a single channel for deactivation of the ^2E_g state or several competing channels. Systematic approaches for the mechanistic evolution of pressure-dependent quantum yields and lifetimes are presented. The implications of the published pressure dependencies depend on the mechanistic model proposed. For example, the single channel, back intersystem crossing model ($^4T_{2g} \leftarrow {}^2E_g$) requires a volume of activation for NH_3 aquation from the $^4T_{2g}$ state, $\Delta V^{\ddagger}_{NH_3} \simeq -13 \pm 2$ cm^3 mol^{-1}, while a model assuming multiple competing channels for doublet decay results in $\Delta V^{\ddagger}_{NH_3} = -4$ cm^3 mol^{-1}. Both of these models imply a strongly associative pathway for ($^4T_{2g}$) $Cr(NH_3)_6^{3+}$ aquation. Other models are considered, and photosubstitution in the most plausible of these also appears to be associative. Thus prevailing theories, based on dissociative photoreaction pathways, are probably inconsistent with the published pressure effects.

INTRODUCTION

Volume changes which occur along the reaction coordinate contribute to the pressure dependence of chemical reaction rates.[1–5] However, the accompanying mechanistic information is often difficult to extract, especially in systems with competing reaction pathways. A number of research groups[6–10] have recently been using the pressure dependence of photochemical and photophysical

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processes as mechanistic probes of excited state behavior in transition metal complexes. A complicating feature of the photochemistry and photophysics of these compounds is that there are often two or more photoactive electronic excited states close in energy. Such situations have rarely been treated properly in the literature. This is specifically a problem in studies of the coordination complexes of chromium(III) for which both the lowest energy quartet and doublet electronic excited states are often reported to be photoactive. The energy difference between these states is usually less than 4×10^3 cm^{-1}. Inferring mechanistic information from such a system is actually very difficult. However, valid inferences can be extracted, based on limiting models for the photochemical and photophysical behavior of the electronically excited system. In order to do this it is necessary to know the fractions of products which are generated following population of each of the photoactive states, the pressure dependence of the quantum yields of products and the pressure dependence of the lifetime of the lowest energy excited state. Meaningful mechanistic inferences are not possible unless all this information is available.

A variety of photochemical mechanisms have been proposed for the excited state behavior of Cr(III) complexes, and, in their limiting forms, these mechanistic models lead to dramatically different interpretations of the pressure-dependent photophysical and photochemical parameters. There are, in principle, several pathways for relaxation or product formation for a photoactive electronic excited state. If these pathways are independent, each can have a different pressure dependence. We will consider a simple three-state system, with two photoactive states. This is the simplest scheme applicable to chromium(III). Treatment of the upper state is relatively straightforward and we will simply assume that all processes are independent and kinetically competitive in the upper state. It is necessary to consider two general limiting categories of behavior for the lowest energy excited state: (a) there is only one channel for escape from this state; and (b) there are several kinetically competitive channels (reaction, nonradiative relaxation, etc.) for escape from this state. In the most general case, the behavior of intermediates (I) must be considered in addition to the behavior of excited states.

The mechanistically useful, pressure-dependent experimental parameters are defined by

$$-\mathrm{RT}\left\{\frac{\partial \ln \phi(\mathrm{X})}{\partial P}\right\}_{\mathrm{T}} = \Delta V^{\ddagger}_{\phi(\mathrm{X})}$$

$$-\mathrm{RT}\left\{\frac{\partial \ln \tau(\mathrm{D})}{\partial P}\right\}_{\mathrm{T}} = \Delta V^{\ddagger}_{\tau(\mathrm{D})}$$

The necessary photochemical and photophysical quantities have been reported for $\mathrm{Cr(NH_3)_6^{3+}}$ [8,9,11–13] and for the photoaquation of ammonia in $\mathrm{Cr(NH_3)_5NCS^{2+}}$.[8,9,11,13] These parameters are collected in Table I.

Single Channel for Lower State Decay

The most commonly cited mechanistic models proposed[14–19] for chromium(III) photochemical or photophysical behavior can be regarded as limiting single-channel models of the ^{2}E state. For two

TABLE I

Experimental parameters pertinent to analysis of pressure-dependent photochemical and photophysical properties of $\mathrm{Cr(NH_3)_6^{3+}}$ and $\mathrm{Cr(NH_3)_5NCS^{2+}}$

Parameter	Numerical Values Found for $\mathrm{Cr(NH_3)_6^{3+}}$	 $\mathrm{Cr(NH_3)_5NCS^{2+}}$
$\phi(\mathrm{NH_3})$	0.45[a]	0.42[b,c]
$\phi(\mathrm{NCS^-})$		0.02[b,c]
f^u	0.25[d]	0.25[b,d,e]
f^q	0.75[d]	0.75[b,d,c]
$\Delta V^{\ddagger}_{\phi(\mathrm{NH3})}$ cm^{3}mol^{-1}	-6.7 ± 0.5[c,f]	-6.4 ± 0.1[c,f]
$\Delta V^{\ddagger}_{\phi(\mathrm{NCS-})}$ cm^{3}mol^{-1}		-9.8 ± 0.2[c]
$\Delta V^{\ddagger}_{\tau(\mathrm{D})}$ cm^{3}mol^{-1}	-4.3 ± 0.4[f]	-6.9 ± 0.1[f]

[a] Ref. 12.
[b] Ref. 13.
[c] Ref. 8.
[d] Ref. 11.
[e] For $\mathrm{NH_3}$ photoaquation.
[f] Ref. 9.

photoactive states, Q and D, the quantum yield for formation of product X is formulated

$$\phi(\mathrm{X}) = \eta_{\mathrm{isc}} k_{\mathrm{I}}^{\mathrm{D}} \tau(\mathrm{D}) p_{\mathrm{X}}^{\mathrm{D}} + k_{\mathrm{I}}^{\mathrm{Q}} \tau(\mathrm{Q}) p_{\mathrm{X}}^{\mathrm{Q}} \tag{1}$$

where η_{isc} is the crossing efficiency from Q to populate D, $k_{\mathrm{I}}^{\mathrm{R}}$ is the rate constant for generating the product-forming intermediate from excited state R (R = Q or D), $\tau(\mathrm{R})$ is the lifetime of state R and $p_{\mathrm{X}}^{\mathrm{R}}$ is the probability that product X is formed from any intermediate species produced in the reactive decay of state R. In any mechanism which postulates a single channel for escape from D, $k_{\mathrm{I}}^{\mathrm{D}} = [\tau(\mathrm{D})]^{-1}$, and Eq. (1) reduces to

$$\phi(\mathrm{X}) = \eta_{isc} p_{\mathrm{X}}^{\mathrm{D}} + k_{\mathrm{I}}^{\mathrm{Q}} \tau(\mathrm{Q}) p_{\mathrm{X}}^{\mathrm{Q}} \tag{2}$$

1. *Back Intersystem Crossing.* If the only pathway for relaxation of the lower excited state is by means of thermal repopulation of the upper state, $p_{\mathrm{X}}^{\mathrm{D}} = p_{\mathrm{X}}^{\mathrm{Q}} = p$. In this kind of model, one must allow for multiple passes through the lower state. With these considerations, Eq. (2) becomes,

$$\phi(\mathrm{X}) = \eta_{\mathrm{X}} p \left[1 + \sum_{n=1}^{\infty} \eta_{isc}^{n} \right] = \eta_{\mathrm{X}} p/(1 - \eta_{isc}) \tag{3}$$

and

$$\Delta V_{\phi(\mathrm{X})}^{\ddagger} = \Delta V_{\eta(\mathrm{X})}^{\ddagger} + \Delta V_{p}^{\ddagger} + (\eta_{isc} \Delta V_{\eta(isc)}^{\ddagger})/(1 - \eta_{isc}) \tag{4}$$

Since

$$\Delta V_{\eta(i)}^{\ddagger} = (1 - \eta_i) \Delta V_i^{\ddagger} - \sum_{j \neq i} \eta_j \Delta V_j^{\ddagger}$$

(where the sum includes all kinetically competitive processes except the ith), Eq. (4) can be re-expressed in terms of parameters for the individual kinetically competitive steps

$$\Delta V_{\phi(\mathrm{X})}^{\ddagger} = [1 - \eta_{\mathrm{X}} - \eta_{\mathrm{X}} \eta_{isc}/(1 - \eta_{isc})] \Delta V_{\mathrm{X}}^{\ddagger} - \eta_{ic} \Delta V_{ic}^{\ddagger}/(1 - \eta_{isc}) + \Delta V_{p}^{\ddagger} \tag{5}$$

For $Cr(NH_3)_6^{3+}$, $\phi(X) = 0.45$ and about 75% of the photoreaction is quenched when the doublet state is quenched.[17] If $p \simeq 1$, these experimental parameters substituted into Eq. (3) yield: $\eta_X = 0.12$; $\eta_{ic} = 0.13$; $\eta_{isc} = 0.75$.[20] The experimental volumes of activation are $\Delta V^{\ddagger}_{\phi(X)} = -6.7 \pm 0.5$ cm^3 mol^{-1} and $\Delta V^{\ddagger}_{\tau(D)} = -4.3 \pm 0.4$ cm^3 mol^{-1}.[9] Since the difference in molar volumes of the excited doublet and quartet states is approximately 3.5 ± 0.5 cm^3 mol^{-1},[9,21] $\Delta V^{\ddagger}_{isc} \simeq +0.8 \pm 0.9$ cm^3 mol^{-1} for this model. Assuming that $\Delta V^{\ddagger}_{ic}$ and $\Delta V^{\ddagger}_{p}$ are both about zero in Eq. (5), $\Delta V^{\ddagger}_{X} \simeq -13 \pm 2$ cm^3 mol^{-1}. This implies that the transition state for product formation has a significantly smaller molar volume than the quartet excited state from which it is formed. Thus, the limiting back intersystem crossing model is only consistent with a strongly *associative* pathway for excited state reaction in chromium(III) systems. The most commonly cited theoretical treatments of chromium photochemistry have *assumed* a dissociative reaction pathway.[22-27] Very similar inferences are obtained for $Cr(NH_3)_5NCS^{2+}$ (Table II).

2. *Direct Reaction.* An alternative single-channel approach postulates that the (^{2}E)Cr(III) excited state can only be relaxed by means of a direct chemical reaction.[18] This suggests a limiting model in which the immediate photoproducts are electronically correlated with (^{2}E)Cr(III) and back intersystem crossing can be ignored; thus

$$\phi(X) = \eta_{isc} p_X^D + k_I^Q \tau(Q) p_X^Q \tag{6}$$

$$\tau(D) = (k_I^D)^{-1}$$

and

$$\Delta V^{\ddagger}_{\phi(X)} = (f^u - \eta_X)\Delta V^{\ddagger}_{XQ} + f^q \Delta V^{\ddagger}_{isc} - \eta_{ic}\Delta V^{\ddagger}_{ic} + f^q \Delta V^{\ddagger}_{p(X,D)} + f^u \Delta V^{\ddagger}_{p(X,Q)}$$

where f^q and f^u are the quenchable and unquenchable fractions of reaction, respectively. In this model $\Delta V_{\phi(X)}$ is predominately a quartet state property. If we assume that $\Delta V^{\ddagger}_{ic}$ and $\Delta V^{\ddagger}_{isc}$ are each

TABLE II

Mechanistic parameters inferred for various, limiting photochemical models

	Values Calculated[a] (or Assumed) Based On							
	A. Single Channel Models						B. Multiple Competing Channel Models	
	1. B.I.S.C.		2. Direct Reaction		3. Crossing to Intermediate			
Parameter	$Cr(NH_3)_6^{3+}$	$Cr(NH_3)_5NCS^{2+}$	$Cr(NH_3)_6^{3+}$	$Cr(NH_3)_5NCS^{2+}$	$Cr(NH_3)_6^{3+}$	$Cr(NH_3)_5NCS^{2+}$	$Cr(NH_3)_6^{3+}$	$Cr(NH_3)_5NCS^{2+}$
$\eta_{X,Q}$	0.12	0.11	0.12	0.105	0.25[b]	0.25[b]	0.12	0.11
η_{ic}	0.13	0.14	0.55	0.56	0.25[b]	0.25[b]	(0)	(0)
η_{isc}	0.75	0.75	0.33	0.33	0.75	0.75	0.88	0.89
$\eta_{X,D}$	[c]	[c]	[c]	[c]	[c]	[c]	0.34	0.35
η_{nr}	[c]	[c]	[c]	[c]	[c]	[c]	0.66	0.65
$p_{X,Q}$	(1)	(1)	(1)	(1)	0.45[d]	0.44[d]	(1)	(1)
$p_{X,D}$	[c]	[c]	(1)	(1)	0.45[d]	0.44[d]	(1)	(1)
$\Delta V^{\ddagger}_{X,Q}$ cm^3 mol^{-1}	-13 ± 2[e]	-11 ± 2[e]	-50 ± 20	-46 ± 21	[f]	[f]	-7 ± 2	-3 ± 1

$\Delta V^{\ddagger}_{X,D}$ cm^3 mol^{-1}	[c]	[c]	4.3 ± 2	7 ± 2	4.3[c]	6.9[c]	−4 ± 3	−1.5 ± 3
$\Delta V^{\ddagger}_{ic}$ cm^3 mol^{-1}	(0)	(0)	−1.5 ± 3	−1.5 ± 3	[c]	[c]		
$\Delta V^{\ddagger}_{isc}$ cm^3 mol^{-1}	0.8 ± 0.9	−1.5 ± 3	−1.5 ± 3	−1.5 ± 3	[c]	[c]	(−4)	(−4)
$\Delta V^{\ddagger}_{nr}$ cm^3 mol^{-1}	[c]	[c]	[c]	[c]	4.3 ± 0.4	6.9 ± 0.1	8.3 ± 2	11 ± 2
$\Delta V^{\ddagger}_{p(X,Q)}$ cm^3 mol^{-1}	(0)	(0)	(0)	(0)	−6.5 ± 1[d]	−6.5 ± 1[d]	(0)	(0)
$\Delta V^{\ddagger}_{p(X,D)}$ cm^3 mol^{-1}	(0)	(0)	(0)	(0)	−6.5 ± 1[d]	−6.5 ± 1[d]	(0)	(0)

[a] For NH_3 photoaquation only. Values in parenthesis have been assumed to establish limiting conditions.

[b] For these estimates it was assumed that the same intermediate formed from the quartet and doublet states, so that $\Delta V^{\ddagger}_{X,D} = \Delta V^{\ddagger}_{X,Q} + 3.5$ cm^3 mol^{-1}.

[c] Only one channel is defined for relaxation of doublet state.

[d] In this model it is assumed that return to the ground state and formation of products occur after entry into the relaxation channel, so that $\eta_{r,Q} = \eta_{X,Q} + \eta_{ic}$ and $\eta_{r,D} = \eta_{X,D} + \eta_{nr}$, where $\eta_{r,i}$ is the total relaxation efficiency of the state i. For purposes of this calculation we have assumed a common intermediate is generated from the doublet and quartet states.

[e] For $\Delta V^{\ddagger}_{ic} = 0$ cm^3 mol^{-1}.

[f] Competing contributions to this term approximately cancel in this limit.

about -1.5 ± 3 cm^3 mol^{-1} and $P^{R}_{X} = 1$, then $\Delta V^{\ddagger}_{X} \simeq -50 \pm 20$ and -46 ± 21 cm^3 mol^{-1} for the quartet states and 4.3 and 6.9 cm^3 mol^{-1} for the doublet states of $Cr(NH_3)_6^{3+}$ and $Cr(NH_3)_5NCS^{2+}$, respectively. Apparently the pressure dependence of ammonia aquation and of the doublet state lifetime implicates very different reaction pathways for the quartet and doublet state (strongly associative and weakly dissociative, respectively) in the direct reaction limit. The values of $\Delta V^{\ddagger}_{X,Q}$ inferred for the quartet state are unrealistically negative, and this limiting form of the direct reaction model is not mechanistically useful.

3. *Surface Crossing to a Ground-State Reaction Intermediate.* This mechanistic proposal can be treated if we assume that the same intermediate is formed from quartet and doublet state reactions; i.e., $p^{D}_{X} = p^{Q}_{X} = p_X$. If we further assume that partitioning along the reaction trajectory, after the surface crossing, can result in return to the ground state or product formation, and that this is the only pathway for regeneration of the original ground state, then $p_X = 0.45$, $\eta_X = 0.25$, $\eta_{isc} = 0.75$, $\Delta V^{\ddagger}_{\phi(X)} = \Delta V^{\ddagger}_{p} \cong -6.5$ cm^3 mol^{-1} and $\Delta V^{\ddagger}_{\tau(D)}$ is simply the difference between the molar volumes of the doublet state and the intermediate species. Thus, in order for this limiting situation to appropriately describe the ammonia substitution pathway, the molar volume of the intermediate would have to be as large as, or larger than, the molar volume of the quartet excited state. It is to be emphasized that the limiting form assumed for this model requires a photochemical intermediate which can competitively form the solvent-substituted product or regenerate the ground state. The partitioning between these two decay modes of the intermediate is presumed to be pressure dependent.

MULTIPLE, COMPETING CHANNELS FOR DOUBLET STATE DECAY

In this approach $\phi(X)$ is given by Eq. (1) and, neglecting back intersystem crossing and radiative relaxation rates,

$$[\tau(D)]^{-1} = k^{D}_{X} + k^{D}_{nr}$$

If we neglect the $\Delta V^{\ddagger}_{p(\mathrm{X,R})}$ terms, then

$$\Delta V^{\ddagger}_{\phi(\mathrm{X})} \simeq f^{q}(1 - \eta_{\mathrm{X,D}})\Delta V^{\ddagger}_{\mathrm{X,D}} + (f^{u} - \eta_{\mathrm{X,Q}})\Delta V^{\ddagger}_{\mathrm{X,Q}}$$

$$- f^{q}\eta_{nr}\Delta V^{\ddagger}_{nr} - \eta_{ic}\Delta V^{\ddagger}_{ic} + (f^{q} - \eta_{isc})\Delta V^{\ddagger}_{isc}$$

The algebra can be unscrambled if we set $\eta_{ic} \simeq 0$, so that $\eta_{\mathrm{X,Q}} = 0.12$, $\eta_{isc} = 0.88$, $\eta_{\mathrm{X,D}} = 0.34$ and $\eta_{nr} = 0.66$ for photoaquation of NH_3 in either $Cr(NH_3)_6^{3+}$ or $Cr(NH_3)_5NCS^{2+}$. On making the further assumption that the same transition state is formed from the quartet and doublet state reactions, $\Delta V^{\ddagger}_{\mathrm{X,D}} = \Delta V^{\ddagger}_{\mathrm{X,Q}} + 3.5$, we find very similar parameters for these two compounds: the mean values of $\Delta V^{\ddagger}_{\mathrm{X,D}}$ and $\Delta V^{\ddagger}_{\mathrm{X,Q}}$ are -3 ± 3 and -5 ± 2 cm^3 mol^{-1}, respectively, and a mean value of $\Delta V^{\ddagger}_{nr} = 10 \pm 3$ cm^3 mol^{-1} (see Table II). Thus this form of the competing channels model would imply an associative reaction pathway, but expansion of the coordination sphere along the thermally activated channel which quenches the doublet state nonreactively.

THE PATHWAY FOR PHOTOAQUATION OF NCS$^-$ FROM $Cr(NH_3)_5NCS^{2+}$

While aquation of NH_3 is the dominant photochemical process following ligand-field excitation of $Cr(NH_3)_5NCS^{2+}$ ($\phi(NH_3) = 0.42$), there is a small probability for NCS$^-$ aquation ($\phi(NCS) = 0.02$). Unfortunately, there is no precise information about the extent to which this reaction is associated with population of the doublet or the quartet excited states. However, it has been reported that the ratio $\phi(NH_3):\phi(NCS^-)$ decreases as the excitation energy decreases.[28] This suggests a simple model in which NH_3 photoaquation is a quartet state property and NCS$^-$ photoaquation is a doublet state property,[13,28] and back intersystem crossing must play an important role in order for this model to be consistent with the observations on $\phi(NH_3)$.[13] In its limiting form, this model is only a slight variation on the simple B.I.S.C. model discussed above, and results in $\Delta V^{\ddagger}_{\mathrm{NCS}^-} = -11 \pm 2$ cm^3 mol^{-1}. This is not significantly different, even allowing for the difference in molar volumes of the quartet and doublet states, from the value of

$\Delta V^{\ddagger}_{NH_3} = -11 \pm 2$ cm^3 mol^{-1} found for the limiting B.I.S.C. model (Table II).

Of course, adding a kinetically competitive NCS$^-$ aquation step to back intersystem crossing is to propose a multiple competing channels model for doublet state decay. Unfortunately, the general multiple channel model involves too many parameters to be evaluated with the experimental information now available.

SUMMARY AND CONCLUSIONS

The pressure dependence of photochemical and photophysical parameters in systems with two or more photoactive states can be used to impose important constraints on proposed photochemical mechanisms. Thus, the observed pressure dependencies appear to require an associative reaction pathway for most mechanistic models which have been proposed for Cr(III) photochemistry and photophysics. This indicates that the prevailing theories of these processes, theories based on a dissociative reaction pathway, must be considered less than meaningful. However, interpretation of the pressure dependence of excited state behavior in such complex systems requires a great deal of photochemical and photophysical information, and only idealized limiting cases can be examined with the experimental information now available. Even this limited kind of analysis is so far possible for only two compounds. The pressure dependence of the quantum yields and lifetimes, combined with other necessary photophysical information, does lead to some strong mechanistic inferences with regard to these two compounds. In any case, the experimental determination of a substantial number of parameters is necessary for definitive mechanistic conclusions in such complex photochemical systems. It is obvious that meaningful mechanistic inferences cannot be based on the determination of the pressure dependence of only one photochemical or photophysical parameter.

Only very restricted or limiting models of photochemical and photophysical behavior of Cr(III) complexes have been considered in this Comment in order to illustrate the possible significance and the limitations of mechanistic inferences based on the reported pressure dependence of photochemical parameters. The available information does not permit the evaluation of a general treatment of the multiple state problem which includes the possibility of competing channels for decay of each state, the possibility of equilibrium between states, etc. One must also be concerned that all the mechanistic discussions to date treat the idealized limit in which only one quartet and one doublet state are considered. The energy of the $^2T_1$ state is usually intermediate between the ^2E and the $^4T_2$ state energies and the $^2T_1$ state has not been demonstrated to play a mechanistically innocent role. Furthermore, several quartet and doublet components are expected in complexes with microsymmetries lower than O_h, and each component of the multiplets might be expected to exhibit different photophysical behavior based on the different nuclear distortions, the different degrees of configurational mixing, etc.

Clearly the multiple state problem, which one must confront in mechanistic discussions of Cr(III) photochemistry, is far too complicated to be resolved by any single kind of measurement. Nevertheless, progress can be made by the systematic consideration of limiting mechanistic models, *if* the assumptions of the models are clearly identified.

JOHN F. ENDICOTT and CHONG KUL RYU
Department of Chemistry,
Wayne State University,
Detroit, Michigan 48202

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