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Commentationes

Excited States in the Photochemistry of Chromium(III) Complexes*

G. B. Porter and S. N. Chen

Department of Chemistry, University of British Columbia, Vancouver, Canada

H. L. Schläfer and H. Gausmann

Institut für physikalische Chemie der Universität Frankfurt am Main, Germany

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Experimental data for chromium(III) complex ions on the spectroscopic properties, photoreactions, and intermolecular energy transfer are analyzed in terms of the primary photophysical and photochemical processes. It is suggested that the lowest excited quartet state, ${}^4T_{2g}$ in O_h symmetry, is the immediate precursor to photoaquation and that the lowest doublet state, ${}^2E$, is substitution inert except via the ${}^4T_{2g}$ state reached by back intersystem crossing.

Experimentelle Daten von Chrom-(III)-Komplex-Ionen in bezug auf spektroskopische Eigenschaften, Photoreaktionen und intermolekularen Energieübertragung wurden mit dem Begriffssystem der photophysikalischen und photochemischen Primärprozesse analysiert. Und zwar wird vorgeschlagen, daß der tiefste angeregte Quartettzustand, ${}^4T_{2g}$ in O_h-Symmetrie, der unmittelbare Vorläufer der Photoaquatisierung ist und daß der tiefste Doublettzustand, ${}^2E$, inert gegenüber Substitutionen ist, außer über den ${}^4T_{2g}$ Zustand, wenn er durch Re-"intersystem crossing" erreicht wird.

In the investigation of photochemical reactions of chromium complexes, particularly with reference to primary processes, definitive information about the role of excited states cannot be obtained from studies of the photochemistry alone. Recourse must be made to other techniques such as spectral measurements, quenching and energy transfer reactions, and kinetic spectroscopy, in order to sort out complexities of the primary photochemical and photophysical processes.

Solutions of octahedral chromium(III) complexes are known to undergo such photochemical reactions as: aquation, anation, racemization and isomerization [1–3]. Unlike many other transition metal complexes, those of chromium(III) generally are not susceptible to photochemical oxidation-reduction reactions.

In the following, we shall describe the photochemical reactions of some chromium(III) complexes in terms of what is known about the excited electronic states: their energies, lifetimes, quenching, etc. The available information will then be used to assess the role of the various excited states in the photochemical reactions.

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* Dedicated to the memory of Professor Hans-Ludwig Schläfer.

1. Spectral Properties

Absorption spectra furnish a basic understanding of the low-lying excited states which may be reached in the course of a photochemical reaction of an octahedral complex [4, 5]. A typical absorption spectrum, that of $[Cr(NH_3)_6]^{3+}$, is shown in Fig. 1 [6]. The main features of such spectra are: in the red region (700 to 820 nm) a set of sharp lines of low intensity assigned to the transition $^2E_g \leftarrow {}^4A_{2g}$ (in octahedral symmetry) and other spin-forbidden transitions; in the visible region two (or sometimes three) broad structureless bands of relatively low intensity (ε_{max} of the order of $50\,M^{-1}\,cm^{-1}$), representing the Laporte forbidden transitions $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{1g} \leftarrow {}^4A_{2g}$; and, usually in the UV and near UV region of the spectrum, a number of intense bands which are intraligand and/or charge-transfer bands.

In emission spectra, two types of transitions have been observed: phosphorescence, $^2E_g \rightarrow {}^4A_{2g}$, and fluorescence, $^4T_{2g} \rightarrow {}^4A_{2g}$ [7, 8]. No other emission has been reported for chromium(III) complexes, although charge-transfer and intraligand transitions have been characterized from the emission spectra of other transition metal complexes [8]. Usually, phosphorescence is the only emission which can be readily observed, and then best at low temperatures, but there are some cases for which fluorescence emission is comparable in intensity with the phosphorescence and still others which show only fluorescence [9]. Which of these occur has been correlated with the relative energies of the ^2E_g and $^4T_{2g}$ states [10].

Phosphorescence spectra, like the corresponding absorption spectra, consist of a set of sharp lines, one of which occurs strongly in both absorption and emission and represents the origin of the band or the zero-zero transition. Other lines in the spectra are vibronic in nature and lie to the blue of the origin in absorption and to the red of the origin in emission except for "hot" bands originating in excited vibrational levels. The fluorescence spectra, on the other hand, are invariably broad and structureless (except possibly at 4 °K in

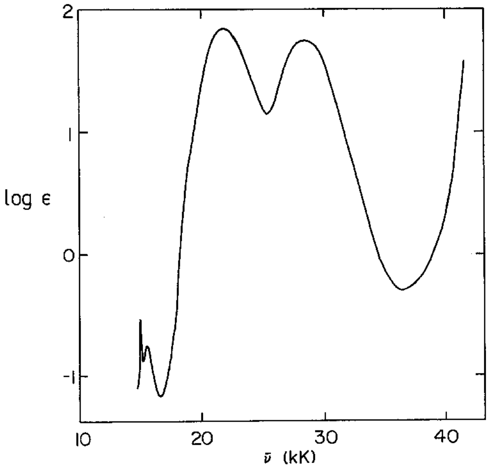

Fig. 1. Absorption spectrum of $[Cr(NH_3)_6]^{3+}$

crystalline samples). There is a mirror image relationship of the fluorescence band with the corresponding $^4T_{2g} \leftarrow {}^4A_{2g}$ absorption band, but the maximum in emission lies at longer wavelength than the maximum in absorption. Because of this relatively large Stokes' shift, $\Delta\bar{\nu}_s$, and the absence of structure, the origin of this transition cannot be located with any precision. When fluorescence is too weak to be measured, as is the case for most chromium(III) complexes, only an approximate upper bound can be placed on the zero-zero energy.

2. The Excited Electronics States

The various low-lying excited states of chromium(III) complexes, illustrated in the form of a Jablonski diagram in Fig. 2, can be interpreted within the framework of ligand field theory [4, 5]. Simple crystal field theory is based on the electrostatic interaction of the ligands with the *d* orbitals of the chromium ion. The (field-free) degenerate *d* orbitals are split according to the symmetry and strength of the field. Energy levels can be obtained from one-electron orbitals by including electron repulsion and spin-orbital coupling[1]. Although the electrostatic "crystal field theory" gives remarkably good results, it cannot be used to interpret the finer points, because it does not provide for any contribution from covalent bonding at all.

Ligand field theory is now considered to be the application of molecular orbital theory to complexes [4]. The splitting of the orbitals arises from the bonding and antibonding nature of the molecular orbitals formed from the ligand and metal orbitals. A typical scheme is that shown in Fig. 3 for an octahedral field. The *d* electrons of an octahedral complex ion occupy the orbitals t_{2g} and e_g, which are non-bonding or π anti-bonding (t_{2g}) and σ anti-bonding (e_g). In the d^3 system, to which chromium(III) belongs, the ground state orbital configuration is t_{2g}^3. The splitting of the two sets of orbitals, Δ, arises from the anti-bonding character of the e_g orbitals primarily, but may also be affected by π bonding of the t_{2g} orbitals, because the orbital occupancy of the $^4T_{2g}$ state is $t_{2g}^2e_g$. Thus a large value of Δ for a given complex means that a complex in the $^4T_{2g}$ state is expected to have considerably larger chromium-ligand separations than the

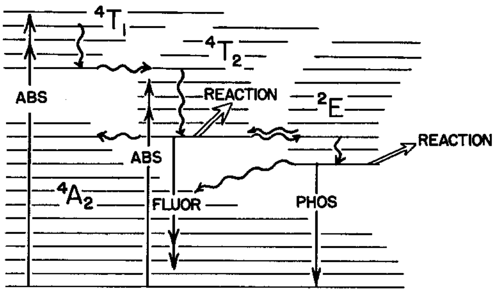

Fig. 2. Jablonski diagram for a typical chromium(III) complex

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[1] This is the so-called strong field approach. The weak-field method starts with the states of the free ion which are then considered to be split by the ligand field. The two methods give identical results [11].

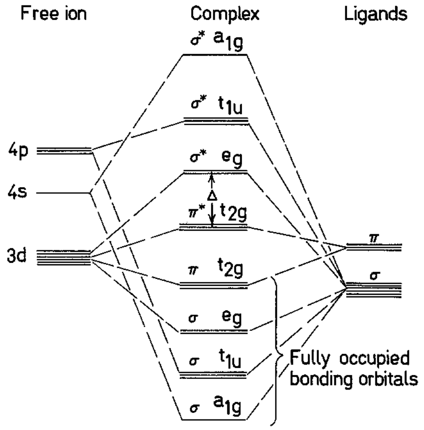

Fig. 3. Ligand field scheme of one electron orbitals

ground state molecule because of the decrease in overall bond character when a t_{2g} electron is promoted to an anti-bonding e_g orbital. We can expect then that the value of Δ (obtained from the absorption maximum of ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and thus corresponding to vibronic transitions with maximum Frank-Condon overlap) will be influenced not only by the separation of the origins of the electronic states themselves, but also by this change in equilibrium nuclear configuration. These considerations then lead to the prediction that the Stokes' shift, $\Delta\bar{v}_s$, between the absorption maximum and the fluorescence maximum should increase markedly as Δ increases for a series of complexes. It may well be that the increase in internuclear configuration of the ${}^4T_{2g}$ state compensates for an increase in Δ, so that the position of the fluorescence maximum may not change appreciably as Δ changes. Very little data are available on this point, however, because of the difficulty of detection of fluorescence for complexes with large Δ. An indication of this effect is obtained by comparing the urea [12] and cyano complexes [13]. The absorption and fluorescence emission maxima for $[Cr(urea)_6]^{3+}$ are at 15050 and 12550 cm^{-1}, respectively, while for the complex, $[Cr(CN)_6]^{3-}$, are at 26700 and approximately 12000 cm^{-1}, respectively. Thus a change of Δ from 15050 to 26700 cm^{-1} corresponds to a change in the Stokes' shift from 2500 to 14700 cm^{-1}.

3. Lifetimes and Equilibration of Excited States

Absorption of radiation by chromium(III) complexes populates one of the excited electronic states, usually with a considerable excess of vibrational energy over equilibrium. This is so because of the operation of the Franck-Condon Principle together with the fact that the equilibrium nuclear configuration of the excited quartet state is different from that of the ground state [10]. Excitation into one of the doublet bands would give an excited molecule without appreciable vibrational energy, but practical photochemistry is then difficult because of the low extinction coefficents and overlap with stronger absorption bands. We must examine then the fate of molecules in the $^4T_{2g}$ and $^4T_{1g}$ states with upwards of 5 kcal/mole of excess vibrational energy.

Although there are few experimental data that bear directly on the problem of vibrational deactivation of inorganic complexes in condensed media, there can be little question that it does occur. Since the collision rate with solvent is of the order of 10^{13} sec^{-1}, it is quite unlikely that excess *vibrational* energy could survive for as long as 10^{-12} sec. For a photochemical reaction to compete to any appreciable extent, it must have a pseudo first order rate constant of the order of 10^{11} sec^{-1}. Although this is feasible, there are other reasons for ruling out the possibility, as will be explored in a later section.

If the initial excitation is such that the $^4T_{1g}$ state (or a higher state) is populated, electronic as well as vibrational relaxation must be considered. Again there is no direct information concerning such processes. An analogy can be made to organic molecules in solution (considered dangerous by Adamson [14]) for which, with a few exceptions, electronic relaxation to the lowest excited state within one spin manifold occurs rapidly [15]. Such information is deduced from the absence of fluorescence from upper singlet states, implying an upper state lifetime of less than 10^{-11} sec. Whether or not relaxation occurs so rapidly for chromium(III) complexes cannot be decided at present, in part because the natural lifetime, particularly of the $^4T_{1g}$ state, may be abnormally long. Again, the possibility of photochemical reaction via upper states will be examined in the later discussion.

Aside from photochemical reaction, there are three unimolecular degradative processes that can occur from the vibrationally equilibrated $^4T_{2g}$ state: fluorescence, internal conversion to high vibrational levels of the ground state, and intersystem crossing to either the $^2T_{1g}$ or ^2E_g states. Much recent research has been aimed at the investigation of the relative importance of these three processes and of photochemical reaction.

On a theoretical basis, the transition probability for the radiative process, $^4T_{2g} \rightarrow {}^4A_{2g}$, fluorescence, can be estimated from the intergrated absorption coefficient through the oscillator strength [7]. The reciprocal of the transition probability is the natural lifetime of the $^4T_{2g}$ state, i.e. the radiative lifetime in the absence of competing non-radiative processes. As has been discussed by Adamson [14], however, the lifetime so obtained, which is of the order of 10^{-5} sec, may be appreciably in error. Among the factors that could lead to a significant error is a large distortion of the upper state relative to the ground state. As we have seen above, the distortion is expected to increase with increasing ligand field strength. Thus we can expect, on this basis, that although the theoretical lifetime may be nearly correct for complexes with low ligand field strengths, it could be appreciably shorter than the actual natural lifetime for such complexes as $[Cr(CN)_6]^{3-}$. The available lifetime data support this conclusion as is indicated by the experimental lifetimes of the $^4T_{2g}$ state at 77 °K for various complexes [13] given in Table 1. The natural lifetime is longer by the factor $1/\phi_f$, which must be at least 10^3. The reciprocals of the lifetimes given in Table 1 represent sums of the rate constants for fluorescence, internal conversion, intersystem crossing and photochemical reaction. For the hexacyano complex, Forster *et al.* [16] have found a value of 0.1 for the efficiency of intersystem

Table 1. *Lifetimes of the* $^4T_{2g}$ *state of* Cr(III) *complexes in rigid glass at 77° K* [13]

Complex	τ(μ sec)
$[Cr(CN)_6]^{3-}$	50
$[Cr(NCS)]^{3-}$	8
$Cr(acac)_3$	8
$[Cr\ en_3]^{3+}$	11

Table 2. *Lifetimes of the* ^2E_g *state of some representative* Cr(III) *complex ions*

Complex	τ(μ sec)	Ref.
$[Cr(NH_3)_6]^{3+}$	56	[18]
$[Cr(NCS)_6]^{3-}$	4400	[13]
$[Cr(en)_3]^{3+}$	100	[18]
$[Cr(CN)_6]^{3-}$	3450	[13]
trans-$[Cr(NH_3)_2(NCS)_4]^-$	310	[18]

crossing, therefore we can estimate $k_{isc} = 2 \times 10^3$ sec^{-1} and $k_{ic} = 2 \times 10^4$ sec^{-1} on the basis that the fluorescence quantum yield is small even at 77 °K. These rate constants are far smaller than has been expected for chromium complexes (typically $k_{isc} \cong 10^8$ sec^{-1} for many organic systems [15]). That the $^4T_{2g}$ state is relatively long-lived has important consequences in any discussion of the role of this state in photochemical reactions.

However, intersystem crossing is of major importance in the relaxation of excited states, as judged by the appearance of phosphorescence, $^2E_g \rightarrow {}^4A_{2g}$, regardless of the state reached on excitation (except when ^2E_g lies appreciably above the origin $^4T_{2g}$ [10]). Relaxation within the doublet manifold is expected to occur rapidly following intersystem crossing, so that only the equilibrated ^2E_g state participates in a radiative process. Back intersystem crossing to the $^4T_{2g}$ state could occur [10, 17] with an activation energy equal to the endothermicity, which is the separation of the zeroth levels of $^4T_{2g}$ and $^2E_{2g}$. It has been postulated by Camessei and Forster that this is the principal degradative process of the ^2E_g state [17], other than phosphorescence and possible photochemical decomposition.

The lifetime of the ^2E_g state is relatively long, particularly at low temperatures, as is shown by the representative data in Table 2 [13, 18]. Further, the natural lifetimes preducted through the oscillator strength formulation seem to fit well with the experimental measurements, in contrast to the situation outlined above for the lowest energy quartet-quartet transition.

4. Photochemical Processes

Aquation is the principal photoreaction that has been studied for chromium complexes in aqueous solution [1]. Some quantum yields are given in Table 3 for octahedral CrA_6 and $Cr(AA)_3$ complexes. All investigations of compounds with

Table 3. *Quantum yields for photoaquation of some* CrA_6 *and* $Cr(AA)_3$ *complexes*

Complex ion	Φ	Wavelengths studied	Ref.
$[Cr(H_2O)_6]^{3+}$	0.1	254—730 nm	[28]
$[Cr(urea)_6]^{3+}$	0.10	452—735	[20]
$[Cr(NH_3)_6]^{3+}$	0.5	254	[29]
	0.3	320—652	[20]
$[Cr(CN)_6]^{3-}$	0.15	305, 370	[30]
$[Cr(NCS)_6]^{3-}$	0.26	546, 600	[20]
$[Cr(en)_3]^{3+}$	0.35	250—434	[31]

only one ligand type present report the quantum yield to be independent of the wavelength of excitation. These results can be best interpreted as meaning that photoaquation does not occur directly from the vibronic level reached in the absorption process nor from other than the *lowest excited state* of one multiplicity. Considerable effort has been directed at measurement of the quantum yield on irradiation in the region of the sharp absorption bands, in order to populate the doublet states directly rather than through intersystem crossing [19, 20]. The idea is to bypass the $^4T_{2g}$ state so that if it were responsible for the photochemical reaction, the yield would be decreased. If, on the other hand the ^2E_g state were the immediate precursor to photoaquation, the yield might be larger, on the grounds that intersystem crossing is not 100% efficient. However these experiments are difficult to carry out. So far there is no firm evidence that the quantum yields are any different for excitation in the region of the doublet bands.

Rather more information can be obtained when there are two different ligands attached to the Cr(III) ion [21–23]. There are two important features to the data on the pentaammine complexes. One is that, for the complex $[Cr(NH_3)_5NCS]^{2+}$, the ratio of thiocyanate aquation to ammonia aquation yields changes with

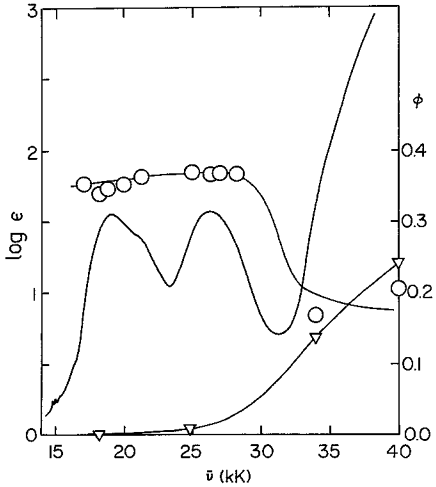

Fig. 4. Absorption spectrum of $[Cr(NH_3)_5Br]^{2+}$, with quantum yields of NH_3 aquation, ○, and of Br^- aquation, ▽

wavelength [21]. Thus, while the yield of thiocyanate, although small, is nearly constant over the range studied, the ammonia yield decreases somewhat for excitation at 652 nm. For the $[Cr(NH_3)_5Br]^{2+}$ ion [22], see Fig. 4, ammonia release is the major photo-process in the visible region, but bromide ion is released in much larger yield in the ultra-violet region, where there is an intense charge-transfer absorption band. The tentative conclusion one might draw from these data is that ammonia aquation occurs via the $^4T_{2g}$ state and that Br^- is released via a charge-transfer state.

5. Energy Transfer

Intermolecular energy transfer has the possibility of indicating in a direct way the participation of specific electronic states in photochemical reaction. Forster *et al.* [16] have used organic molecules with long-lived triplet states to sensitize the phosphorescence of Cr(III) complexes at low temperatures in fluid solution. However, except in the case of the hexacyanochromate complex (and perhaps not even then) can they be sure that the observed energy transfer populates the doublet states directly rather than the quartet, either of which are allowed on energetic and spin correlation grounds. Adamson *et al.* [24] have studied energy transfer from various organic donors to several different chromium complexes by following the photosensitized aquation reactions of the latter. A detailed study of the system biacetyl-$[Cr(NH_3)_5NCS]^{2+}$ was carried out with irradiation of the biacetyl only, at 410 nm. From the quenching of biacetyl phosphorescence and absence of quenching of fluorescence, the triplet state of biacetyl is definitely identified as the donor. Although the acceptor state is not known definitely, the aquation is almost exclusively of NH_3 rather than NCS^-, hence Adamson [24] concludes that the quartet state is populated by energy transfer.

We have studied energy transfer [25, 26] between complexes in solutions as a means of exploring the details of photochemical reactions. At moderately low temperatures, e.g. −65 °C, in fluid solution, phosphorescence quenching of reineckate ion and phosphorescence sensization of $[Cr(CN)_6]^{3-}$ occurs [25].

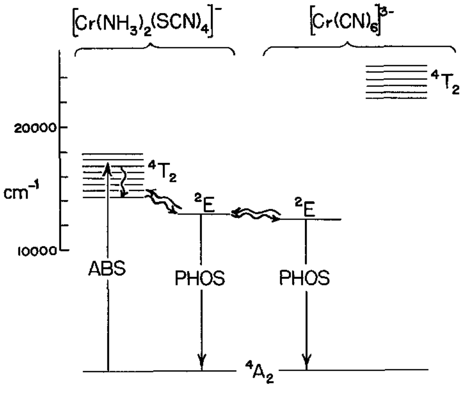

Fig. 5. Energy level scheme for energy transfer between *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ and $[Cr(CN)_6]^{3-}$

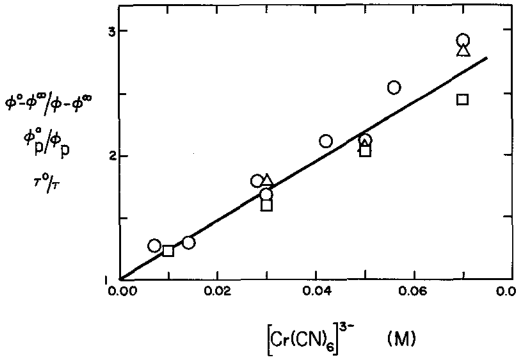

Fig. 6. Stern Volmer plots for $\phi^0 - \phi^\infty/\phi - \phi^\infty$, △, for ϕ_p^0/ϕ_p, ○, and for τ^0/τ, □, of *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ against concentration of acceptor, $[Cr(CN)_6]^{3-}$

Both yields and lifetimes fit the expected Stern-Volmer relationship with $k_{et} = 7 \times 10^5\ M^{-1}$, showing that energy transfer depopulates the phosphorescing state of reineckate and populates the corresponding state of $[Cr(CN)_6]^{3-}$. The nature of the temperature dependence precludes participation of the excited quartet states in the transfer process (see Fig. 5). In this same temperature range, photoaquation can also be studied. We have found that the photochemical quantum yield of the reineckate ion is reduced in the presence of $[Cr(CN)_6]^{3-}$, but not as much as the phosphorescence of reineckate is quenched, as shown in Fig. 6 [26]. Although the limited solubility of the cyano complex prevents a complete study of the concentration dependence, the data up to 0.07 M^- $[Cr(CN)_6]^{3-}$ all give a constant value for ϕ^∞.

We propose that part of the photoaquation, represented by the limiting value of ϕ^∞, occurs via the $^4T_{2g}$ state (in O_h symmetry), while the quenchable part must occur through the lowest doublet state as an intermediate. The photoaquation quantum yield should approach a limiting value given by:

$$\phi = \frac{\phi^0 \phi_p - \phi \phi_p^0}{\phi_p - \phi_p^0} \cong 5 \times 10^{-3}$$

where ϕ^0 and ϕ_p^0 are the photoaquation and phosphorescence quantum yield in the absence of $[Cr(CN)_6]^{3-}$. We further suggest that the actual path of the quenchable reaction is via back intersystem crossing to the lowest excited quartet state (see Fig. 5) which then undergoes aquation. However, this path cannot be distinguished from one in which the doublet itself undergoes aquation.

6. Discussion

The general picture of the primary photochemical processes in chromium (III) complexes has been somewhat clarified by the collected data on luminescence, photochemical reaction and energy transfer. It seems now reasonable to attribute most or all of the photochemical reaction to the lowest excited quartet state of the complexes as the reactive species. In a naive sense, the one-electron orbital occupancy for the $^4T_{2g}$ state, $t_{2g}^2 e_g$, suggests that this state might be more labile than the lowest doublet state, with t_{2g}^3. The principal objection to the $^4T_{2g}$ as the photo-active species, according to Schläfer [27], has been the expected maximum lifetime of 10^{-8} sec for the $^4T_{2g}$ state. As this estimate has now been revised upward by several orders of magnitude [13], there is no reason to rule out participation of the $^4T_{2g}$ state.

It is important to realize that, in attributing the photochemical reaction to the $^4T_{2g}$ state (or its equivalent in lower symmetries) nothing can as yet be said about further details of the process. For example, it is conceivable that the actual path of reaction is via high vibrational levels of the ground state reached by internal conversion of the quartet. This would not affect the conclusion about the role of the quartet state, however, because direct aquation of the $^4T_{2g}$ state and aquation via the ground state are, so far, kinetically indistinquishable. It does become difficult to rationalize quantum yields different from unity by the latter path.

With regard to participation of doublet states, it is apparent, at least for the reineckate ion, that molecules in these states can undergo photoaquation. But the data are consistent with the proposal that the doublet states are themselves substitution inert and react only via the quartet state. The activation energy associated with the lifetime of the phosphorescence fits well with the expected separation of the $^4T_{2g}$ and ^2E_g origins for a number of complexes. This suggests that the principal mode of degradation of the ^2E_g state, particularly near room temperature, is via the $^4T_{2g}$ state [17, 26]. To confirm back intersystem crossing would require some measurement technique, such as observation of delayed fluorescence, but even prompt fluorescence is too weak to be detected in general.

There is the further problem of non-octahedral complexes, in which there may be two different ligands susceptible to photoaquation. Adamson [14] has proposed a set of empirical rules for predicting which positions in a complex will be photolabile.

The series of complexes, $[Cr(NH_3)_5X)^{2+}$, fit a pattern in which NH_3 is the principal species aquated on irradiation throughout the visible region of the spectrum with nearly constant quantum yield [21–23]. Schläfer's measurements on the complexes with $X = Cl$ or Br [22, 23] show that the yield of halide ion rises sharply in the ultraviolet region, where the absorption is into an intense charge-transfer type band. Because that band can be attributed to a ligand-to-metal orbital transition, it may well be that aquation of halide is initiated as a redox reaction, but because of the great reducing power of divalent chromium, the halogen atom could well be reduced before it can leave the solvent cage. However, that reaction would have to be extremely fast because of the lability of Cr(II) complexes. Nevertheless, those results do mean that the charge-transfer excited state must be able to undergo reaction at a rate competitive with crossing to ligand field excited states.

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Professor G. B. Porter
Department of Chemistry
University of British Columbia
Vancouver 8, Canada