

THE PRIMARY PHOTOPROCESSES OF CHROMIUM(III) COMPLEXES

by

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ABSTRACT

Energy transfer between Reineckate ion (donor) and hexacyanochromate(III) ion (acceptor) has been studied through quenching of donor phosphorescence (lifetime and intensity) and sensitization of acceptor phosphorescence. Results from all measurements fit the expected Stern-Volmer relationship with a quenching constant $k_{QH} = 7.2 \times 10^5 \text{ M}^{-1}\text{sec}^{-1}$ at -65°C . The pre-exponential factor and activation energy of k_{QH} are $6.6 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$ and 4.8 Kcal/mol respectively. The constant, k_{QH} , is attributed entirely to an energy transfer rather than a quenching process. The electronic states directly involved are the 2E_g (and/or $^2T_{1g}$) states of both donor and acceptor. Energy transfer is a diffusion-controlled (collisional) process. Hexacyanochromate(III) ion is itself quenched in the presence of Reineckate ion. The quenching constant, k'_{QH} , which may be attributed to back energy transfer from acceptor to donor, has a pre-exponential factor of $2 \times 10^{12} \text{ M}^{-1}\text{sec}^{-1}$ and an activation energy of 7.6 Kcal/mol.

In the same system, quenching of photoaquation has also been studied at -65°C . The photoaquation quantum yield of Reineckate ion is 1.02×10^{-2} . It is reduced in the presence of hexacyanochromate(III) ion, but not as much as the phosphorescence of Reineckate ion is reduced. The limiting unquenchable part, $\phi_{\text{chem}}^\infty$, occurs via the $^4T_{2g}$ state, while

the quenchable part must occur through the 2E_g state as an intermediate. The actual path for the quenchable part proposed is back intersystem crossing from the 2E_g to the $^4T_{2g}$ state, which then undergoes aquation.

The primary processes of 2E_g state molecules have been investigated through the temperature dependence of phosphorescence lifetimes of some Cr(III) complexes. All the available evidence supports the idea of the thermally activated back intersystem crossing. According to this mechanism, the origins of the $^4T_{2g}$ states of Cr(III) complexes reached by crossing are far lower in energy than has been expected.

Assuming the occurrence of back intersystem crossing, the application of energy transfer to the determination of intersystem crossing quantum yield, ϕ_{isc} , has been demonstrated. The values of ϕ_{isc} for Reineckate and hexacyanochromate(III) ions are estimated to be 0.52 and 0.35, respectively. The variation of ϕ_{isc} with temperature for these Cr(III) complexes has also been measured, which suggests that in general, internal conversion has a strong temperature dependence.

From the rise of phosphorescence with time after pulse excitation, a new parameter, τ_x , has been obtained which represents population of the phosphorescing state and is believed to be the lifetime of the $^4T_{2g}$ (or less likely $^2T_{1g}$) state. Efforts have been made to confirm and identify this parameter. Studies of τ_x have been carried out as a function

of temperature. Mechanisms based on different tentative assignments of τ_x are proposed and their implications examined. All primary processes, except the intrinsic radiative transitions, seem to consist of at least two components, which take different pathways and are different functions of temperature.

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CHAPTER I

INTRODUCTION

Stimulated by the great strides taken in the studies of the chemical and physical nature of excited molecules in general, the photochemistry of coordination compounds has recently quickened its pace and emerged as an interesting new branch of photochemistry. Numerous reviews have been published in the last few years,¹⁻¹⁰ and the importance of this new field is now being gradually acknowledged. However, as in any other field in its infancy, most of the existing data and results of the photochemistry of coordination compounds are only phenomenological and are rather scattered and isolated. It is thus essential to have more systematic mechanistic studies.

The family of chromium(III) complexes is one of the most suitable systems for both intensive and extensive photochemical investigation. A large number of Cr(III) complexes with widely varying ligand field strength have been prepared, their thermal stabilities are usually moderately satisfactory, and their ground state chemical reactions have been well characterized and studied.^{1,11} The bonding properties of the electronic states are relatively clear and the spectroscopic bands have been well assigned.¹²⁻¹⁸ Unlike Co(III) complexes, Cr(III) complexes only undergo

photosubstitution, with no known photoredox reactions, hence this largely simplifies the problem. In addition, quite a few Cr(III) complexes phosphoresce in fluid solutions at low temperatures, or even at room temperature, for example, $[\text{Cr}(\text{en})_3]^{+3}$. Emission studies where possible are an essential adjunct to photochemical studies.

In the following sections the theoretical and empirical facts which are important for this work are briefly outlined. More detailed descriptions can be found in the references cited in this chapter.

1. Thermal Reactions^{1,11}

Cr(III) complexes have half-filled t_{2g} orbitals and are therefore considered to be substitutionally inert. Ligand exchange reactions in the absence of light take place only slowly. They consist of aquation, anation, isomerization, and racemization. Their activation energies range from 15 to 17 Kcal/mol.

2. Electronic States¹²⁻¹⁸

The molecular orbital diagram for a transition metal complex of O_h symmetry is shown in Figure 1. The d electrons of an octahedral complex ion occupy the orbitals t_{2g} and e_g , which are non-bonding or π antibonding (t_{2g}^*) and σ antibonding (e_g^*). In the d^3 system, to which chromium(III) belongs, the ground state orbital configuration is t_{2g}^3 . The

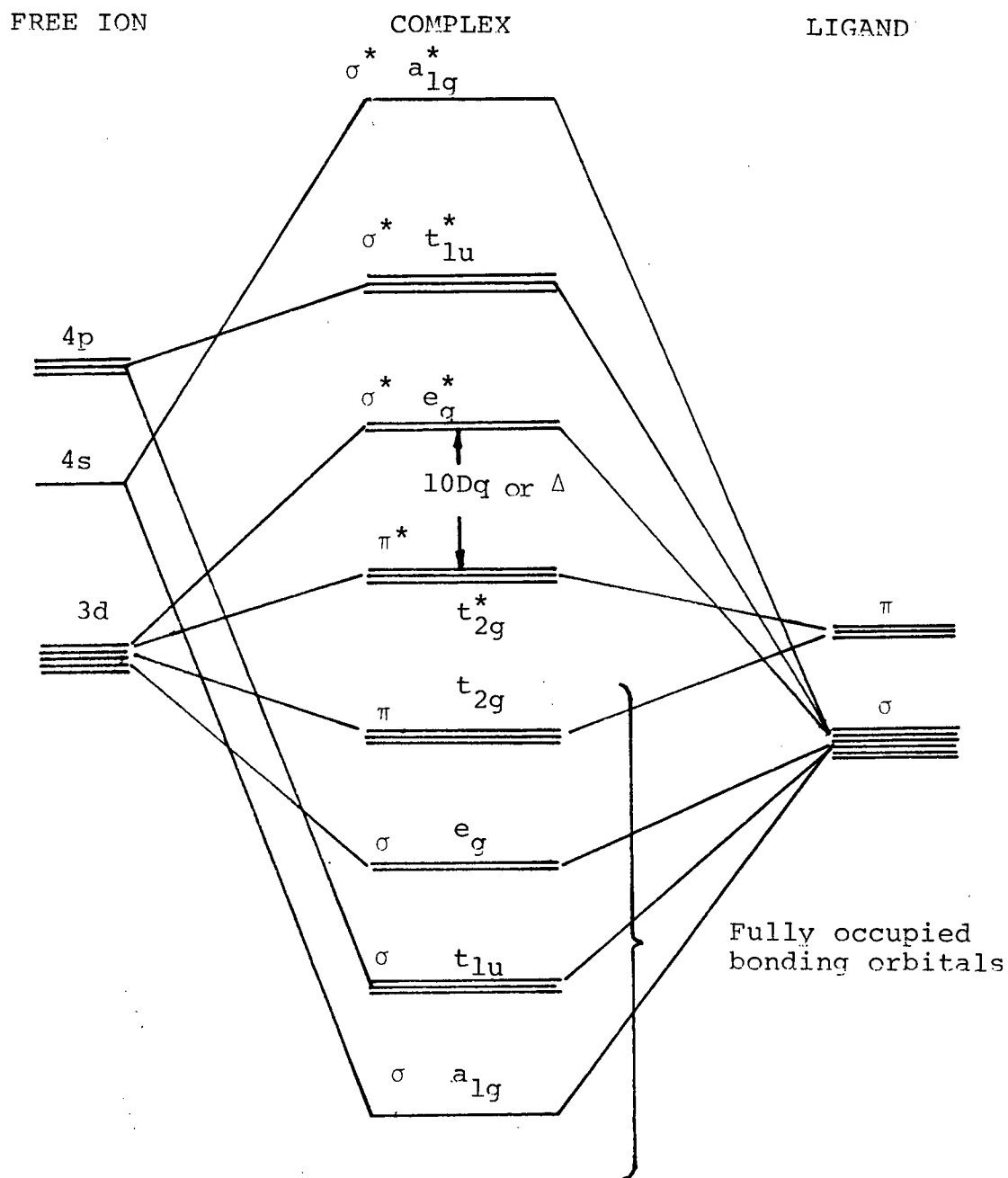


Figure 1. Molecular orbital diagram of transition metal complex of O_h symmetry.

splitting, $10Dq$, of the two sets of orbitals arises primarily from the anti-bonding character of the e_g orbitals. However, it may also be affected by π bonding of the t_{2g} orbitals. Thus a large value of $10Dq$ for a given complex means that a complex in the ${}^4T_{2g}(t_{2g}^2e_g)$ state is expected to have considerably larger chromium-ligand separations than the ground state molecule because of the decrease in the overall (σ and π) bonding force when a t_{2g} electron is promoted to an anti-bonding e_g orbital. In other words, it is expected that the value of $10Dq$ (obtained from the absorption maximum of ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and thus corresponding to the vibronic transition with maximum Franck-Condon overlap) will be determined not only by the separation of the origins of the electronic states themselves, but also by the change in the equilibrium nuclear configuration. Therefore, phenomenologically, the Stokes' shift between the absorption maximum and the fluorescence maximum should increase markedly as $10Dq$ increases for a series of complexes.

The energy level diagram from the strong-field calculations of Tanabe and Sugano in the simplified form is shown in Figure 2. Also arising from the configuration t_{2g}^3 are three doublet states 2E_g , ${}^2T_{1g}$, and ${}^2T_{2g}$. The degeneracy of the 2E_g and ${}^2T_{1g}$ states is removed by spin-orbital coupling and by deviation of the ligand field from octahedral symmetry.

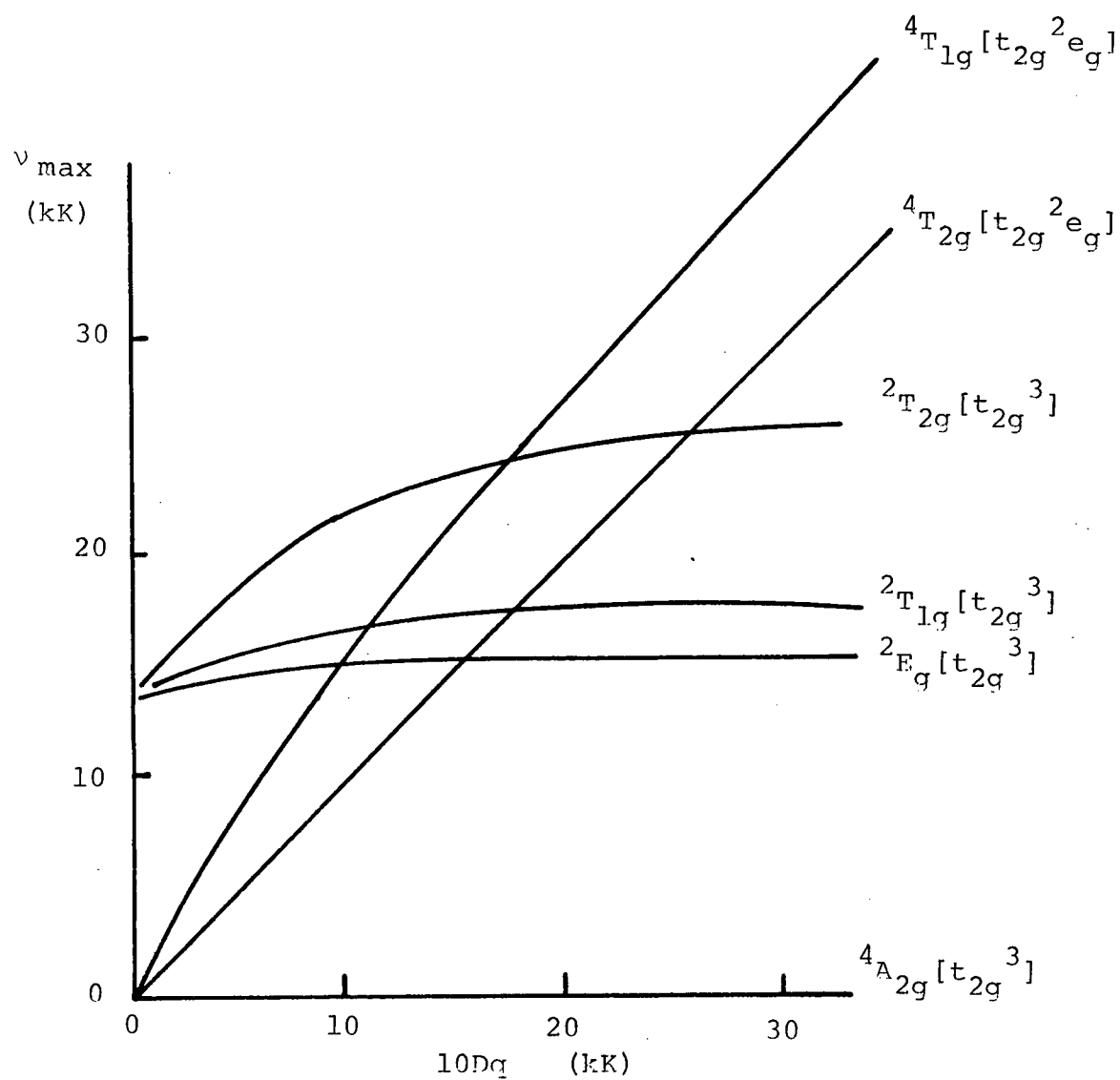


Figure 2. Simplified energy level diagram for the octahedral d^3 configuration.

The next lowest electronic configuration, $t_{2g}^2 e_g$, gives rise to the quartet states ${}^4T_{2g}$ and ${}^4T_{1g}(F)$. The other quartet state ${}^4T_{1g}(P)$ which is not shown in the figure arises from the $t_{2g}^2 e_g$ configuration.

3. Spectral Properties¹³⁻¹⁸

The main features of the absorption spectra of Cr(III) complexes are: in the red region (700 to 820 nm) a set of sharp lines of low intensity assigned to the transition ${}^2E_g \leftarrow {}^4A_{2g}^{++}$ and other spin-forbidden transitions; in the visible region two (or sometimes three) broad structureless bands of relatively low intensity ($\epsilon_{\max}$ of order of $50 \text{ M}^{-1} \text{ cm}^{-1}$), 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, ${}^4T_{2g} \rightarrow {}^4A_{2g}$. Here fluorescence is the radiation transition between two electronic states of the same spin multiplicity, while phosphorescence is of different spin multiplicities. Usually, phosphorescence is the only emission which can be readily observed in Cr(III) complexes, but there are some cases for

⁺⁺The O_h symmetry designation is used throughout this thesis for simplicity, even though some complexes are not octahedral, for example, $\text{trans-[Cr(NH}_3)_2(\text{NCS})_4]^-$ is of D_{4h} symmetry.

which fluorescence emission is comparable in intensity with the phosphorescence and still others which show only fluorescence.¹⁹ Which of these occur has been correlated with the relative energies of the 2E_g and $^4T_{2g}$ states.²⁰

Phosphorescence spectra, which are usually the mirror images of the corresponding spin-forbidden absorption spectra, consist of a set of sharp lines, one of which occurs distinctly in both absorption and emission and represents the origin of the band or the zero-zero transition. This indicates that the equilibrium nuclear configurations of the $^4A_{2g}$ and the 2E_g states must be nearly identical. The fluorescence spectra, on the other hand, are invariably broad and structureless. There is mirror image relationship of the fluorescence band with the corresponding $^4T_{2g} \leftarrow ^4A_{2g}$ absorption, but the Stokes' shift is relatively large. This indicates that the equilibrium nuclear configurations of the $^4A_{2g}$ and the $^4T_{2g}$ states must be quite different.

4. Primary Photophysical Processes

The Jablonski diagram for chromium(III) complexes involving the $^4T_{2g}$, $^2T_{2g}$, $^2T_{1g}$, 2E_g , and $^4A_{2g}$ states is shown in Figure 3. For simplicity, the electronic states are described in O_h symmetry for all the complexes studied in this work, and the $^2T_{1g}$ and 2E_g states, because of small energy separation between them, are assumed to be in rapid

equilibrium and are considered an equilibrated state unless otherwise specified.

It is generally believed that after excitation to the Frank-Condon levels of the excited electronic states, because the vibrational relaxation and internal conversions between higher excited states are very fast, the molecule must reach its lowest excited electronic states within 10^{-12} sec. The lifetime of the $^4T_{2g}$ state has been estimated from oscillator strength and fluorescence quantum yield to be less than 10^{-7} sec. However, the observed values for complexes which fluoresce are in the order of 10^{-6} sec or a little less. Intersystem crossing, k_4 , completes favorably with the other processes, and internal conversion, k_2 (and/or intersystem crossing, k_6), should be significant as judged from the sum of photochemical and emission quantum yields which is usually far smaller than unity.

Primary processes from the 2E_g state have been better studied. The phosphorescence radiative rate constants, k_5 , have been approximately evaluated through a simple spin-orbit-coupling model.¹⁸ Although phosphorescence emissions are readily detectable at liquid nitrogen temperature, the yields are usually less than a few percent. Intersystem crossing to the ground state, k_6 , is the dominant degrading pathway at low temperatures, and thermally activated intersystem crossing, k_{-4} , may be important at higher temperatures.

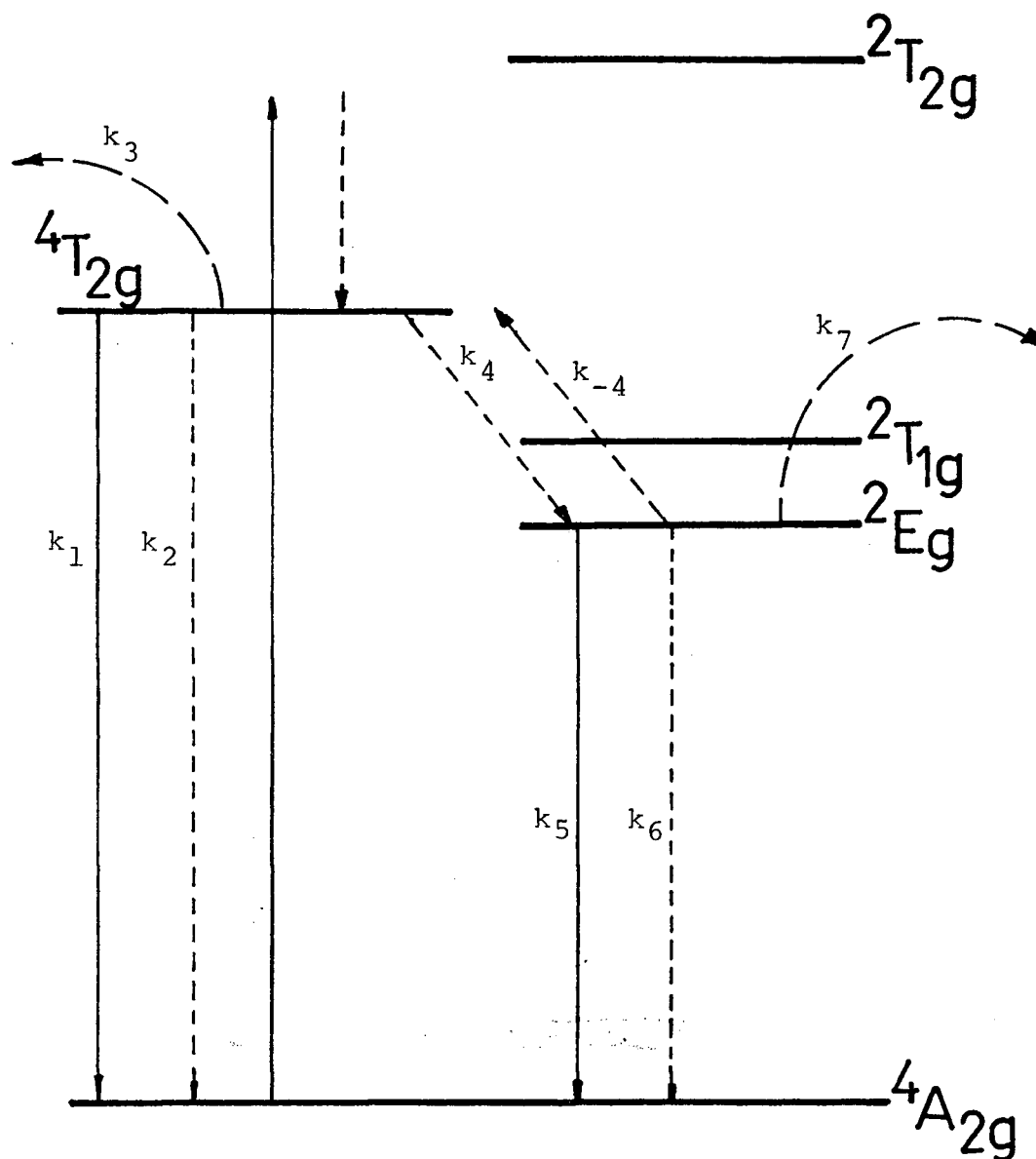


Figure 3. Primary processes involving the lowest excited states. k_1 , intrinsic fluorescence emission; k_2 , internal conversion; k_3 , photochemical reaction from the $4T_{2g}$ state; k_4 , intersystem crossing; k_{-4} , thermally activated reverse intersystem crossing; k_5 , intrinsic phosphorescence emission; k_6 , intersystem crossing to the ground state; k_7 , photochemical reaction from the $2E_g$ state.

5. Photochemical Processes

Aquation is the principal photoreaction that has been studied for chromium(III) complexes in aqueous solution. The photoaquation quantum yields range from less than 0.1 to 0.5. The low quantum yields are not due to cage effects as is evident from the studies of the photosubstitution of $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$ by oxygen-18 enriched water--although the solvent cage is one of the reactants, the quantum yield is still low.²¹ All investigations of complexes with 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.

The immediate precursor to the photochemical reactions of Cr(III) complexes has been sought for years. It has been suggested to be the $^4\text{T}_{2g}$ state, based on the bonding character and electronic structure.²² However, it has also been held that the lifetime of the lowest excited quartet, $^4\text{T}_{2g}$, is no greater than 10^{-7} sec, which is too brief to enable aquation to compete effectively with other decay processes.²³ The lowest excited doublet state, $^2\text{E}_g$, is relatively long-lived so chemical reaction may well compete with intersystem crossings and phosphorescence.^{22,24}

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.^{25,28} 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.

It has also been proposed that the reacting species may be a vibrationally excited or hot ground-state molecule which is formed through isoenergetic transitions from the electronically excited states.²⁶ However, the reaction patterns and activation parameters are quite different between photochemical and thermal reactions.²⁷ And recent evidence has shown that while photosubstitution does not depend on the solvent composition thermal substitution does.²⁹ Moreover, considering the fact that the lifetimes of the non-equilibrated, highly excited vibrational levels are extremely short (about 10^{-12} sec), this supposition is generally not favored.

6. A Brief Description of this Work

The main rationale of this work was to investigate the role played by the $^4T_{2g}$ and 2E_g states in the photoaquation of Cr(III) complexes. Instead of populating the doublet state by direct excitation, the more efficient energy transfer technique was used.

The first step was to search for the suitable energy transfer systems. One of the systems, $\text{trans}-[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ as a donor and $[\text{Cr}(\text{CN})_6]^{-3}$ as an acceptor, is considered in Chapter III. The emphasis there is not only on the application of energy transfer to photochemical studies but also on the energy transfer itself as a primary process.

The application of energy transfer to the studies of the photochemistry of $\text{trans}-[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ in the energy transfer system is described in Chapter IV.

It was clear at this stage that definitive information about the role of excited states cannot be obtained from studies of the photochemistry alone. Studies of the other primary processes are needed.

In order to identify the quenchable part of the photoaquation, the primary processes from the 2E_g state were investigated as described in Chapter V. The main effort was to confirm that the thermally activated intersystem crossing, k_{-4} , occurs.

In Chapter VI, the possible methods available to determine intersystem crossing quantum yields from energy transfer and quenching are considered. Intersystem crossing

quantum yields were measured as functions of temperature in the hope that this would provide some information about the $^4T_{2g}$ state.

In Chapter VII, a transient species or state, believed to be either of the $^4T_{2g}$ state or of the $^2T_{1g}$ state, was characterized by the rise of the phosphorescence intensity with time after pulse excitation.

In Chapter VIII, assuming the newly observed lifetime to represent that of, first, the $^4T_{2g}$ state and then that of the $^2T_{1g}$ state, three mechanisms are proposed and examined.

Finally, in Chapter IX, the spectroscopic origin of the $^4T_{2g}$ state is studied. Some speculations are described and suggestions for further investigations are made.

CHAPTER II

GENERAL EXPERIMENTAL PART

Experimental information common to the entire thesis is outlined in this chapter. This includes details of the setup of equipment, experimental techniques, and the sources and purification procedures of the chemicals used. Specific information and minor modifications limited only to a certain investigation will be mentioned in the chapter where it is described.

1. Emission Measurements

A block diagram of the setup for the steady-state emission measurements is shown in Figure 4. All measurements were carried out in a dark chamber. The right angle optical arrangement was adopted mainly to avoid scattered light. Fortunately for all the systems studied the inner filter effect is negligible.

1.1 Excitation Light Source

The light source was a 100-watt, point-source mercury arc lamp (PEK 110) powered by a stabilized DC power supply (PEK model 401). A short focal-length quartz lens (1" diam. 27 mm F.L.) was placed right before the lamp in order to collect the maximal amount of light from the arc. The lamp housing was similar to that described by Calvert and Pitts.³⁰ The light beam was so focused that it passed through the sample with nearly constant cross-section.

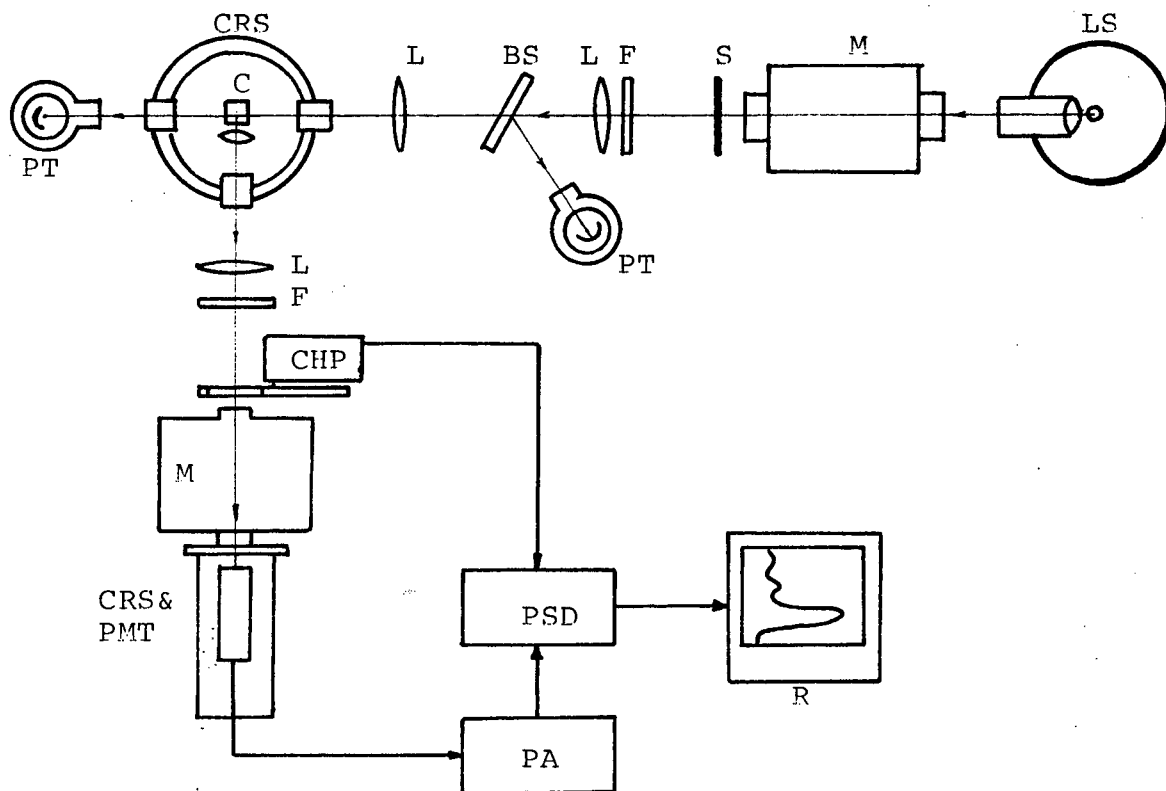


Figure 4. Schematic of the setup for emission measurements.

LS = light source; M = monochromator; S = shutter,
 F = glass filter; L = lens; BS = beam splitter; CRS =
 cryostat; C = sample cuvette; PT = phototube; CHP = light
 chopper for the lock-in amplified; PMT = photomultiplier
 tube; PA = preamplifier; PSD = phase sensitive detector;
 R = recorder.

Each of the mercury lines at 456, 436, or 366 nm, isolated from the total output of the arc by a monochromator, was employed as the monochromatic excitation light. For the 546 nm line, a yellow glass filter (Corning 3-74) was added to eliminate the second order uv radiation. The monochromator used was a Bausch & Lomb Monochromator (33-86-25) with a visible grating (33-86-02) of 1350 groove/mm and 500 nm blaze. The reciprocal linear dispersion is 6.4 nm/mm. The entrance and exit slits were 5.36 and 3.00 mm respectively.

The output of the lamp at 546 nm was about 12 mw. Although its short-term stability was better than 1%, sometimes it could drift as much as 5% over 10 hours. Therefore the relative intensity of the excitation light was monitored continuously through a beam splitter, a phototube (RCA 935), and a 10-mv recorder. The fluctuation in the excitation light was properly corrected for in the calculations.

1.2 Sample Cryostat

The cylindrical sample cryostat was built of Plexiglass and insulated thermally with thick Styrofoam. Three double-layered quartz windows were made for the exciting, transmitting and emitting light beams respectively. The outer windows were blanketed with streams of warm air to prevent them from frosting when necessary.

The sample cell--a 1-cm quartz luminescence cuvette--could be positioned reproducibly on a copper block. A glass tubing connected to the cell and protruding out of the cryo-

stat served as the conduit to introduce and withdraw the sample, to carry a thermocouple lead, and to maintain a continuous flow of nitrogen over the solution. A short focal-length quartz lens was placed very close to the cell in order to collect the maximal amount of emission.

The cold nitrogen used to cool the sample was spread evenly onto the cell walls through the holes on the inlet copper tubing which was extended to encircle the cell base. In order to ensure a reasonably homogeneous temperature, a tiny Teflon-clad magnetic bar was placed in the cell to stir the solution. Fortunately, when the solution becomes too viscous to be stirred, the emission becomes insensitive to the temperature, thus stirring is not critically required.

1.3 Temperature Control and Measurement

Temperature was controlled manually by controlling the flow rate of cold nitrogen gas, evaporated from liquid nitrogen, that was in turn controlled by the current to the heater in a 50 l Dewar containing liquid nitrogen. Temperature was probed with a glass-clad copper-constantan thermocouple which was immersed directly into the solution with its junction close to but out of the excitation light. The emf developed was measured with a Rubicon potentiometer.

1.4 Detecting System

The detecting system consisted of a sharp-cut red filter, lenses, a chopper for the lock-in amplifier, an ana-

lyzing monochromator, and a Phillips 150 CVP photomultiplier. The red filter (Corning CS 2-58) was used to eliminate further the scattered excitation light. The analyzing monochromator was a Jarrell-Ash 0.25 meter Ebert monochromator (Model 82-400) with two gratings of 1180 groove/mm and blazed at 300 and 600 nm respectively. The linear dispersion is 33 nm/mm. The entrance and exit slits used were both 100 microns. The scanning speed was 25 nm/min. The monochromator was laid on its side wall to make the entrance slit horizontal in order to allow the image of the emission, which has been carefully focused, to fall entirely onto it. Before reaching the monochromator, the emission light was chopped by a PAR Model BZ-1 chopper which was operated at 100 Hz and placed right before the entrance slit of the monochromator.

The red sensitive (S-1 spectral response) Phillips 150 CVP photomultiplier was placed in a cryostat and cooled with liquid nitrogen. It was powered by a Kepco ABC 1500 DC high voltage supply. The voltage applied to the photomultiplier was 1.3 kv, the optimal value. The signal voltage across the load resistor of the photomultiplier was amplified by a Brookdeal LA350 Low-Noise Amplifier. The amplified signal from it as well as the reference signal from the chopper was again fed into a Brookdeal Phase Sensitive Detector/Meter Unit PM322 which carried out the lock-in detection. The resulting signal was then recorded on a Leeds and Northrup 10-mv recorder. The linearity of the system has been checked to be satisfactory with a series of neutral density filters.

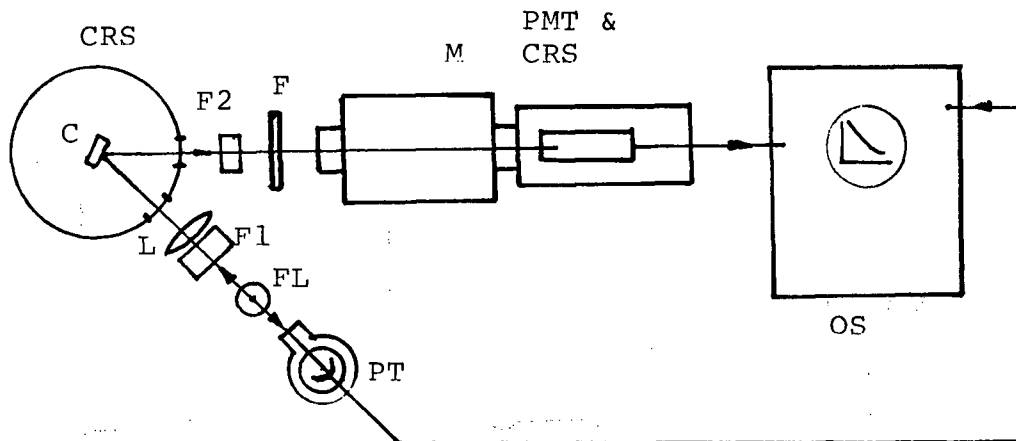


Figure 5. Schematic of the setup for lifetime measurements.

OS = oscilloscope; PMT = photomultiplier tube; CRS = cryostat; M = monochromator; F = glass filter; F1 = CuSO_4 solution filter; F2 = $\text{K}_2\text{Cr}_2\text{O}_7$ solution filter; L = lens; C = sample cuvette; FL = flash lamp; PT = phototube.

2. Lifetime Measurements

The block diagram of the setup for lifetime measurements is shown in Figure 5. The emission was detected at an angle 45° to the excitation light.

2.1 Flash Lamp

The nitrogen flash lamp was made in this laboratory. Operated at 5 atm and 15 kv, it has a rise time of 60 nsec and half-height width of 200 nsec with 5×10^{14} photons/pulse. The details of its construction and characteristics will be published by Pfeil and Porter.³¹ The flash lamp was filtered with a 5-cm saturated CuSO_4 solution to provide the excitation light from about 300 to 500 nm. It was focused to a small spot onto the sample cuvette.

2.2 Sample Cryostat

The cryostat consisted mainly of two cylindrical cans. The inner one can be filled with liquid nitrogen or circulated with cold nitrogen gas. A copper block attached to the lower end of this cooling can served as the cell holder. The sample cell was a specially blown Pyrex cuvette with about 1 ml capacity and 2 mm path length. The space between the inner and outer cans, where the cuvette was, was evacuated before cooling. The cuvette was tightly capped, however it allowed a small quartz-clad thermocouple to be inserted through the cap and immersed directly into the solution. The junction point of the thermocouple was situated at the point of focus of the flash light to monitor the true temperature. There were two quartz windows at 45° to each other on the outer cylinder for the exciting and emitting lights respectively. Temperature control and measurements were similar to those described in the emission measurements. Temperature was changed very slowly and measurements were taken only after the temperature became apparently steady.

2.3 Detecting System

The detecting system consisted of filters, a monochromator, and a photomultiplier. A red glass filter (Corning CS 2-64) and a 2-cm saturated $K_2Cr_2O_7$ solution were used to eliminate the scattered excitation light. The analyzing monochromator was a Bausch & Lomb Monochromator (33-86-25) with an infrared grating (33-86-03) of 675 groove/mm and 1.0

micron blaze. The reciprocal linear dispersion is 12.8 nm/mm. The entrance and exit slits were set at 3.4 and 6 mm respectively. However, the monochromator was used in such a way that the exit served as an entrance and the entrance an exit. The photomultiplier, its cooling system and power supply were the same type as those used in emission measurements except the bleeder network of the photomultiplier was wired specially for fast response applications. The voltage applied to the photomultiplier was between 0.9 and 1.5 kv. The signal, measured across a 1,000-ohm load resistor, was preamplified with a Tektronix Type L Plug-In and displayed on a Type 543B Oscilloscope. The combined unit has a rise time of 15 nsec and sensitivity of 5 mv/cm. It was triggered either internally or externally with signal from a phototube. The decay curves were recorded with a Du Mont Oscillograph Record Camera Type 302 and Polaroid Type 410 film. The pictures obtained were then enlarged with a Delineascope (American Optical Co.).

3. Photolysis Measurements

A block diagram of the setup for photolysis studies is shown in Figure 6. The light source was exactly the same as that described in the emission measurements except that the light beam was so focused that it filled most of the photolysis cell.

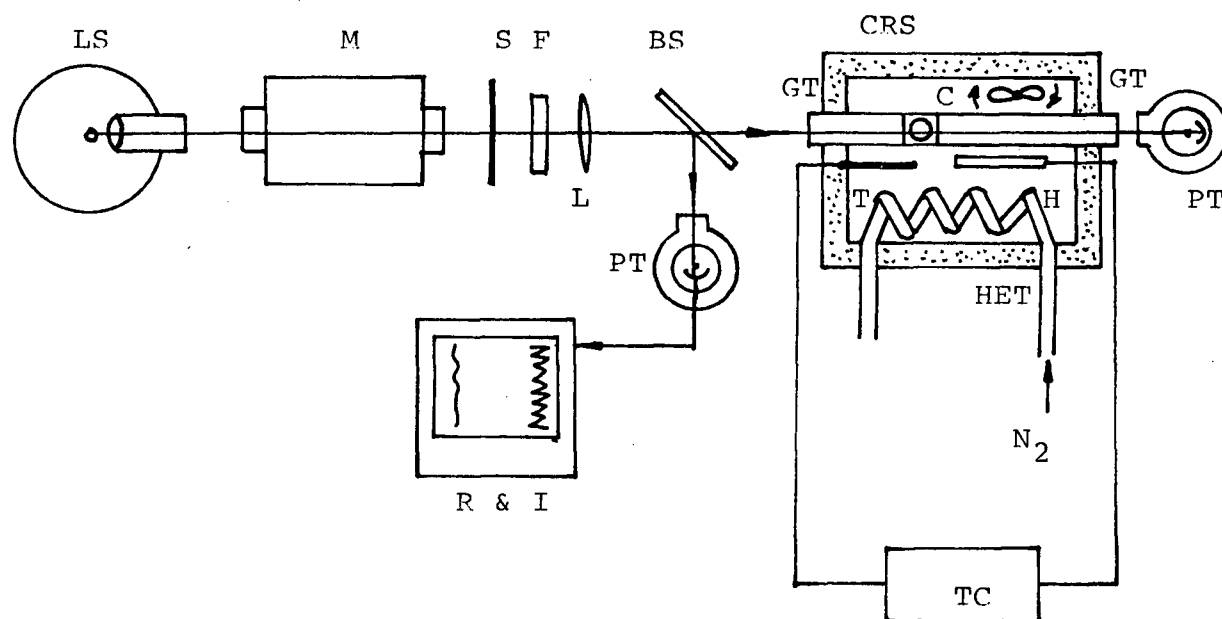


Figure 6. Schematic of the setup for photolysis measurements.

LS = light source; M = monochromator; S = shutter; F = glass filter; L = lens; BS = beam splitter; PT = phototube; GT = guard tube; CRS = cryostat; C = sample cuvette; T = thermistor; H = heater; HET = heat-exchange tube; TC = temperature controller; R & I = recorder and integrator.

3.1 Photolysis Cell

The photolysis cell was a 1-cm cylindrical quartz cuvette. It was extended at both ends with long, evacuated guard tubes. The opening of the cuvette was connected to a long glass tube which served as the conduit to introduce and withdraw samples, to place a thermocouple, and to maintain a flow of nitrogen above the solution during photolysis. The photolysis cell was immersed in a low temperature bath with the guard tubes protruded partly outside it.

3.2 Temperature Control and Measurements

The low temperature isothermal bath was built of a square copper vessel insulated with thick Styrofoam, and containing methanol as the coolant. Cooling was achieved by passing cold nitrogen gas through a copper tubing heat exchanger immersed in the coolant. Temperature was kept within 0.2°C of the desired temperature by a heater which was controlled by a Cole Parmer Versatherm Electronic Controller and a low temperature thermistor probe. The solution introduced was allowed to reach equilibrium with the outside coolant before photolyzing. Temperature was measured with a copper-constantan thermocouple immersed directly into the solution.

3.3 Photon Counting System

The intensity of the incident light was measured with the beam splitting technique as shown in Figure 6. A small part of the radiation was reflected from the beam splitter and detected by a RCA 935 phototube. The signal from the

phototube was recorded and integrated with a Brown (MH) Recorder (Model 143x58) equipped with a Disc Chart Integrator (Model 201). The ratio of photons reaching the photolysis cell to the integrator counts was determined with a Reineckate actinometer²⁸ in the same photolysis cell.

4. Absorption Measurements

Absorption spectra and absorbances were measured with a Cary 14 Spectrophotometer at room temperature.

5. Deoxygenation Techniques

All solution preparations were carried out in a nitrogen box. Solutions were deoxygenated by bubbling pure nitrogen via a fritted glass gas dispenser through them. Canadian Liquid Air Co. L grade nitrogen (oxygen content 20 ppm max.) was washed successively through two bottles of vanadous solution and one of dilute NaOH solution before use.³² The component solvents had been purged with nitrogen for a long time (days) before they were used to make up the mixed solvent. After adding the solute, the resulting solution was again purged with nitrogen for at least ten minutes before measurement. All solutions under measurement, if open to the atmosphere, were covered under a continuous flow of nitrogen to keep off the oxygen. The solutions for lifetime measurements were prepared and introduced into the sample cuvette in the nitrogen box and were tightly capped before being transported to the sample cryostat. The solutions for emission

and photolysis measurements were transported with a 10-ml syringe with a long flexible Teflon needle to their cells, which were already under flows of nitrogen gas.

6. Chemicals

6.1 Potassium Hexathiocyanatochromate(III)

Anhydrous potassium hexathiocyanatochromate(III), $K_3[Cr(NCS)_6]$, obtained from Alfa Inorganics Inc., was recrystallized more than three times from cold 95% alcohol under evacuation. It was then dried over P_2O_5 in a drying pistol and stored over P_2O_5 in a vacuum desiccator. The molar fraction of the free thiocyanate ion is less than 0.5%.

6.2 Potassium Hexacyanochromate(III)

Electronic grade potassium chromicyanide, $K_3[Cr(CN)_6]$, from City Chemical Co. was recrystallized twice from water and washed with ethanol and then with ether. It was stored over P_2O_5 in a vacuum desiccator. The molar fraction of the free cyanide ion is less than 0.5%.

6.3 Potassium Tetrathiocyanatodiamminechromate(III)

Potassium tetrathiocyanatodiamminechromate(III), trans- $K[Cr(NH_3)_2(NCS)_4]$, was prepared from Fisher Certified grade Reinecke's salt as described by Wegner and Adamson.²⁸ The sample was further recrystallized from cold alcohol and dried over P_2O_5 in a vacuum desiccator. The molar fraction of the free thiocyanate ion is less than 0.3%.

6.4 Tris(ethylenediamine)chromate(III) Perchlorate

Tris(ethylenediamine)chromate(III) perchlorate was prepared from its chloride salt, $[\text{Cr}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]\text{Cl} \cdot 3\frac{1}{2}\text{H}_2\text{O}$, which was available from Alfa Inorganics Inc. It was recrystallized twice from water and then dried and stored over P_2O_5 in a vacuum desiccator.

6.5 Chromium(III) Acetylacetonate

Chromium(III) acetylacetonate, $\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)_3$, obtained from Alfa Inorganics Inc., was recrystallized three times from benzene under evacuation.

All the above compounds are light sensitive, and therefore were purified under dim red light and stored in a vacuum desiccator in the dark.

6.6 Methanol

Eastman Kodak Spectro grade or Fisher Certified A.C.S. Spectroanalyzed methanol was used without further purification.

6.7 Ethylene Glycol

Eastman Kodak reagent grade or Fisher Certified grade ethylene glycol was used without further purification.

6.8 Water

Water used was distilled water.

6.9 The Mixed Solvent

The solvent used to make up the Cr(III) complex solutions consisted of two parts (in volume) of methanol, one part of ethylene glycol, and one part of water. It forms clear glass below about -100°C . The glass cracks at about -150°C . The solution remains clear whether it is cooled down or warmed up slowly.

CHAPTER III

ENERGY TRANSFER AND QUENCHING STUDIES

In order to elucidate the kinetics and mechanisms of the photophysical and photochemical primary processes, it is important to be able to selectively populate, depopulate, or bypass a certain excited state of a molecule. In organic photochemistry, energy transfer has been proven to be the most efficient and versatile technique in this aspect.^{33,34,35}

For Cr(III) complexes, the direct excitation to the doublet state has often been attempted,^{25,28} but owing to technical difficulties and diverse results, more attention has been directed recently to excitation energy transfer.

Quenching of organic triplets by Cr(acac)₃ has been observed,³⁶ but it was not certain then that energy transfer was involved. Only recently has energy transfer from excited organic molecules to Cr(III) complexes been demonstrated clearly through sensitized emission³⁷ and photoaquation.³⁸ Unfortunately, there is still some ambiguity about the state of the inorganic acceptor reached. It is imperative to identify the donating and accepting electronic states for both theoretical and practical reasons. The situation will be clearer if a system is so chosen that the lowest spin-allowed and spin-forbidden bands of the donor are, respectively, lower and higher than those of the acceptor. Accordingly [Cr(CN)₆]⁻³

is the best among the Cr(III) complexes as an acceptor. In fact, energy transfer from a series of Cr(III) double salts containing $[\text{Cr}(\text{CN})_6]^{-3}$ in the crystalline state has been studied.³⁹ However, there is evidence that the observed effect is not caused by energy transfer but by a crystal perturbation.⁴⁰

The energy transfer between the potassium salts of the Reineckate ion, $\text{trans}-[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$, and the hexacyanochromate(III) ion, $[\text{Cr}(\text{CN})_6]^{-3}$, was investigated in this work.

Experimental Section

The concentration of $\text{trans}-[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ was kept constant at 0.05 M; while that of $[\text{Cr}(\text{CN})_6]^{-3}$ varied from 0 to 0.07 M. All the solutions were deoxygenated. The absorption spectra were measured in 1 mm cells at room temperature.

Quantum yield measurements were made with 546 nm radiation at -65°C . Since the absorption spectra of the two ions are sufficiently different (see Figure 7), this wavelength is absorbed only by the Reineckate ion in solutions containing both ions. Both donor and acceptor emission spectra were scanned. Since the phosphorescence intensity is very sensitive to temperature, the average value was taken from at least three separate measurements.

Lifetime measurements were made from -110° to -40°C . The flashlamp was filtered with a yellow glass filter to provide radiation near 500 nm so that again only Reineckate ion was excited. The phosphorescence decays of the donor and

acceptor were measured separately at 751 and 840 nm respectively.

Results

The absorption spectrum of the solution containing both ions, as shown in Figure 7, is exactly the sum of the separate absorption spectra of the $[\text{Cr}(\text{CN})_6]^{-3}$ and $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$ solutions. Therefore, the two ions in the same solution do not interact with each other noticeably in the sense of ion-pairing.

Excitation of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$ only with 546 nm radiation in the presence of $[\text{Cr}(\text{CN})_6]^{-3}$ results in the appearance of phosphorescence of the latter and the decrement of the phosphorescence intensity of the former. That the observed emission is sensitized phosphorescence is established by the fact that at the same conditions, but in the absence of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$, no emission from $[\text{Cr}(\text{CN})_6]^{-3}$ is detectable. Therefore, on the whole $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$ acts as donor and $[\text{Cr}(\text{CN})_6]^{-3}$ as acceptor in this system. The two phosphorescence spectra are easily separable as shown in Figure 8.

The results of phosphorescence quenching and sensitization from quantum yield measurements at various acceptor concentrations are presented in Figures 9 and 10. The intensities of the donor and acceptor emissions were taken at the phosphorescence maxima, that is, 751 nm for $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$

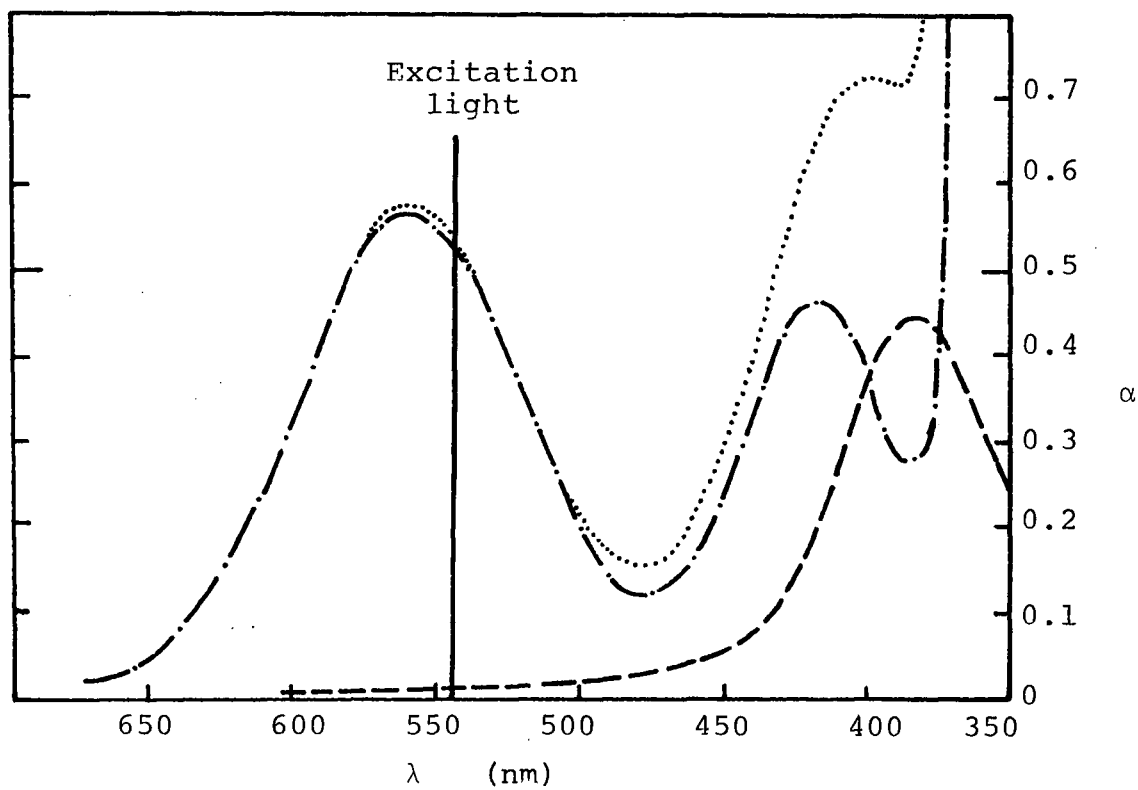


Figure 7. The absorption spectra of the $[\text{Cr}(\text{CN})_6]^{3-}$ and $\text{trans-}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ system.

- 0.05 M $[\text{Cr}(\text{CN})_6]^{3-}$ 1 mm path-length;
- · - · - 0.05 M $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ 1 mm path-length;
- 0.05 M $[\text{Cr}(\text{CN})_6]^{3-}$ 1 mm + 0.05 M $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ 1 mm path-length.

and 806 and 825 nm for $[\text{Cr}(\text{CN})_6]^{-3}$. The intensities of the acceptor emission at both wavelengths have been corrected for the small donor emission (see Figure 8). For quenching of the donor, according to Stern-Volmer mechanism,

$$\frac{I_0^D}{I^D} = 1 + k_{QH} \tau_O^D [A] \quad (3.1)$$

where I^D and I_0^D are the intensities of the quenched and unquenched emission, k_{QH} , τ_O^D , and $[A]$ are, respectively, the total quenching constant, the lifetime of the donor in the absence of the acceptor, and the concentration of the acceptor. Figure 9 shows that the plot of (I_0^D/I^D) against the concentration of $[\text{Cr}(\text{CN})_6]^{-3}$ yields a straight line. Its slope, equal to $k_{QH} \tau_O^D$, is estimated to be 24.3 M^{-1} . Since τ_O^D is 33 μsec , k_{QH} is $7.7 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$.

For the sensitized emission of the acceptor, it can be shown that

$$\frac{1}{I^A} = \frac{k_{QH}}{K k_{et}} + \frac{1}{K k_{et} \tau_O^D [A]} \quad (3.2)$$

where I^A is the intensity of the sensitized acceptor emission, k_{et} the energy transfer rate constant, and K an experimental proportionality constant. Figure 10 shows that the plot of the reciprocal intensity, $1/I^A$, against the reciprocal concentration of acceptor yields a straight line. It can be seen that $k_{QH} \tau_O^D$ is equal to the ratio of the intercept to the slope of the line of Equation 3.2. The values estimated for

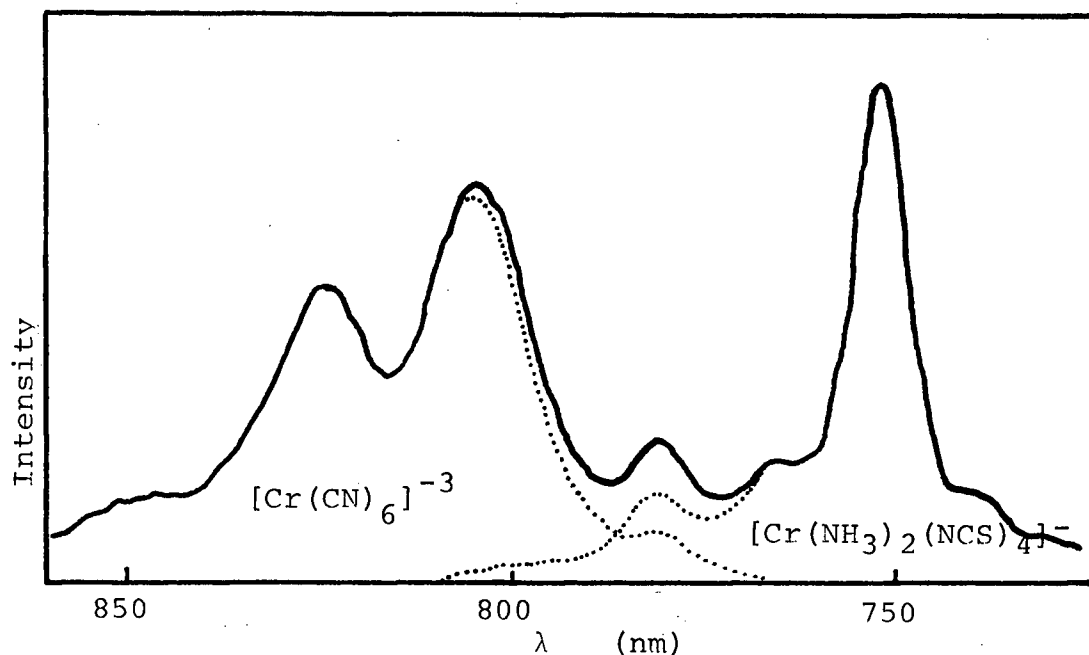


Figure 8. The emission spectra of the $[\text{Cr}(\text{CN})_6]^{-3}$ and $\text{trans-}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$ system.

$k_{\text{QH}}\tau_{\text{O}}^{\text{D}}$ are 20.7 and 21.8 at 806 and 825 nm respectively. Consequently, k_{QH} is 6.8 and $7.2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ from these data.

For the lifetime measurements, the phosphorescence decay rate constant k^{D} , or $1/\tau^{\text{D}}$, of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$ at various acceptor concentrations as functions of temperature is presented in Figure 11. It is straightforward to derive the expression

$$k^{\text{D}} = 1/\tau^{\text{D}} = 1/\tau_{\text{O}}^{\text{D}} + k_{\text{QH}}[\text{A}] \quad (3.3)$$

Figure 12 shows that the plot of k^{D} at -65°C against the acceptor concentration yield a straight line. The slope of

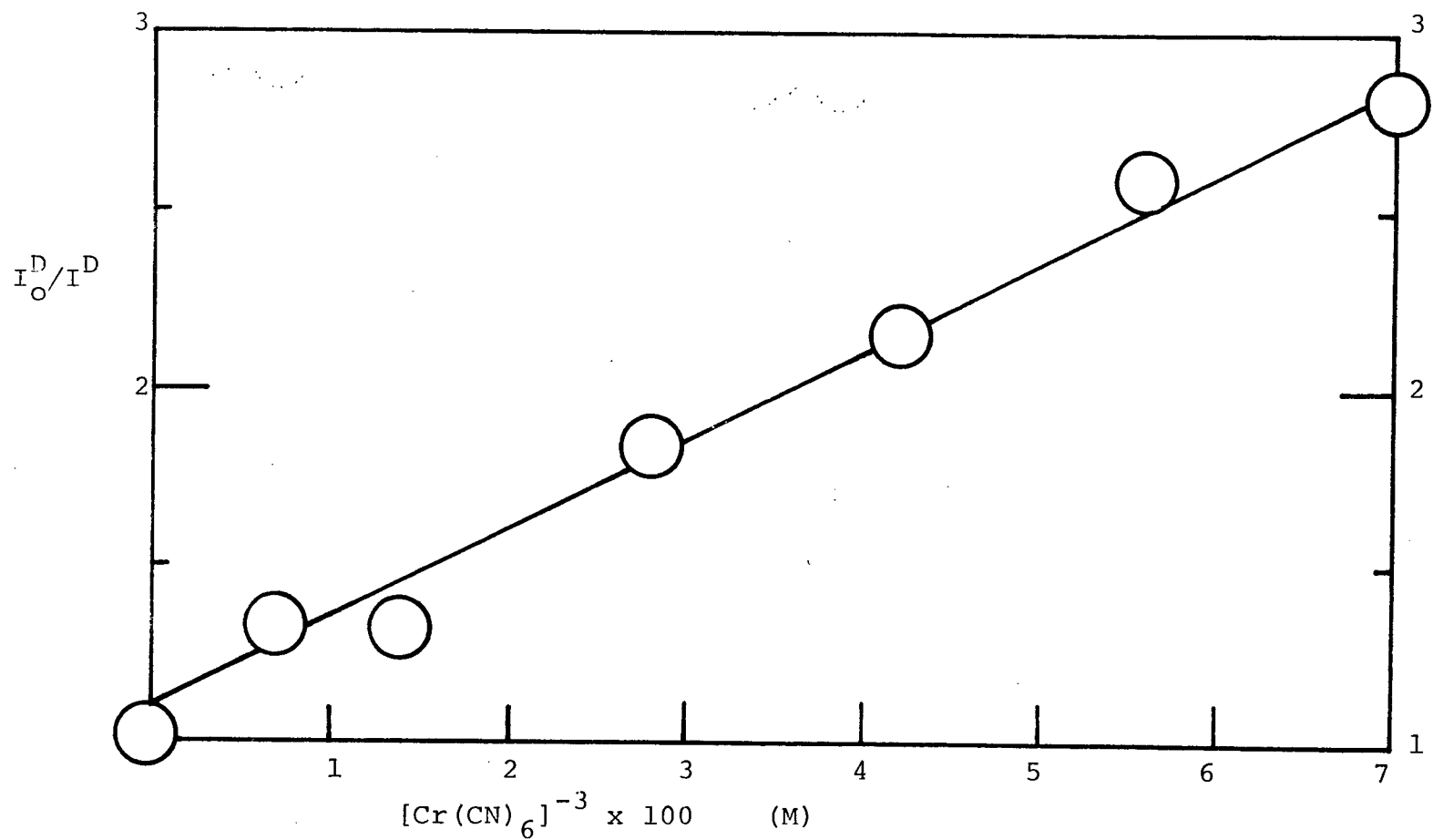


Figure 9. Stern-Volmer quenching of donor phosphorescence intensity at -65°C .

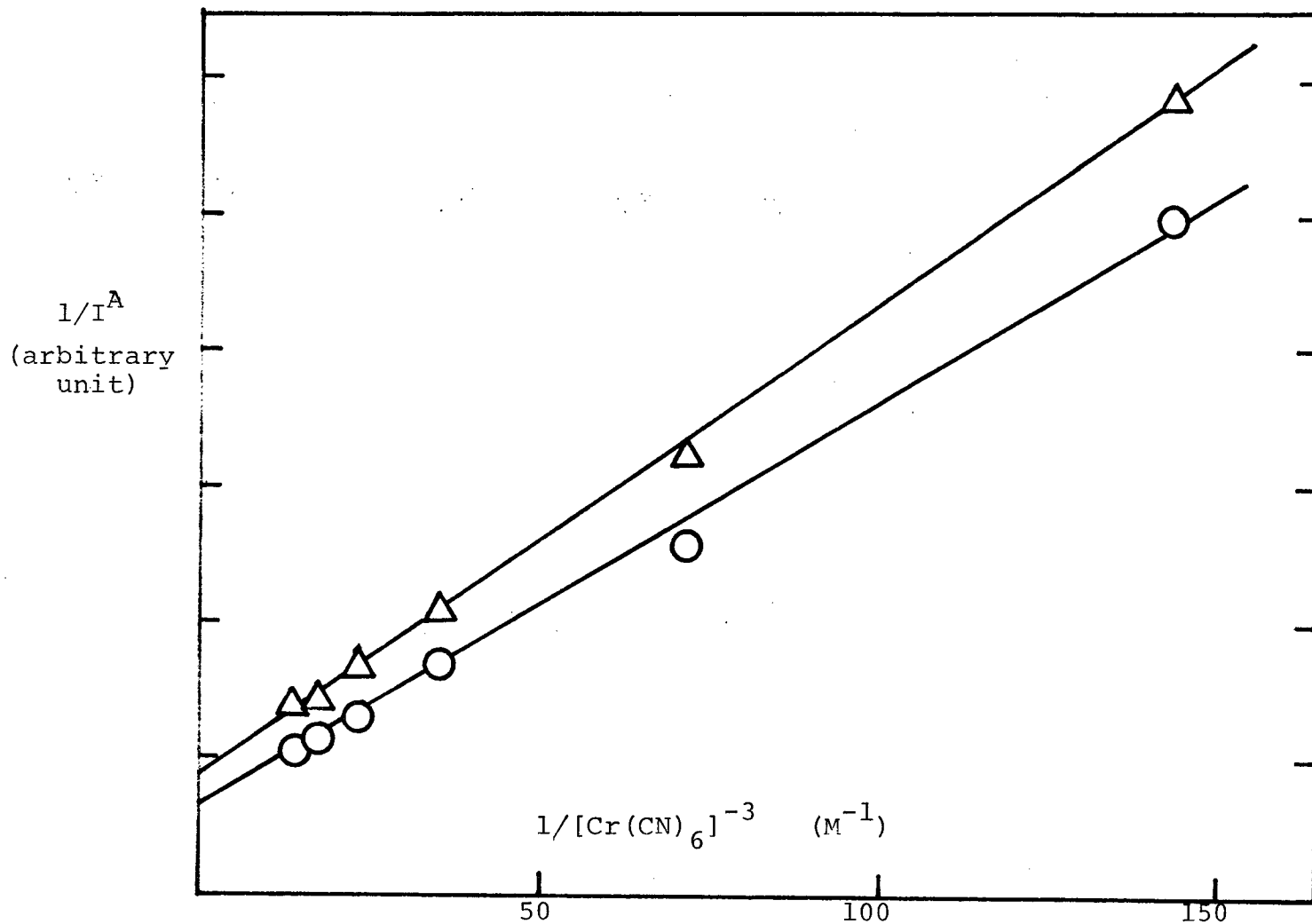


Figure 10. Sensitization of acceptor phosphorescence monitored at 806 nm (O) and at 825 nm (Δ). [D] = 0.05 M at -65°C

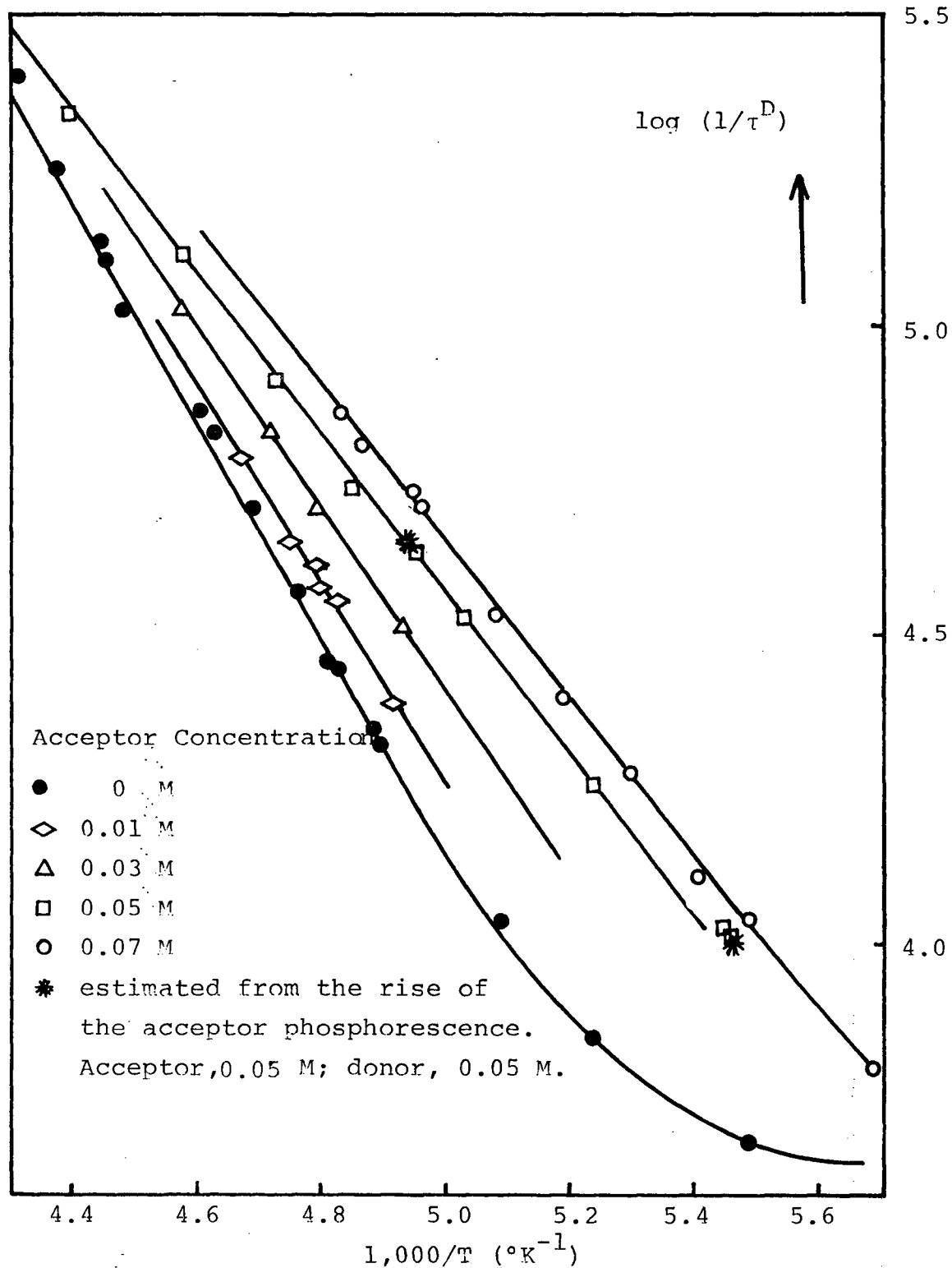


Figure 11. The donor phosphorescence decay rate constants at various acceptor concentrations as functions of temperature.

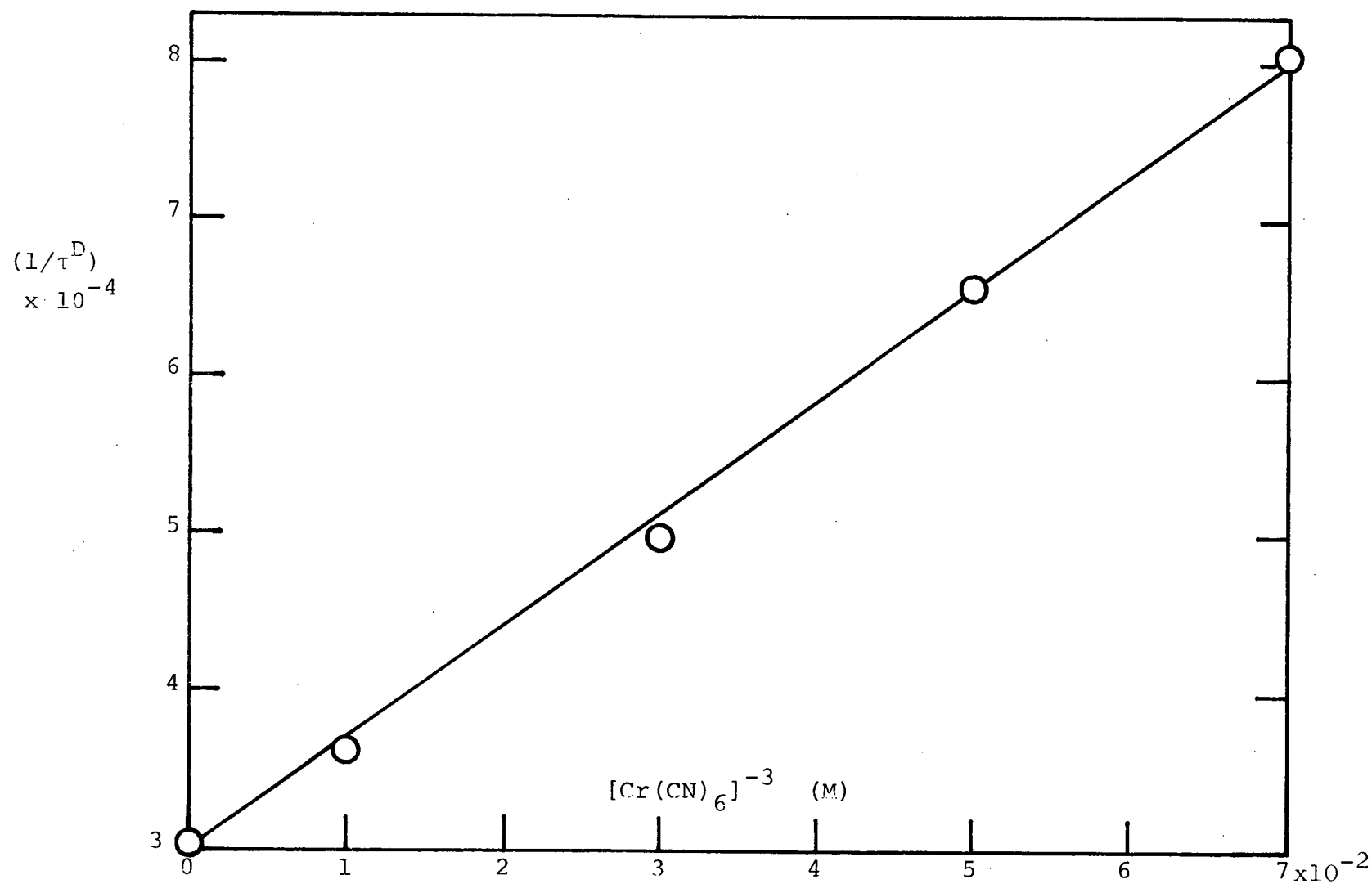


Figure 12. Stern-Volmer quenching of donor phosphorescence lifetime at -65°C . Donor concentration at 0.05 M.

the line gives directly the value of k_{QH} as $7.2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$, in good agreement with those found from the quantum yield measurements. Figure 13 shows the Arrhenius plot of $\log(k_{\text{QH}})$ against reciprocal temperature as a straight line. The frequency factor and activation energy obtained for k_{QH} are $6.6 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ and 4.8 Kcal/mol respectively.

The results of the lifetime measurements of $[\text{Cr}(\text{CN})_6]^{-3}$ in the energy transfer system are especially interesting. Firstly, the phosphorescence lifetime of the acceptor, τ^{A} , was found to be shortened considerably in the presence of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ as shown in Figure 14. Apparently $[\text{Cr}(\text{CN})_6]^{-3}$ is quenched by $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ too. Although there are not sufficient experimental data to check the Stern-Volmer relationship, the quenching constant, k'_{QH} has been estimated from two points. The Arrhenius plot of k'_{QH} against reciprocal temperature is shown in Figure 15. The frequency factor and activation energy obtained for k'_{QH} are $2.2 \times 10^{12} \text{ M}^{-1} \text{ sec}^{-1}$ and 7.6 Kcal/mol respectively, although there is a large experimental uncertainty in these values.

Secondly, when the emission of $[\text{Cr}(\text{CN})_6]^{-3}$ at 840 nm was followed with an oscilloscope, the traces of the emission showed an initial increase in intensity with time and followed by a longer decay, as shown in Figure 16. As derived in the Appendix, the dependence of phosphorescence intensities of the donor and acceptor on time, after an ideal pulse excitation of the donor only can be expressed as:

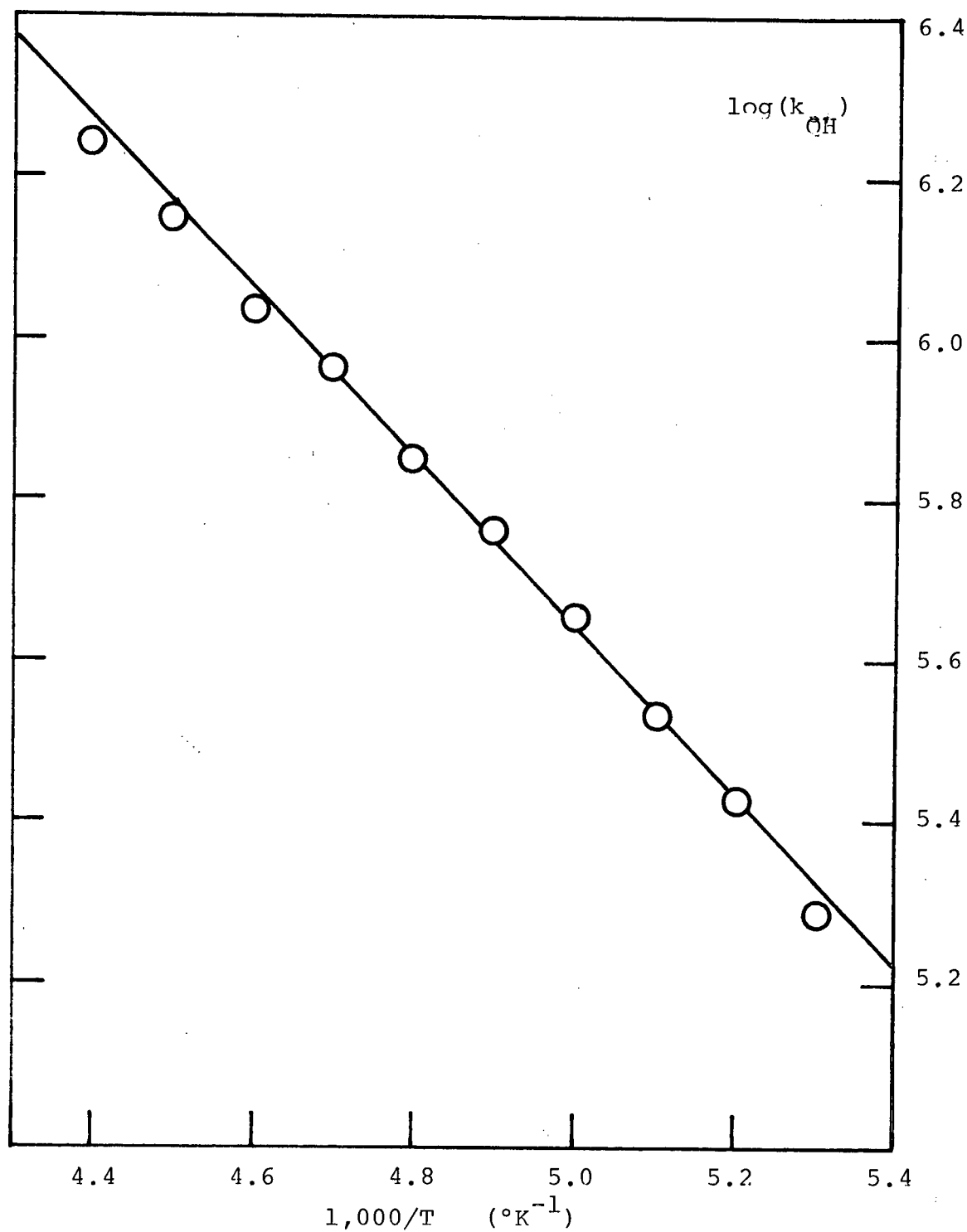


Figure 13. Arrhenius plot of k_{OH} .

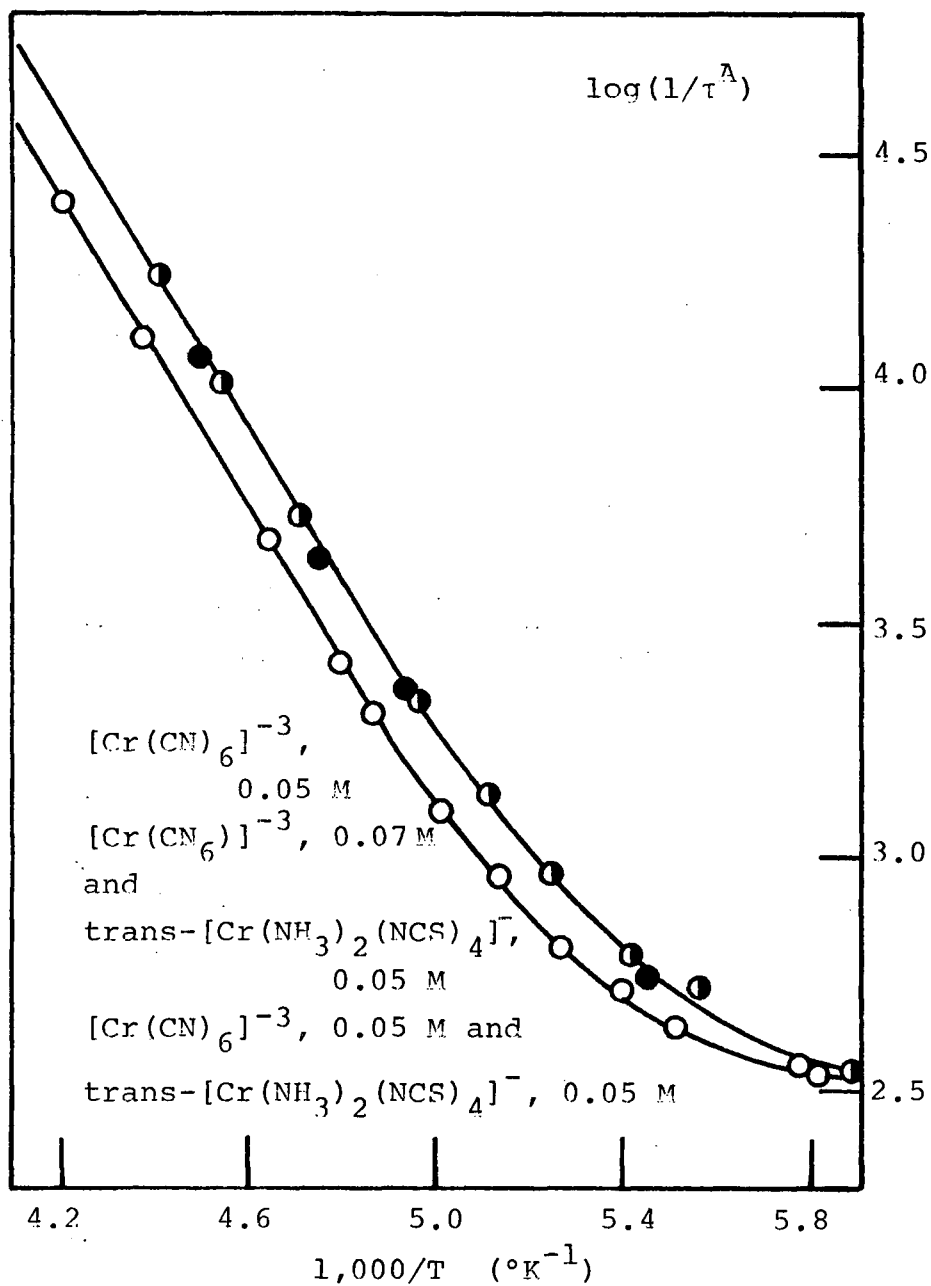


Figure 14. Quenching of the phosphorescence lifetime of $[\text{Cr}(\text{CN})_6]^{-3}$ in the presence of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$.

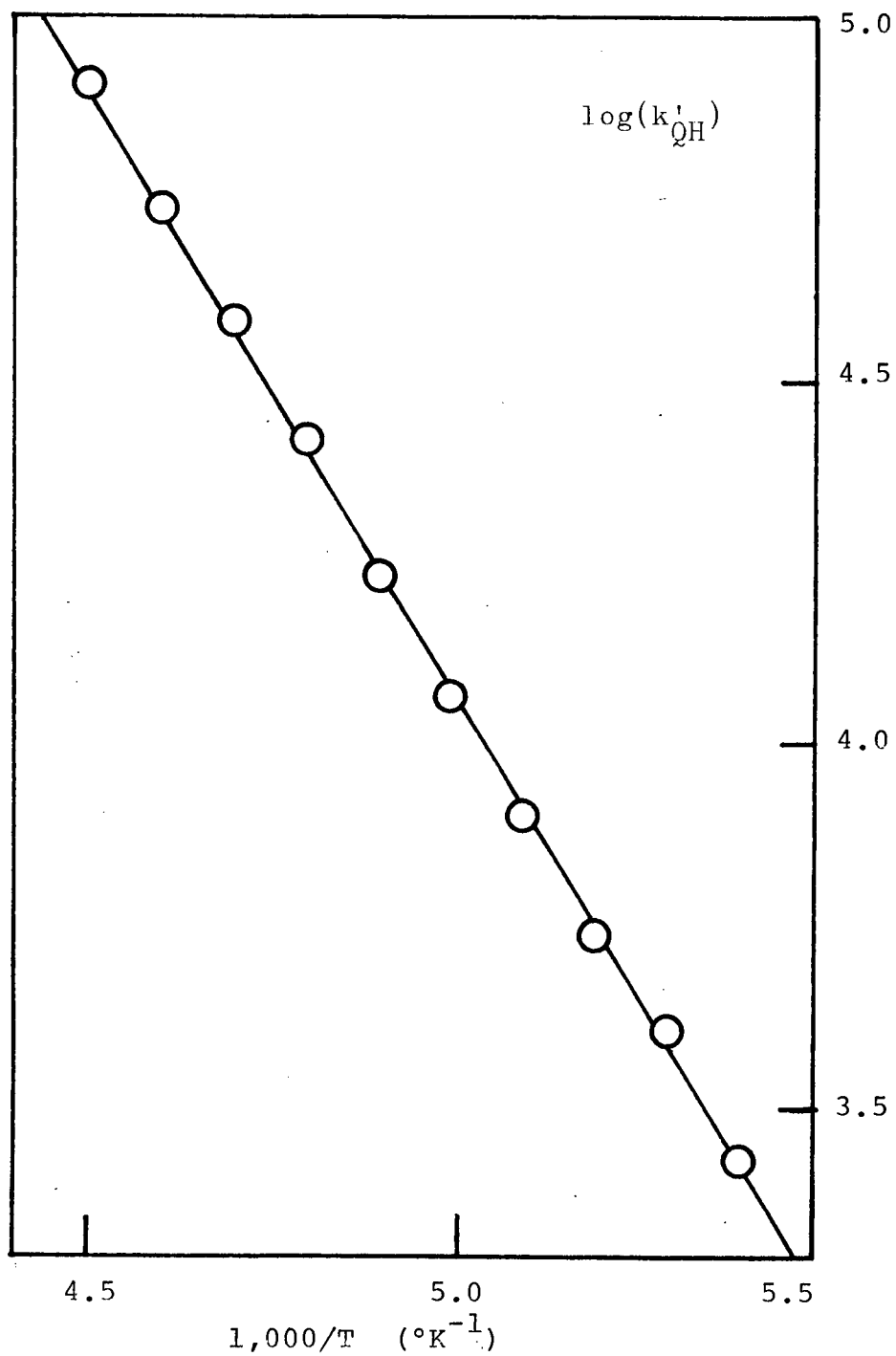


Figure 15. Arrhenius plot of k'_{QH} .

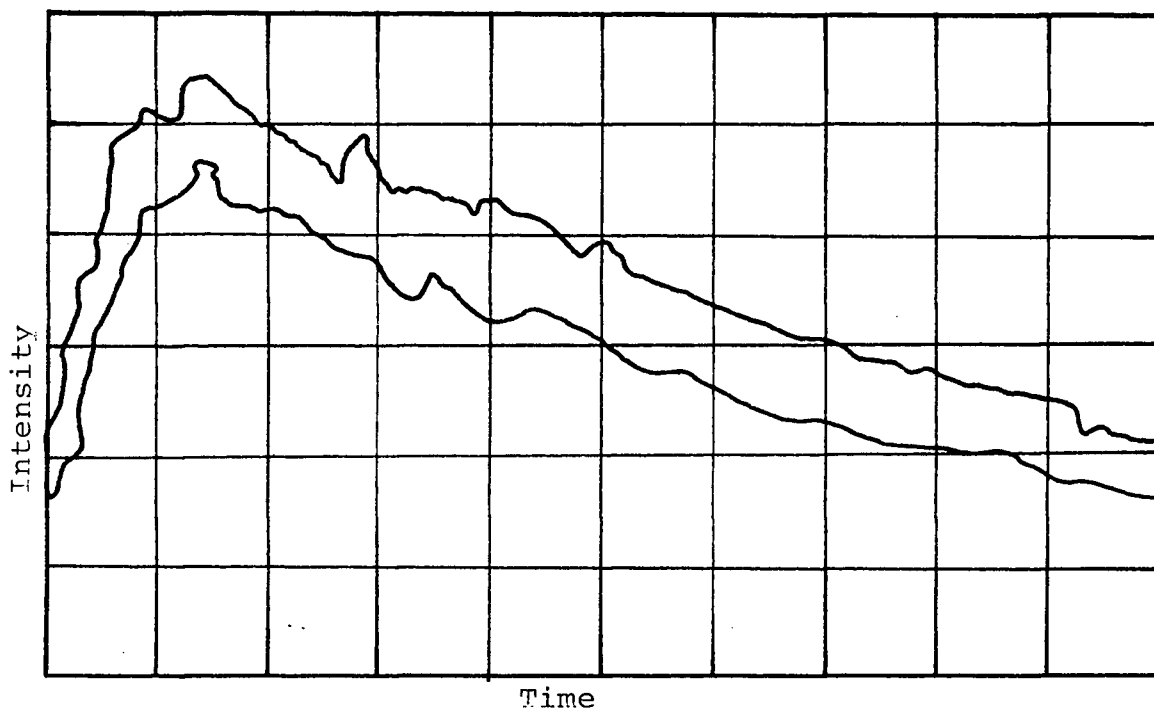


Figure 16. The rise and decay trace of the phosphorescence of the acceptor. Donor, 0.05 M and acceptor, 0.05 M, detected at 840 nm, at -70.7°C . Time scale: 50 μsec per division.

$$I^D = K_1 \exp(-t/\tau^D) \quad (3.4)$$

$$I^A = K_2 [\exp(-t/\tau^A) - \exp(-t/\tau^D)] \quad (3.5)$$

where K_1 and K_2 are adjustable parameters. Because the instantaneous intensity of the donor emission is much greater than that of the acceptor and that the slits of the monochromator used were large at the setting of 840 nm a small part of the Reineckate emission was still detectable. Therefore, the total intensity has the following form:

$$I_{\text{total}} = I^A + K_3 I^D \quad (3.6)$$

$$= K_2 \exp(-t/\tau^A) + (K_3 K_1 + K_2) \exp(-t/\tau^D) \quad (3.7)$$

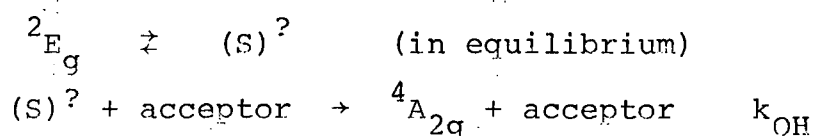
where K_3 is a weighting factor.

The values of the donor lifetime, τ^D , at various temperatures obtained from the intensity traces of emission at 840 nm according to Equation 3.7 are shown as starred points in Figure 11. The values so obtained agree with those found directly from the phosphorescence decay of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ in the same system. This clearly indicates that the donating electronic state of the Reineckate ion is the phosphorescent state, 2E_g .

Discussion

With 546 nm radiation, the ${}^4T_{2g}$ state of the Reineckate ion is populated directly, followed by intersystem crossing to the 2E_g state which emits phosphorescence.⁴¹ The results on quenching, sensitization, and especially lifetime measurements establish unequivocally that the 2E_g state of the Reineckate ion is the donating state, or the state being quenched.

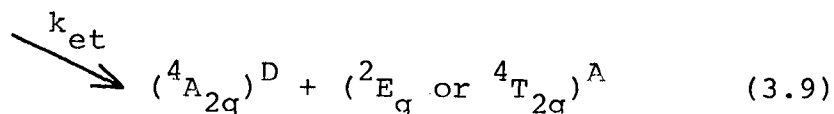
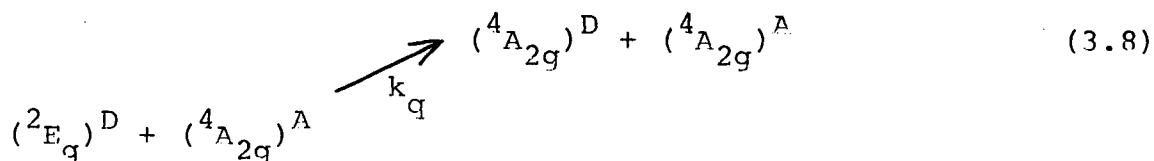
However, it is conceivable that, instead of the phosphorescent state, 2E_g , some thermally activated electronic excited state $(S)^?$, of the Reineckate ion in equilibrium with the 2E_g state, can be the immediate precursor to quenching.⁴²



It is kinetically indistinguishable whether the 2E_g or some other doublet state, e.g., the $^2T_{1g}$ state is directly involved. However, based on the following arguments, it can be estimated that the thermally activated state, (S)?, if any, can not be the $^4T_{2g}$ state. Firstly, the $^4T_{2g}$ state undergoes many relaxation processes and has a decay constant, $1/k_{QH}$, at least an order of magnitude bigger than that of the 2E_g state (see Chapter VII). Therefore, the $^4T_{2g}$ state is not in equilibrium with the 2E_g state. In fact, the thermally activated transition $^2E_g \rightarrow ^4T_{2g}$ is the rate-determining step of degrading the excitation energy of the 2E_g state via the $^4T_{2g}$ state (see Chapter V). Even if the $^4T_{2g}$ state is quenched, the 2E_g state will not be affected. Secondly, the $^4T_{2g}$ state, lying about $3,000\text{ cm}^{-1}$ above the 2E_g state (see Chapter V), is much too high in energy to be involved in energy transfer--the activation energy of k_{QH} is only about $1,700\text{ cm}^{-1}$.

The values obtained for the total quenching constant, k_{QH} , from both the quantum yield and the lifetime measurements are the same within experimental errors. This indicates that the intersystem crossing quantum yield of the donor, $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$, is not changed by the presence of $[\text{Cr}(\text{CN})_6]^{-3}$. In fact, it is highly probable that the $^4T_{2g}$ state of the donor is not perturbed at all in the energy transfer system.

There are two modes for quenching of the donor 2E_g state.



The first process is equivalent to an intramolecular radiationless transition facilitated or enhanced by interaction with the quencher; while the second process is an intermolecular energy transfer. As to the relative importance of energy transfer, Equation 3.9 and quenching, Equation 3.8, no quantitative assessment can be made from the data on phosphorescence intensity and lifetimes. Equations 3.1, 3.2, and 3.3 incorporate only the sum of their rate constants:

$$k_{QH} = k_q + k_{et} \quad (3.10)$$

not their individual values or their ratio.

The participation of energy transfer is clearly demonstrated by the sensitized emission of the acceptor. If quenching as in Equation 3.8 occurred, without the involvement of any electronically excited states of the acceptor molecule, there is no reason to expect $[\text{Cr}(\text{CN})_6]^{-3}$ to be any different in quenching than the donor itself. Yet such self-quenching does not occur, as is demonstrated by the fact that the phosphorescence lifetime of the Reineckate ion is independent

of its concentration. Therefore, quenching cannot be an important reaction and k_{QH} as measured, represent energy transfer, k_{et} , only.

Although energy transfer from the 2E_g state of the donor to either of the 2E_g or $^4T_{2g}$ states of the acceptor are spin-allowed,⁴³ the state of the acceptor is, like that of the donor, probably too high in energy to be involved in energy transfer. It is assumed that energy transfer occurs only via the lowest doublet states of donor and acceptor. Then the energy transfer efficiency, $k_{et}/(k_{et} + k_q)$ can be estimated from the following equations.

$$\phi_{sp}^A = \phi_{isc}^D \frac{k_{et}[A]}{(1/\tau_O^D) + (k_q + k_{et})[A]} k_p^A \tau_O^A \quad (3.11)$$

$$\phi_p^D = \phi_{isc}^D \frac{k_p^D}{(1/\tau_O^D) + (k_q + k_{et})[A]} \quad (3.12)$$

From Equations 3.10, 3.11, and 3.12, one can derive the energy transfer efficiency as

$$\frac{k_{et}}{k_{et} + k_q} = \frac{1}{\tau_O^A k_{QH}[A]} \frac{k_p^D}{k_p^A} \frac{\phi_{sp}^A}{\phi_p^D} \quad (3.13)$$

where ϕ_p^D , ϕ_{isc}^D , and k_p^D are the quantum yield of the quenched phosphorescence, the quantum yield of intersystem crossing, and the intrinsic radiative rate constant respective, of the

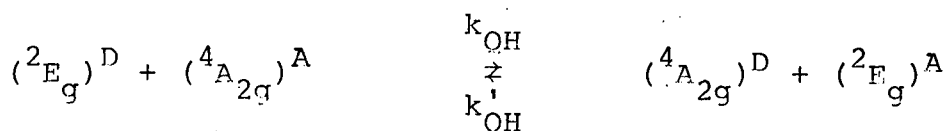
donor; and ϕ_p^A and k_p^A are the quantum yield of the sensitized phosphorescence and the intrinsic radiative rate constant of the acceptor.

At -65°C and $[A] = 0.07\text{ M}$, the ratio ϕ_{sp}^A/ϕ_p^D is equal to 1.6---evaluated by comparing the areas under the quenched and the sensitized phosphorescence spectra. The sensitivity of S-1 photomultiplier is relatively flat in this region. k_p^D and k_p^A are 200 and 16 sec^{-1} respectively.¹⁸ The value of the energy transfer efficiency obtained according to Equation 3.13 is about 1.1. This indicates that $k_{QH} = k_{et}$, and agrees with the conclusion previously made. From this it can also be shown that the $^4T_{2g}$ state cannot be the accepting state because, if so, then the energy transfer efficiency obtained (taking $\phi_{isc}^A = 0.1$) will be 11 which is not possible.

Energy transfer does not occur at temperatures below -130°C where the solvent becomes a rigid glass. This eliminates long-range energy transfer, complex formation, and trivial process of reabsorption. The activation energy of k_{QH} is very close to that of solvent fluidity, $5 \pm 0.5\text{ Kcal/mol}$, and the magnitude of k_{QH} is close to the estimated rate of diffusion controlled process, about $4 \times 10^6\text{ M}^{-1}\text{ sec}^{-1}$ for this solvent, estimated from viscosity measurements. All these facts suggest that the energy transfer is essentially a diffusion controlled process.

Figure 14 shows that the 2E_g state of $[\text{Cr}(\text{CN})_6]^{-3}$ is also quenched in the presence of Reineckate ion. Similarly, two modes of quenching are possible: the enhanced intramolecular radiationless transition k'_q and the intermolecular energy transfer k'_{et} . Again energy transfer is favored. Since the self-quenching of $[\text{Cr}(\text{CN})_6]^{-3}$ is not noticeable as is evidenced from Figure 14, the process k'_q , similar to self-quenching, should not be operative. In fact, the decay curve of the $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ emission at 740 nm (see Figure 17) becomes non-exponential and decays more slowly in the later part. This may be due to the delayed phosphorescence caused by the back energy transfer from the 2E_g state of $[\text{Cr}(\text{CN})_6]^{-3}$ to that of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$. Unfortunately, the instantaneous intensity of the delayed phosphorescence is too small and the curve at that part too noisy to allow rigorous analysis.

In the following energy transfers



k_{QH} is assumed to be equal to the diffusion-controlled rate constant given by Debye equation

$$k_{QH} = \frac{8RT}{3000 \eta} = s_{QH} \exp(-\Delta E_{fl}/RT) \quad (3.14)$$

where ΔE_{fl} is the activation energy of the solvent fluidity.⁴⁴ It is further assumed that the reverse energy transfer, k'_{QH} , which is endothermic, requires an Arrhenius activation energy

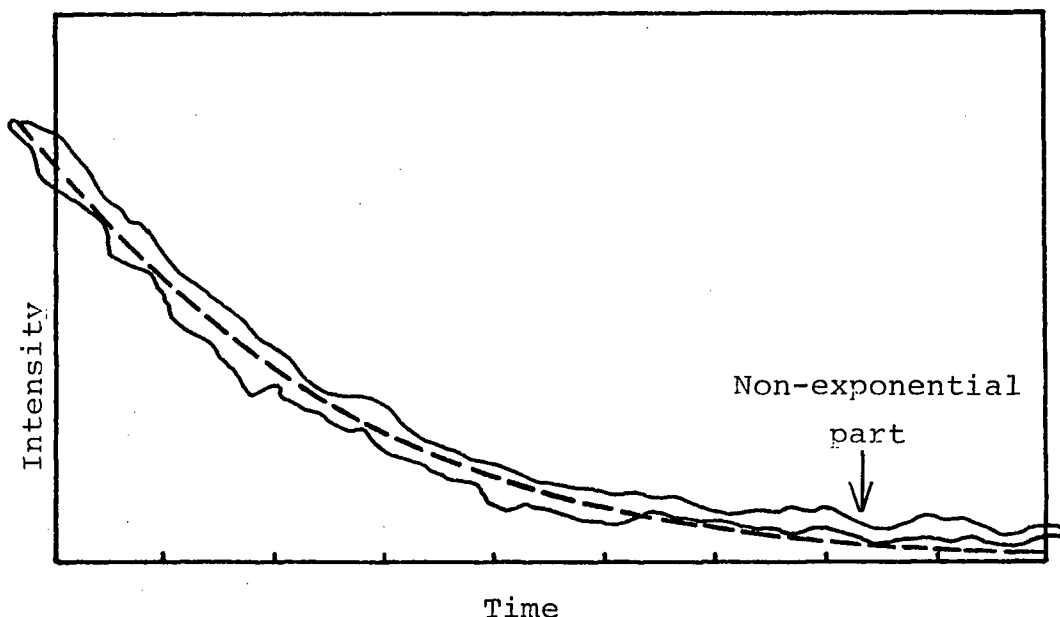


Figure 17. Non-exponential decay of the $\text{trans-}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ in the energy transfer system. Donor concentration: 0.05 M; acceptor concentration: 0.05 M, at -38°C . Time scale: 1 μsec per division. ----- indicates the ideal exponential decay trace.

equal to the energy difference, ΔE , between the 2E_g states of the donor and acceptor. Therefore,⁴⁵

$$\begin{aligned} k'_{\text{QH}} &= s_{\text{QH}} \exp(-\Delta E_{\text{fl}}/RT) \exp(-\Delta E/RT) \\ &= s_{\text{QH}} \exp[-(\Delta E_{\text{fl}} + \Delta E)/RT] \end{aligned} \quad (3.15)$$

The activation energy of k_{QH} obtained does agree with ΔE_{fl} (4.8 vs 5 Kcal/mol). The activation energy of k'_{QH} obtained, 7.6 Kcal/mol, is about 2.6 Kcal/mol more than ΔE_{fl} . The

difference is equal to ΔE . The value of ΔE evaluated from the emission spectra of $[\text{Cr}(\text{CN})_6]^{-3}$ and $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$ is 870 cm^{-1} (2.5 Kcal/mol). The two values from different methods are in agreement with each other.

CHAPTER IV

PHOTOCHEMICAL STUDIES

Energy transfer has been used successfully in organic photochemistry to investigate the role played by singlet and triplet states.^{33,34,35} However the application of this technique to the study of inorganic photoreactions has only been reported in a few cases. And almost all of the investigations were made on the photosensitized reactions of metal complexes by organic donors, particularly biacetyl. Vogler and Adamson⁴⁶ have studied the photosensitized reduction of some Co(III) amines. Porter⁴⁷ has studied the photosensitized aquation of cobalticyanide ion; and Sastri and Langford⁴⁸ the tetrachloroplatinate(III) ion. As for Cr(III) complexes, Adamson, Martin, and Camessei³⁸ have investigated the photosensitized aquation of $[\text{Cr}(\text{NH}_3)_5(\text{NCS})]^{+2}$, $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$ and $[\text{Cr}(\text{NCS})_6]^{-3}$. Recently, some work on the photosensitized aquation of $[\text{Cr}(\text{en})_3]^{+3}$ by biacetyl has been reported by Balzani, Ballardini, Gandolfi, and Moggi.⁴⁹ However, because the accepting states were not known for sure, a clear-cut conclusion on the reactivity of the various excited electronic states is still far from certain. Furthermore, there is the complication that the excited biacetyl may react directly with the ligands of the complex ions.⁴⁹

General Principles

The general principles and criteria of making use of energy transfer measurements to obtain information concerning photoreactive states have been described.^{33-35,50} The ideal systems are those in which only the phosphorescent states of the donor and acceptor are involved. A photoreactive molecule under study may be used as either a donor or an acceptor. If it is used as an acceptor, populating its phosphorescent state and simultaneously bypassing its fluorescent state allow a study to be made of the reactivity of the former. That is, the phosphorescent state can be determined to be reactive or inert depending on whether the photoreaction still occurs or not at all. However, usually because of the uncertainties of the energy transfer efficiency and of the intersystem crossing quantum yield of the donor, the reactivity of the phosphorescent state is very difficult to evaluate quantitatively. It is relatively easy to obtain quantitative results, if the molecule is used as a donor. By quenching the phosphorescent state, the maximal reduction in the overall photochemical quantum yield at very high quencher concentration is taken as a measure of the photochemical quantum yield from the phosphorescent state, while the unaffected portion is equal to the photochemical quantum yield from the fluorescent state.

The above statements have to be considerably modified if back intersystem crossing is appreciably involved. For Cr(III) complexes, for example, the back intersystem crossing, k_{-4} , has been considered to be the main pathway for depletion of the 2E_g state (see Chapter V). If so, then direct population of the 2E_g state by energy transfer (or direct excitation) does not bypass the $^4T_{2g}$ state. In this case, if the photochemical quantum yield obtained from sensitization is greater than that from direct photolysis, the phosphorescent state is reactive; if smaller, the fluorescent state is reactive. As pointed out quantitative data are difficult to obtain from sensitization, a qualitative result of merely observing photosensitized reaction cannot be used to conclude unambiguously that the phosphorescent state is reactive. As for the quenching method, the unquenchable part of the photochemical quantum yield still is the photochemical quantum yield from the fluorescent state. However, the maximal quenchable part may not be the quantum yield directly from the phosphorescent state now. Careful analyses have to be made to determine whether quenching of photoreaction or intersystem crossing or both from the phosphorescent state is responsible for the decrease in overall photochemical quantum yield.

In Chapter III energy transfer between $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ and $[\text{Cr}(\text{CN})_6]^{3-}$ has been shown clearly to take place via doublet states of each ion. In this chapter quenching studies of the photoaquation of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ are described.

Experimental and Results

Photolysis of the Reineckate ion was carried out at $-65.0 \pm 0.2^\circ\text{C}$ in the deoxygenated solution of methanol, water, and ethylene glycol (2:1:1). Irradiation was at 546 nm and lasted typically one hour. During irradiation the solution was kept under a flow of pure nitrogen gas in order to keep off oxygen. The concentration of the Reineckate ion was 0.03 M, while that of $[\text{Cr}(\text{CN})_6]^{-3}$ varied from 0 to 0.07 M. For all the solutions the radiation was only absorbed by the Reineckate ion. The photochemical quantum yield was measured according to the thiocyanate ion produced. A solution of the same amount and through the same operations except irradiation served as the blank. Thiocyanate ion was analyzed by the technique of Adamson and Wegner,²⁸ except that ethanol was added with the $[(\text{CH}_3)_4\text{N}]\text{Cl}$ to precipitate $[\text{Cr}(\text{CN})_6]^{-3}$ as well as the unreacted Reineckate ion. The filtered solution was then made alkaline and allowed to stand overnight before adding ferric perchlorate solution and measuring the absorbance of the ferric-thiocyanate complex. The molar extinction coefficient taken for the ferric-thiocyanate complex was $4.30 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$.²⁸ Quantum yields were determined by reference to the room temperature Reineckate actinometer,²⁸ taking account of the fact that the analysis releases four thiocyanate ions per aquated complex. The photoaquation quantum yields of the Reineckate ion at several concentrations of $[\text{Cr}(\text{CN})_6]^{-3}$

are listed in Table I, together with the relative phosphorescence quantum yield of the same ion for comparison. The value at each point is averaged from at least three runs.

Table I
Photoaquation Quantum Yields of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ as
Donor

Concentration Donor	M/l Acceptor	$\phi_{\text{chem}} \times 10^2$ (donor)	I^D (relative)	$\phi_{\text{chem}}^\infty$ (donor)
0.03	0	1.02 ± 0.02	1	--
0.03	0.03	0.79 ± 0.04	0.58	0.49×10^{-2}
0.03	0.05	0.76 ± 0.01	0.45	0.55×10^{-2}
0.03	0.07	0.69 ± 0.01	0.37	0.51×10^{-2}

The acceptor is $[\text{Cr}(\text{CN})_6]^{-3}$.

Discussion

It is clear from these data that the photoaquation of the Reineckate ion is quenched in the presence of $[\text{Cr}(\text{CN})_6]^{-3}$, but less so than the phosphorescence. Since the $^4\text{T}_{2g}$ state of the Reineckate ion is not quenched in this system, and the extent of quenching of the $^2\text{E}_g$ state can be estimated from quenching of phosphorescence, the maximal quenchable portion of the photoaquation can be calculated accordingly to the following equation:

$$(\phi_{\text{chem}}^{\text{O}} - \phi_{\text{chem}}^{\infty}) = (\phi_{\text{chem}}^{\text{O}} - \phi_{\text{chem}}) \left(\frac{I_{\text{O}}^{\text{D}}}{I_{\text{O}}^{\text{D}} - I^{\text{D}}} \right) \quad (4.1)$$

$\phi_{\text{chem}}^{\infty}$ is the limiting photoaquation quantum yield at high concentration of $[\text{Cr}(\text{CN})_6]^{-3}$ when the phosphorescent state is totally quenched. The solubility of $[\text{Cr}(\text{CN})_6]^{-3}$ precludes a direct measurement of $\phi_{\text{chem}}^{\infty}$, however, the values obtained for it from Equation 4.1, as listed in Table I, are consistent and have an average value of 5.2×10^{-3} . By rearranging Equation 4.1 and making use of Equations 3.1 and 3.3 the following equations can be derived.

$$\frac{\phi_{\text{chem}}^{\text{O}} - \phi_{\text{chem}}^{\infty}}{\phi_{\text{chem}}^{\text{O}} - \phi_{\text{chem}}} = \frac{I_{\text{O}}^{\text{D}}}{I^{\text{D}}} = \frac{\tau_{\text{O}}^{\text{D}}}{\tau^{\text{D}}} = 1 + k_{\text{OH}} \tau_{\text{O}}^{\text{D}} [\text{A}] \quad (4.2)$$

Plots of the photoaquations quantum yield, phosphorescence intensity, and phosphorescence lifetime against the concentration of $[\text{Cr}(\text{CN})_6]^{-3}$ according to Equation 4.2 are shown in Figure 18. The fact that all the lines are practically coincident demonstrates that part of photoaquation, given by $(\phi_{\text{chem}}^{\text{O}} - \phi_{\text{chem}}^{\infty})$, and the phosphorescence occur via the same state.

Two conclusions can be drawn from these experiments:

(1) half of the total photoaquation at -65°C (with $\phi = 5 \times 10^{-3}$) is not quenched by $[\text{Cr}(\text{CN})_6]^{-3}$ and thus occurs from excited molecules that have not been through equilibrated doublet states, and (2) the rest of the photoaquation, again

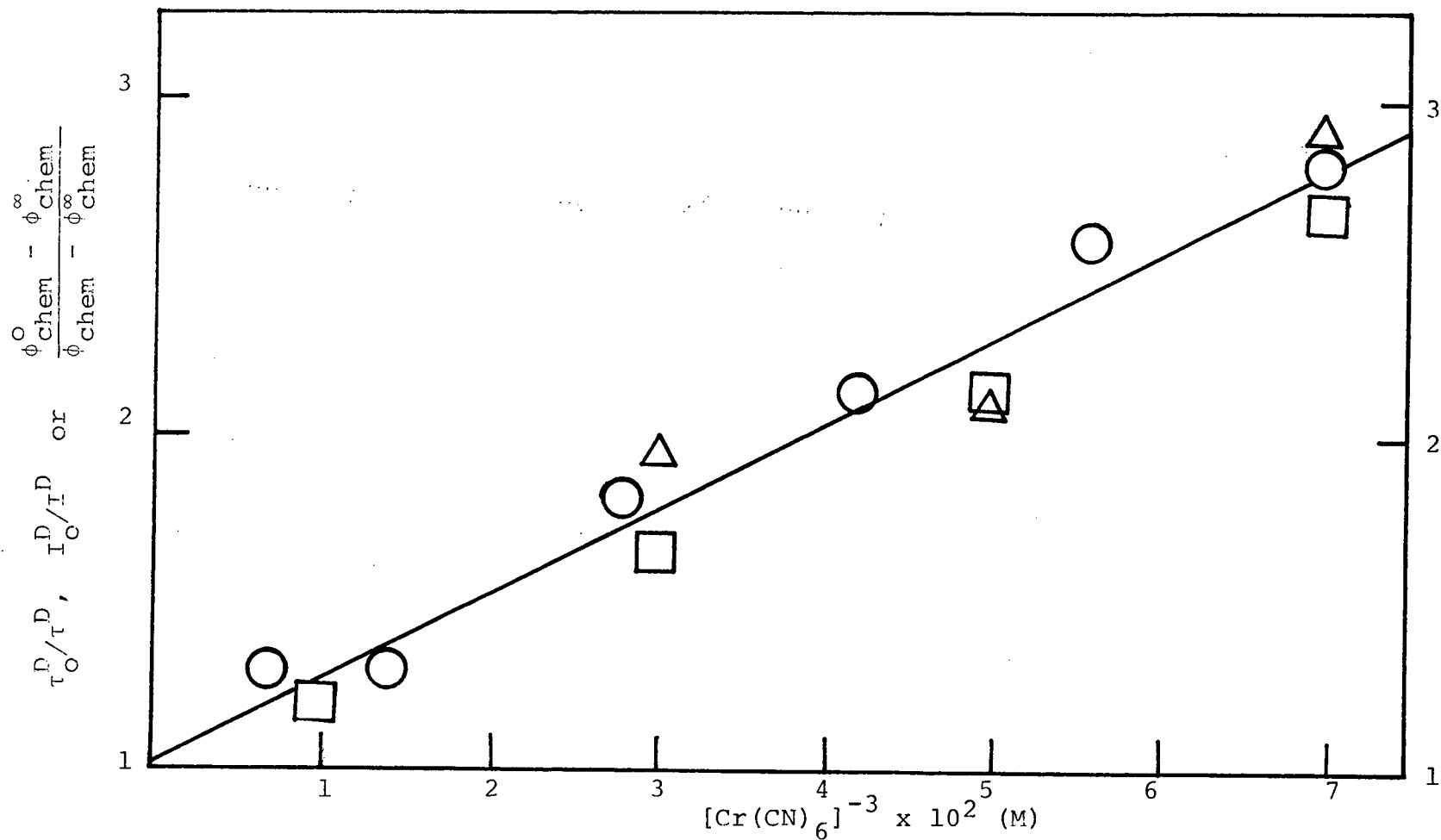


Figure 18. Stern-Volmer plots $(\phi_{\text{chem}}^{\text{O}} - \phi_{\text{chem}}^{\infty})/(\phi_{\text{chem}} - \phi_{\text{chem}}^{\infty})$, (Δ); for $I_{\text{O}}^{\text{D}}/I^{\text{D}}$, (O); and for $\tau_{\text{O}}^{\text{D}}/\tau^{\text{D}}$, ($\square$).

with $\phi = 5 \times 10^{-3}$, can be quenched and therefore must occur via either the phosphorescent state or some other state reachable by thermal activation from the phosphorescent state.

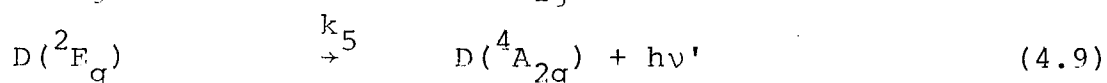
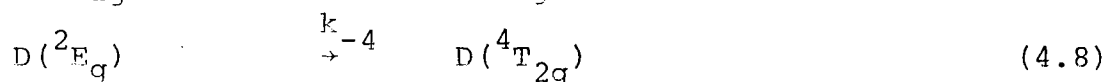
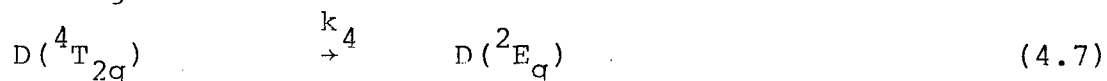
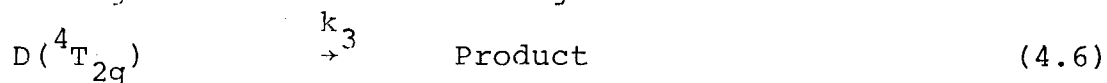
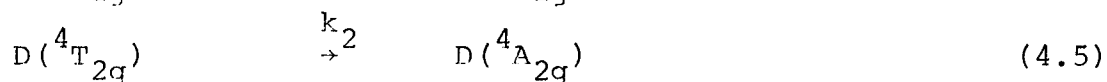
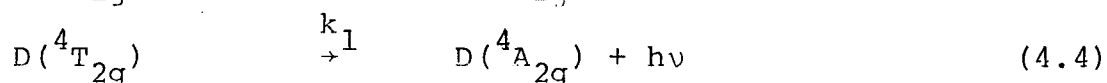
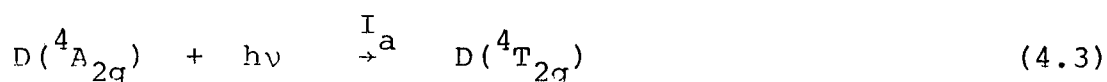
The results are therefore interpreted in the following way. After excitation to a high vibrational level of the lowest excited quartet state, rapid degradation results in a vibrationally equilibrated excited quartet molecule. Photo-aquation then occurs from this state, in competition with intersystem crossing to the doublet state manifold and internal conversion to the ground state, $^4A_{2g}$. Molecules in the doublet manifold must degrade to the lowest doublet state, 2E_g , as the phosphorescence lifetime is still 33 μsec at 65°C. Such molecules undergo aquation in competition with phosphorescence and intersystem crossing to the ground state--all of which can be quenched by energy transfer. There are two paths to be considered for this latter part of the aquation reaction: direct substitution of the complex in the doublet state by water, or back intersystem crossing to the lowest excited quartet state, with an activation energy equal to the energy difference between the two states, followed by aquation of the resulting quartet state molecule. The second explanation is favored from the studies of the temperature dependence of the phosphorescence lifetime. This means that the 2E_g state is essentially substitutionally inert. The detailed arguments are presented in Chapter V. However, at

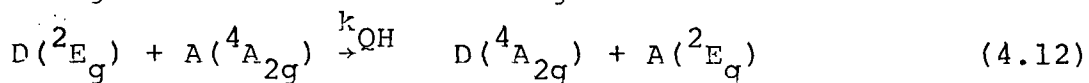
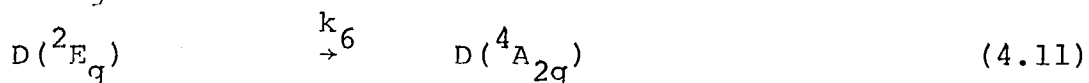
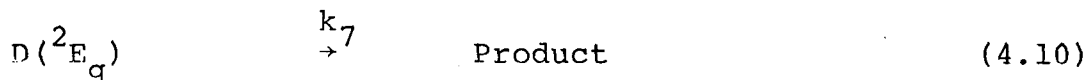
-65°C, back intersystem crossing of the Reineckate ion occurs with an efficiency of about 90%. A forward intersystem crossing efficiency of about 52% would then be required in order that the aquation quantum yields via the two paths be equal (see Chapter VI).

Kinetic Treatment

Since the above conclusions, as well as those in Chapter III, were deduced from the experimental results through the conventional analyses which are in fact based on a mechanism which does not include back intersystem crossing, it is necessary to demonstrate that even if back intersystem crossing is included the data treatment made and the conclusions drawn are still valid.

The complete mechanism is





The reverse of process 4.12, i.e., reverse energy transfer is omitted for the sake of convenience. In the transient studies, the apparent lifetime of the donor can be expressed, as shown in the Appendix and Chapter V, as

$$\frac{1}{\tau^D} = k_D = k_5 + k_6 + k_7 + (1 - \alpha) k_{-4} + k_{QH}[A] \quad (4.13)$$

$$= \frac{1}{\tau_O^D} + \frac{k_{QH}[A]}{k_4} \quad (4.14)$$

$$\text{where } \alpha = \frac{k_4}{k_1 + k_2 + k_3 + k_4} \quad (4.15)$$

$$\text{and } \tau_O^D = \frac{1}{k_5 + k_6 + k_7 + (1 - \alpha)k_{-4}} \quad (4.16)$$

Equation 4.14 is therefore exactly the same as Equation 3.3.

In the phosphorescence intensity and photoaquation quantum yield measurements where the steady-state approximation is justified, the steady-state concentrations of the Reineckate ions in the 2E_g and $^4T_{4g}$ states can be derived as

$$(^2E_g)_D^{ss} = \frac{k_4 I_a}{(k_1 + k_2 + k_3 + k_4)(k_{-4} + k_5 + k_6 + k_7 + k_{QH}[A]) - k_4 k_{-4}} \quad (4.17)$$

$$({}^4T_{2g})_{ss}^D = \frac{(k_{-4}+k_5+k_6+k_7+k_{QH}[A])I_a}{(k_1+k_2+k_3+k_4)(k_{-4}+k_5+k_6+k_7+k_{QH}[A]) - k_4k_{-4}} \quad (4.18)$$

Therefore quantum yields of the phosphorescence and photoaquation can be expressed as

$$\phi_{phos} = \frac{k_4k_5}{(k_1+k_2+k_3+k_4)(k_{-4}+k_5+k_6+k_7+k_{QH}[A]) - k_4k_{-4}} \quad (4.19)$$

$$\phi_{chem} = \frac{k_3(k_{-4}+k_5+k_6+k_7+k_{QH}[A]) + k_4k_7}{(k_1+k_2+k_3+k_4)(k_{-4}+k_5+k_6+k_7+k_{QH}[A]) - k_4k_{-4}} \quad (4.20)$$

From Equation 4.18, it can be shown that

$$\frac{I_o^D}{I^D} = \frac{p_{phos}^o}{p_{phos}} = 1 + \frac{k_{QH}[A]}{k_5+k_6+k_7+(1-\alpha)k_{-4}} \quad (4.21)$$

$$= 1 + k_{QH}\tau_o^D[A] \quad (4.22)$$

Thus, Equation 4.22 is also exactly the same as Equation 3.1.

Now, from Equation 4.19

$$\phi_{chem}^{\infty} = \lim_{[A] \rightarrow \infty} \phi_{chem} = \frac{k_3}{k_1 + k_2 + k_3 + k_4} \quad (4.23)$$

This shows the unquenchable part of the photoaquation is still equal to the quantum yield of photoaquation from the quartet state. It can further be shown that

$$\frac{\phi_{\text{chem}}^{\text{O}} - \phi_{\text{chem}}^{\infty}}{\phi_{\text{chem}} - \phi_{\text{chem}}^{\infty}} = 1 + \frac{k_{\text{QH}}[\text{A}]}{k_5 + k_6 + k_7 + (1 - \alpha)k_{-4}} \quad (4.24)$$

$$= 1 + k_{\text{QH}}\tau_{\text{O}}^{\text{D}}[\text{A}] \quad (4.25)$$

This is again exactly the same as Equation 4.2. We therefore can conclude that Equations 3.1, 3.3, and 4.2 are generally valid whether back intersystem crossing is included in the mechanism or not.

CHAPTER V

TEMPERATURE-DEPENDENCE OF THE PHOSPHORESCENCE

LIFETIMES

It has long been known that the phosphorescence lifetimes of Cr(III) complex ions are strongly dependent on temperature. A few investigations have been made in the attempt to clarify the mechanisms. Targos and Forster⁵¹ found that the phosphorescence decay constants consisted of a temperature-independent, a slightly temperature-dependent, and a strongly temperature-dependent term. The second term, as well as part of the first, was assigned to intersystem crossing from the 2E_g to the ground $^4A_{2g}$ state. The third term, which is overwhelmingly dominant at relatively high temperatures, although not definite then, was postulated to represent the thermally activated intersystem crossing from the 2E_g back to the $^4T_{2g}$ state. Such crossing, $^2E_g \rightarrow ^4T_{2g}$, certainly does occur in those complexes, e.g. $[\text{Cr}(\text{urea})_6]^{+3}$, which have rather small energy separation between the 2E_g and the $^4T_{2g}$ states.^{52,53} However, the first definite evidence for the process came from studies of ruby and emerald at high temperatures. In both crystals the calculated activated energy of the temperature-dependent component agreed reasonably well with the energy difference between the zero-vibrational levels of the $^4T_{2g}$ and 2E_g states, and emission of delayed

fluorescence was also observed.^{18,54} Recent work of Camassei and Forster⁵⁵ have demonstrated unambiguously the involvement of $^2E_g \rightarrow ^4T_{2g}$ in a group of Cr(III) complex ions in various crystalline hosts that fluoresce only at sufficiently high temperature. Unfortunately, all the above-mentioned complexes have small $10Dq$ values and accordingly, probably have small $^4T_{2g}(v=0) - ^2E_g(v=0)$ separations.²⁰ For those complexes which have large $10Dq$ values and generally do not exhibit delayed fluorescence, it is interesting to inquire whether the thermal activated $^2E_g \rightarrow ^4T_{2g}$ still prevails (especially in solutions where photoreactions may be competitive). Schlafer *et al.*⁵⁶ have studied the temperature dependence of the phosphorescence intensity of Cr(III) complex ions in solutions. Zander⁵⁷ has extensively investigated the temperature effect on the phosphorescence lifetimes of many Cr(III) complexes in both crystalline state and solution. Without additional support, they simply concluded that the strong thermal quenching of the phosphorescent state was due to the thermal activated $^2E_g \rightarrow ^4T_{2g}$. However, their solutions were not de-oxygenated, and therefore their data are not reliable.⁺⁺ In fact, for the Cr(III) complexes with a large

⁺⁺Oxygen quenching of the phosphorescent state of some Cr(III) complexes in solutions has been demonstrated in this laboratory.⁵⁸

10Dq value, the identification of the strongly temperature-dependent depleting component of 2E_g with the thermal activated $^2E_g \rightarrow ^4T_{2g}$ transition remained thus, at best, merely as a plausible speculation.

Aside from the interest in thermal activated back intersystem crossing itself, there are important reasons for clarifying the speculation. Firstly, at room temperature, the relaxation of the 2E_g state proceeds almost entirely by the strongly temperature-dependent component. Without confirming or ruling out the proposed mechanism, studies of the reactivity of the 2E_g state, even by solely populating or depleting it by direct excitation or energy transfer, could hardly be interpreted unambiguously. Secondly, if the proposed mechanism is confirmed by making use of the activation energies it offers us a way to estimate the zero-vibrational level of the $^4T_{2g}$ state which is, in general, not available from spectroscopic studies. Knowledge of the location of the zero-vibrational level of the $^4T_{2g}$ state is very important for the understanding of the primary photoprocesses originating from the $^4T_{2g}$ state and of its geometrical distortion.

Presented in this chapter are the experimental results for the temperature dependence of the phosphorescence lifetime of some Cr(III) complexes with large 10Dq values in well deoxygenated solutions as well as the arguments to support the thermal activated intersystem crossing. The other photo-

processes originating from the 2E_g state are also discussed here. Studies extended to the zero-vibrational level of the ${}^4T_{2g}$ state will be discussed in Chapters VIII and IX.

Results

The lifetimes of the complex ions $[Cr(CN)_6]^{-3}$, $[Cr(en)_3]^{+3}$, $[Cr(NCS)_6]^{-3}$, $[Cr(NCS)_4(NH_3)_2]^{-1}$, and $[Cr(acac)_3]$ have been measured as functions of temperature from about 0° to $-140^\circ C$ in the deoxygenated solution of methanol, water, and ethylene glycol (2:1:1). The concentrations of all the complex ions were 0.05 M except $Cr(acac)_3$ which was 0.01 M. The emission was monitored at the known phosphorescence maxima. The results, plotted as the logarithm of the reciprocal lifetime vs the reciprocal absolute temperature, are shown in Figures 19, 20 and 21.

According to Targos and Forster⁵¹ the reciprocal lifetime, or decay rate constant, can be expressed as

$$k_D = 1/\tau_D = k_0 + k_a + k_b \quad (5.1)$$

$$= k_0 + s_a e^{\frac{-E_a}{RT}} + s_b e^{\frac{-E_b}{RT}} \quad (5.2)$$

where k_0 includes the radiative ${}^2E_g \rightarrow {}^4A_{2g}$ transition probability and the temperature-independent nonradiative rate constant. However, the fact that all the experimental curves become quite straight at both ends may indicate that k_0 is not important over this temperature range and that k_a and k_b each dominates at one end of the temperature range (in this

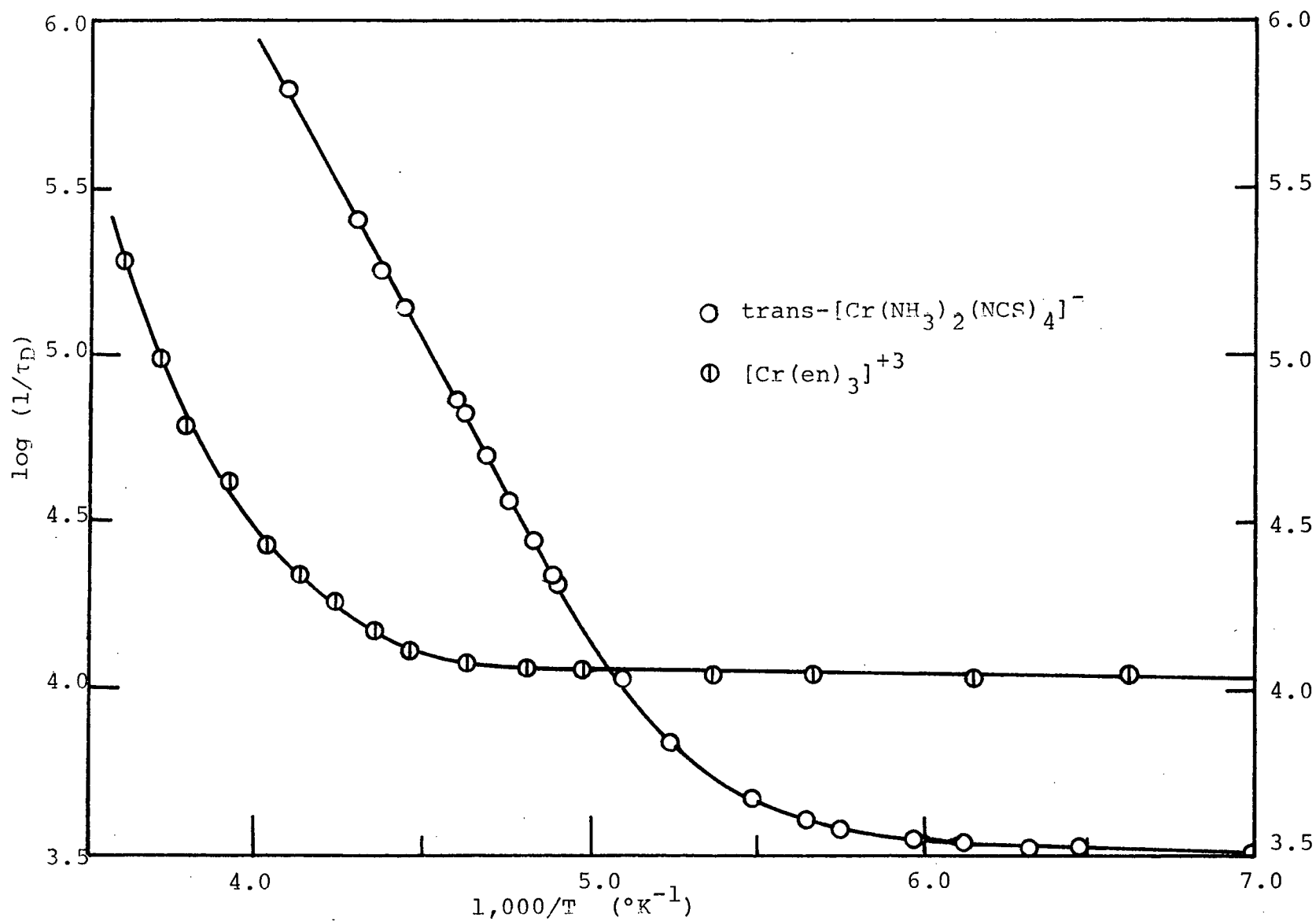


Figure 19. The lifetimes of the 2E_g states of $\text{trans-}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ and $[\text{Cr}(\text{en})_3]^{+3}$ as functions of temperature. 67

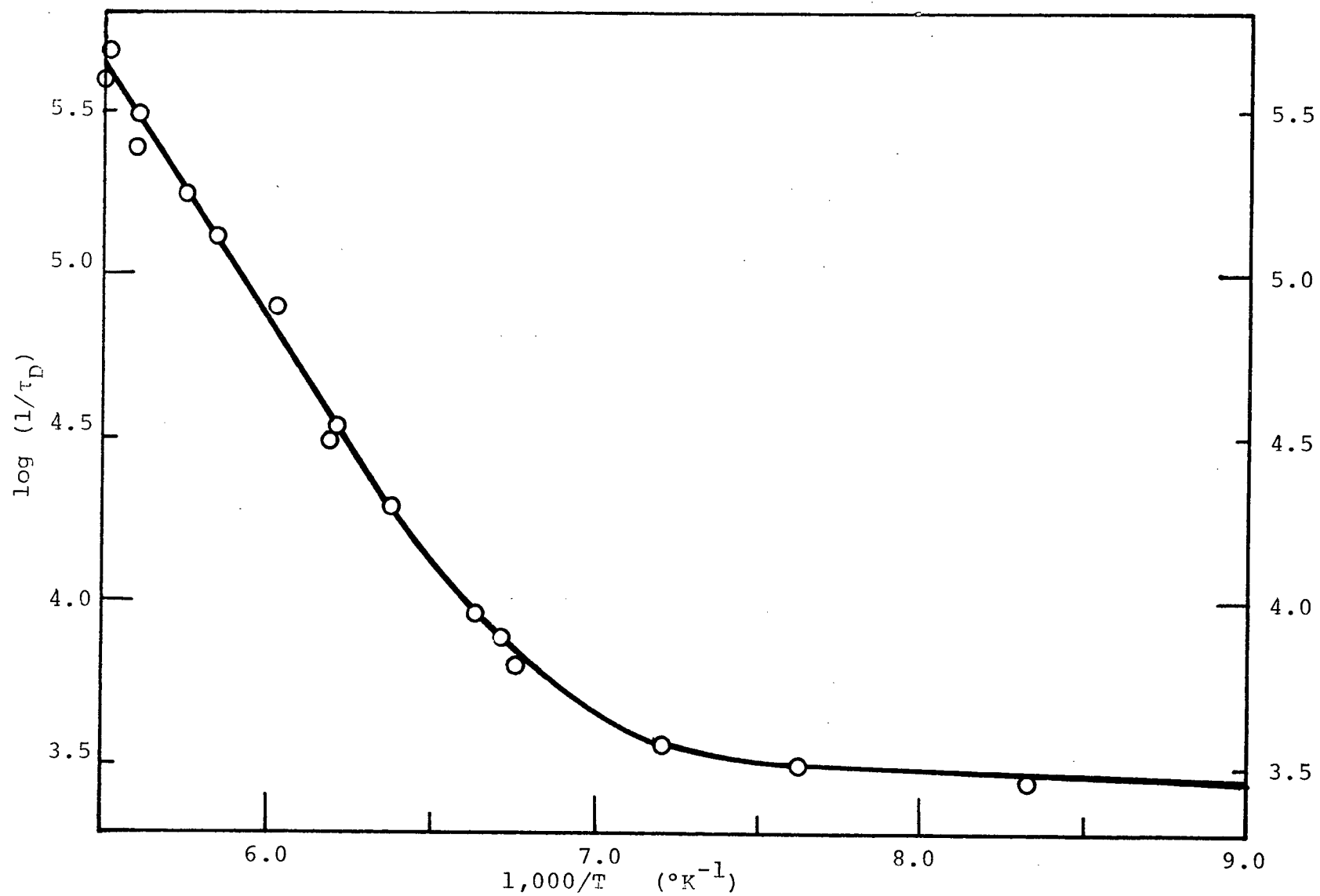


Figure 20. The lifetime of the 2E_g state of $\text{Cr}(\text{acac})_3$ as a function of temperature.

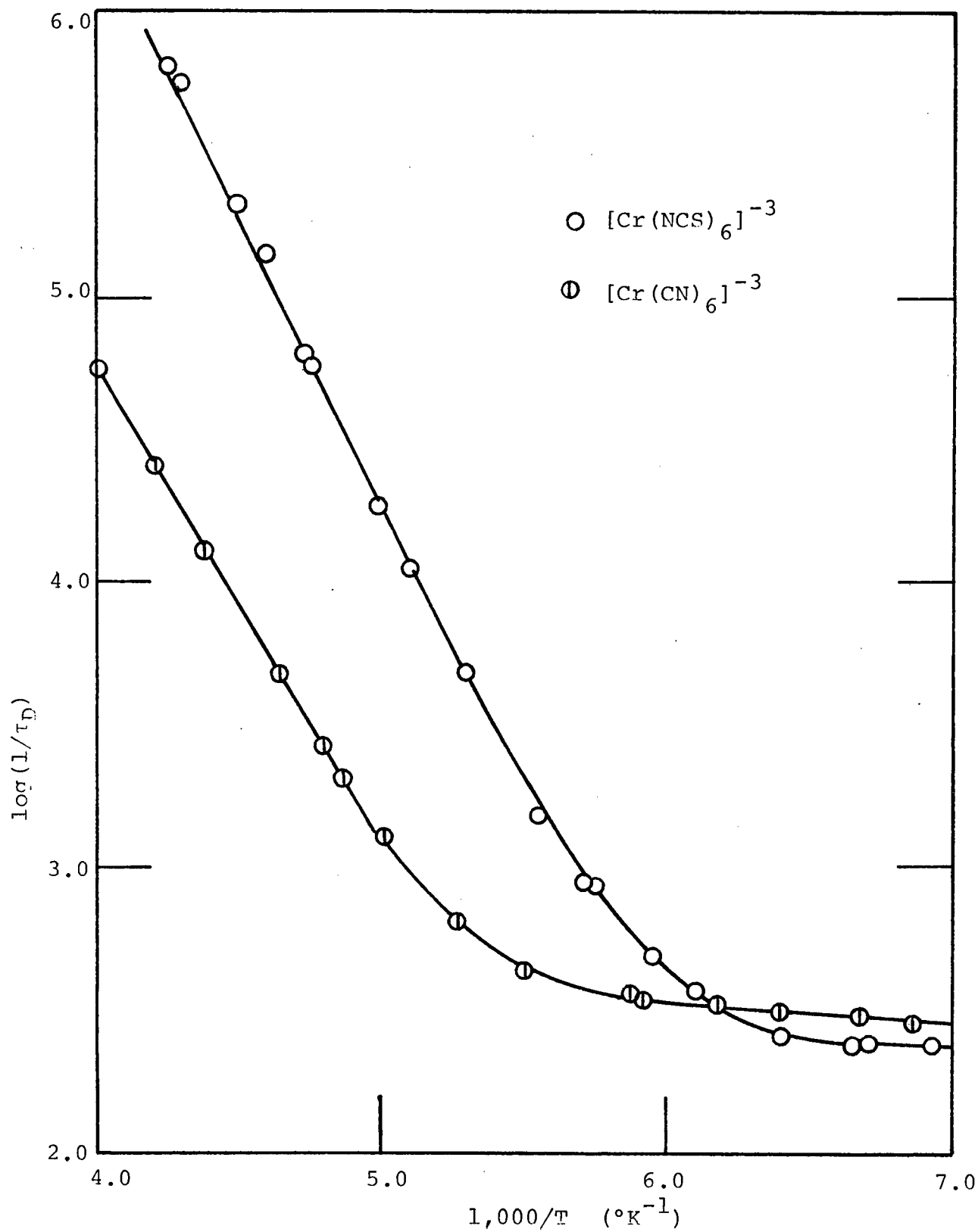


Figure 21. The lifetimes of the 2E_g states of $[\text{Cr}(\text{NCS})_6]^{-3}$ and $[\text{Cr}(\text{CN})_6]^{-3}$ as functions of temperature.

work). The decay rate constants were therefore decomposed into two temperature-dependent terms only:

$$k_D = s_a e^{\frac{-E_a}{RT}} + s_b e^{\frac{-E_b}{RT}} \quad (5.3)$$

The estimated values of s_a , E_a , s_b , and E_b are summarized in Table II where some of Targos and Forster's and Zander's data are also included for comparison. The smooth curves in Figures 17, 18, and 19 are plotted according to Equation 5.3 with parameters from Table II.

Table II

Frequency factors and activation energies of the temperature-dependent processes of the 2E_g state

Complex	s_a (sec^{-1})	E_a (Kcal/mol)	s_b (sec^{-1})	E_b (Kcal/mol)
$[\text{Cr}(\text{CN})_6]^{-3}$	7.2×10^2	0.26	8.7×10^{11}	8.2
$[\text{Cr}(\text{NCS})_6]^{-3}$	4.6×10^2	0.19	2.1×10^{14}	9.2
$\text{trans}-[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$	4.3×10^3	0.076	7.2×10^{13}	9.0
$[\text{Cr}(\text{en})_3]^{+3}$	1.6×10^4	0.10	1.5×10^{13}	10.2
$[\text{Cr}(\text{en})_3]^{+3}$ a	2.5×10^3	0.08	9×10^{12}	9.9
$[\text{Cr}(\text{en})_3](\text{ClO}_4)_3$ c	1.8×10^3	0.06	8.5×10^{11}	9.2
$\text{Cr}(\text{acac})_3$	6.2×10^3	0.18	6.9×10^{14}	7.7
$\text{Cr}(\text{acac})_3:\text{Al}(\text{acac})_3$ b	6×10	0.4	6×10^{12}	8.0

- From Zander's data, in water and glycerin(1:1) without de-oxygenation. $[\text{Cr}(\text{en})_3]^{+3}$ was known not to be quenched by oxygen.⁵⁸
- From Targos and Forster's data.
- Calculated from Zander's data in solid state.⁵⁷ The phosphorescence decay is exponential in solid state for this complex. Estimated from three points.

Discussion

An overall examination of the curves reveals that the onset temperature, at which the lifetime begins to shorten drastically, is a strong function of the solute. This is not compatible with the proposed explanation²² that the onset temperature corresponds to the temperature at which the solution starts to fluidify or solidify. Certainly, the environment does affect the relaxation processes, but it is apparently that the influence is rather continuous and differentiable over the temperature range.

On the whole, it is common rather than exceptional that the lifetime depends very much on temperature in solution. In some organic compounds, this has been shown⁵⁹ to be due to the diffusion controlled quenching by impurities since the activation energy of this depleting process for different solutes was practically the same as the activation energy of the solvent fluidity. In the case of Cr(III) complex ions, there is much evidence to rule out the intermolecular mechanisms. Quenching by oxygen⁵⁸ and by the other Cr(III) complex ions via energy transfer (see Chapter III) has been well studied. Even if we assume the presence of a noticeable amount of oxygen or some other possible complex ions, the quenching effect is still far too small to be adequately accounted for, not to mention that the solutions have been well deoxygenated and the Cr(III) complexes carefully purified. Impurities in the organic solvents are not impossible.

However, thanks to the low lying 2E_g state, organic impurities would be very unlikely to meet the necessary conditions to quench it. Self-quenching, if any, is not important at this concentration.⁵⁷ Furthermore, the activation energies, E_a 's and E_b 's in the same solvent are well spread and all are quite different from the activation energy of the solvent fluidity--about 5 Kcal/mol for the mixed solvent used. All these facts clearly rule out the possibility of any diffusion controlled quenching. There is also some evidence to support the supposition that s_a , s_b , E_a , and E_b are all mainly intramolecular parameters.⁵¹ Conclusive evidence comes from the fact that although s_a and s_b change with environment, E_a and E_b are practically invariant in different environments. For example, E_a and E_b respectively remain the same for $[Cr(en)_3]^{+3}$ in the methanol:water:ethylene glycol (2:1:1) mixture, the water:glycerin (1:1) mixture, and in solid state. This is also true for $Cr(acac)_3$ in solution and in crystalline host $Al(acac)_3$ (see Table II).

The possible intramolecular pathways for depopulation of the excited 2E_g state, as shown in Figure 3, are: (1) phosphorescence $^2E_g \rightarrow ^4A_{2g}$, (2) intersystem crossing to the ground state $^2E_g \rightarrow ^4A_{2g}$, (3) photochemical reactions, and (4) thermal activated intersystem crossing $^2E_g \rightarrow ^4T_{2g}$. The radiative $^2E_g \rightarrow ^4A_{2g}$ transition, assumed to be temperature-independent, is included in k_0 in Equation 5.2. Phosphorescence quantum

yields for the complex are usually very small and thus not an important competitive process in this temperature range.

Since E_a is too small to be due to the thermal excitation from 2E_g to $^4T_{2g}$, k_a has been assigned to a direct transition from 2E_g to $^4A_{2g}$.⁵⁵ Although the radiative transition probability k_5 may be temperature dependent due to the fact that it is vibronically induced, to identify k_a with k_5 cannot be justified on the grounds that the phosphorescence quantum yield is generally far too small. Therefore, k_a is assigned to the intersystem crossing from 2E_g to $^4A_{2g}$ and thus identified with k_6 .

Modern theories of radiationless transition by Robinson and Frosch,⁶⁰ Siebrand,⁶¹ and Lin⁶² all indicate that there may be but a small temperature dependence for radiationless deactivations. Lin and Bersohn have derived from Lin's theory an explicit equation relating to the temperature effect on triplet-state lifetimes.⁶¹ At sufficiently low temperature

$$1/\tau = 1/\tau_0 + a/\tau_0 e^{-\theta/T} \quad (5.4)$$

where τ_0 is the lifetime at $T=0^\circ K$. In most aromatic compounds studied, the value of θ ranges from about 300 to 800 cm^{-1} .⁶³ Lin suggested that some of the lower-frequency intramolecular vibrations (out-of-plane bends) may be responsible for the temperature dependence.⁶³ For Cr(III) complexes, from Table II, s_a is generally less than 300 cm^{-1} . Taking the lower frequencies of the metal-ligand vibrations into account,

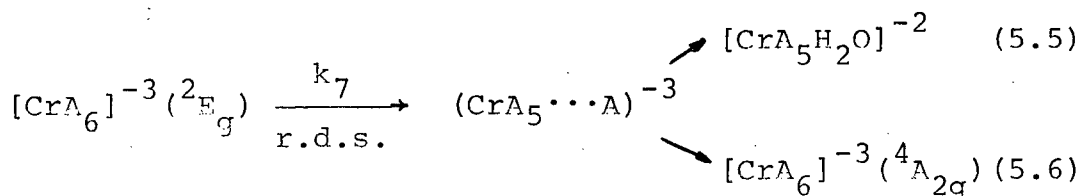
these values are reasonably satisfactory.

For the second temperature-dependent component k_b , the last one to be identified, it can again be (1) intersystem crossing k_6 , (2) photochemical reaction k_7 , or (3) thermally activated intersystem crossing k_{-4} . Evidence confirming that k_b is actually k_{-4} comes mainly from photochemical studies. In studies of the energy transfer between trans- $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ and $[\text{Cr}(\text{CN})_6]^{-3}$, it was well demonstrated (see Chapter III) that the phosphorescence state of the former was quenched by the latter. Further photochemical studies of the same system at -65°C indicated (see Chapter IV) that photoaquation of trans- $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ was quenched too, but to a less extent than phosphorescence. This requires that k_b is a process leading to photochemical reaction and rules out the first possible case, i.e., $k_b = k_6$. Wegner and Adamson²⁸ studied the photoaquation yields of trans- $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ and $[\text{Cr}(\text{NH}_3)_6]^{+3}$ at room temperature by direct excitation into the lowest doublet excited state and found within experimental error that the photoaquation quantum yield was essentially the same--about 0.3 for both complexes--whether the excitation was into the excited quartet or doublet states. Since the depletion process of the 2E_g state at room temperature is practically entirely caused by process k_b , if $k_b = k_6$ or $k_b = k_7$, the photoaquation quantum yield should be 0 or 1, respectively, upon

direct excitation into the 2E_g state. Apparently, this was not the observation. Therefore, both the first and second possible cases, i.e., $k_b = k_6$ and $k_b = k_7$ have to be ruled out. If the possible cases listed are exhaustive, then k_b must be identified with k_{-4} --the last possible case. In fact, by assuming $k_b = k_{-4}$, it becomes possible to explain consistently all the experimental results. It is certainly true that the thermally activated intersystem crossing k_{-4} is not a photoreactive process in itself, and to accept $k_b = k_{-4}$ implies that the 2E_g state is substantially inert. However, process k_{-4} activates complex ions in the 2E_g state up to the $^4T_{2g}$ state and from this state photosubstitution as well as the other primary processes (with possible recyclings of $^4T_{2g} \rightarrow ^2E_g \rightarrow ^4T_{2g}$) occurs. Therefore, it is clear that k_{-4} is a process leading to photoaquation. And the decrease in photoaquation quantum yield caused by quenching the 2E_g state actually results from a quenching of the thermally activated intersystem crossing k_{-4} . From the same mechanism, it follows that the complex ions formed in the 2E_g state via direct excitation at room temperature will entirely be activated to the $^4T_{2g}$ state from where further relaxations proceed--a situation, as far as photoaquation is concerned, not different from direct excitation into the quartet bands. Therefore, the fact that the photoaquation quantum yield was the same whether excitation was into the 2E_g state or the excited quartet states is self-evident.

The above arguments and interpretations may be criticized on the grounds that due attention has not been paid to the possible alternative mechanisms other than $k_b = k_{-4}$. Phenomenologically, k_b may consist of two routes: one leads to the photochemical reaction and the other to a non-radiative transition. From the straightness of the Arrhenius plots of k_b 's, it requires that the two routes either undergo the same rate-determining step or have quite close activation energies. A non-radiative transition with such a large activation energy is hard to understand from theories. However, Hammond has illustrated in the case of the photoisomerization of olefinic compounds⁶⁴ that the photochemical process and the internal conversion are virtually the same. An equivalent case in the photosubstitution of Cr(III) complexes can be, as suggested in rigid media by Chatterjee and Forster,⁴¹ that k_b is a process involving bond breaking and immediate recombination can be operative because of a cage effect. Actually, Cr(III) photochemistry has been thought²⁷ to be essentially that of cage reactions.

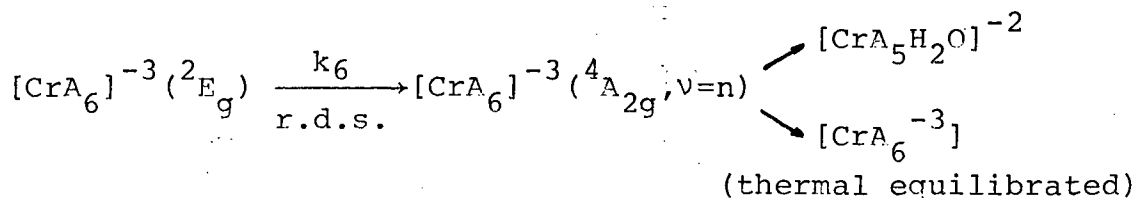
Taking $[\text{CrA}_6]^{-3}$ as an example,



In this interpretation, the bond breaking process--virtually k_7 --is the rate-determining step. If it is followed by

diffusion away of the leaving ligand, then a net chemical reaction occurs; if it is followed by recombination, then a net intersystem crossing to the ground state occurs. Apparently, a large activation energy for the non-radiative transition can thus be rationalized with this mechanism. But if it is true, then the photoaquation quantum yield should be strongly dependent on the cage structure. Langford has studied the solvolysis of $[\text{Cr}(\text{NCS})_6]^{-3}$ in acetonitrile-water mixtures and found²⁹ that, in contrast to the thermal aquation, the photoaquation quantum yield is independent of the solvent composition.⁺⁺ This indicates cage effect may not be important in the photoaquation of Cr(III) complexes and therefore makes this mechanism improbable.

The other interpretation is that k_b is essentially k_6 , but after isoenergetic intersystem crossing to the ground state, vibrational relaxation and aquation from the highly excited vibrational levels of the ${}^4A_{2g}$ state can be competitive. Taking $[\text{CrA}_6]^{-3}$ as an example,



⁺⁺It has to be noted that larger part of the photoaquation may come from the lowest excited quartet states and the results may largely reflect the properties of those states. However, if cage effect is not important for the lowest excited quartet states, there are no reasons why it should be important for the longer-lived lowest excited doublet states.

In this mechanism, the large activation energy for the non-radiative transition k_6 is hard to explain.⁺⁺ Moreover, for the photochemical route, the mechanism is essentially that of the thermal accelerated model which has long been thought to be improbable based on the short, lifetime of the non-equilibrated vibrational excited states and on the different reaction patterns and characteristics between thermal and photochemical reactions.^{27,29}

It is not impossible that k_b may consist of independent chemical process and intersystem crossing to the ground state. But the large activation energy for the non-radiative transition is again hard to rationalize.⁺⁺ Unfortunately, to rule out the interpretation with experimental evidence seems extremely difficult. However, the fact that the activation energies for those two independent processes are the same or nearly the same for all the Cr(III) complexes studied seems far too casual to be possible.

From the above evidence and arguments, it is clear that the identification of the strongly temperature-dependent term k_b with the thermally activated intersystem crossing k_{-4} from the 2E_g to $^4T_{2g}$ state is overwhelmingly favored.

Additional support comes from the locations of the zero-vibrational level of the $^4T_{2g}$ state, which can be

⁺⁺ Intersystem crossings through the intersection points of the potential energy surfaces (Teller crossing) may account for a large activation energy. However, to the author's knowledge, no precedent examples with such a large activation energy have been reported.

estimated by adding E_b 's to the known ${}^2E_g(v=0)$ states. For all the Cr(III) complexes studied, fluorescence has been detected near and only near the phosphorescence maxima. Therefore the fluorescence maximum should lie fairly closely to the phosphorescence maximum (see Chapter VI). It is found that the estimated ${}^4T_{2g}(v=0)$ levels all lie about in the central region between the absorption and fluorescence maxima. Secondly, studies of the intersystem crossing from the ${}^4T_{2g}$ state to the excited doublet states (see Chapter VII) revealed a thermally activated process assigned to ${}^4T_{2g} \rightarrow {}^2T_{2g}$. If the corresponding activation energies are added to the ${}^4T_{2g}(v=0)$ levels respectively, the energy levels so obtained for the ${}^2T_{2g}$ state agree very well with those predicted theoretically (see Chapter VIII). These all support indirectly the thermally activate back intersystem crossing from the 2E_g state to the ${}^4T_{2g}$ state.

A Further Comment

Since the phosphorescence decay rate constant k_D was determined by the conventional method which tacitly assumes no appreciable back intersystem crossing, a careful analysis to investigate the limitations of the data treatments and the validity of the arguments is indispensable when the back intersystem crossing is known to be greatly involved.

After an ideal instantaneous excitation, the phosphorescence intensity as a function of time can be expressed (see the Appendix) as

$$I_p = A (e^{-k_\alpha t} - e^{-k_\beta t}) \quad (5.7)$$

$$\text{where } k_\alpha = \frac{1}{2} (k_E + k_T) - \frac{1}{2} [(k_T - k_E)^2 + 4k_4k_{-4}]^{\frac{1}{2}}$$

$$k_\beta = \frac{1}{2} (k_E + k_T) + \frac{1}{2} [(k_T - k_E)^2 + 4k_4k_{-4}]^{\frac{1}{2}}$$

and

$$k_E = k_5 + k_6 + k_7 + k_{-4}$$

$$k_T = k_1 + k_2 + k_3 + k_4$$

In the Cr(III) complexes studied in this work, k_β generally greater than k_α , therefore the second term decreases much faster than the first term. Because the apparent decay rate constant k_p was determined from the decaying part of the curve well past the maximum, in practice

$$I_p = Ae^{-k_\alpha t} \quad (5.8)$$

Therefore $k_D = k_\alpha$, and this part of the decay curve should be exponential as observed.

Assuming k_T is sufficiently greater than k_E which is certainly the case over the studied temperature range, then k_α can be approximated as (see the Appendix)

$$k_D = k_\alpha = k_5 + k_6 + k_7 + (1 - \phi_{isc})k_{-4} \quad (5.9)$$

Since ϕ_{isc} can only be between 0 and 1, and it is not very temperature dependent over the studied temperature range (see Chapter VI), the factor $(1 - \phi_{isc})$ is essentially constant comparing to the greatly varying k_{-4} . Therefore the parameters s_a , s_b , E_a , and E_b estimated are justified except that s_b has to be corrected by a factor of $(1 - \phi_{isc})$.

CHAPTER VI

QUANTUM YIELD OF INTERSYSTEM CROSSING AS A FUNCTION OF TEMPERATURE

Except for a few Cr(III) complexes that fluoresce, the kinetic parameters of the ${}^4T_{2g}$ state are generally inaccessible. The only probe obtainable from 2E_g parameters that can be used to provide some information about the ${}^4T_{2g}$ state is the quantum yield of intersystem crossing or the quantum yield of doublet formation.

From the observations of phosphorescence emission in most Cr(III) complexes, it is evident that intersystem crossing from the ${}^4T_{2g}$ to 2E_g state certainly takes place to an appreciable extent. However, Forster et al. have demonstrated both theoretically and experimentally^{18,41,55} that its quantum yield is generally substantially less than unity and therefore concluded that internal conversion from the ${}^4T_{2g}$ to ${}^4A_{2g}$ state is important.

The quantum yield of intersystem crossing can be expressed as

$$\phi_{isc} = \frac{\phi_p}{k_5 \tau_p} \quad (6.1)$$

It is interesting to note that even when back intersystem crossing occurs, Equation 6.1 still holds. This can be verified through Equation 4.19 and the definition

$$\phi_{isc} = \frac{k_4}{k_1 + k_2 + k_3 + k_4} \quad (6.2)$$

The phosphorescence lifetimes of some Cr(III) complexes as functions of temperature have been discussed in Chapter V. Further, k_5 has been estimated theoretically for many Cr(III) complexes.^{18,41} If we assume that k_5 is temperature invariant, then measurements of phosphorescence quantum yields as functions of temperature will enable us, through Equation 6.1, to determine the temperature effect on the quantum yield of intersystem crossing.

Experimental and Results

Except the Cr(acac)₃ solution which was 0.01 M, all the complex solutions used were 0.05 M and absorbed the excitation light totally. The irradiation was at 546 nm for [Cr(NCS)₆]⁻³, [Cr(NH₃)₂(NCS)₄]⁻, [Cr(CN)₆]⁻³, and Cr(acac)₃; and at 436 nm for [Cr(en)₃]⁺³ and [Cr(CN)₆]⁻³. In order to minimize the photochemical reaction, irradiating time was kept as short as possible. Therefore, for each complex, only the intensity at the emission maximum was used as a measure of the relative phosphorescence quantum yield. However, the whole spectrum was scanned intermittently to ensure that the spectral distribution was reasonably constant over the temperature range.

No measurements of the absolute quantum yield were attempted in this work. According to Chatterjee and Forster⁴¹ the phosphorescence quantum yield reaches a limiting value at low temperature and the value remains the same in different

solvents. The absolute phosphorescence quantum yields used in this chapter were estimated by fixing the low-temperature limiting intensities at the values obtained by Chatterjee and Forster for the absolute phosphorescence quantum yields. The values for k_5 and limiting low-temperature ϕ_p are listed in Table III.

Table III

Intrinsic Phosphorescence Rate Constants and Low-Temperature
Limiting Phosphorescence Quantum Yields

Complex	k_5 ($\text{sec}^{-1} \times 10^3$)	ϕ_p^{lim}
$[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$	0.20	0.011
$[\text{Cr}(\text{NCS})_6]^{-3}$	0.23 ⁺⁺	0.23
$[\text{Cr}(\text{CN})_6]^{-3}$	0.016	0.0042
$[\text{Cr}(\text{en})_3]^{+3}$	0.15	0.0090
$[\text{Cr}(\text{acac})_3]$	0.13	0.021

⁺⁺ Value taken from phosphorescence decay constant at liquid nitrogen temperature.

The phosphorescence quantum yields were plotted as functions of temperature for these five Cr(III) complexes, as shown in Figures 22, 23, 24. The quantum yields of intersystem crossing were then evaluated via Equation 6.1 and are shown as functions of temperature in Figure 25, 26.

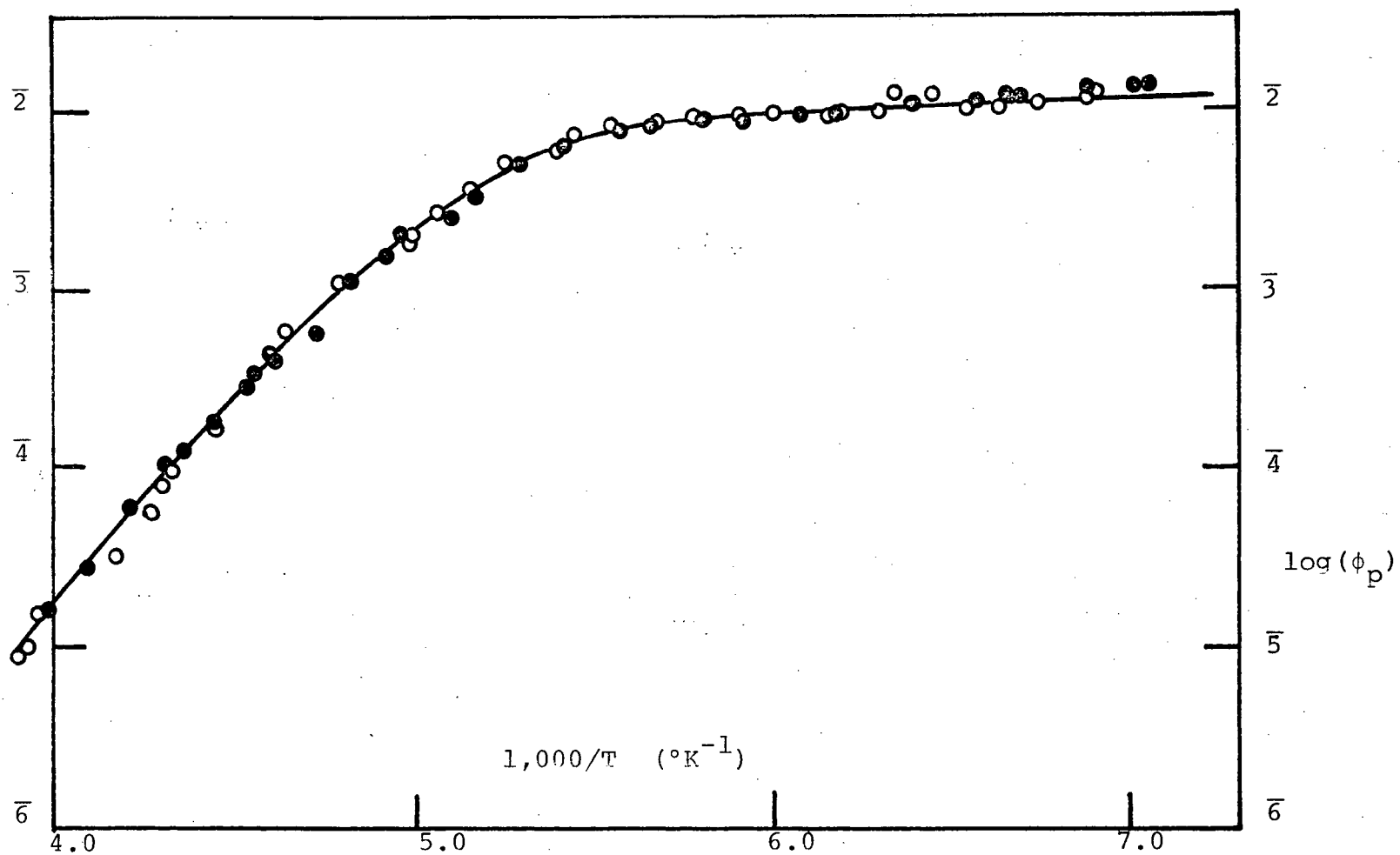


Figure 22. The phosphorescence quantum yield of Reineckate ion as a function of temperature.

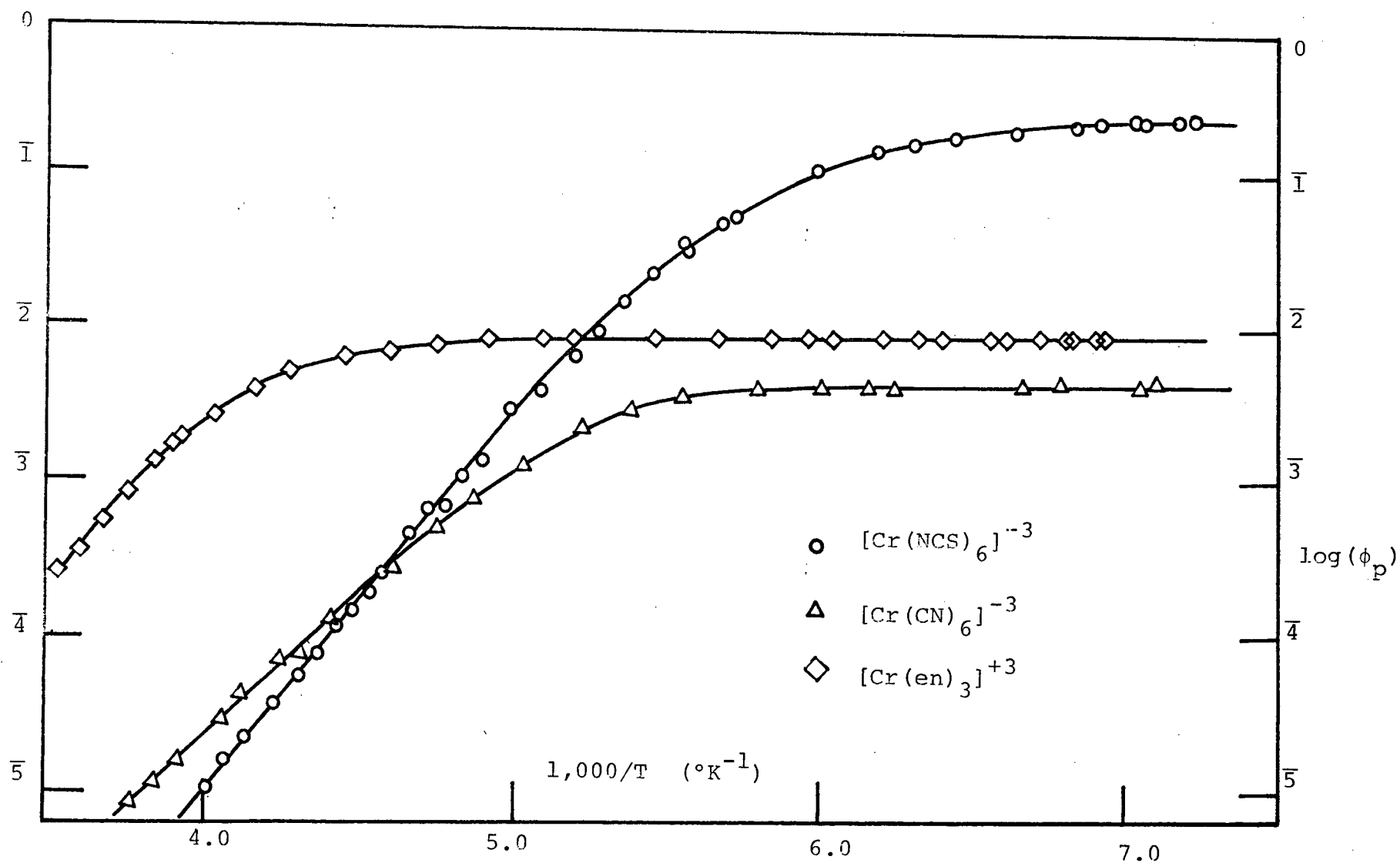


Figure 23. Phosphorescence quantum yields as functions of temperature.

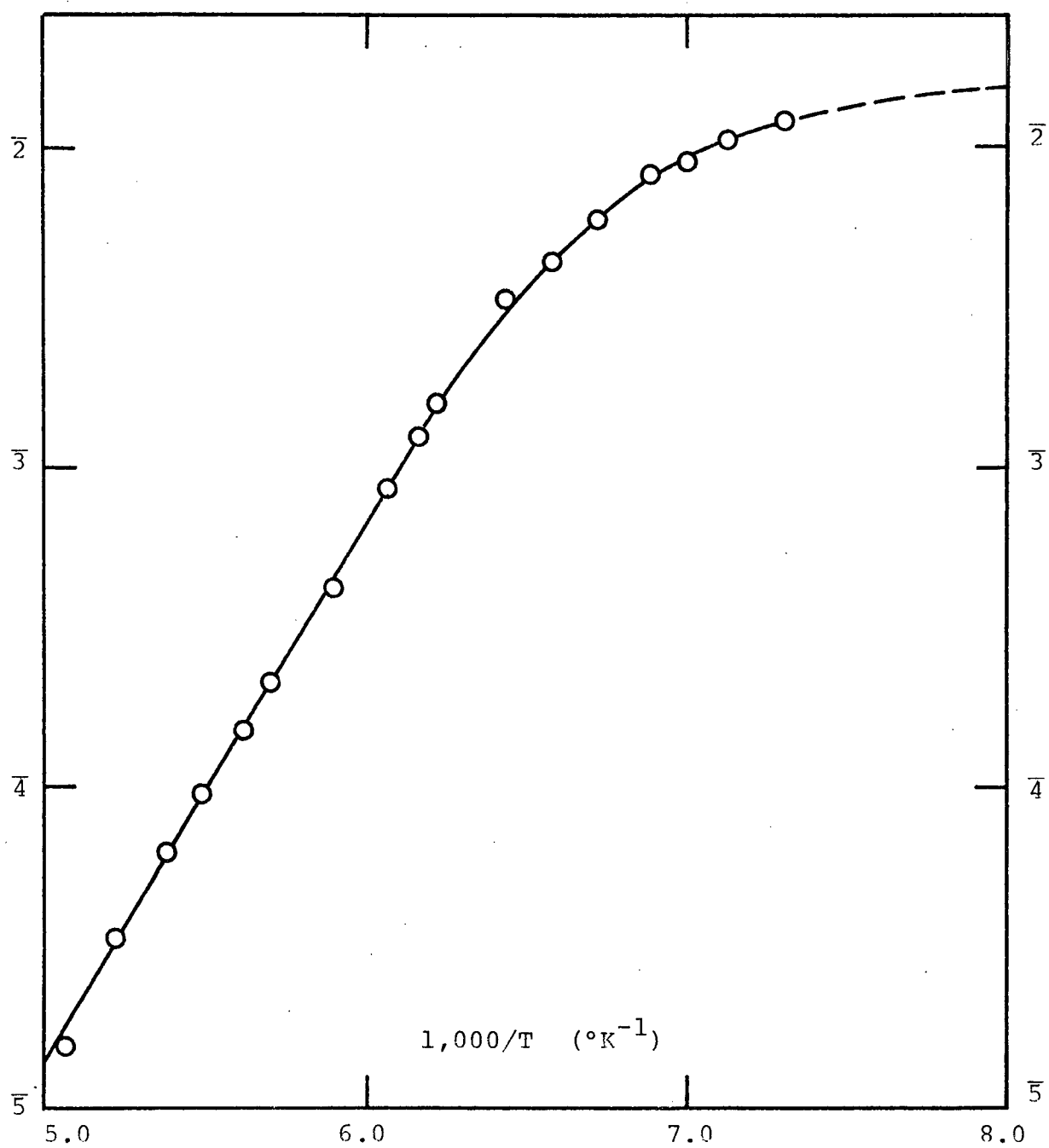


Figure 24. The phosphorescence quantum yield of $\text{Cr}(\text{acac})_3$ as a function of temperature.

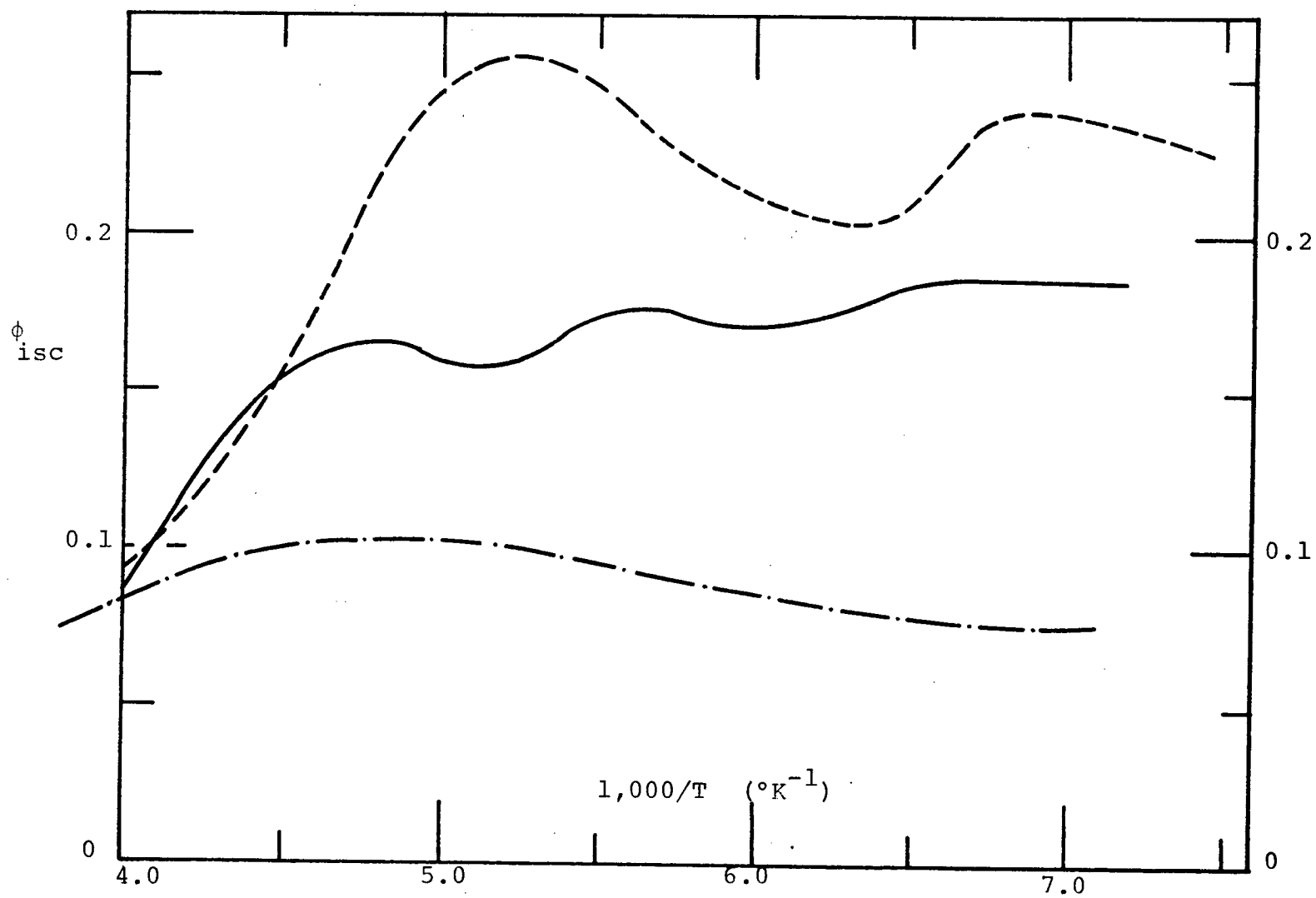


Figure 25. Quantum yields of intersystem crossing for $[\text{Cr}(\text{NCS})_6]^{-3}$ (-----), $\text{trans-}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$ (—), and $[\text{Cr}(\text{CN})_6]^{-3}$ (-.-.-).

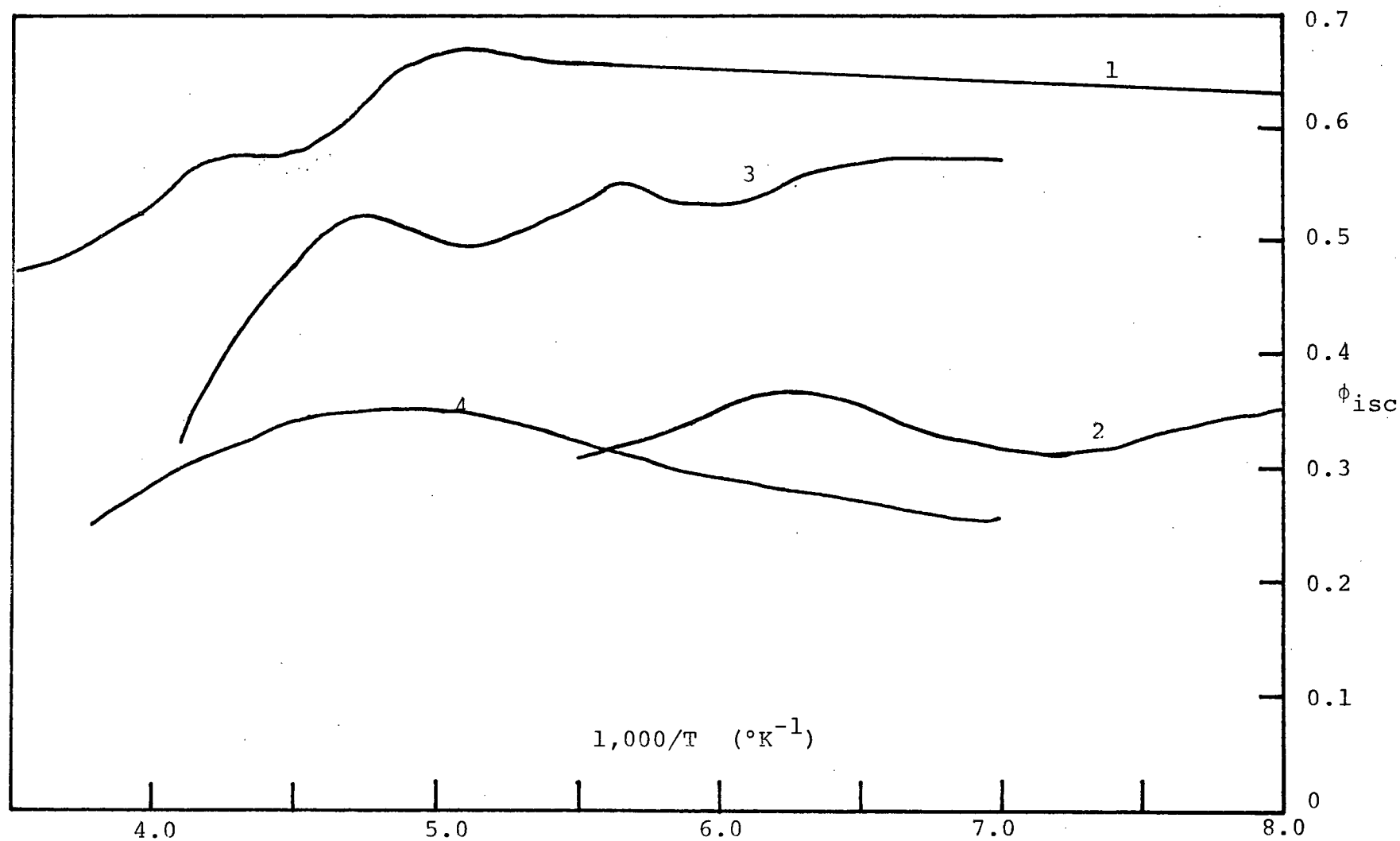


Figure 26. Quantum yields of intersystem crossing for (1) $[\text{Cr}(\text{en})_3]^{+3}$; (2) $\text{Cr}(\text{acac})_3$; (3) $\text{trans-}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$, set $\phi_{isc} = 0.52$ at 65°C ; (4) $[\text{Cr}(\text{CN})_6]^{-3}$, set $\phi_{isc} = 0.35$ at 65°C .

Discussion

On the whole, the quantum yield of intersystem crossing, ϕ_{isc} , does not change much with temperature for the Cr(III) complexes studied. The values calculated for ϕ_{isc} range from 0.1 for $[\text{Cr}(\text{CN})_6]^{-3}$ to 0.7 for $[\text{Cr}(\text{en})_3]^{+3}$. The small oscillations in the curves can probably be attributed to experimental errors, but, the steady decreasing of the curves at the high temperature ends must be considered to be real.

Since there are uncertainties in both the evaluations of k_5 and the determinations of ϕ_p , the absolute values estimated for ϕ_{isc} are not very reliable. However, ϕ_{isc} for $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ has been estimated from photochemical studies, and the same method can be extended to other Cr(III) complexes. Assuming $k_7 = 0$ and $[A]=0$, it can be shown through Equation 4.20 that

$$\frac{\phi_{chem}^{\infty}}{\phi_{chem}} = 1 - \phi_{isc}\phi_{isc}^r \quad (6.3)$$

$$\text{where } \phi_{isc}^r = \frac{k_{-4}}{k_{-4} + k_5 + k_6} \quad (6.4)$$

ϕ_{isc}^r is not readily available, but it can be estimated from studies of the temperature-dependence of phosphorescence lifetimes. From results in Chapter V,

$$\frac{(1 - \phi_{isc})k_{-4}}{(1 - \phi_{isc})k_{-4} + k_5 + k_6} = \frac{k_b}{k_D} \quad (6.5)$$

For $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ at -65°C , $\phi_{\text{chem}}^\infty/\phi_{\text{chem}} = 0.0052/0.0102 = 0.51$ from Chapter IV and $k_p/k_D = 0.89$ from Chapter V. Equations 6.3, 6.4, and 6.5 can be solved to give a value of 0.52 for the quantum yield of intersystem crossing in $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$, and 0.94 for ϕ_{isc}^r .

The quantum yield of intersystem crossing can also be estimated through the studies on the sensitized phosphorescence. In the energy transfer system of $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ and $[\text{Cr}(\text{CN})_6]^{-3}$, the energy transfer efficiency is unity and 2E_g is the accepting state (see Chapter II). The mechanism predicts:

$$\phi_{\text{sp}}^A = \phi_{\text{isc}}^D \left(\frac{k_{\text{QH}}[A]}{k_O^D + k_{\text{QH}}[A]} \right) \left(\frac{k_p^A}{k^A} \right) \quad (3.12)$$

$$\phi_p^A = \phi_{\text{isc}}^A \left(\frac{k_p^A}{k^A} \right) \quad (6.6)$$

From the above two equations

$$\phi_{\text{isc}}^A = \left(\frac{\phi_p^A}{\phi_{\text{sp}}^A} \right) \left(\frac{k_{\text{QH}}[A]}{k_O^D + k_{\text{QH}}[A]} \right) \phi_{\text{isc}}^D \quad (6.7)$$

At -65°C and $[A] = 0.07 \text{ M}$, $\phi_p^A = 6.3 \times 10^{-4}$ (Figure 23), $\phi_{\text{sp}}^A = 5.9 \times 10^{-4}$, $k_{\text{QH}}[A]/(k_O^D + k_{\text{QH}}[A]) = 0.63$ (Chapter III), and $\phi_{\text{isc}}^D = 0.52$. Substituting these values into Equation 6.7, one obtains $\phi_{\text{isc}}^A = 0.35$ for $[\text{Cr}(\text{CN})_6]^{-3}$.

The quantum yields of intersystem crossing for $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ and $[\text{Cr}(\text{CN})_6]^{-3}$ obtained in this way are three times greater than those estimated from Equation 6.1

(0.52 and 0.35 vs 0.17 and 0.11). Since lifetime measurements are comparatively certain, this constant factor could arise from a systematic error either in the evaluations of k_5 or in the absolute determinations of ϕ_p . However, applying this factor to $[\text{Cr(en)}_3]^{+3}$ would result in a quantum yield of intersystem crossing far greater than unity that, of course, is not acceptable. However, absolute emission quantum yields are notoriously difficult to measure and it is likely that these values may be in error.

All the quantum yields of intersystem crossing obtained become constant below -70°C . This indicates that internal conversion and intersystem crossing yields from the $^4\text{T}_{2g}$ state are temperature independent or only slightly temperature dependent in this temperature range. However, they do monotonically decrease at higher temperatures. For this, two other factors must first be considered: photochemical reaction and the variation of k_5 with temperature. Photochemistry, as established in the previous chapters, occurs from the $^4\text{T}_{2g}$ state, and its yield increases with temperature, but its quantum yield rarely exceeds 0.1 below -30°C . It therefore cannot cause the quantum yield of intersystem crossing to decrease appreciably. Change of k_5 with temperature has been noticed in ruby (213 and 244 sec^{-1} at 77° and 300°K).⁶⁵ Because the transition $^2\text{E}_g \leftarrow ^4\text{T}_{2g}$ is vibronically induced, it is possible that k_5 does have a temperature dependence. In fact, the

spectral distribution of $[\text{Cr}(\text{CN})_6]^{-3}$ emission changes below -130°C . However, the spectra of the emissions studied do not change appreciably from -120° to -30°C . It is believed that the decrease of ϕ_{isc} is still too large to be accounted for by any variation of k_5 .

From Equation 6.2, by neglecting fluorescence process, k_1 , and photochemical reaction, k_3 , the following expression can be obtained.

$$\frac{1}{\phi_{\text{isc}}} = 1 + \frac{k_2}{k_4} \quad (6.8)$$

Both internal conversion, k_2 , and intersystem crossing, k_4 , may consist of a temperature-independent (or only slightly dependent) component and a temperature-dependent component. Below -70°C , the temperature-independent component parts of each are dominant, therefore ϕ_{isc} does not change much with temperature. Above -70°C , the temperature-dependent parts become important and ϕ_{isc} starts to decrease. Since k_4 is unlikely to decrease with temperature, the fact that ϕ_{isc} decreases with rising temperature implies that at least internal conversion is temperature-dependent. If the above interpretation is right, then an Arrhenius plot of $\log(1/\phi_{\text{isc}} - 1)$ against $1/T$ will yield the difference in the activation energies of k_2 and k_4 , provide the temperature range is sufficiently high.

The Arrhenius plot has been done for $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ and $[\text{Cr}(\text{CN})_6]^{-3}$ with the corrected ϕ_{isc} from Figure 25. The resulting lines are slightly curved as shown in Figure 27. The activation energy differences estimated from the high-temperature end are about 5 Kcal/mol for $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ and 2 Kcal/mol for $[\text{Cr}(\text{CN})_6]^{-3}$. Therefore, the activation energies for their internal conversions must be greater than 5 and 2 Kcal/mol respectively. They are surprisingly large values for internal conversions, since the present theories all predict^{60,61,62} that the temperature dependence of non-radiative transitions should be small or none at all. However, internal conversion has not really been measured in detail for any molecule. Confirmation at this point will require direct study of the $^4\text{T}_{2g}$ state.

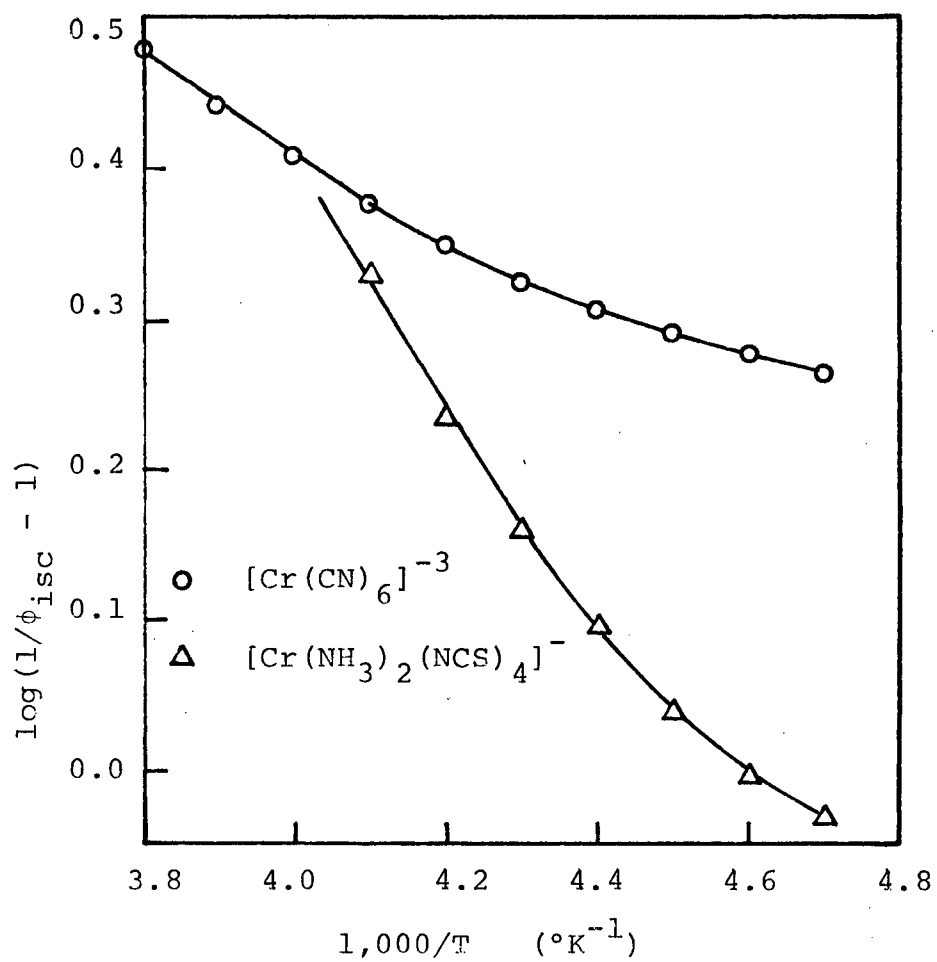


Figure 27. Plots of $\log(1/\phi_{isc} - 1)$ vs $1/T$.

CHAPTER VII

THE LIFETIME OF THE $^4T_{2g}$ OR $^2T_{1g}$ STATE

In the lifetime measurements of energy transfer between Reineckate and hexacyanochromate(III) ions, an initial rise preceding a longer decay of the phosphorescence of the acceptor was noticed. It was immediately recognized to be the population process of the phosphorescent state of the acceptor (see Chapter III). Out of curiosity, the initial part of the decay curve of the donor, Reineckate ion, was reinvestigated. It was a sort of serendipity to find that there was an initial rise in the donor phosphorescence too, although in a shorter period.

It has been established from subsequent studies that an initial rise of phosphorescence after a pulse excitation is a general phenomenon among the individual Cr(III) complexes. Figure 28A shows, as a typical example, the population and decay curve of $\text{Cr}(\text{acac})_3$ phosphorescence. The only exception observed is $[\text{Cr}(\text{CN})_6]^{-3}$ whose decay curve consists of a faster and a much slower component as shown in Figure 28B.

Similar to the case of energy transfer, the initial rise of phosphorescence relates to the population process of the 2E_g state. The importance of being able to observe the population process is apparent. However, first of all,

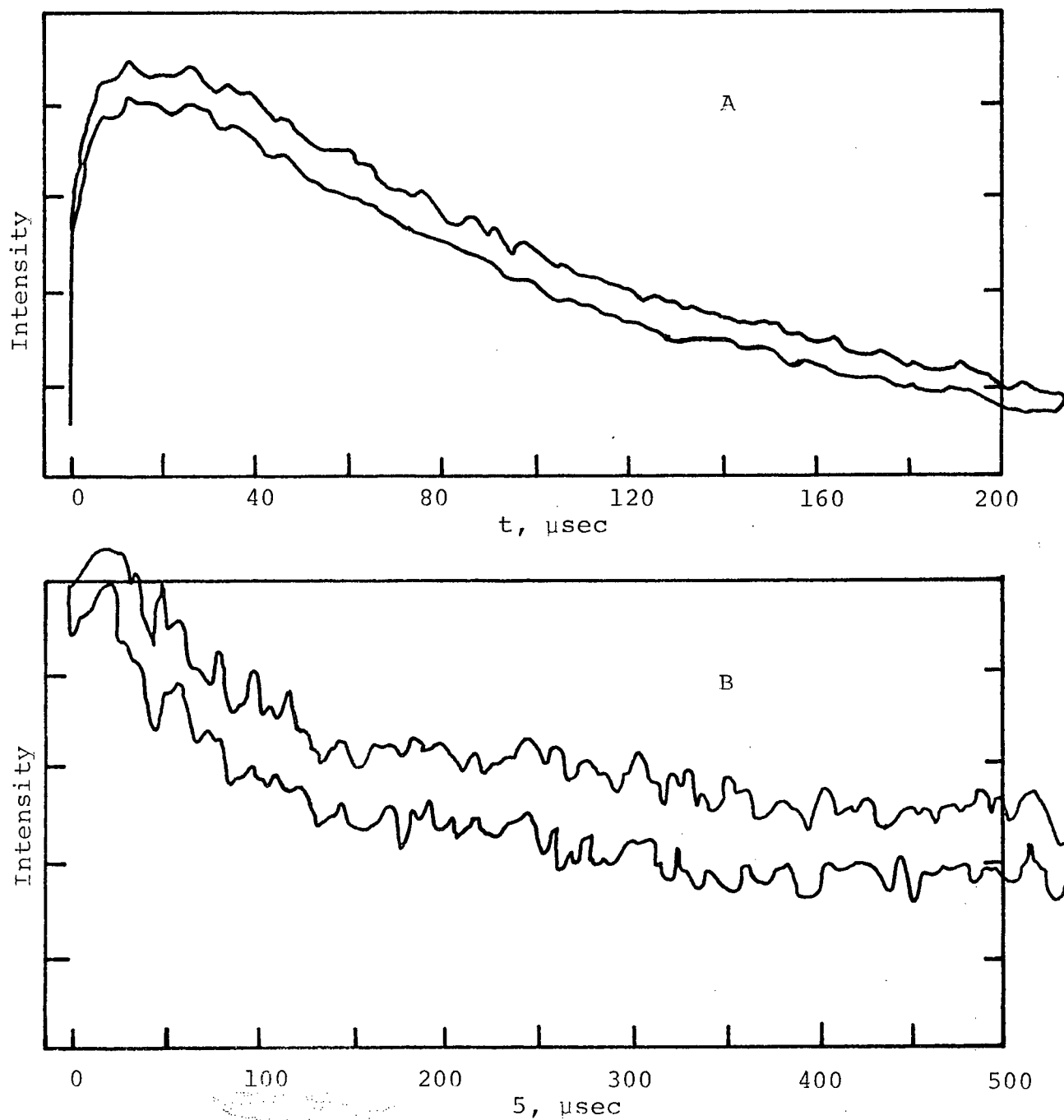


Figure 28. Oscilloscope traces of luminescence decay:

(A) $\text{Cr}(\text{acac})_3$, (B) $[\text{Cr}(\text{CN})_6]^{-3}$.

we have to prove that the phenomenon is not due to instrumental factors or from impurities.

The half-height width of the flash lamp was less than 200 nsec and its scattered light from the blank solution was not detectable at the sensitivity used. From these facts one could conclude that the lamp did not interfere with the emission. In the case of $[\text{Cr}(\text{CN})_6]^{-3}$ this implied that the initial faster decay could not be caused by the tail of the lamp output. A more probable source of distortion, if any, might come from the detecting and recording systems. However, the photomultiplier was wired specially for fast response applications. In fact, the bleeder resistors have been changed to achieve a higher bleeder current, but still no appreciable change has thus been caused in the population and decay curve. The oscilloscope has a rise time of 15 nsec at the sensitivity used and is therefore sufficiently fast. Different capacitors were used individually across the load resistor to alleviate the noise, but the RC time constant was kept to be less than that of the rise time studied by a factor of about 100. And the curves remained the same average figure upon decreasing the RC time constant or eliminating the external capacitor after all. In fact the detecting system can easily follow the 50 nsec rise and 150 nsec decay of the flash lamp. Moreover, the rise times of the phosphorescence does vary with temperature. All these rule out the possibility of having instrumental distortions.

For impurity to cause a rise in the decay curve, the only way can be thought about is that the impurities absorb large part of the excitation radiation and transfer it slowly to the Cr(III) complex under study. Judging from the absorbances, it is highly improbable to have so much of impurities in the sample. Of course, impurities with fast decay and high emission quantum yield can cause a faster decay component before the slower phosphorescence decay of hexacyanochromate(III) ion. However, calculations based on some reasonable assumptions show that the amount of impurity needed is still too high to be probable in the compound used.

It is therefore believed that the initial rise and the initial fast component are intrinsic phenomena of the Cr(III) complexes.

Results

It was found that all the phosphorescence intensity-time curves could be fitted satisfactorily to the following equation

$$I = A[\exp(-t/\tau_p) + \alpha \exp(-t/\tau_x)] \quad (7.1)$$

where τ_p is the lifetime of the 2E_g state, τ_x is the lifetime of a state preceding the 2E_g state as will be shown in the next section. Both A and α are proportionality constants. A is arbitrary. The values of α depend on the wavelength monitored. The data from liquid nitrogen temperature measurements are collected in Table IV. Temperature dependence of

τ_x has also been studied for $[\text{Cr}(\text{NCS})_6]^{-3}$, $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$, $[\text{Cr}(\text{en})_3]^{+3}$, and $\text{Cr}(\text{acac})_3$; and the results are presented in Figures 29, 30, and 31.

Table IV
Rate Constants (sec^{-1}) in Luminescence Decay
of Cr(III) Complexes

Complex	$(1/\tau_p)$ $\times 10^{-3}$	$(1/\tau_f)$ $\times 10^{-4}$	k_1 (calcd) $\times 10^{-4}$	α^{++}	$\phi_f \times 10^4$
$[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{-}$	3.0	13	30	-0.38	6
$[\text{Cr}(\text{NCS})_6]^{-3}$	0.23	12	20	-0.47	2
$[\text{Cr}(\text{CN})_6]^{-3}$	0.29	2.0	10	+1.6	3
$\text{Cr}(\text{acac})_3$	2.8	12	10	-0.40	2
$[\text{Cr}(\text{tn})_3]^{+3}$	9.3	13	--	-0.47	-
$[\text{Cr}(\text{en})_3]^{+3}$	10.0	8.9	23	-0.38	3

⁺⁺The values of α depend on the wavelength monitored. The values reported are at their phosphorescence maxima.

The accuracy in evaluating τ_x depends very much on the noise level of the curve. At liquid nitrogen temperature, the values calculated fluctuate within 40%, while at higher temperatures, they can fluctuate as much as 100%. Usually the average value of τ_x at each temperature was determined from three oscillograms.

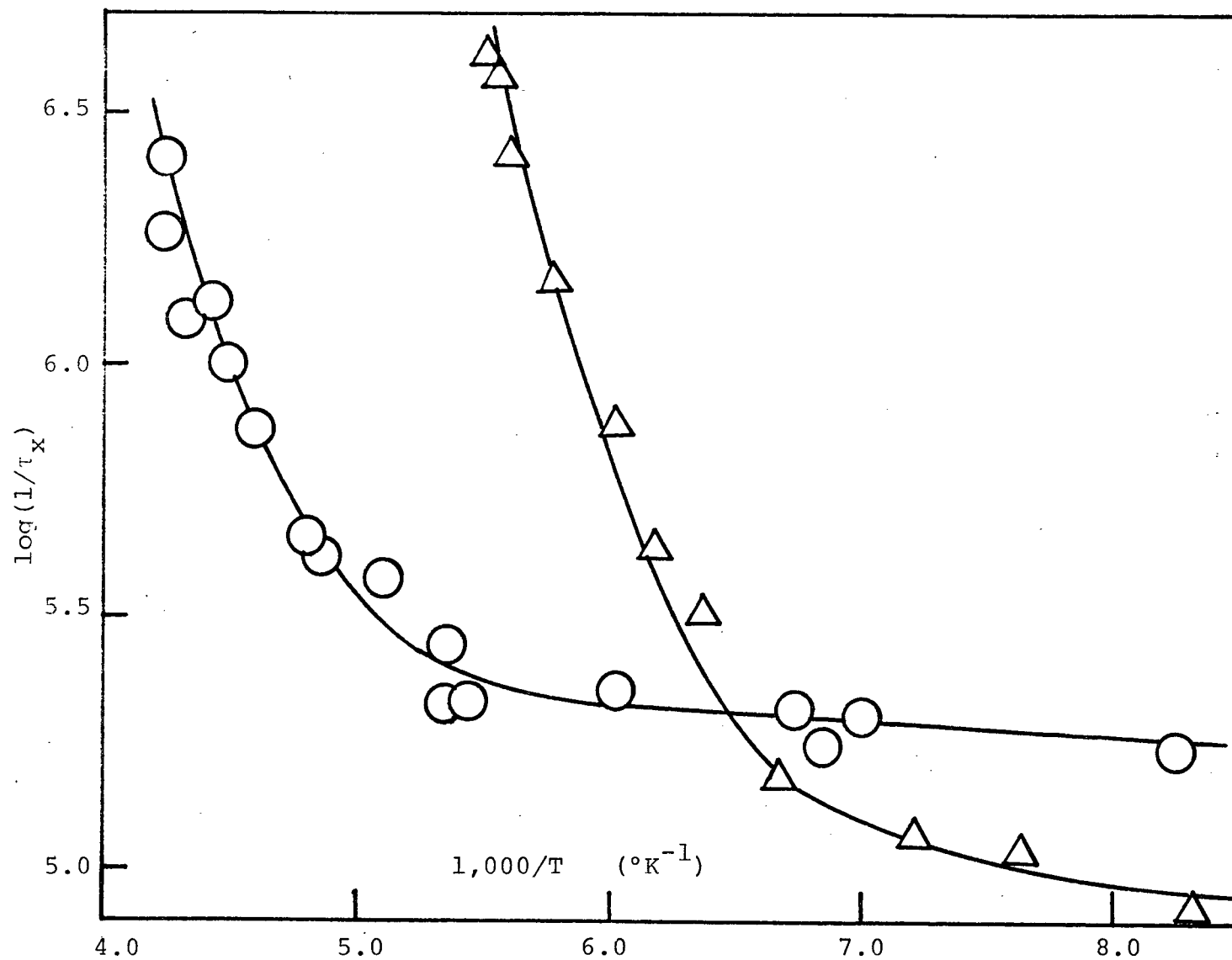


Figure 29. τ_x as functions of temperature for $\text{trans-}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ (O), and $\text{Cr}(\text{acac})_3$ (Δ).

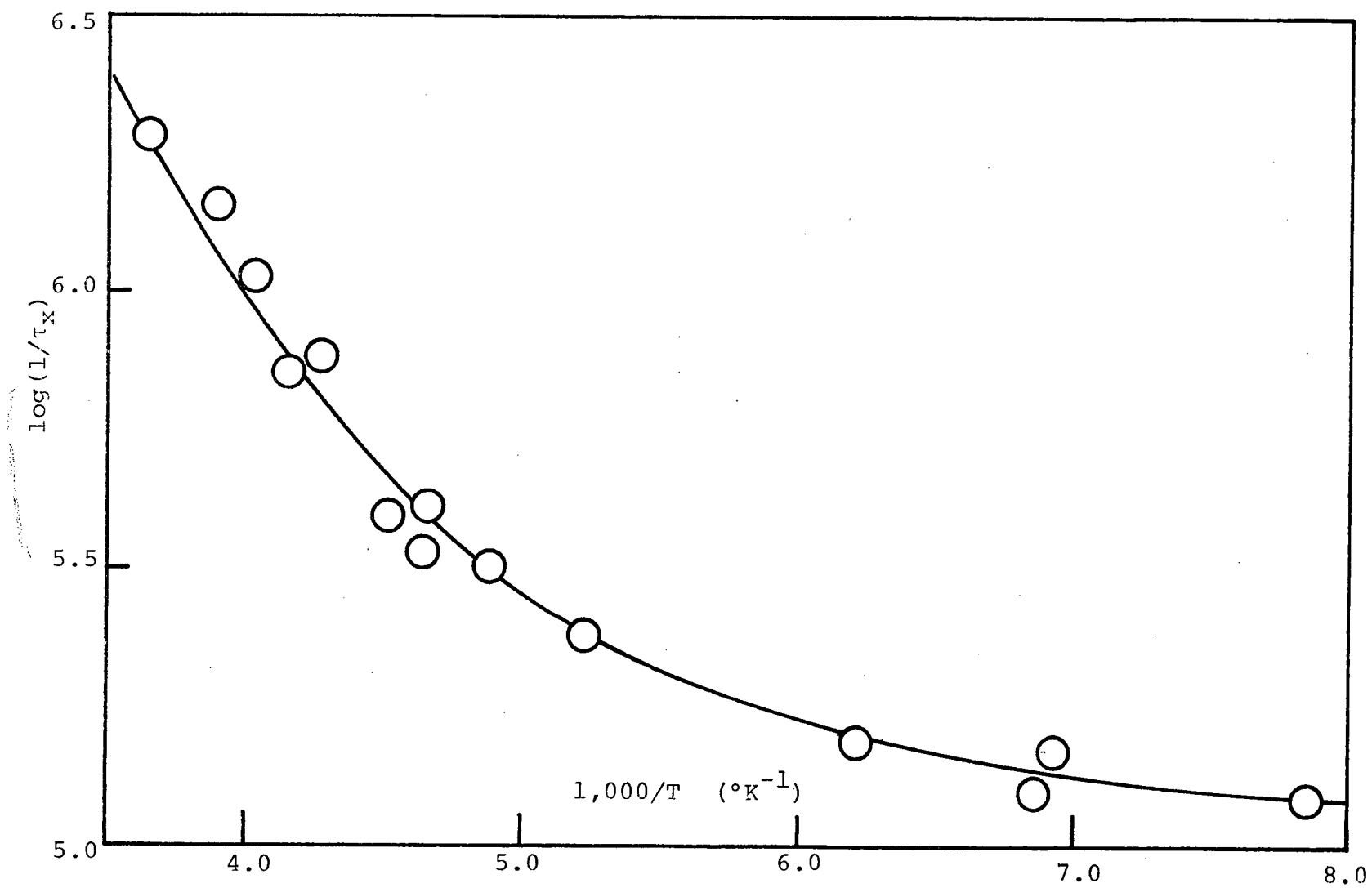


Figure 30. τ_x as a function of temperature for $[\text{Cr}(\text{en})_3]^{+3}$.

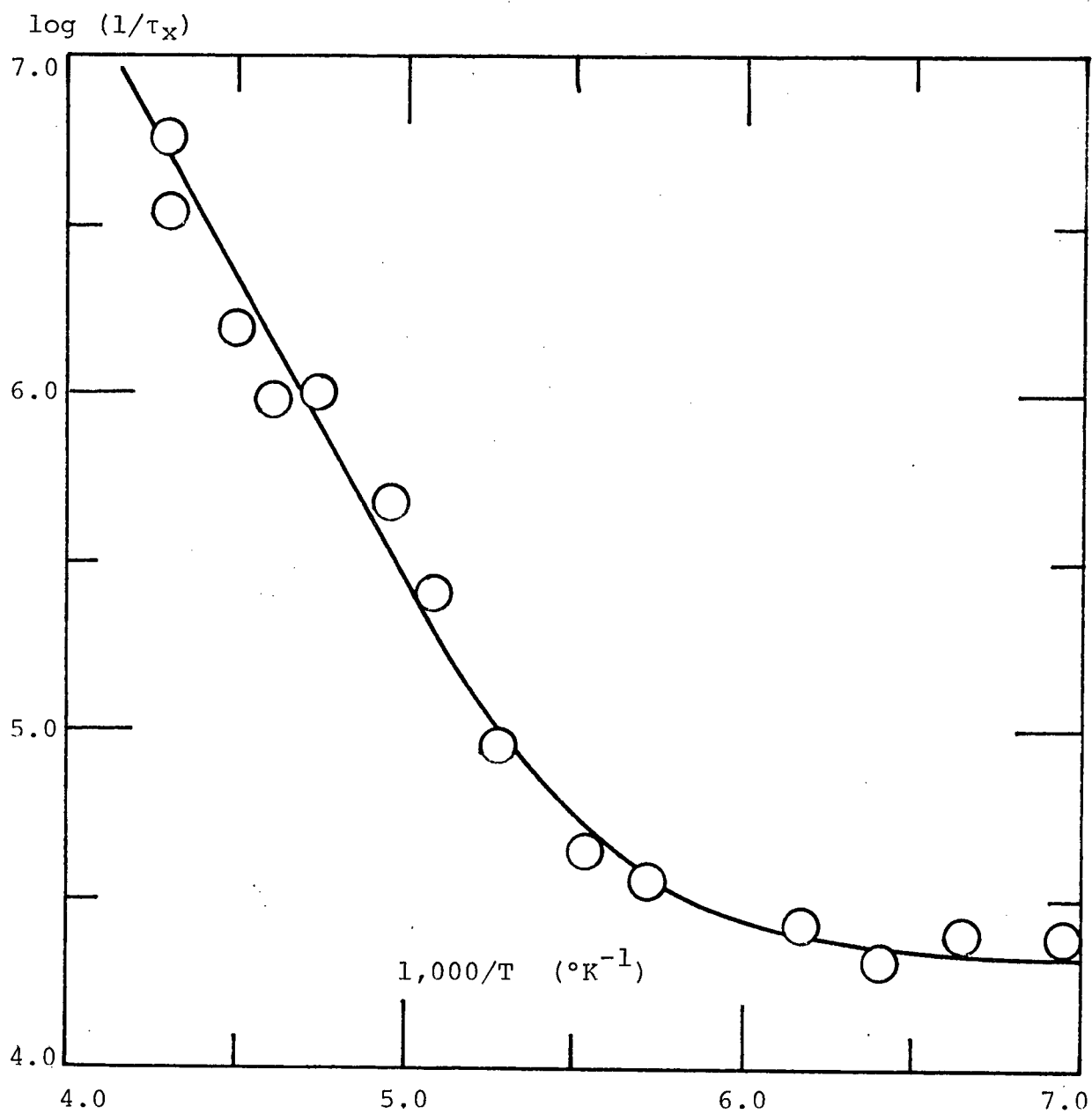


Figure 31. τ_X of $[\text{Cr}(\text{NCS})_6]^{-3}$ as a function of temperature.

Discussion

Since the complex is mainly pumped into the $^4T_{2g}$ and $^4T_{1g}$ states in the pulse excitation, the possible known electronic states preceding the 2E_g state are $^4T_{1g}$, $^4T_{2g}$, $^2T_{2g}$, and $^2T_{1g}$ states. The $^4T_{1g}$ and $^2T_{2g}$ states can be confidently ruled out as the comparatively long-lived state (ca. 10 μ sec). If they were, then emissions would have occurred at wavelengths much shorter than the phosphorescence. The transition between $^2T_{1g}$ and 2E_g states has been assumed to be very fast. Therefore the following discussion will be based on the assumption that the $^4T_{2g}$ state is the long-lived precursor from which the excitation energy is transfer to the 2E_g state. However, a mechanism containing $^2T_{1g}$ instead of $^4T_{2g}$ as the long-lived precursor will be discussed in Chapter VIII.

If $^4T_{2g}$ is the long-lived precursor to the 2E_g state, then according to the derivations in the Appendix, the intensity of fluorescence and of phosphorescence at any one wavelength as a function of time after a pulse excitation can be expressed as

$$I_f = A_f \exp(-t/\tau_f) \quad (7.2)$$

$$I_p = A_p [\exp(-t/\tau_p) - \exp(-t/\tau_f)] \quad (7.3)$$

Equation 7.3 does not agree with the empirical Equation 7.1, because the value of α is not generally -1. There are two possible explanations: (1) both fluorescence and phosphorescence are in fact detected at the wavelength monitored,

therefore the total intensity is actually

$$I = A_p \{ \exp(-t/\tau_p) + [(A_f/A_p) - 1] \exp(-t/\tau_f) \} \quad (7.4)$$

$$\text{thus } \alpha = (A_f/A_p) - 1 \quad (7.5)$$

Since A_f and A_p are positive proportionality constants, α must be equal to or greater than -1, as observed. (2) The 2E_g state is populated in part through some very fast transitions and in part through the slower direct $^4T_{2g} \rightarrow ^2E_g$ transition. Therefore, the instantaneous intensity can be expressed as

$$I_p = A'_p [\exp(-t/\tau_p) - \exp(-t/\tau_f)] + A''_p \exp(-t/\tau_p) \quad (7.6)$$

$$= (A'_p + A''_p) [\exp(-t/\tau_p) - \frac{A'_p}{(A'_p + A''_p)} \exp(-t/\tau_f)] \quad (7.7)$$

$$\text{therefore } \alpha = -A'_p / (A'_p + A''_p) \quad (7.8)$$

Since both A'_p and A''_p are positive constants, α can only be between 0 and -1. Unfortunately, this explanation is inadequate for $[\text{Cr}(\text{CN})_6]^{-3}$ which has a positive α . A slight modified scheme of this explanation will be discussed again in Chapter IX.

If fluorescence and phosphorescence are both detected at the same wavelength, by making use of Equations 7.2 and 7.3, the steady-state emission intensities can be related as

$$\left(\frac{I_f}{I_p}\right)_\lambda^{ss} = \frac{\int_0^\infty I_f(t) dt}{\int_0^\infty I_p(t) dt} = \frac{\tau_f A_f}{\tau_p A_p - \tau_f A_f} \quad (7.9)$$

$$= (\tau_f A_f)/(\tau_p A_p) \quad (\because \tau_p \gg \tau_f) \quad (7.10)$$

Since τ_p , τ_f , and (A_f/A_p) can be obtained through Equations 7.1 and 7.5, the ratio of the steady-state intensity of fluorescence to that of phosphorescence can be estimated from Equation 7.10. As all the emission spectra of Cr(III) complexes are readily available, the fluorescence spectra can be roughly constructed. Figure 32 shows the fluorescence spectrum of $[\text{Cr}(\text{CN})_6]^{-3}$ by this technique.

If Equation 7.10 is further integrated with respect to the wavelength, λ , then

$$\frac{\phi_f}{\phi_p} = \frac{\tau_f}{\tau_p} \int \frac{A_f}{A_p} d\lambda \quad (7.11)$$

Phosphorescence quantum yields of Cr(III) complexes have been given by Forster,¹⁸ therefore by making use of Equation 7.11, the fluorescence quantum yield can be very roughly estimated. The calculated values are listed in Table IV. They represent minimum values because the fluorescence spectra may be broader.

For all the complexes studied, the fluorescence maximum occurs near the phosphorescence maximum; and therefore far away from the absorption maximum. $[\text{Cr}(\text{CN})_6]^{-3}$ represents the extreme case to have the separation between the absorption and fluorescence maximum well over $14,000 \text{ cm}^{-1}$. The extraordinary Stokes' shift implies that the equilibrium nuclear

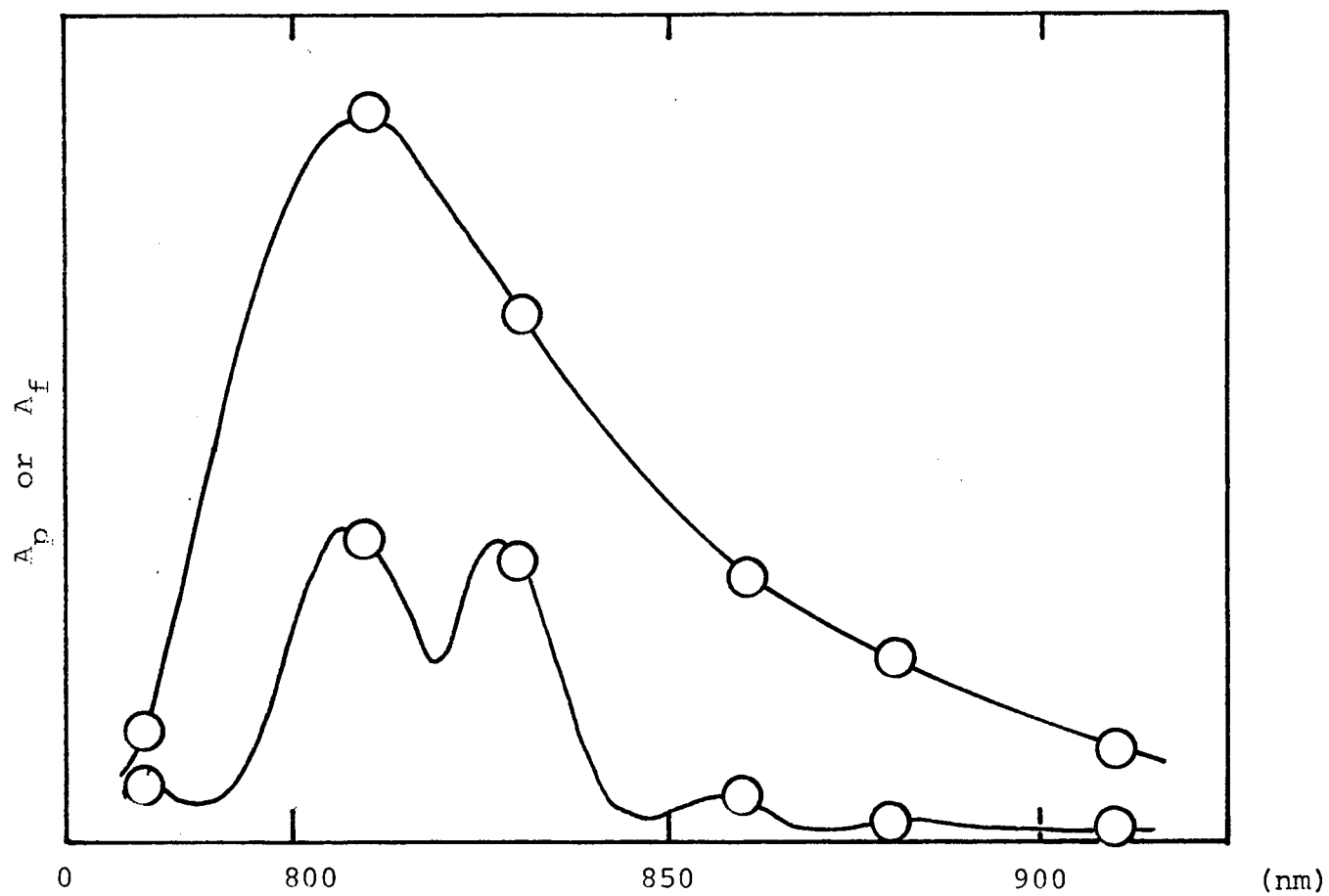


Figure 32. Luminescence spectra obtained from decay curves for $[\text{Cr}(\text{CN})_6]^{-3}$ in rigid glass solution at 77°K. The upper curve is fluorescence; the lower is phosphorescence with details of the spectrum sketch in from steady-state measurements.

configuration of the ${}^4T_{2g}$ state is indeed very different from that of the ground state. This is also supported by the evidence from the studies of the thermally activated back intersystem crossing, which indicates that the zero-vibrational levels are very far below the absorption maxima of the ${}^4T_{2g}$ state (see Chapters V and VIII).

Because the fluorescence was not detected in steady-state measurements for these complexes, it has been widely held that the lifetime of the ${}^4T_{2g}$ state should be shorter than 10^{-8} sec. From data given by Forster,¹⁸ the intrinsic fluorescence rate constant, k_1 , can be calculated using the oscillator strengths, f , for the transition ${}^4T_{2g} \rightarrow {}^4T_{2g}$ according to

$$k_1 = n^2 f \bar{\nu}^2 / 1.5 \quad (7.12)$$

assuming $\bar{\nu}$ to be at the same wavelength as the phosphorescence maximum and $n=1$. The calculated values of k_1 are included in Table IV. In every case k_1 is larger than the observed $1/\tau_f$, where it should in fact be smaller, since

$$k_1 = \phi_f / \tau_f \quad (7.13)$$

The values for the observed k_1 (according to Equation 7.13) are also included in Table IV. In general, the observed k_1 is about four orders of magnitude smaller than the calculated one (according to Equation 7.12). The large discrepancy no doubt reflects the errors inherent in the application of Equation 7.12. Adamson²² has described in detail the argu-

ments for the disparity based on the expected difference in equilibrium nuclear configurations of the ${}^4T_{2g}$ and ${}^4A_{2g}$ states. Strictly speaking, Equation 7.12 is applicable only to atomic systems, whose transitions are sharp. Although a modified equation of Strickler and Berg has been proposed for broad molecular bands when the transition is strongly allowed,⁶⁶ there are still no equations derived for the fluorescence which is symmetry-forbidden and has a large Stokes' shift. Birks and Dyson⁶⁷ have shown in the diphenylpolyene series that $k_1(\text{obs.})/k_1(\text{cal.})$ progressively decreases as the Stokes' shift becomes larger and larger, that is, the lowest excited state becomes distorted more and more from the ground state. The extraordinarily small value for $k_1(\text{obs.})/k_1(\text{cal.})$ in these Cr(III) complexes seems consistent with the large Stokes' shift.

The Cr(III) complexes with relatively small $10Dq$ value have been known to fluoresce.²⁰ The fluorescence lifetimes of them have recently been measured conventionally by Zander,⁵⁷ the results at liquid nitrogen temperature are reproduced in Table V.

The fluorescence quantum yields for these complexes have not been reported, but if we assume them to be about 0.01, then $k_1(\text{obs.})/k_1(\text{cal.})$ still will be one or two orders of magnitude less than unity, although not so much less as in the group of Cr(III) complexes described in this work. It is known that the Stokes' shift increases as $10Dq$ increases,

Table V

Fluorescence Lifetimes at liquid Nitrogen
Temperature

Complex	$\tau_f \times 10^6 \text{ sec}$
$[\text{Cr}(\text{atp})_6](\text{ClO}_3)_3$	20
$[\text{Cr}(\text{atp})_6](\text{ClO}_4)_3$	6.5
$[\text{Cr}(\text{atp})_6] \text{I}_3$	6.0
$[\text{Cr}(\text{urea})_6](\text{ClO}_4)_3$	0.36
CrCl_3	4.8
$[\text{CrF}_6](\text{NH}_4)_3$	1.4

therefore, it is expected that the value of $k_1(\text{obs.})/k_1(\text{cal.})$ for the complexes with smaller $10Dq$ value should be greater than that for the one with larger $10Dq$ value. This certainly is the observation.

Although we cannot be certain that the new lifetime, τ_x , is really the lifetime of the ${}^4T_{2g}$ state, the observations from the studies of $[\text{Cr}(\text{urea})_6]^{+3}$ at very low temperatures (below 25°K) by Dingle⁵² do give some support. The emission from the $14,222 \text{ cm}^{-1}$ region (${}^4T_{2g}$?) has a fast decay component (prompt fluorescence ?) of $\tau \sim 50 \text{ } \mu\text{sec}$ and a slow component (delay fluorescence ?) of $\tau \sim 300\text{-}400 \text{ } \mu\text{sec}$, while emission

from $14,196\text{ cm}^{-1}$ region (2E_g) does not reach a maximum until 50 - 70 μsec after the pulse. Although no detailed quantitative analysis was given, the build-up process of the 2E_g state seems to correspond very well with the prompt decay of the $^4T_{2g}$ state.

Although the detailed mechanism still remains unknown, the $^4T_{2g}$ state has been shown to be chemically reactive (see Chapter IV). From this the lifetime of $^4T_{2g}$ state would be expected to be longer than 10^{-7} sec^{-1} .

The internal conversion rate constant, k_2 , has been shown, without using any of the quartet state parameters, to be strongly dependent on temperature at the higher temperature range. Therefore the lifetime of the $^4T_{2g}$ state in this region too should be strongly dependent on temperature. The results obtained in this chapter support this conclusion.

CHAPTER VIII

THE PRIMARY PHOTOPROCESSES

The intersystem crossing rate constant, k_4 , can be evaluated according to the following equation:

$$k_4 = \phi_{isc}/\tau_f \quad (8.1)$$

If we assume that the newly observed lifetime, τ_x , is the fluorescence lifetime, τ_f , then with the results for ϕ_{isc} and τ_f reported in Chapters VI and VII respectively, k_4 as a function of temperature can be obtained. The results are shown in Figures 33, 34, 35, and 36. It has to be noted that the absolute value, due to the uncertainties in ϕ_{isc} and τ_f , can only be accurate, at best, to within 100% for $[\text{Cr}(\text{en})_3]^{+3}$ and $\text{Cr}(\text{acac})_3$ and within 50% for $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ and $[\text{Cr}(\text{CN})_6]^{-3}$. The curves so obtained for k_{isc} , i.e., k_4 as a function of temperature are found to have the following form:

$$k_4 = k_c + k_d \quad (8.2)$$

$$= s_c \exp(-E_c/RT) + s_d \exp(-E_d/RT) \quad (8.3)$$

The best values of the parameters for the four complexes are collected in Table VI, where the Arrhenius parameters for k_D are also included for convenience.

The temperature dependence of intersystem crossing in some aromatic compounds, e.g., anthracene, naphthalene, pyrene,

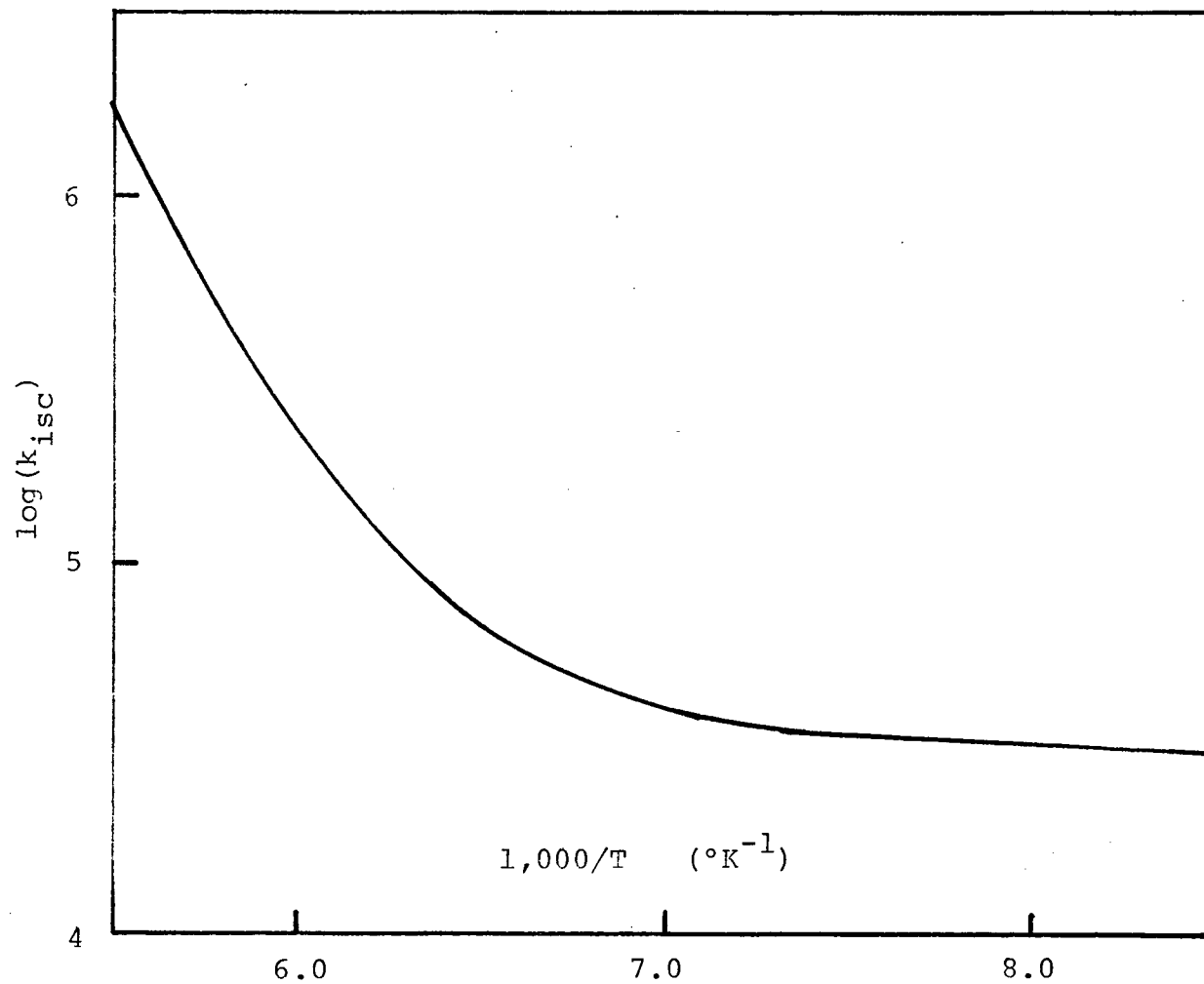


Figure 33. Intersystem crossing rate constant of $\text{Cr}(\text{acac})_3$ as a function of temperature. According to Mechanism I.

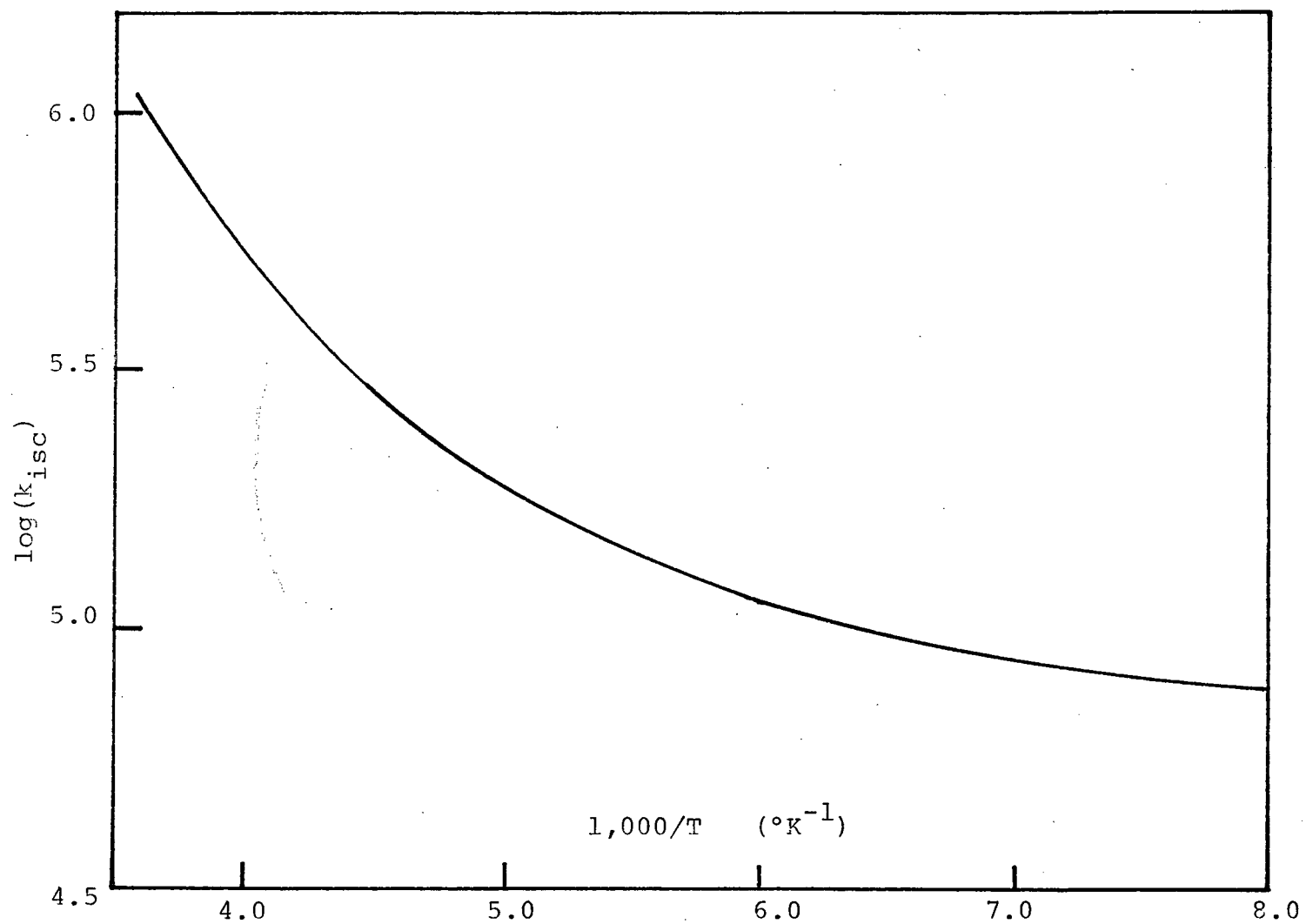


Figure 34. Intersystem crossing rate constant of $[\text{Cr}(\text{en})_3]^{+3}$ as a function of temperature. According to Mechanism I.

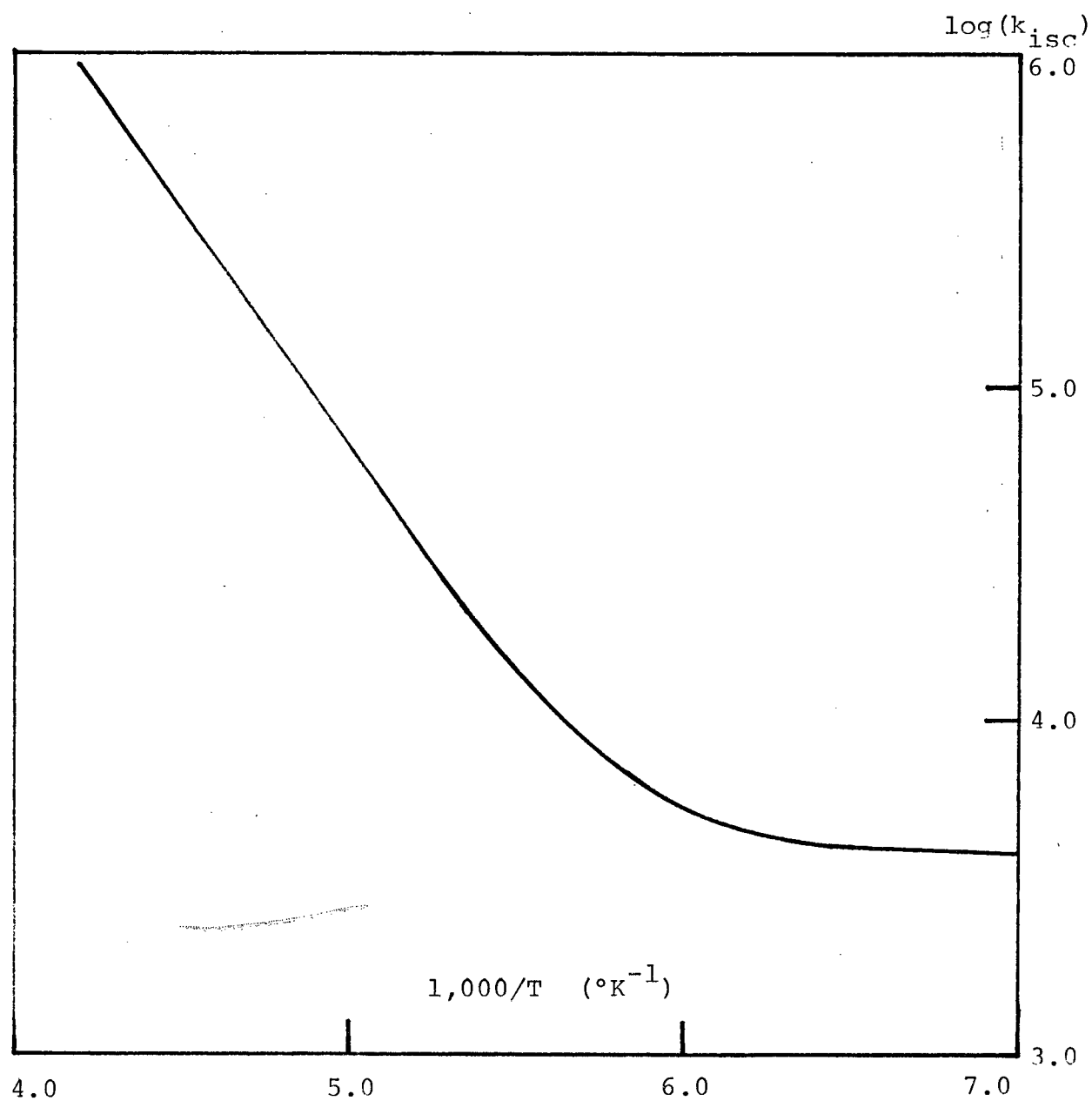


Figure 35. Intersystem crossing rate constant of $[\text{Cr}(\text{NCS})_6]^{-3}$ as a function of temperature. According to Mechanism I.

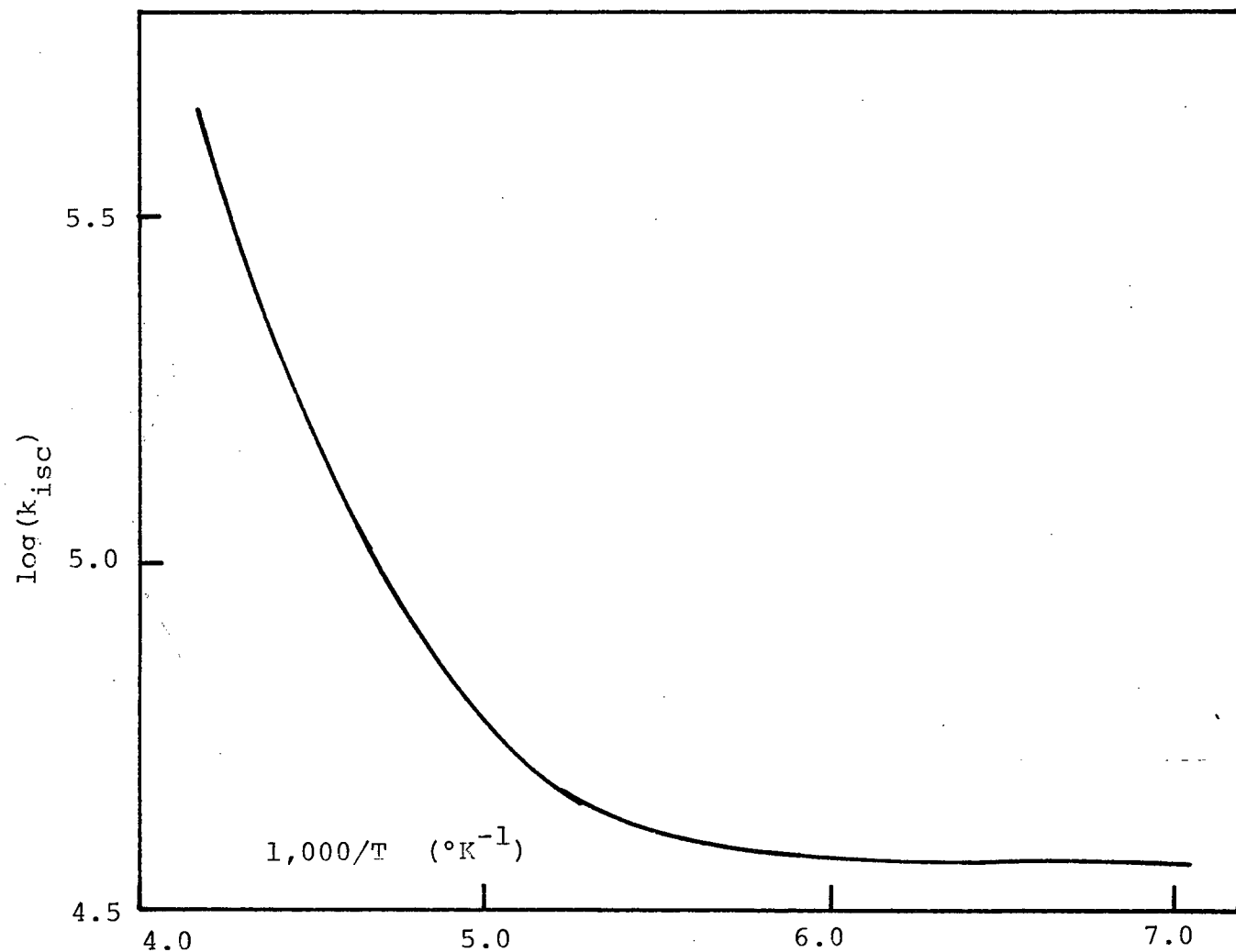


Figure 36. Intersystem crossing rate constant of $\text{trans-}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ as a function of temperature. According to Mechanism I.

Table VI

The Arrhenius Parameters of k_{isc} based on Mechanisms I and II. The frequency factors are in sec^{-1} and the activation energies in Kcal/mol.

Complex	s_a	E_a	s_b	E_b	s_c	E_c	s_d	E_d
$[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$	4.3×10^3	0.08	7.2×10^{13}	9.0	1.2×10^5	0	3.1×10^{12}	7.0
$\text{Cr}(\text{acac})_3$	6.2×10^3	0.18	6.9×10^{14}	7.7	7.1×10^4	0.20	2.6×10^{15}	7.8
$[\text{Cr}(\text{NCS})_6]^{-3}$	4.6×10^2	0.19	2.1×10^{14}	7.9	7.9×10^3	0.20	1.0×10^{12}	7.5
$[\text{Cr}(\text{en})_3]^{+3}$	1.6×10^4	0.10	1.5×10^{13}	10.2	2.1×10^5	0.26	3.6×10^6	3.3

and their derivatives has been studied by several research groups.⁶⁸⁻⁷³ It was found that their intersystem crossing rate constants consisted of both temperature independent and dependent components. The former was assigned to the direct intersystem crossing from the lowest excited singlet state to the lowest triplet state while the latter from the same state to a higher triplet state.

Similarly, in the Cr(III) complexes, the process k_c can be assigned to the intersystem crossing from the lowest vibrational levels of the $^4T_{2g}$ state directly to the isoenergetic vibronic levels of the $^2T_{1g}$ and/or 2E_g states. And the strongly temperature dependent process k_d may correspond to the intersystem crossing via high vibrational levels (higher than the zero-vibrational level by an average of E_d) of the $^4T_{2g}$ state to the $^2T_{2g}$ state.

In the following sections, the overall mechanistic schemes in the Cr(III) complex are discussed with all the available information.

Mechanism I

In this mechanism let us assume that process k_a is the intersystem crossing from the 2E_g state to the ground state $^4A_{2g}$, process k_b the thermally activated intersystem crossing from the 2E_g to $^4T_{2g}$ state, process k_c the intersystem crossing from the $^4T_{2g}$ to 2E_g state, and process k_d intersystem crossing from the $^4T_{2g}$ to $^2T_{2g}$ state (see Figure 37). All

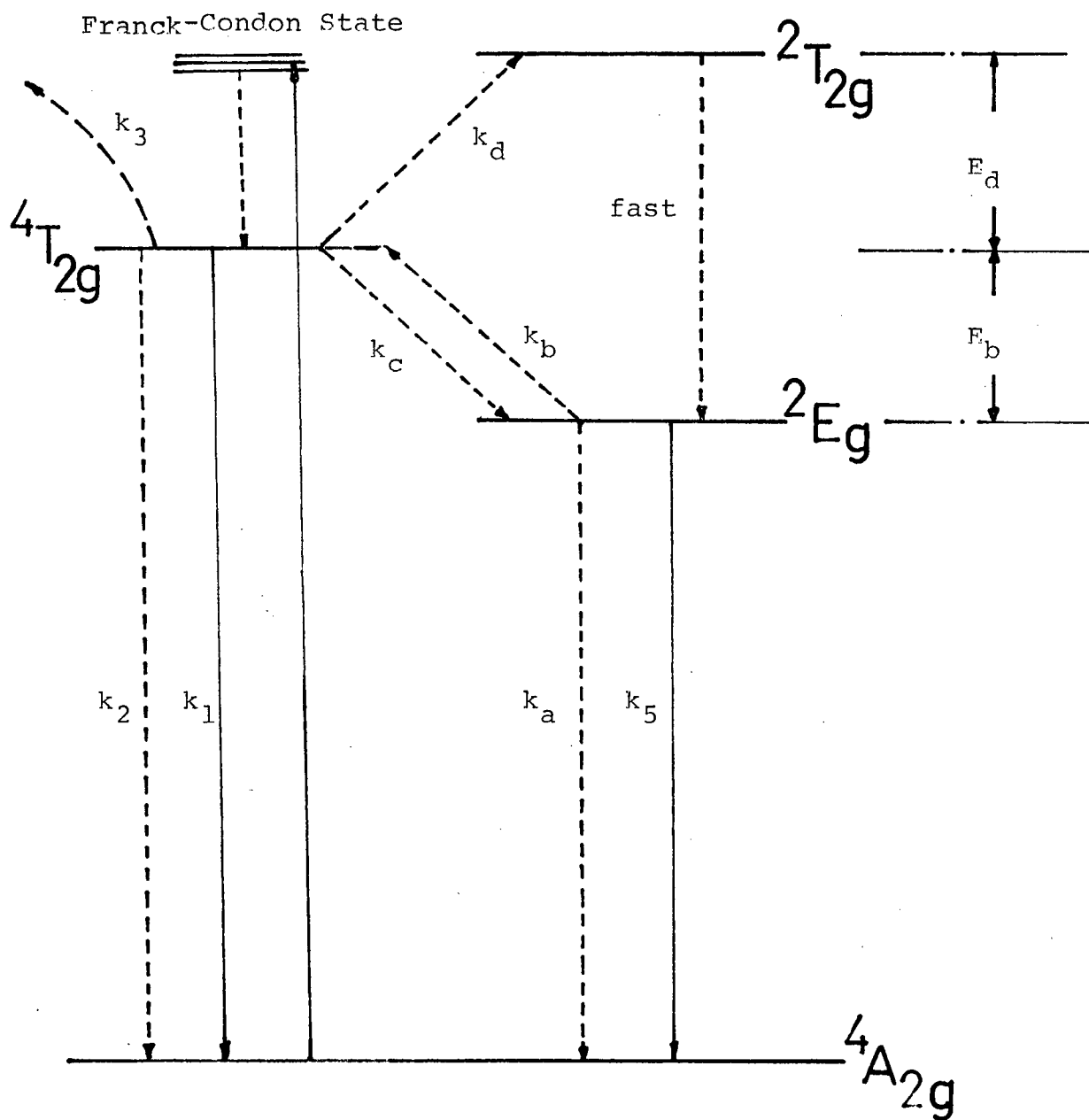


Figure 37. Schematic of Mechanism I.

the four processes are assumed to proceed via a tunnelling mechanism.⁶⁰

Accordingly, the zero-vibrational level of the ${}^4T_{2g}$ state can be expressed as

$$\bar{\nu}_{0-0}({}^4T_{2g}) = \bar{\nu}_{0-0}({}^2E_g) + E_b \quad (8.4)$$

and the location of the ${}^2T_{2g}$ state can be estimated by

$$\bar{\nu}({}^2T_{2g}) = \bar{\nu}_{0-0}({}^4T_{2g}) + E_d \quad (8.5)$$

The zero-vibrational levels of the 2E_g state are mostly known. The values estimated for $\bar{\nu}_{0-0}({}^4T_{2g})$ and $\bar{\nu}({}^2T_{2g})$ are listed in Table VII. Since the zero-vibrational levels of the ${}^4T_{2g}$ states of these Cr(III) complexes have never been observed spectroscopically, a direct confirmation of this assignment is out of the question. However, the ${}^2T_{2g}$ band has been observed in some Cr(III) complexes,⁷⁴ $\bar{\nu}({}^2T_{2g})$ lies from $18,000 \text{ cm}^{-1}$ to $21,000 \text{ cm}^{-1}$. Within experimental errors, the values listed in Table VII fall quite well within the region.

In spite of the satisfactory argument based on energetic considerations for this mechanism, there are some difficulties with it too. Firstly, the frequency factors, s_c and s_d , supposedly being the transition probabilities between the isoenergetic levels of the ${}^4T_{2g}$ and 2E_g states and of the ${}^4T_{2g}$ and ${}^2T_{2g}$ states, differ by as much as seven orders

of magnitude. In the aromatic compounds studied, the frequency factors of the two components of intersystem crossing are of comparable magnitude. Since the ${}^2T_{2g}$ state lies not much closer to the ${}^4T_{2g}(\bar{\nu}_{0-0})$ than the 2E_g state (comparing E_d and E_b), the fact that s_d is much more efficient than s_c is not applicable on the energy gap hypothesis.^{60,76}

Table VII

The predicted locations of the ${}^4T_{2g}$ and ${}^2T_{2g}$ states according to Mechanism I and II. Wave number in kK

Complex	$\bar{\nu}_{0-0}({}^2E_g)$	Mechanism I		Mechanism II
		$\bar{\nu}_{0-0}({}^4T_{2g})$	$\bar{\nu}({}^2T_{2g})$	$\bar{\nu}_{0-0}({}^4T_{2g})$
trans-[Cr(NH ₃) ₂ (NCS) ₄] ⁻	13.33	16.5	18.9	14.0
[Cr(CN) ₆] ⁻³	12.38	15.2	-	-
[Cr(NCS) ₆] ⁻³	12.85	15.6	18.2	13.0
[Cr(en) ₃] ⁺³	14.98	18.6	19.7	17.4
Cr(acac) ₃	12.84	15.5	18.3	12.8

It is considered to be due to the fact that the doublet states, 2E_g , ${}^2T_{1g}$, and ${}^2T_{2g}$, have nearly the same equilibrium nuclear configuration with the ground state ${}^4A_{2g}$, while the ${}^4T_{2g}$ state is strongly distorted from the ground state. Therefore, the intersystem crossing from ${}^4T_{2g}(\bar{\nu}_{0-0})$ to the ${}^2T_{1g}$ and

2E_g states is strongly forbidden by the Frank-Condon principle. On the other hand, because of the $^2T_{2g}$ state and the Frank-Condon state (absorption maximum) of the $^4T_{2g}$ state are close together in both energy and nuclear geometry, the interaction between them is expected to be large, consequently, the radiationless transition probability between them is high.

Unfortunately, more serious difficulty comes from the other pair of frequency factors, s_c and s_b , supposedly being the forward and reverse transition probabilities of the intersystem crossing between the zero-vibrational level of the $^4T_{2g}$ state and the isoenergetic levels of the 2E_g state. They are expected to be of the same magnitude, but they are in fact different by from seven to ten orders of magnitude from each other. Although radiationless transitions between two electronic states which differ very much in equilibrium nuclear configuration have never been explored theoretically or experimentally, the extreme large discrepancy between the forward and reverse transitions observed on this mechanism may be possible but can hardly be reasonable.

Mechanism II

In this mechanism, to obviate the difficulties in Mechanism I, we assume (see Figure 38) that processes k_d and k_b are the forward and reverse transitions of the thermally activated intersystem crossing and assume they do not proceed via a tunneling mechanism but instead via Teller crossing

through the intersection boundaries of the multi-dimensioned potential energy surfaces of the $^4T_{2g}$ and 2E_g state. Of course, process k_c is still assumed to be the tunneling intersystem crossing. It has to be noted that the tunneling process and Teller crossing have not been reported to be competitive in the same molecule for any other compound studied. But theoretically there is no reason why they should not be.

According to this mechanism, the zero-vibrational level of the $^4T_{2g}$ state is now expressed as

$$\bar{\nu}_{0-0}(^4T_{2g}) = \bar{\nu}_{0-0}(^2E_g) + E_b - E_d \quad (8.6)$$

The values so obtained for $\bar{\nu}_{0-0}(^4T_{2g})$ are also listed in Table VII.

The only difficulty with this mechanism is that it requires the location of the zero-vibrational level of the $^4T_{2g}$ state to be very low in energy. However, this is not impossible, as a matter of fact, the location of $\bar{\nu}_{0-0}(^4T_{2g})$ has never been determined, for these complexes.

Now the frequency factors s_d and s_b are of comparable magnitude as they should be according to this mechanism.

It is interesting to note that the energy separation between the $^4T_{2g}$ and 2E_g states estimated⁵⁵ from delayed fluorescence is the difference in the activation energies of the forward and reverse intersystem crossing. The values found for ruby and emerald agree with the values obtained spectroscopically (see Ref. 18). If the lifetimes of these

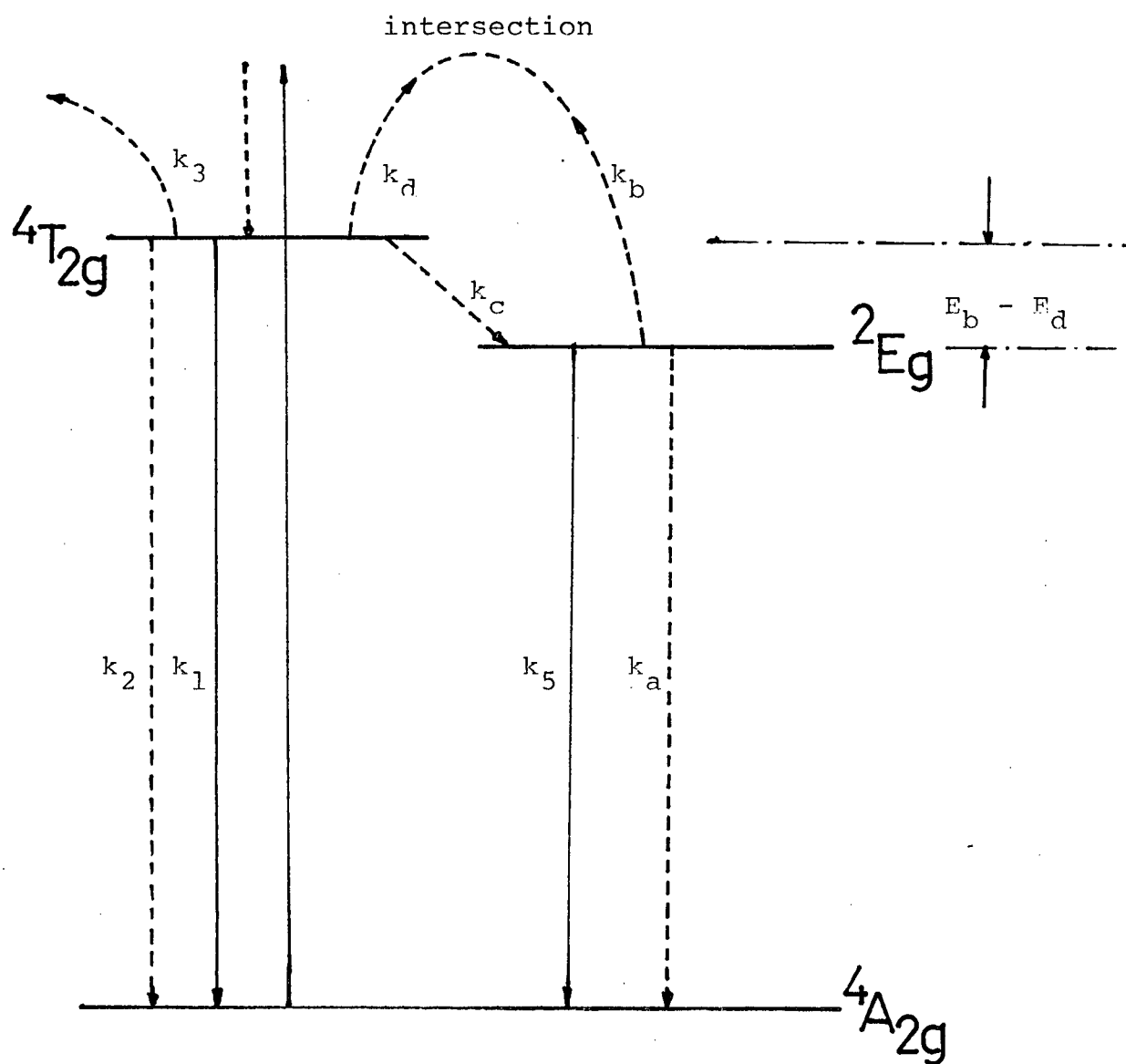


Figure 38. Schematic of Mechanism II.

compounds are studied, the component corresponding to the thermally activated intersystem crossing may have an activation energy which is E_b higher than the energy separation between the $^4T_{2g}$ and 2E_g state predicted from the delayed fluorescence studies.

Mechanism III

In this mechanism (see Figure 39), we assume that the newly found lifetime, τ_x , to be the lifetime of the $^2T_{1g}$ state. Now let us decompose τ_x into two components

$$1/\tau_x = k_y + k_z \quad (8.8)$$

$$= s_y \exp(-E_y/RT) + s_z \exp(-E_z/RT) \quad (8.9)$$

The values for s_y , E_y , s_z , and E_z are collected in Table VIII. Because of the difficulty in the measurement of τ_x , s_y is uncertain by $\pm 50\%$, and s_z is known only within two orders of magnitude, E_y is ± 0.03 Kcal/mol, and $E_z \pm 1$ Kcal/mol.

Since the 2E_g and $^2T_{1g}$ states are assumed to be populated promptly and the transition $^2T_{1g} \rightarrow ^2E_g$ is the slow rate-determining step, the mechanism automatically fits Equation 7.1 with α between 0 and -1 (refer to Equations 7.6, 7.7, and 7.8). However, in order to explain the positive α for $[\text{Cr}(\text{CN})_6]^{-3}$ and the fact that α changes with wavelength, it is necessary to assume that phosphorescence from the $^2T_{1g}$ state is also detected. Unfortunately, the spectra so attributed to the $^2T_{1g}$ phosphorescence (see Chapter VII) are

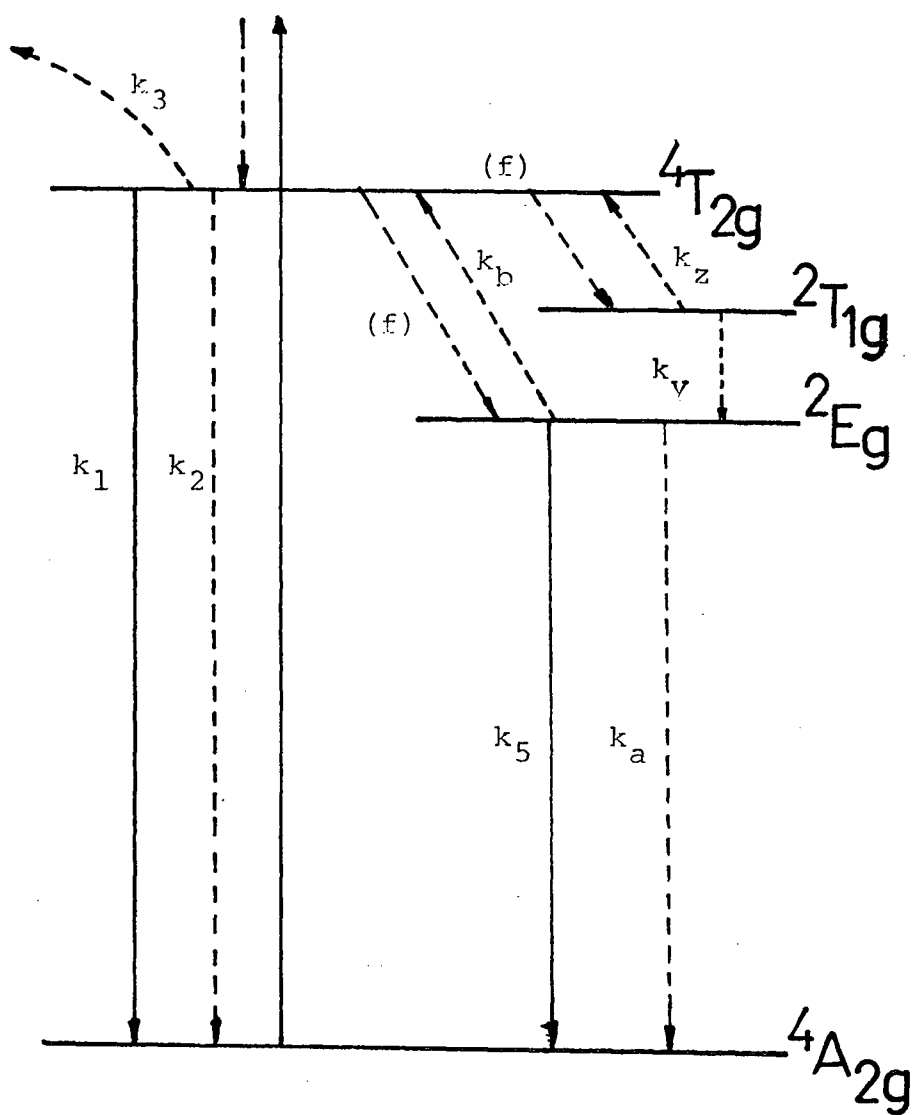


Figure 39. Schematic of Mechanism III.

located near or even at longer wavelengths than those of the 2E_g phosphorescence. A large Stokes' shift in the $^2T_{1g}$ phosphorescence is unlikely (because that of the 2E_g phosphorescence is only about 100 cm^{-1}) but is not impossible.

Depletion of the $^2T_{1g}$ state and further population of the 2E_g state are achieved by process k_y at lower temperatures and by process k_z to the $^4T_{2g}$ state followed by rapid inter-system crossing to the 2E_g state at higher temperatures.

If we assume process k_b and k_z proceed via a tunneling mechanism, then

$$\bar{v}(^2T_{1g}) - \bar{v}(^2E_g) = E_b - E_z \quad (8.10)$$

The values for $(E_b - E_z)$ are 0.4, 0.6, -0.9, and 6.6 Kcal/mol for $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$, $[\text{Cr}(\text{NCS})_6]^{-3}$, $\text{Cr}(\text{acac})_3$, and $[\text{Cr}(\text{en})_3]^{+3}$ respectively. However, the energy separation of the 2E_g and $^2T_{1g}$ is known to be about 2 Kcal/mol.⁷⁴ The values predicted for $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ and $[\text{Cr}(\text{NCS})_6]^-$ may be considered satisfactory within experimental error, but those for $[\text{Cr}(\text{en})_3]^{+3}$ and $\text{Cr}(\text{acac})_3$ can not be.

In this mechanism, judging from s_b and s_z , the lifetime of the $^4T_{2g}$ state must be at the order of 10^{-10} sec or less. In fact, Kisliuk and Moore estimated the lifetime of the $^4T_{2g}$ in ruby to be less than 10^{-3} sec.⁵⁴ But comparing to the fluorescence-only complexes, the values speculated are much shorter (10^{-7} vs 10^{-10} sec). Since the only apparent

Table VIII
The Arrhenius Parameters of $1/\tau_x$

Complex	s_y (sec^{-1})	E_y (Kcal/mol)	s_z (sec^{-1})	E_z (Kcal/mol)
$[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$	3.4×10^5	0.15	1.2×10^{14}	8.6
$\text{Cr}(\text{acac})_3$	1.8×10^5	0.14	1.5×10^{17}	8.7
$[\text{Cr}(\text{NCS})_3]^{-3}$	5.9×10^4	0.18	5.9×10^{14}	8.6
$[\text{Cr}(\text{en})_3]^{+3}$	2.0×10^5	0.12	1.2×10^9	3.6

difference between the phosphorescence and the fluorescence-only Cr(III) complexes is the participation of intersystem crossing in the former, if we assume the shortening of the quartet lifetime from the latter to the former is caused mainly by intersystem crossing, then we would expect the doublet formation quantum yield to be unity. The ϕ_{isc} obtained in Chapter VI, according to this mechanism, should be the quantum yield of the 2E_g state formation. Since ϕ_{isc} is substantially less than unity, we are led to the conclusion that intersystem crossing from the $^2T_{1g}$ state to the ground state is very efficient. This is different from the 2E_g state (10^6 vs 10^4 sec^{-1}). From considerations of nuclear configuration and energy level, the 2E_g and $^2T_{1g}$ states are

expected to behave similarly with respect to the ground states. Moreover, the transition ${}^2T_{1g} \rightarrow {}^2E_g$ is too slow to be rationalized, as the separation between the two states is small.⁺⁺

In order for the chemical reaction to compete with other processes in the ${}^4T_{2g}$ state, the rate constant of chemical reaction must be larger than 10^{10} sec^{-1} . The difficulty is why a reaction proceeding so fast in solution is not subjected to the cage effect.

In $[\text{Cr}(\text{urea})_3]^{+3}$, it is known that the ${}^2T_{1g}$ state lies above the ${}^4T_{2g}$ state in energy. Therefore, it is expected that at extremely low temperatures, the intersystem crossing ${}^4T_{2g} \rightarrow {}^2T_{1g}$ must be negligible and the ${}^2T_{1g}$ state thus not appreciably populated. If so, this would result in a phosphorescence curve without a rise. In fact, Dingle observed the phosphorescence from $[\text{Cr}(\text{urea})_6]^{+3}$ at 25°K did show an initial rise before decay.⁵²

Recently, an experimental upper limit of 4 nsec has been determined for the lifetime of the ${}^4T_{2g}$ state of ruby. And it also has been shown that the ${}^2T_{1g}$ and 2E_g states are practically in thermal equilibrium as is evident from the fact that the phosphorescence of the ${}^2T_{1g}$ states is observed at 300°K but not at 77°K.²⁵ This contradicts the assumption made in Mechanism III. However, the difference in primary processes between the ionic and molecular Cr(III) compounds should not be overlooked.

⁺⁺The energy gap hypothesis should be valid if the initial and final states of a transition are not too different in the equilibrium nuclear configuration.

From the above considerations, although it is still favored that τ_x is the lifetime of the $^4T_{2g}$ state, it is undeniable that none of the mechanisms proposed has been unambiguously confirmed or negated. Some more research is needed to clarify this problem. These will be discussed in Chapter IX.

No matter which mechanism is true, on the whole, all the primary processes behave quite "normally" at low temperatures. But as soon as the temperature rises sufficiently, the primary processes start to change their courses to the thermally activated routes and result in an "abnormal" and complicated mechanistic scheme.

CHAPTER IX

SOME FINAL REMARKS

The primary photoprocesses in Cr(III) complexes are very different in behavior from those known in organic compounds. For example, in Cr(III) complexes, the intrinsic fluorescence lifetimes are much longer than predicted theoretically, the quantum yields of internal conversions are large, and the fluorescent states instead of the phosphorescent states are direct precursors to photochemical reactions. All these can be explained consistently by the fact that the equilibrium nuclear configuration of the ${}^4T_{2g}$ state is distorted very much from that of the ground state, ${}^4A_{2g}$. Before investigating the possible roles the distortion plays in the primary processes, let us first study the distortion as a function of $10Dq$, the ligand field strength. The distortion is qualitatively measured by the quantity $\bar{\nu}_{\max}({}^4T_{2g}) - \bar{\nu}_{0-0}({}^4T_{2g})$.

The arguments and discussions in the following sections are based more on intuition than on solid evidence, therefore they should be considered to be tentative and speculative.

9.1 The Origin of the Lowest Quartet State

Three methods are used to estimate roughly the location of the zero-vibrational level of the ${}^4T_{2g}$ state: (1) for

those complexes which fluoresce, the origin is assumed to be at the center of absorption and fluorescence maxima. The necessary data are taken from the review by Fleischauer and Fleischauer.¹⁷ (2) from the temperature-dependence studies of delayed fluorescence. The results are given by Camassei and Forster.⁵⁵ (3) From the activation energies of the thermally activated primary processes (see Chapter VIII). Figure 40 shows the plot of the origin of the $^4T_{2g}$ state against $10Dq$.

It can be seen that the location of the origin is very insensitive to $10Dq$. And to our surprise, the origin of the $^4T_{2g}$ state is lower in energy for complexes with very large $10Dq$ value than for those with smaller $10Dq$ value. This indicates the inadequacy of the present bonding theories for the excited electronic states. Ligand Field Theory may well be justified in the prediction of absorption maxima in metal complexes because the excited vibronic states (Frank-Condon states) reached by the vertical transition have the same nuclear configuration as the ground state. But in general, the Molecular Orbital Theories at present stage are rather impotent to predict the origins (not to mention the geometry) of the excited states, because the equilibrium nuclear configuration may be different in different electronic states. This is certainly true in the case that a bonding or non-bonding electron is excited to an anti-bonding orbital. Transitions from the ground state to the excited quartet

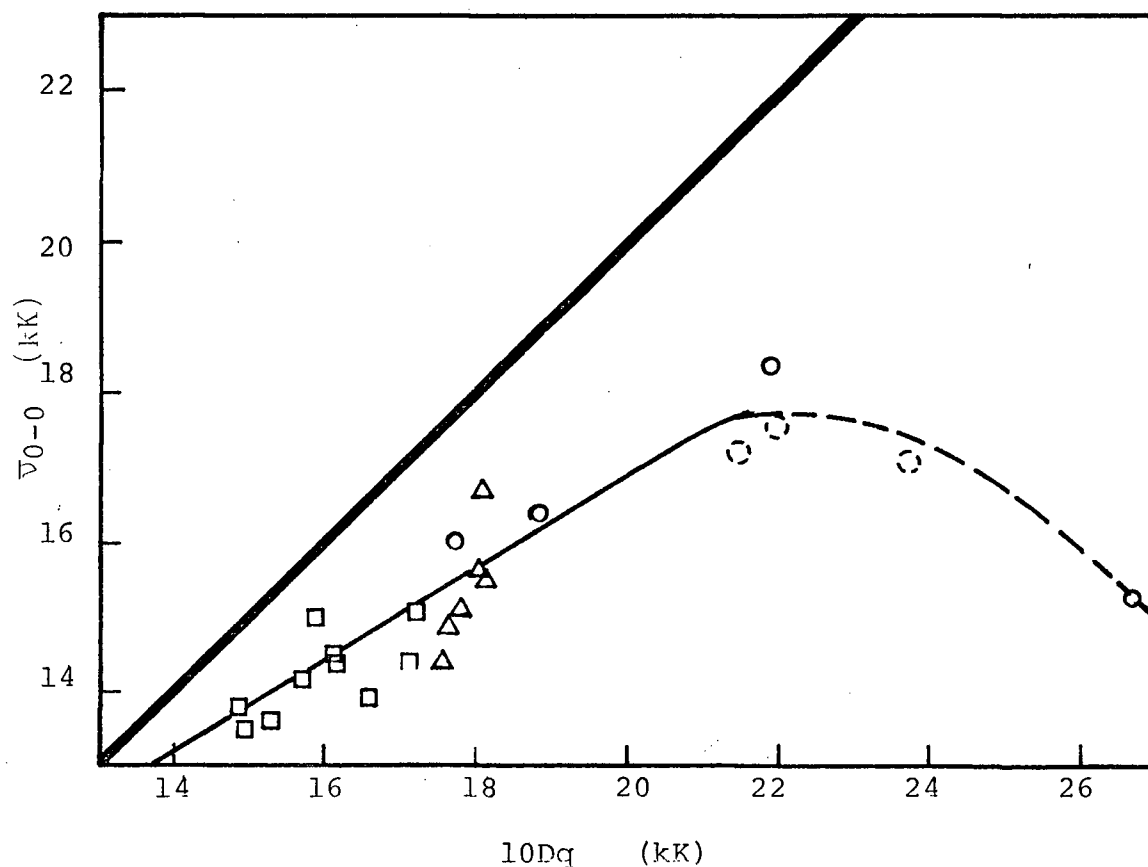


Figure 40. The origin of the ${}^4T_{2g}$ state of Cr(III) complexes as function of ligand field strength. $\square$, Method 1; Δ , Method 2; and $\circ$ Method 3, according to Mechanism I. The broken circles are data from Zanders.⁵⁷ The origins are even lower according to Mechanism II or III. The heavy line represents the limiting condition that the initial and final states have identical equilibrium nuclear configuration.

states in Cr(III) involve excitation of an electron from the bonding orbital (t_{2g}) to an anti-bonding orbital (e_g), strong distortion of the quartet excited states is thus expected. From Figure 40 it can also be seen that the distortion of the $^4T_{2g}$ state increases as $10Dq$ increases.

9.2 Tunneling Mechanism and Teller Crossing

The competition between tunneling and Teller crossing has not been observed for radiationless transitions in aromatic compounds. It is believed that tunneling is the more efficient route for transitions between two electronic states which have the same equilibrium nuclear configuration so that their potential energy surfaces intersect at a very high energy level or do not intersect at all. The Teller crossing can become competitive with the tunneling process if the two electronic states are quite different from each other in the equilibrium nuclear configuration; and therefore the intersection lines of their potential energy surfaces lie very low in energy with reference to the zero-vibrational level of the initial electronic state. At low temperature, unless the intersection lines go right through the minimum in the potential energy surface of the initial state, the tunneling process is always dominant; however, at high temperature, Teller crossing gradually stands out. At the intersection boundaries, Teller crossing must take place

in a few vibrations. Therefore, the net process is expected to have an activation energy equal to the separation between the zero-vibrational level and the intersection lines; and to have a pre-exponential factor of about 10^{12} to 10^{13} sec^{-1} , that is, about the rate constant of the vibration.

For process k_b and k_d , we cannot tell whether transitions occur via tunneling or Teller crossing, because higher electronic states are available. But at least Teller crossing has to be assumed to occur in the internal conversion which also has a thermally activated component with a large activation energy.

9.3 Primary Processes and Ligand Field Strength

In this section the efficiencies of the primary processes from the ${}^4T_{2g}$ state are discussed in terms of energy gaps⁶⁰ and barrier widths⁷⁶ between the initial and the final states of the transitions when they take place via tunneling mechanism; and in terms of the energy separations between the intersections and the origins of the initial states when they take place via Teller crossing.

Since the origin of the ${}^4T_{2g}$ state does not change much with ligand field strength, $10Dq$, the more likely effect of $10Dq$ on the primary processes is the change it causes in the equilibrium nuclear configuration of the ${}^4T_{2g}$ state. With increasing $10Dq$, the ${}^4T_{2g}$ state is generally distorted more and more from both the lowest doublet states and the

ground state. It can be seen from the simplified two-dimensional potential energy surfaces that this results in wider barrier widths between the $^4T_{2g}$ state and the 2E_g and $^2T_{1g}$ state and a narrower barrier width between the $^4T_{2g}$ state and the ground state. Therefore, intersystem crossings and internal conversion are expected to decrease and increase respectively with increasing $10Dq$.

At liquid nitrogen temperature, only intersystem crossing and internal conversion are important in depleting the $^4T_{2g}$ state, the quantum yield of intersystem crossing will be smaller; and the quantum yield of internal conversion larger as $10Dq$ increases. In fact, the quantum yields of intersystem crossing for Cr(III) complexes with low $10Dq$ values are known to be close to unity, but for those with high $10Dq$ values, they are substantially less than unity.

9.4 Suggestions for Further Work

Although many problems have been cleared up in this work, there are more new questions introduced, and the mechanisms of the primary photoprocesses are far more complicated than were expected before. Besides being comparatively less explored, the $^4T_{2g}$ state is bound to be the focus of research on Cr(III) complexes in the near future. Three parameters will be widely used: photochemical quantum yield, doublet formation quantum yield, and especially the lifetime of the

$^4T_{2g}$ state. The following are some suggestions for further work.

(1) The $^4T_{2g}$ state has been proven to be the immediate precursor to the photosubstitution in Reineckate ion, but more Cr(III) complexes have to be studied (by the same technique) to establish the generality of the conclusion. Especially interesting will be the work extended to those Cr(III) complexes, for example, $[Cr(NH_3)_5(NCS)]^{+2}$, which exhibit two modes of photosubstitution and are thought to have two different photoreactive intermediates.^{22,27}

(2) The temperature-dependence studies of the photochemical quantum yields of the Cr(III) complexes in deoxygenated solutions are essential to understand the reactivity of the $^4T_{2g}$ state. In the case that the lifetime of the $^4T_{2g}$ state is available, the rate constant and the activation energy of the photochemical reaction can be evaluated. Correlation of the activation energy with the ligand field strength will give us an insight into the detailed mechanism of the $^4T_{2g}$ state chemistry and will provide some clue to the relationship between structure and reactivity.

In the case that the lifetime of the $^4T_{2g}$ state is not available, only the apparent activation energy can be estimated, and it is difficult to interpret unambiguously.

However, at sufficiently high temperature, repopulation of the $^4T_{2g}$ state causes practically complete depletion of the 2E_g state; there are only two efficient pathways to degrade

the excitation energy, therefore,

$$\phi_{\text{chem}} = \frac{k_3}{k_2 + k_3} \quad (9.1)$$

or

$$(\phi_{\text{chem}} - 1) = \frac{k_2}{k_3} \quad (9.2)$$

(These can also be derived from Equation 4.20 by assuming the 2E_g state is substitutionally inert.) The Arrhenius plot of $\log(1/\phi_{\text{chem}} - 1)$ vs $1/T$ will yield the difference between the activation energies of the photochemical reaction and internal conversion.

(3) The confirmation of the lifetime of the $^4T_{2g}$ state is of utmost importance for subsequent studies of the $^4T_{2g}$ state. The rise of phosphorescence in Cr(III) complexes should be studied more extensively and systematically. And the accuracy of the data must be improved. This can be achieved with a more intense flash lamp and a more sensitive but less noise detecting system.

Direct observation of the excited state whose lifetime is τ_x is possible and promising by using the submicrosecond flash-kinetic spectrophotometric method. The millisecond flash-kinetic studies of the Cr(III) complexes have recently been reported.^{77,78} However, from the fact that $\tau_x \doteq 10^{-5}$ sec, we know there are practically no detectable excited

$^4T_{2g}$ (or $^2T_{1g}$) state molecules remaining after millisecond delay times. Therefore only the absorption spectra of 2E_g states of Cr(III) complexes can be observed. The submicrosecond flash-kinetic method has the potential to detect the excited state having τ_x and will eventually lead us to the identification of it. This can be achieved with a pulsed laser.

(4) The three mechanisms mentioned in Chapter VIII for the primary processes can be confirmed or negated once the locations of the $^2T_{1g}$ and $^2T_{2g}$ states and the origin of the $^4T_{2g}$ state are known. There are scattered data for the $^2T_{1g}$ and $^2T_{2g}$ states, but a more systematic study is desired. To look for the origin of the $^4T_{2g}$ state spectroscopically is a difficult task. However, careful investigations of the absorption spectra of these Cr(III) complexes at an extremely low temperature, say, at 2°K, may reveal the locations of the origins of the $^4T_{2g}$ state.

(5) It is clear that the environmental structure plays an important role in all the primary processes of Cr(III) complexes. However, for a fixed solvent, the viscosity of the solvent does not seem to affect the primary processes at all. Since the effect of viscosity of the solvent on the primary processes has been stressed,⁵⁹ it is interesting to have a systematic study by varying the composition of the solvent gradually.

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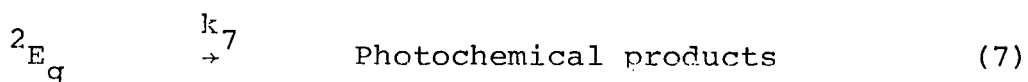
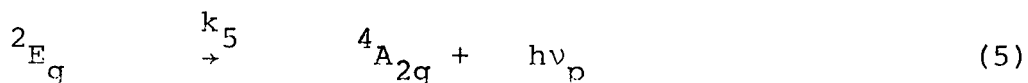
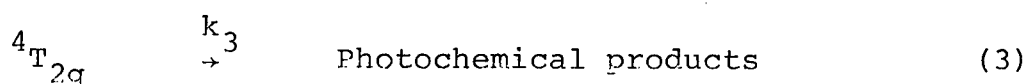
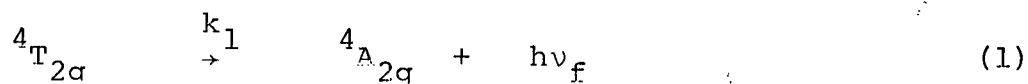
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A P P E N D I X

According to the following mechanistic scheme (see Figure 3):



after an ideal instantaneous excitation, suppose that only the ${}^4T_{2g}$ state is immediately populated, the rate equations can be expressed as

$$-\frac{d[{}^4T_{2g}]}{dt} = (k_1 + k_2 + k_3 + k_4)[{}^4T_{2g}] - k_{-4}[{}^2E_g] \quad (8)$$

$$-\frac{d[{}^2E_g]}{dt} = (k_5 + k_6 + k_7 + k_{-4})[{}^2E_g] - k_4[{}^4T_{2g}] \quad (9)$$

and

$$[{}^4T_{2g}] = [{}^4T_{2g}]_0; \quad [{}^2E_g] = 0 \quad (10)$$

The solutions are:

$$[{}^2E_g] = \frac{k_4 [{}^4T_{2g}]_0}{k_\beta - k_\alpha} \{ e^{-k_\alpha t} - e^{-k_\beta t} \} \quad (11)$$

$$[{}^4T_{2g}] = \frac{[{}^4T_{2g}]_0}{k_\beta - k_\alpha} \{ (k_E - k_\alpha) e^{-k_\alpha t} + (k_E - k_\beta) e^{-k_\beta t} \} \quad (12)$$

$$\text{where } k_\alpha = \frac{1}{2}(k_E + k_T) - \frac{1}{2}[(k_T - k_E)^2 + 4k_4 k_{-4}]^{\frac{1}{2}} \quad (13)$$

$$k_\beta = \frac{1}{2}(k_E + k_T) + \frac{1}{2}[(k_T - k_E)^2 + 4k_4 k_{-4}]^{\frac{1}{2}} \quad (14)$$

$$\text{and } k_E = k_5 + k_6 + k_7 + k_{-4} \quad (15)$$

$$k_T = k_1 + k_2 + k_3 + k_4 \quad (16)$$

Since emission intensities are proportional to the concentrations of the emitting species, therefore,

$$I_p = K (e^{-k_\alpha t} - e^{-k_\beta t}) \quad (17)$$

$$I_f = K' [(k_E - k_\alpha) e^{-k_\alpha t} - (k_E - k_\beta) e^{-k_\beta t}] \quad (18)$$

In the case that reverse process 4 does not occur, that is, $k_{-4} = 0$, then the above equations can be simplified to

$$I_p = K (e^{-k_E t} - e^{-k_T t}) \quad (19)$$

$$I_f = K'' e^{-k_T t} \quad (20)$$

If processes k_{-4} do occur, but k_T is much greater than k_E , then

$$\begin{aligned}
k_{\alpha} &= \frac{1}{2}(k_E + k_T) - \frac{1}{2}(k_T - k_E) \left[1 + \frac{4k_4 k_{-4}}{(k_T - k_E)^2} \right]^{\frac{1}{2}} \\
&\doteq \frac{1}{2}(k_E + k_T) - \frac{1}{2}(k_T - k_E) - k_4 k_{-4} / (k_T - k_E) \\
&\doteq k_E - k_4 k_{-4} / k_T \\
&= k_E - \phi_{isc} k_{-4} \\
&= k_5 + k_6 + k_7 + (1 - \phi_{isc}) k_{-4}
\end{aligned}$$

where $\phi_{isc} = k_4 / (k_1 + k_2 + k_3 + k_4)$

Similarly, we can obtain

$$k_{\beta} \doteq k_T$$

This mechanistic scheme and the above derivations can be applied equally well to the energy transfer system with the terms properly changed.