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Effects of Molecular Structure on Quenching Reactions

by

Sze-Ming Y. Huang

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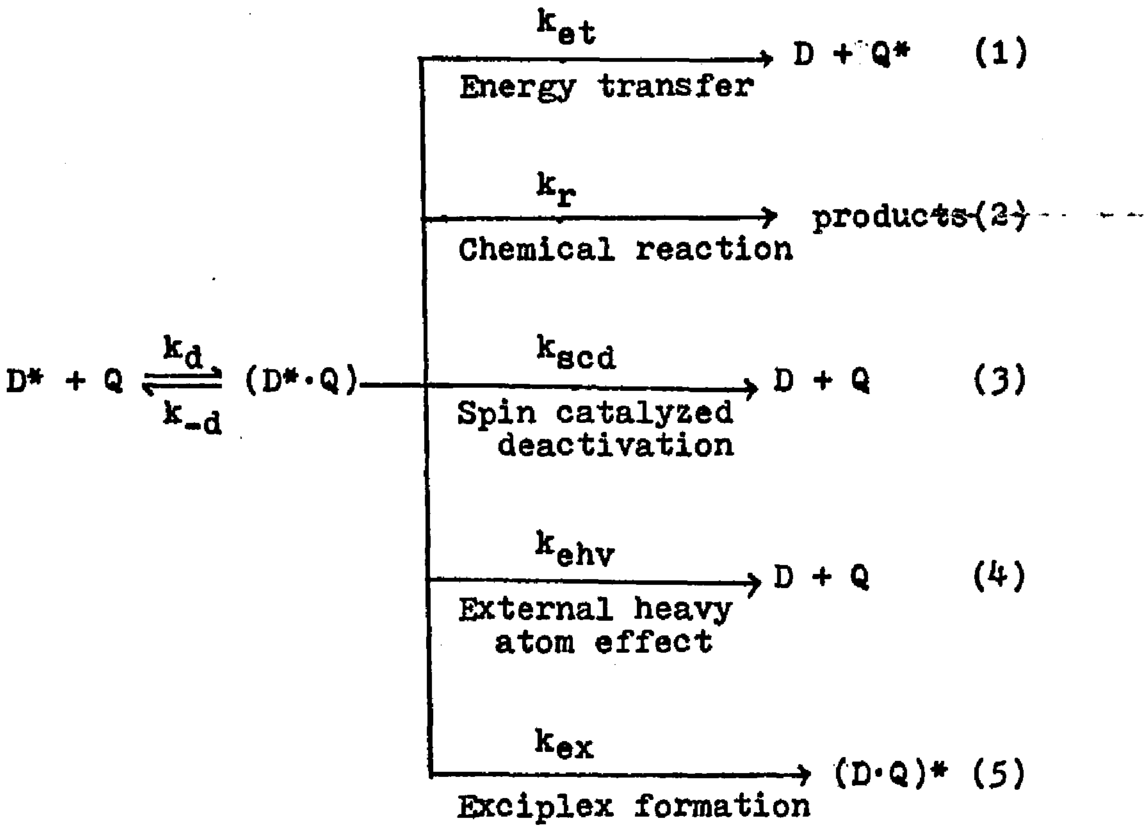
CHAPTER 1

Introduction

Pressed by the dwindling fossil fuel reserves, and spurred by the fascination with the role of radiant energy on the environment, there has developed an extraordinary interest in the photophysical and photochemical processes of a wide variety of compounds. In recent years, this surge of interest and activity has led to some progress in the understanding of the chemistry of the excited state. The development and continued growth of this understanding arises from a detailed knowledge of not only those states which are observed in the absorption spectrum, but also those states where direct population by absorption of light energy is forbidden by various selection rules. In the field of organic chemistry, sensitization and quenching techniques have been shown to be powerful tools to obtain information on these excited states.[1] Recently these techniques have been introduced with some success as probes of the interesting, but varied photophysical and photochemical behavior of transition metal complexes.[2]

In fluid solution, the first step in a sensitization or quenching reaction is the quenching encounter. The quenching encounter can take place by two basic mechanisms:[2] (1) dynamic quenching (diffusional quenching) where the donor and quencher diffuse to within a reaction volume, or (2) static quenching (associative quenching) where the donor and quencher form a nonluminescent pair dictated by a thermal equilibrium. A dynamic quenching process is a bimolecular interaction between an electronic excited state of a donor and a ground state quencher, in which the donor is deactivated or converted into a different compound. As indicated by equations 1 through 5, the quenching of an excited molecule may take place by several distinct mechanisms, the most important of which are: (1) electronic energy transfer, (2) chemical reaction, (3) spin-catalyzed deactivation, (4) external heavy-atom effect, and (5) complex (excimer and exciplex) formation.[2]



where D* represents an excited donor and Q represents a quencher. The rate constants k_d and k_{-d} describe the formation and dissociation of an encounter pair indicated by the brackets. The brackets are not intended to imply composition or structure but simply imply that D* and Q exist within an effective reaction volume or solvent cage for some finite period of time.

(1) Electronic Energy Transfer

In fluid solutions, electronic energy transfer, equation 1, may occur by means of Coulombic (dipole-dipole) or exchange interaction.[1] A Coulombic interaction can take place over an intermolecular distance much larger than the molecular diameter. They are important, however, only in the case in which the transitions in the donor and acceptor are spin allowed. The exchange interaction, on the other hand, can only take place over distances of the order of the collision diameters. Its magnitude, however, is not related to the oscillator strength of the transition in either the donor or the acceptor. The low-energy ligand-field absorption bands of transition metal complexes are Laporte forbidden.[3] Since these transitions are forbidden, it has been suggested that Coulombic interactions would play a small role in an energy transfer process. With most transition metal complexes, energy transfer occurs by an exchange interaction requiring a collisional mechanism.[2]

Unlike most organic molecules, the ground state of a transition metal complex may have a high spin multiplicity.[3] For example, the ground state of a Cr(III) complex is a quartet. For electronic energy transfer, this high spin multiplicity of the complex allows a number of processes to satisfy Wigner's rules of conservation of spin momenta.[4] Energy transfer from triplet donors, ${}^3D^*$, to both spin-forbidden doublet, ${}^2Cr(III)^*$, and spin-allowed quartet, ${}^4Cr(III)^*$, excited states of a Cr(III) complex is allowed.[2] As indicated by equations 6 and 7, both pairs of reaction products have at least one component of spin the same as the reactants.

$$\underset{5/2,\,3/2,\,1/2}{{}^3D^* + {}^4Cr(III)} \longrightarrow \begin{cases} {}^1D + \overset{1/2}{{}^2Cr(III)^*} & (6) \\ {}^1D + \underset{3/2}{{}^4Cr(III)^*} & (7) \end{cases}$$

The results available show that transition metal complexes can participate in the energy transfer processes as both donors[5] and acceptors[6]. Excitation of $Ru(bipy)_3^{2+}$ in the presence of $Cr(CN)_6^{3-}$ results in emission characteristic of the Cr(III) complex.[6a] This sensitized emission establishes an energy transfer process.

(2) Chemical Reaction

Unlike the complex radical reactions which may occur with organic donors and acceptors,[4a] sensitization of transition metal complexes induces ligand substitution, isomerization, and redox reaction modes.[2] Although postulated in a number of systems, quenching via a chemical mechanism has been unambiguously established in relatively few cases.

For example, the luminescent charge transfer state of $Ru(bipy)_3^{2+}$ is efficiently quenched by Tl^{3+}[7]. The emission spectrum of $Ru(bipy)_3^{2+}$ establishes that the luminescent charge-transfer state lies at energies $\leq$ 19 kK. Since the excited states of Tl^{3+} have energies $\geq$ 30 kK[7], an energy transfer process would be extremely endothermic and can be ruled out. The appearence of the electron transfer products, $Ru(bipy)_3^{3+}$ and Tl^{2+}, however, led to the suggestion that quenching occurs via a redox mechanism, equation 8.

$$*Ru(bipy)_3^{2+} + Tl^{3+} \longrightarrow Ru(bipy)_3^{3+} + Tl^{2+} \quad (8)$$

Tl^{2+} is unstable and rapidly disproportionates to Tl^{3+} and Tl^{1+}. With many systems, quenching via an electron transfer mechanism can not be established simply by the reaction stoichiometry. For example, photolysis of $Ru(bipy)_3^{2+}$ in the presence of Fe^{3+} leads to no net chemical change.[8] Flash photolysis experiments, however, show an efficient electron transfer quenching reaction,[8] equation 9

$$*Ru(bipy)_3^{2+} + Fe^{3+} \xrightarrow{k=2\text{x}10^9 M^{-1}sec^{-1}} Ru(bipy)_3^{3+} + Fe^{2+} \quad (9)$$

followed by a rapid reverse reaction, equation 10.

$$Ru(bipy)_3^{3+} + Fe^{2+} \xrightarrow{k=5.2\text{x}10^6 M^{-1}sec^{-1}\ ^{9}} Ru(bipy)_3^{2+} + Fe^{3+} \quad (10)$$

Thus, the absence of electron transfer products does not necessarily negate the occurrence of an electron transfer process.

Unfortunately, the observation of electron transfer products does not in itself unambiguously establish the quenching mechanism. Alternatively, an energy transfer mechanism might be postulated.[2] The first step would be energy transfer from $*\mathrm{Ru(bipy)}_3^{2+}$ to Fe^{3+}, equation 11. A suitable acceptor state in Fe^{3+} lies at an energy of 12.3 kK.[2]

$$*\mathrm{Ru(bipy)}_3^{2+} + \mathrm{Fe}^{3+} \xrightarrow{k_{11}} \mathrm{Ru(bipy)}_3^{2+} + *\mathrm{Fe}^{3+} \qquad (11)$$

If one further assumes that $*\mathrm{Fe}^{3+}$ is a strong oxidant, equation 11 could be followed by an electron transfer reaction, equation 12.

$$*\mathrm{Fe}^{3+} + \mathrm{Ru(bipy)}_3^{2+} \xrightarrow{k_{12}} \mathrm{Fe}^{2+} + \mathrm{Ru(bipy)}_3^{3+} \qquad (12)$$

The products are the same in both quenching schemes, but the dynamics of the two schemes are different. In the first scheme, equations 9 and 10, the oxidation of the $*\mathrm{Ru(bipy)}_3^{2+}$ would take place at the same rate as the quenching reaction. In the second scheme, however, if $k_{12} < k_{11}$, the rate of oxidation of $*\mathrm{Ru(bipy)}_3^{2+}$ would be less than the quenching rate. Thus, kinetically the reaction mechanisms can be distinguished. Of course, if $k_{12} > k_{11}$, an experimental distinction between the two schemes would not be possible. Lin and Sutin, however, have used an ingenious series of steady state experiments which provide strong evidence for first scheme.[10] It was suggested by these investigators " that most (if not all) of the quenching events result in net electron transfer from the excited ruthenium(II) to the iron(III)."

(3) Spin Catalyzed Deactivation

Spin catalyzed deactivation is a special case in which a radiationless transition to the ground state of the donor is enhanced by quencher, yet energy transfer to the quencher does not occur. As pointed out by Wilkinson, a spin catalyzed deactivation of an organic triplet donor, $^3D^*$, by a quencher, Q, of spin multiplicity m, can be described by equation 13.[11]

$$^3D^* + {}^mQ \rightleftharpoons {}^m(D^*.Q) \longrightarrow {}^m(D.Q) \longrightarrow {}^1D + {}^mQ \qquad (13)$$

$$m \geq 2$$

Most organic molecules have singlet ground states and this quenching process is forbidden according to Wigner's spin conservation rules. The multiplicities of paramagnetic transition metal ions and complexes, on the other hand, are greater than 1. In the presence of such a complex or ion, the normally spin-forbidden change from triplet to ground state singlet of an organic donor will be permitted, and quenching may occur without energy transfer between the two. The rate of donor deactivation will be dependent on the degree of spin-spin coupling between donor and quencher, and the lifetime of the encounter complex, (D·Q).[11] An additional statistical term is introduced which accounts for the probability that (D·Q) has a spin momentum which correlates with the ground-state products of D and Q.[11] The larger the spin-spin coupling within the encounter complex, the more efficient the quenching. Quenching of triplet naphthalene by a number of transition metal ions in water was rationalized on this basis.[12] However, the lack of correlation between the quenching rate constants and spin multiplicities of the quenchers suggests an alternative mechanism.[2] For example, low energy states of the quencher ions indicated that quenching by energy transfer is possible. It has been suggested that the quenching of triplet naphthalene by transition metal ions is not due to spin-catalyzed deactivation, but rather the more conventional energy transfer mechanism.[2] Although accepted as a plausible quenching mechanism, the process of spin catalyzed deactivation remains to be unequivocally demonstrated.

(4) External Heavy-Atom Effect

Although similar to spin-spin catalyzed deactivation, the external heavy atom effect is attributed to spin-orbit coupling. With quenchers of high atomic number, radiationless deactivation of the excited donor can be enhanced by a spin-orbit coupling mechanism.[2] A radiationless transition, which is normally spin forbidden, may then have a non-zero probability due to this spin-orbit coupling. The effect is short ranged, however, and requires a quencher of high atomic number in close proximity to the donor. For example, the quenching of naphthalene by propyl chloride, propyl bromide and propyl iodide is attributed to this effect.[1] For the quenching of organic donors by first row transition metal ions or complexes, this effect is expected, but has not been experimentally demonstrated. For the quenching of the excited states of transition metal complexes, however, the external heavy atom effect is thought to be small.[13] Since spin-orbit coupling falls off rapidly with distance, the spin-orbit coupling induced by an external heavy atom would be small in comparison to that due to the metal ion of the complex. Thus, an external heavy atom is thought to have little effect on the decay of the excited state of a transition metal complex.

(5) Exciplex Formation

An exciplex is an excited molecular complex of definite stoichiometry.[1] The complex exists only during the lifetime of the excited state and dissociates on relaxation to the ground state. The formation of the exciplex may be followed by physical or chemical processes, such as exciplex emission, or chemical reaction.[2] In some organic systems, the formation of a dimer through a reaction involving the excited singlet state has been attributed to exciplex formation.[1] The appearance of a new emission at 560-nm led Balzani and coworkers to suggest the formation of an exciplex in the quenching of the charge-transfer luminescence of cis-Ir(phen)$_2$Cl$_2^+$ by naphthalene.[14] Recently, however, these results have been questioned. In the absence of a characteristic emission, exciplex formation is difficult to demonstrate experimentally. For cases involving coordination compounds, little evidence of exciplex formation is available.

In dealing with organic moleucles in fluid solutions, it has generally been found that electronic energy transfer is nearly diffusion controlled when spin and energy requirements are satisfied.[4a,15] This is not generally true, however, when transition metal complexes are involved.[2] When one of the partners is a transition metal complex, the quenching rate constants may be three orders of magnitude less than the diffusion controlled rate. Even lower rates are found when both the donor and acceptor are transition metal complexes, indicating that there are characteristics of transition metal complexes which reduce the quenching efficiency. A priori, these factors may include the nature of the metal and/or ligand, ionic charge, the orbital nature of the excited states involved, the geometry of the complex, the coordination number and solvation of the complex. Few experimental results are available, however, and it is impossible to assess the role played by each one of these factors.

It has been shown that large ligand effects are involved in determining the quenching efficiency of a complex.[16] Insulating ligands, such as ethylenediamine, en, trismethylenediamine, tn, and ammonia, NH_3, decrease the quenching efficiency. On the other hand, delocalized ligands, such as cyanide, CN^-, thiocyanate, SCN^-, 1,10-phenanthroline, phen, and acetylacetone, acac, appear to enhance the quenching efficiency of the complex. Balzani and coworkers have investigated the quenching of $Ru(bipy)_3^{2+}$ by the isomers of $Cr(en)_2XY^+$.[17] Within this series of Cr(III) complexes, the quenching ability increases in the series $F^- < Cl^- < NCS^- < Br^-$. They suggest this behavior is determined by the conducting ability of the ligands. One might expect that the ligand's conducting ability is correlated with its ability to expand the d orbitals of the metal ion. The ability of the ligand to expand the d orbitals of a metal ion is denoted by the nephelauxetic series.[3a] The authors noted, however, the order of increasing quenching ability does not coincide with the nephelauxetic series.

In the quenching study of phosphorescence of some chromium(III) complexes by molecular oxygen,[18] it was found that Cr(acac)$_3$ was quenched at essentially a diffusion controlled rate, $k = 10^{11}M^{-1}sec^{-1}$, whereas $Cr(CN)_6^{3-}$ and $Cr(NCS)_6^{3-}$ are quenched at considerable lower rates, $k = 2x10^8M^{-1}sec^{-1}$ and $6x10^9M^{-1}sec^{-1}$. It was suggested that the difference in the quenching rates was due to differences in the solvation of the complexes. In the mixed CH_3OH-H_2O solvent, Cr(acac)$_3$, being neutral, is not hydrated to any appreciable extent. $Cr(CN)_6^{3-}$ and $Cr(NCS)_6^{3-}$ are hydrated and this hydration sphere is thought to insulate the complex and decrease the rate of quenching by O_2.

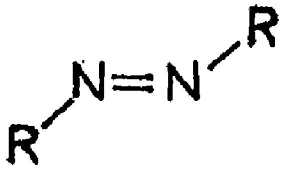
Quenching of anthracene and naphthalene triplets by Co^{2+} ion in mixed aqueous-organic solvents has also been studied.[19] In mixed THF-H_2O solvents, the rate constant for quenching of the anthracene triplet passes through a deep minimum as the solvent composition is changed from an aqueous to an organic solvent. Similarly, in aqueous-alcohol and aqueous-ether solvents, the rate constants for quenching of the naphthalene triplet also went through a minimum as the concentration of organic component of the solvent increased. The depth of the minimum increased in the order $CH_3OH < CH_3CH_2OH < (CH_3)_2CHOH < (CH_3)_3COH$. In ether-THF and ether-dioxane mixed solvents, the minimum found with THF was deeper than that found with dioxane. In the THF-CH_3OH mixtures, however, the quenching rate constant varies little with solvent composition. The results were ascribed to differences in the solvation of the donor and the Co^{2+} ions; the donor was solvated by the organic component of the solvent, whereas the Co^{2+} ion was solvated by the aqueous component. These different environments, one hydrophobic and one hydrophilic, then hindered the close approach of the two species.

Similar results were obtained in a study of the quenching of the triplet state of diphenylketone and its derivatives by Eu^{3+} ion.[20] It was found that varying the solvent from dimethyl ketone to methanol decreased the quenching rate. In methanol, Eu^{3+} ion is more highly solvated and the enhanced solvation decreases the rate by hindering the orbital overlap between the donor and the Eu^{3+} ion.

In general, the role of the solvent in the quenching processes has not yet been clarified, but the effects of solvation are known to be very important, especially for "uncomplexed ions" such as those of rare earths.[2]

In solution, organic donors and quenchers undergo triplet energy transfer by the collisional electron exchange mechanism.[21] Since the effect is short ranged, it would be expected to be sensitive to the steric environment of the donor and acceptor chromophores. Although steric effects are expected to be important in energy transfer, the few studies which have explicitly sought the effect have yielded contradictory results.

Wamser and coworkers studied the steric effect in singlet and triplet energy transfer to azo compounds,[21] I.



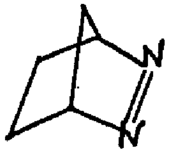
I

R = n-butyl
iso-butyl
sec-butyl
tert-butyl

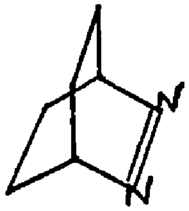
The rate constants for quenching of nine triplet sensitizers by the series of four azobutanes decreased in the order n-butyl > iso-butyl > sec-butyl > tert-butyl. The largest decrease in quenching rate constants, k_q, usually occurs between azo-sec-butane and azo-tert-butane. They attributed this trend to a steric effect on triplet energy transfer. By inspection of molecular models of the trans-azobutanes, access to the n or π electrons of the azo group is only slightly changed between azo-n-butane and azo-iso-butane. Some steric hindrance is introduced in azo-sec-butane, where two alkyl groups are attached to the α-carbon, but the largest difference occurs when a third alkyl group is added to the α-carbon. Except for a small number of rotational isomers, access to the π electrons of the azo chromophore is substantially blocked in the azo-tert-butane. The n electrons remain somewhat more approachable, but the greatest change in their steric environment also occurs between azo-sec-butane and azo-tert-butane.

Since substitution of alkyl groups on the α-carbon increases the electron density of the azo chromophore, an alternative explanation based on inductive substituent effects has been considered. This explanation, however, is not consistent with the observation that azo-tert-butane and azobis(isobutyronitrile), which are sterically similar, but electronically very different, show similar quenching rate constants. In fact, azobis(isobutyronitrile) is less efficient than azo-tert-butane in quenching of various triplet donors. This was explained by the electron-withdrawing effect of the cyano substituent. If this electron withdrawal causes the n and π orbitals of the azo group to be less extended in space, it would require a closer approach of the azo chromophore to the triplet donor. Within this hypothesis, inductive effects induce steric effects and a clear distinction between the two can not be made. The observed trend in k_q, however, is the same for a wide variety of sensitizers such as aryl and alkyl ketones, aromatic hydrocarbons and α-diketones. If the inductive factors were predominant, proceeding from primary to secondary to tertiary alkyl substituents would be expected to smoothly increase k_q. The latter was not observed, however, and the generality of the trend would seem to favor an interpretation of these results in terms of steric rather than electronic factors.

The molecules, 2,3-diazobicyclo[2,2,1]-2-heptene, II, and 2,3-diazobicyclo[2,2,2]-2-octene, III, have steric factors only in the cis configuration about the azo chromophore.



II



III

Unlike the above trans azo compounds, one side of the chromophores is always open in this cis configuration. If only steric considerations are important in determining the quenching efficiency, II and III should be as efficient as the structurally unhindered azo-n-butane. Wamser and coworkers have found that II and III quench high energy triplet donors as efficiently as azo-n-butane and concluded that structural factors are important.[21]

Of the quenchers studied by these workers, azobenzene (in structure I, $R = C_6H_5$) was found to be the most efficient. The high efficiency could be due to the conjugation of the aromatic rings with the azo chromophore. Conjugation would have two effects, both of which would increase k_q. First, conjugation lowers the triplet energy and, second, it increases the size of the chromophore making it more accessible for collisional energy transfer.

In the cases where singlet energy transfer occurs through an exchange interaction, steric effects have been found to be significant in the vapor phase,[22] but insignificant in solution.[23] For example, quenching of naphthalene fluorescence by azo-n-butane and azo-tert-butane shows a steric factor of 9.5 in the vapor phase.[22] Whereas in solution, quenching of a series of related donors yield steric factors of 1.7 to 2.9.[21] The steric factors quoted here are the ratio of k_q for an unhindered quencher relative to that for a hindered quencher. In solution, the observed rate constant for quenching is rarely equal to the rate constant for energy transfer. From studies in the gas phase, the latter is generally taken to be $> 10^{10}$.[21] If the same rate is assumed in fluid solution, k_q is limited by the rate of diffusion to form the encounter complex. A generalized scheme for energy transfer in solution is shown in equation 14.

$$D^* + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (D^* \cdot Q) \xrightarrow{k_{et}} D + Q^* \qquad (14)$$

where $(D^* \cdot Q)$ is an encounter complex in which many collisions can occur. The lifetime of the complex and thus the number of collisions depends directly on the viscosity of the solution. The observed quenching constant, k_q, is given by

$$k_q = k_d \cdot k_{et} / (k_{-d} + k_{et}) \qquad (15)$$

where k_{et} is the rate constant of energy transfer and k_d and k_{-d} are given by equations 1-5. Within this model, the effect of steric factors on singlet quenching can be accounted for. In solution differences in k_{et} may be masked by the large number of collisions before the donor and quencher can diffuse out of the solvent cage. For very efficient energy transfer processes, the rate-limiting diffusion step exerts a leveling effect on the observed quenching rate. In the vapor phase, however, changes in k_{et} are directly reflected in the measured k_q values. Since a solvent cage does not exist in the vapor, the encounter can be considered to be a single collision.

The experimental results obtained in solution for the quenching of the triplet states were compared to the theory of exchange energy transfer. According to Dexter's formulation,[24]

$$k_{et} \propto \exp(-2R/L) \qquad (16)$$

where L is the effective average Bohr radius for the initial and final electronic states of the donor and acceptor, usually taken to be 1Å,[25] and R is the distance of separation of the donor and acceptor. Using the van der Waals radii of methylene, 2.23Å, and of tert-butyl, 3.15Å, it is calculated that azo-n-butane will be 0.92Å closer to the π face of the donor than azo-tert-butane. Using a ΔR of 0.92Å in equation 16, the ratio of k_{et}' for azo-n-butane to that for azo-tert-butane is calculated to be 6.3. Using this ratio of 6.3 in equation 15, the ratio of the k_q's is calculated to be 4.5.[21] The steric factors observed for the quenching of three aromatic triplet sensitizers; 3.6 for naphthalene, 6.3 for 1,4-dibromonaphthalene, and 10.7 for triphenylene, are claimed to bracket the calculated value of 4.5. Similarly, the steric factors for the ketone triplet donors; 5.5 for acetone, 3.3 for acetophenone, 4.4 for benzophenone, and 5.0 for biacetyl, also bracket the theoretical value. This agreement with the theoretical model seems to suggest that quenching requires a close contact between the donor and quencher and that the contact is sensitive to molecular structure.

Ouannés and coworkers have studied the development of optical activity in *trans*-1,2-diphenyl-cyclopropane, *trans*-DPC, when R-(-)3-methyl-1-indanone was irradiated in the presence of a racemic mixture of *trans*-DPC.[26] They proposed a reaction mechanism, equations 17 through 24, in which the development of optical activity was due to differences in the rate of quenching by two enantiomers.

$$D \xrightarrow{h\nu} {}^1D^* \longrightarrow {}^3D^* \tag{17}$$

$${}^3D^* \longrightarrow D \tag{18}$$

$${}^3D^* + \text{t-DPC} \xrightarrow{k_{qt}} T^* + D \tag{19}$$

$${}^3D^* + \text{t}'\text{-DPC} \xrightarrow{k_{qt'}} T^* + D \tag{20}$$

$$^{3}D^{*} + c\text{-}DPC \xrightarrow{k_{qc}} T^{*} + D \qquad (21)$$

$$T^{*} \xrightarrow{k_{t}} t\text{-}DPC \qquad (22)$$

$$T^{*} \xrightarrow{k_{t'}} t'\text{-}DPC \qquad (23)$$

$$T^{*} \xrightarrow{k_{c}} c\text{-}DPC \qquad (24)$$

In this scheme t and t' represent the enantiomers of *trans*-DPC, whereas c represents the optically inactive *cis*-isomer of DPC. T* is a triplet diradical intermediate which may be symmetric or a set of rapidly equilibrating optically active structures. Within this hypothesis, $k_t = k_{t'}$ and the development of optical activity in the products is due to differences in the quenching rates, *i.e.*, $k_{qt} \neq k_{qt'}$. From the value of the optical rotation at the photo-stationary state, the ratio $k_{qt}/k_{qt'}$ was calculated as 1.06.[27] The development of optical activity shows that in the transfer step, equations 19 and 20, there exists some kind of diastereoisomeric relationship between the enantiomers of *trans*-DPC and the sensitizer, (R)-(-)-3-methyl-1-indanone. This may imply a preferential orientation of sensitizer and substrate to allow maximum π-overlap.[28]

The results discussed above suggest that steric effects play some role in determining quenching efficiency.

As mentioned above, however, the results are contradictory in that other experiments suggest that steric factors are not important. For example, the quenching of the type-II photocyclization of the hindered α,α-dimethylvalerophenone and unhindered valerophenone by 2,5-dimethyl-2,4-hexadiene and 2-chloronaphthalene suggests little discrimination on the basis of molecular structure.[25a] Since the Stern-Volmer constants obtained for the quenching of the hindered and unhindered ketones vary with solvent viscosity in a parallel fashion, the authors concluded that energy transfer is indifferent to molecular structure. The authors did note, however, that the quenching of α,α-dimethylvalerophenone by 2,5-dimethyl-2,4-hexadiene, a hindered quencher, as compared to 2-chloronaphthalene or 1,3-pentadiene, unhindered quenchers, does show a slight steric factor of 1.3 to 1.5.

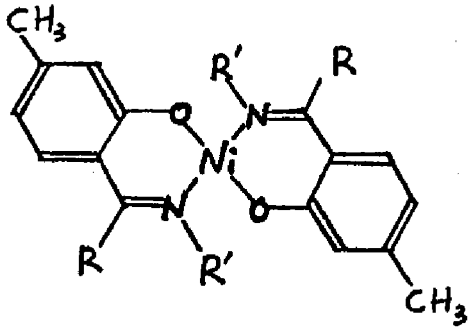
In an extensive study of exothermic singlet-singlet electronic energy transfer from ketones to α-diketones, Yekta and Turro conclude that except for cases where severe steric congestion exists, steric factors are unimportant.[23] They suggest instead that quenching rates are sensitive to the stabilities of cage complexes and the rotomeric populations of the quencher.

Although experiments with organic systems suggest the importance of structural effects, few systematic studies have been reported with coordination compounds.

Using a competitive kinetic method, Hammond and Foss showed that the acetylacetonate complexes were consistently more effective than the dipivaloylmethanate complexes in the quenching of the triplet state of benzophenone.[29] For example, $Fe(acac)_3$ and $Cr(acac)_3$ are 5.4 and 8.4 times more effective than $Fe(dpm)_3$ and $Cr(dpm)_3$. Most dramatic, however, are the results with the Co(III) complexes; $Co(acac)_3$ quenches triplet benzophenone whereas $Co(dpm)_3$ does not. These results led these investigators to suggest that the t-butyl groups in dipivaloylmethanates are a steric hindrance by shielding the unsaturated part of the ligands.

Wilkinson and Farmilo studied the quenching of triplet states of sixteen organic compounds by tris-(beta-diketonate) complexes of Iron(III), Ruthenium(III), and Aluminum(III).[30] As the energy level of the donor approaches an energy level of the metal complex, there is a marked rise in the quenching rate. The quenching efficiency remains constant until the energy of the donor exceeds the energy of the next excited state of the complex. At this point an increase in efficiency is again observed. This characteristic dependence on the energy of the donor and on the energy levels of the complexes establishes energy transfer as the quenching mechanism. The quenching rate constant of $Fe(acac)_3$ is 3.2 times larger than that of Fe(dpm)$_3$ when the charge transfer state of the complex is available for quenching, and 4.5 to 6 times larger when the ligand-field states, $^4T_{2g}$ and $^4T_{1g}$, are available for quenching. These results suggest that steric factors are more important in a quenching encounter involving ligand-field states than in a quenching encounter involving charge-transfer or ligand centered states. Since ligand-field states are essentially metal-centered and embedded within a ligand sheath, a more intimate encounter would be required for energy transfer to occur. The intimacy of the encounter apparently magnifies steric differences.

Adamczyk and Wilkinson studied the quenching of a number of donors by various Schiff base complexes of Ni(II),[11] structure IV



IV

R	R'
CH_3	OH
$C_{11}H_{23}$	OH
CH_3	C_4H_9
$C_{11}H_{23}$	H
CH_3	$(CH_2)_2OH$

The quenching rates were essentially independent of the substituents except for complexes containing the hendecyl group, $C_{11}H_{23}$. The lower quenching efficiency for this substituent probably results from a lower diffusion coefficient. The quenching rates of these Ni(II) complexes are much larger than those of other octahedral coordination complexes, and may be due to the planar structure of the complexes. Since the complexes are planar, the d_{xz}, d_{yz}, and d_{z^2} orbitals, perpendicular to the plane of the molecule, allow a good donor-acceptor orbital overlap. Due to steric crowding, IV becomes a paramagnetic tetrahedral complex when R and R' are t-butyl groups. A paramagnetic octahedral complex, Ni(II)(Hen-sam-OH)$_2$(pyridine)$_2$, was prepared by adding pyridine to trans-planar Ni(II)(Hen-sam-OH)$_2$, where Hen denotes a hendecyl group substituted in the R position and OH in the R' position. For the high energy donor, benzophenone, the quenching rate constants are comparable regardless of whether the complex is tetrahedral, octahedral or trans-planar. For the low energy donor, 1,2-benzanthracene, however, the tetrahedral and octahedral complexes are less efficient than the trans-planar complexes. It was suggested that quenching of a high energy triplet donor is due to energy transfer to a ligand-localized triplet state, and orbital overlap for this type of energy transfer would not be critically dependent on the geometry of the complex. With the lower energy triplet donor, however, an overlap between the donor orbitals and the d orbitals of the metal ion is necessary. Since the d orbitals are more shielded when the ligand array is octahedral or tetrahedral, the complex would be expected to be a less efficient quencher.

Balzani and coworkers have reported the quenching of $Ru(bipy)_3^{2+}$ by cis- and trans-$Cr(en)_2XY^+$ isomers.[17] The quenching rate constant is dependent on ionic strength and the cis- isomers are generally more efficient quenchers than the corresponding trans-isomers. On extrapolation to zero ionic strength, the quenching rate constants of cis-$Cr(en)_2Cl_2^+$, cis-$Cr(en)_2(NCS)Cl^+$, and cis-$Cr(en)_2(NCS)_2^+$ are, respectively, 1.4,1.9 and 5.5 times larger than the corresponding trans- isomers. Although the authors claim these results indicate a structural effect, the results are ambiguous.

Unlike organic systems, in which alkylation of the chromophore causes little or no change in the absorption spectrum,[31] changes in the coordination sphere of a transition metal complex cause not only the desired structural changes, but concurrent changes in the electronic structure of the complex as well.[3a] With these $Cr(en)_2XY^+$ isomers, for example, changing the ligand configuration from cis- to trans- causes substantial changes in the electronic structure of the complex. Thus these experiments are ambiguous in that they do not clearly separate structural differences from electronic differences.

The results of the study of structural effects discussed above are summarized as follows:

(1) The study of the energy transfer to azo compounds led Wamser and coworkers to conclude that steric effects are important in triplet energy transfer in solution and singlet energy transfer in the vapor phase.

(2) The asymmetric induction observed during energy transfer by Ouannès and coworkers led to the suggestion that a preferential orientation of the sensitizer and quencher is required to allow maximum orbital overlap.

(3) Since the dependence on solvent viscosity was the same for hindered and unhindered donors, Wagner and coworkers concluded that steric effects are not important in triplet energy transfer.

(4) The study of singlet energy transfer from ketones to α-diketones also led Yekta and Turro to conclude that steric effects are not important for singlet energy transfer in solution.

(5) From the study of the quenching of benzophenone by acetylacetonate and dipivaloylmethanate complexes, Hammond and Foss suggested that steric effects are important in these quenching encounters.

(6) The study of the quenching of various triplet states by a number of beta-diketonate complexes led Wilkinson and Farmilo to conclude that steric effects are more pronounced in quenching by metal-centered ligand-field states than the ligand-centered or charge-transfer states.

(7) From the study of the quenching of various triplet organic donors by Schiff base complexes of Ni(II), Adamczyk and Wilkinson concluded that the geometry of the complex is important when quenching of a low energy donor involves a ligand-field state.

(8) Balzani and coworkers suggested that structural effects are important in the quenching of $Ru(bipy)_3^{2+}$ by the cis- and trans- isomers of $Cr(en)_2XY^+$.

It is clear from the above discussion that it is difficult to separate structural from electronic factors in quenching encounters which involve transition metal complexes. This difficulty gives rise to an ambiguity which clouds the interpretation of the results. It appears to be necessary that a series of metal complexes be used where structural modification can be made without a concurrent modification of its electronic structure. This requirement is met by the cis- and trans- geometric isomers of the unsymmetrically substituted beta-diketonate complexes.

Fay and Piper have shown that the geometric isomers of the unsymmetrically substituted beta-diketonates can be separated with relative ease by column chromatography.[32] Although the isomers differ in structure, their spectra and therefore their electronic structures are identical.[32] Characterization of the trivalent metal isomers by X-ray[33] and NMR techniques[34] have shown an octahedral arrangement of the ligands about the metal ion. The distinction between the isomeric forms, however, arises from differences in their outer structure. As indicated by Figure 1, the *cis*- isomer possesses a C_3 axis of rotation whereas the *trans*- isomer does not. Thus these isomers offer a unique opportunity to separate electronic and steric factors and to study the effect of the latter on the quenching encounter.

Figure 1

Cis- and *Trans*- Isomers of Asymmetric Beta-diketonate Complex

cis-isomer

trans-isomer

CHAPTER 2

Experimental

I. Materials

A. Preparation of Beta-Diketonate Complexes

a. Cis- and Trans- Trifluoroacetylacetonate Chelates of Cobalt(III) and Chromium(III)

The ligand, 1,1,1-trifluoro-2,4-pentanedione was obtained from Eastman Kodak Company. Tris(1,1,1-trifluoro-2,4-pentanedionato)cobalt(III), Co(tfac)$_3$, and tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III), Cr(tfac)$_3$, were prepared by the method of Fay and Piper.[32b] After refluxing for seven hours, the respective reaction mixtures were filtered and charged onto fluorisil columns. The dark green Co(tfac)$_3$ and dark purple Cr(tfac)$_3$ were eluted with 1:1 benzene-hexane and eluants evaporated to dryness. Since the cis- and trans- isomers have different solubilities in ethanol, a separation was possible. The dry Co(tfac)$_3$ or Cr(tfac)$_3$ residue was extracted with a 5 ml portion of warm ethanol (30°C). The extract, which principally contained the cis- isomer, was decanted off and evaporated to dryness. The residue, which contained principally the trans- isomer, was dissolved in benzene and refluxed for seven hours to convert some of the trans- isomer to the cis- form. The reaction mixture was again evaporated to dryness and the cis- isomer extracted with a warm 5 ml portion of ethanol. This procedure was carried out several times and the 5 ml extracts were combined. After evaporating the ethanol extracts to dryness, the residue was dissolved in 1:1 benzene-hexane and the final purification and separation were made on a 125cm x 2.8cm o.d. florisil column with 1:1 benzene-hexane as the eluting solvent. The eluted fraction was evaporated to dryness and recrystallized from benzene-pentane. The melting points of the recrystallized materials were in good agreement with those expected for these cis- isomers:[35] cis-Co(tfac)$_3$, literature value:127.5-128°C, found:123.5-125°C; cis-Cr(tfac)$_3$, literature value:125-126°C, found: 125-126°C.

The residue remaining after the ethanol extractions contained principally the trans- isomers. This residue was dissolved in 1:1 benzene-hexane and placed on the above florisil column. The trans- isomer was eluted with 1:1 benzene-hexane. The eluants were evaporated to dryness and the trans- isomer recrystallized from benzene-pentane. The melting points were in good agreement with those expected for these isomers:[35] trans-Co(tfac)$_3$, literature value: 158-159°C, found: 156-157°C; trans-Cr(tfac)$_3$, literature value: 154.5-155°C, found: 153.5-154°C.

b. Cis- and Trans- Benzoylacetonate Chelates of Cobalt(III) and Chromium(III)

The ligand, 1-phenyl-1,3-butanedione was obtained from Eastman Kodak Company, Tris(1-phenyl-1,3-butanedionato)cobalt(III), Co(bzac)$_3$, and tris(1-phenyl-1,3-butanedionato)chromium(III), Cr(bzac)$_3$, were prepared by the method of Fay and Piper.[32a] The cis- isomers were concentrated by repeated refluxing and extraction with ethanol and purified on the above florisil column using 19:1 benzene-ether as the eluting solvents. The eluants were evaporated to dryness and recrystallized from benzene-pentane mixtures. The melting points were in good agreement with the literature values:[35] cis-Co(bzac)$_3$, literature value: 158-159°C, found: 153.5-154°C; cis-Cr(bzac)$_3$, literature value: 197.5-198.5°C, found 197.5-198.5°C.

After the ethanol extractions, the residue containing the trans- isomer was dissolved in 1:1 benzene-hexane and placed on the florisil column. The trans- isomer was eluted with 19:1 benzene-ether. The eluants were evaporated to dryness and the trans- isomer recrystallized from a benzene-pentane mixture. The melting points of the trans- isomers were in good agreement with the literature values:[35] trans-Co(bzac)$_3$, literature value: 200.5-201.5°C, found: 203-203.5°C, trans-Cr(bzac)$_3$, literature value: 234-235°C, found: 234.5-235°C.

B. Ru(bipy)$_3$Cl$_2$·6H$_2$O and Ru(bipic)$_3$Cl$_2$·4H$_2$O

Tris(2,2'-bipyridine)ruthenium(II) chloride hexahydrate, Ru(bipy)$_3$Cl$_2$·6H$_2$O, was obtained from J. T. Baker Company and used without further purification. Its absorption and emission spectrum agreed with published spectra.[36]

Tris(2.2'-bi-4-picoline)ruthenium(II) chloride tetrahydrate, Ru(bipic)$_3$Cl$_2$·4H$_2$O,[37] was prepared by refluxing 1.73 g (9.4 mmole) of 2,2'-bi-4-picoline (J. T. Baker) and 0.5 g (1.9 mmole) of RuCl$_3$·3H$_2$O in 200 ml of 95% ethanol. After refluxing for 16 hours, the reaction mixture was evaporated to dryness. The dark orange-red product was taken up in 75 ml of hot water. The unreacted bipicoline was extracted with four 25 ml portions of benzene, and NaCl was added to the aqueous solution to precipitate the product. After cooling, dark red crystals were filtered off and dried by aspiration. Absorption and emission spectra of the product were essentially identical to those of Ru(bipy)$_3$Cl$_2$·6H$_2$O.

Anthracene, 9-methylanthracene, 9-phenylanthracene, pyrene and phenanthrene, purchased from Aldrich Chemical Company, were used without further purification, since the reported purity is greater than 98%. Spectral grade benzene (J. T. Baker) was used in flash experiments, whereas ethanol, chloroform, and formamide used in luminescence measurements were reagent grade.

II. Instrumentation and Photochemical Apparatus

A. Physical Measurements

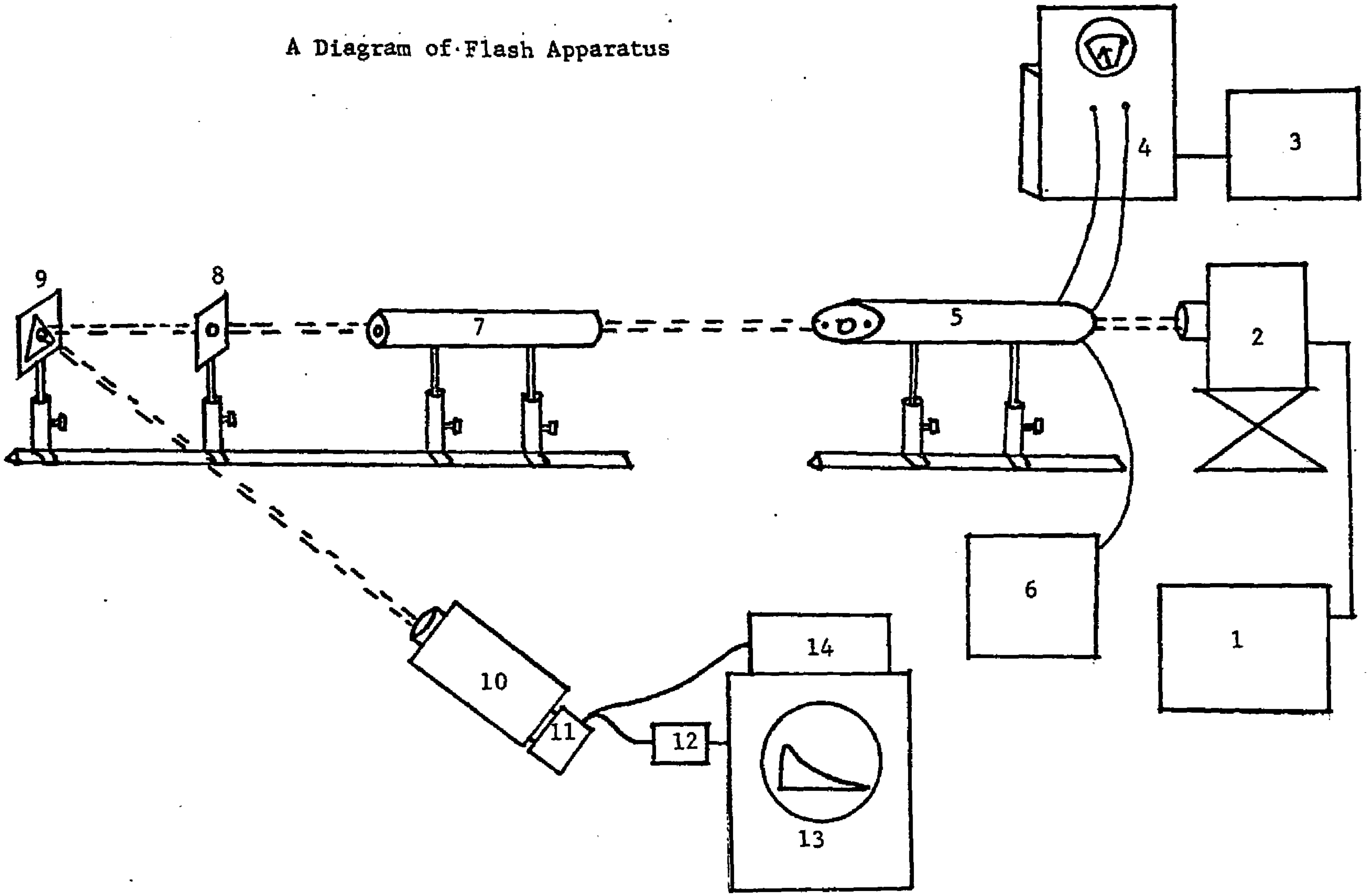
Ultraviolet and visible spectra were recorded on a Cary 14 or a Techtron 635 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer calibrated with a polystyrene film. NMR spectra were recorded on Varian EM360 NMR spectrometer. Luminescence measurements were recorded on a Perkin-Elmer Hitachi MPF-2A fluorescence spectrophotometer equipped with either a Hamamatsu R106 or a red sensitive Hamamatsu R818 photomultiplier. Fused quartz cells, a 10x10x40 mm cell, were used in luminescence measurement. The cells were equipped with a 14/20 ground glass joint and could be fitted to pyrex upper sections. The pyrex upper section had a vacuum stopcock and a 10 ml sidearm for degassing the solution by freeze-thaw techniques. The cell was connected through a 10/30 ground glass joint to a vacuum line. The vacuum line was equipped with an oil diffusion pump, and could be pumped down to a pressure of $\leq 10^{-5}$ torr.

B. Flash Experiments

The flash apparatus used in these experiments is of the general design described by Porter[38] and Linschitz[39] and used in a kinetic-spectrophotometric mode. A diagram of the flash apparatus is shown in Figure 2. The two flash lamps, Xenon Corp. Model FP-100C, are connected in series and across a Sangamo 10 μf capacitor by five inch cables to minimize circuit inductance. The capacitor is charged by a Spellman Model RG10 regulated high voltage power supply. The voltage applied to the capacitor could be varied to dissipate 100- to 500-J per flash. The photolyzing flash, triggered externally with a Xenon Corp. Model C trigger module, has a rise time of 5 μsec, and a half peak duration of 10 μsec, and a total duration of 25 to 30 μsec. Following the flash, the chemical change is detected by monitoring the change in intensity of a collimated beam of light from a 100-W high pressure Xe lamp powered by a Sola filtered DC power supply. The light beam from the Xe lamp is passed through the center of the reaction cell and light baffle onto a mirror which reflects the beam onto the entrance slit of a Bausch and Lomb Model 33-86-76 grating monochromator. The change in intensity of the analyzing beam at a given wavelength is then monitored by an RCA 31034 or Hamamatsu R818 photomultiplier tube powered by a Pacific Photometric Instruments Model 203 regulated negative high voltage power supply. The

Figure 2

A Diagram of Flash Apparatus



1. Lamp Power Supply
2. High Pressure Xe Lamp
3. High Voltage Power Supply
4. Capacitor
5. Sample Holder and Flash Lamps
6. Trigger Module
7. Light Baffle
8. Shutter
9. Reflecting Mirror
10. Monochromator
11. Photomultiplier
12. 150 kΩ Resistor
13. Oscilloscope
14. Photomultiplier Power Supply

photomultiplier current is dropped across a 150 kΩ resistor and the change in voltage as a function of time is displayed on a Hewlett-Packard Model 175A oscilloscope. The oscilloscope sweep is triggered by inductive coupling with the photolyzing flash. Although the RC time constant of the detection circuit is 3.2 μsec, the time resolution of the apparatus is ca. 25 μsec because of the flash duration. For precise kinetic measurements, however, the time resolution is longer due to a tail in the flash profile.

The solution to be flashed is contained in a fused quartz cell, Figure 3. The inner cylindrical sample compartment is 17cm x 1.2 cm diameter and surrounded by an outer annulus which is 20cm x 3.0 cm diameter. The flash cell is connected through a 10/30 joint to an upper section having a side-arm and vacuum stopcock. The apparatus could then be attached through a 10/30 joint to a vacuum line and the solution degassed by repeated freeze-thaw cycles.

C. Continuous Photolysis

An optical train, Figure 4, was assembled to measure the quantum yields. The light from a 350-W Illumination Industries high pressure Xenon-Mercury arc lamp was focussed onto the entrance slit of a Bausch and Lomb Model 33-86-68 grating monochromator. The wavelength scale of the monochromator was calibrated

Figure 3

A Diagram of Flash Cell

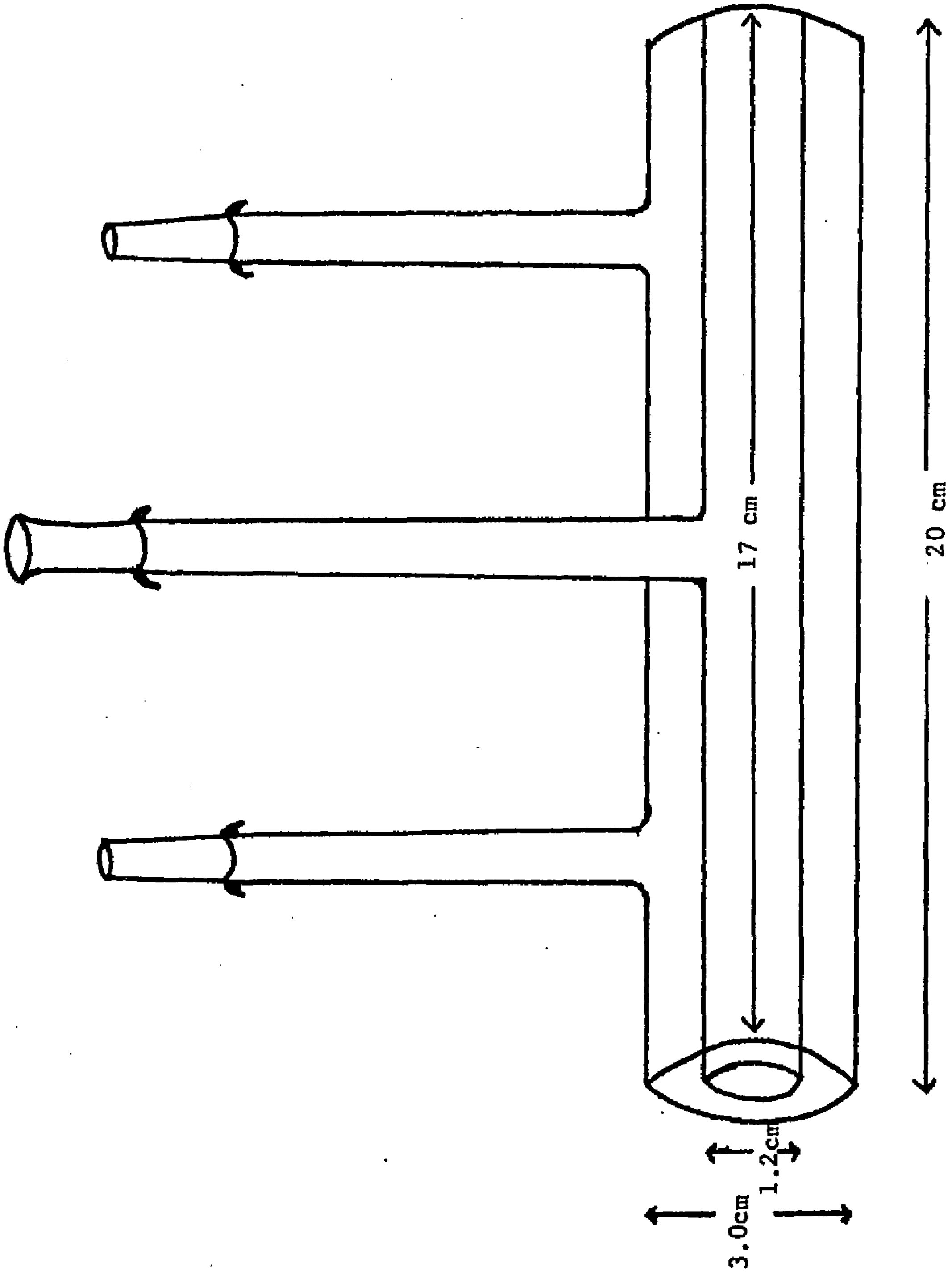
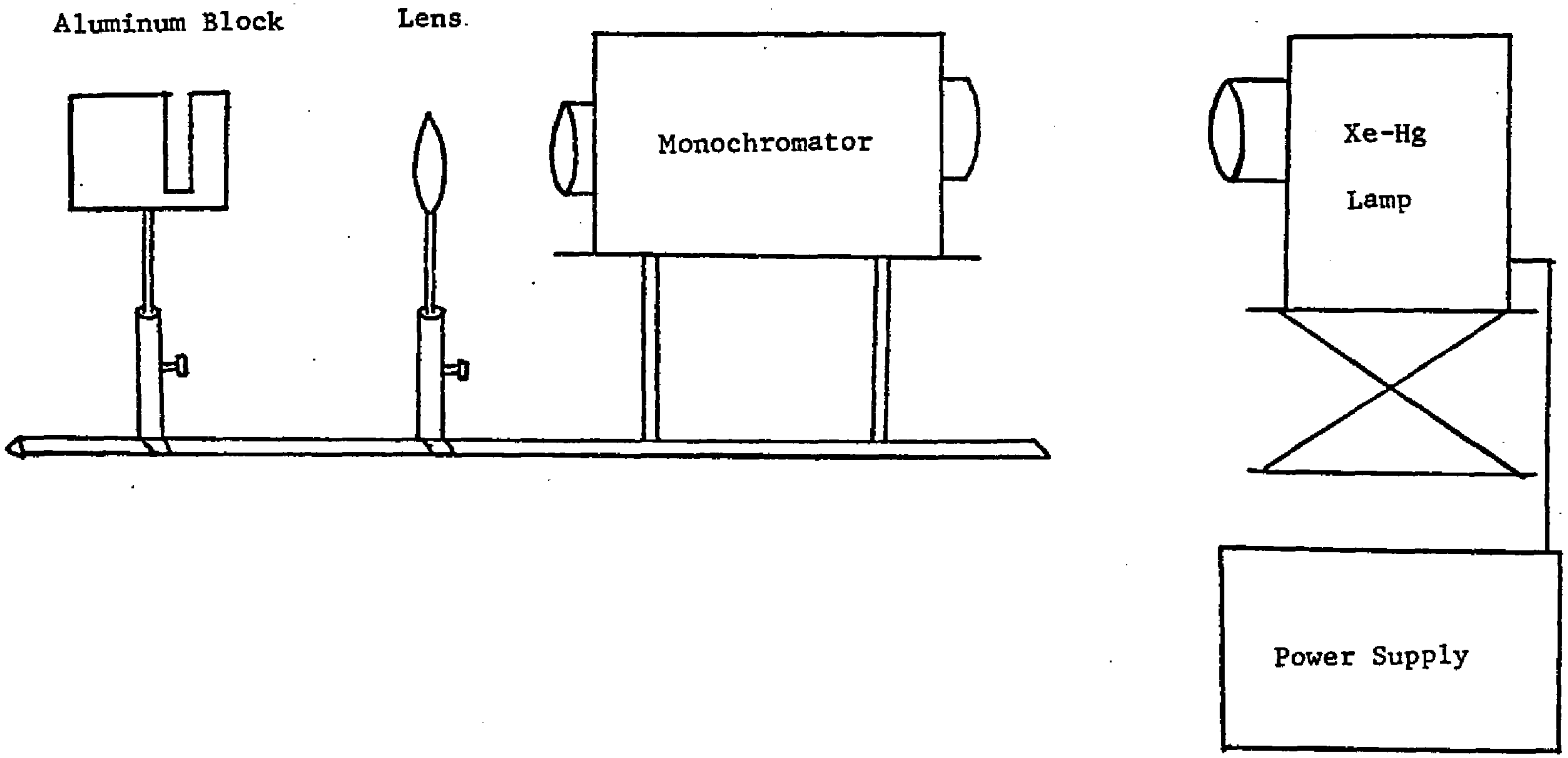


Figure 4

A Diagram of Optical Train



with a low pressure mercury lamp by a procedure adapted from the calibration of a Beckman DU spectrophotometer.[40] The entrance slit, 3.48 mm and exit slit, 1.40 mm were calculated from the manufacturer's reported dispersion of the grating to yield 90% of the radiation within a 10-nm band pass. The light from the monochromator was focussed onto the photolysis cell, mounted in an aluminum block, with a quartz lens.

The reaction cell, a 10 x 10 x 40 mm, fused quartz cell was described in part A.

III. Procedure

A. Quenching of $Ru(bipy)_3^{2+}$ and $Ru(bipic)_3^{2+}$ by the Beta-diketonate Isomers

a. Luminescence Measurements

In the luminescence quenching study, stock solutions containing 10^{-4}M $Ru(bipy)_3Cl_2 \cdot 6H_2O$ or $Ru(bipic)_3Cl_2 \cdot 4H_2O$ in ethanol were used. Ethanol stock solutions of trifluoroacetylacetonate isomers were prepared as needed. Due to the limited solubility in ethanol, however, stock solutions of the <u>cis</u>- and <u>trans</u>-isomers of $Co(bzac)_3$ and $Cr(bzac)_3$ were prepared with chloroform. From these stock solutions, a series of solutions, 10^{-4}M in the Ru(II) complexes and varying concentrations of the <u>cis</u>- or <u>trans</u>- isomers were prepared by diluting the appropriate aliquots with ethanol. The maximum quencher concentrations used in these experiments were 2.5×10^{-3}M in $Cr(tfac)_3$, 10^{-3}M in $Cr(bzac)_3$, 10^{-3}M in $Co(tfac)_3$, 6×10^{-4}M in $Co(bzac)_3$. These concentrations were chosen such that at least 80% of the exciting light was absorbed by donor. Fused quartz cells equipped with degassing bulb were used. Four ml of solution was transfered to the degassing bulb and degassed by three freeze-thaw cycles.

To determine the uncertainty associated with the transmission characteristics of the different cells as well as various pairs of cell faces, the emission intensity of a degassed ethanol solution containing 10^{-4}M $Ru(bipy)_3^{2+}$ was measured at 588-nm. The maximum difference between the cells and pairs of cell faces was 18%. To minimize this uncertainty all measurements were made with specific pairs of faces of the different cells so that the maximum uncertainty was 8.1%.

Samples containing $Ru(bipy)_3^{2+}$ were excited at 452-nm and the emission intensity monitored at 588-nm. With $Ru(bipic)_3^{2+}$, the samples were excited at 460-nm and the emission monitored at 590-nm. The observed emission intensities were corrected for the trivial absorption of the exciting and emitted light by a previously described equation,[41] equation 25.

$$\left(\frac{I_o}{I}\right)_{corr} = \left(\frac{I_o}{I}\right)_{app} \times \frac{A_D}{A_D + A_Q} \times \frac{1 - 10^{-(A_D + A_Q)}}{1 - 10^{-A_D}} \times 10^{-0.5A_Q'} \qquad (25)$$

where I_o represents the emission intensity in the absence of the quencher and I represents the emission intensity in the presence of the quencher. $(I_o/I)_{corr}$ is the corrected ratio of I_o and I and $(I_o/I)_{app}$ is the measured ratio of I_o and I. The other variables in the equation represent the absorption of the donor at the exciting wavelength, A_D, and the absorption of the quencher (assuming a 1 cm path length) at the exciting and emitting wavelengths, A_Q and A_Q' , respectively.

Although these equations involve approximations, it is important to realize that the absorption spectra of both isomers are identical at the excitation and emission wavelengths. Thus potential differences in the Stern-Volmer constants, K_{SV}, obtained with each pair of isomers are not tainted by these corrections. With trifluoroacetylacetonate chelates, absolute ethanol was used as the solvent. The benzoylacetonate chelates, however, are only slightly soluble in ethanol and it was necessary to use 10% chloroform (by volume) in ethanol as the solvent. Chloroform solutions of $Ru(bipy)_3^{2+}$ change color from red-orange to purple when allowed to stand under room light for 3 to 4 days.[74] In 10% chloroform-ethanol solutions, however, spectra of a 10^{-4}M $Ru(bipy)_3^{2+}$ solution recorded periodically showed no detectable change over a three hour period. Nor was any change in the emission intensity of the solution detected over the same time period.

b. Photochemical Experiments

Since the luminescent charge transfer states of these Ru(II) complexes are known to be strong reducing agents,[42] a number of photochemical experiments were carried out to determine if the quenching reaction leads to the formation of electron transfer products. Degassed solutions containing 10^{-4}M $Ru(bipy)_3^{2+}$ and 10^{-3}M _cis_- or _trans_-$Co(tfac)_3$ (or 5 x 10^{-4}M $Co(bzac)_3$) were irradiated at 452-nm (86% of the light is absorbed by Ru(II) complex). The amount of cobalt(II) generated in the photolysis was determined colorimetrically with ammonium thiocyanate.[43] In a 10-ml volumetric flask, a 3ml aliquot of the photolyzed solution and a 1ml aliquot of 6M ammonium thiocyanate, were diluted to volume with acetone. A 3ml aliquot of the unphotolyzed solution was treated in the same manner and the absorbance of the photolyzed sample relative to that of the unphotolyzed sample was measured at 625-nm. The molar extinction coefficient of the $Co(SCN)_4^{2-}$ complex at 625-nm is 1.81 x 10^3 l/mol-cm.[44]

An unusual aspect of an excited state electron transfer reaction of these Ru(II) complexes is that the strong reductant, $*Ru(bipy)_3^{2+}$, is converted on electron transfer to a strong oxidant, $Ru(bipy)_3^{3+}$[45] (The reduction potential of $Ru(bipy)_3^{3+}$ is 1.24V in 1M acid.). Thus, as discussed in the introduction, quenching via electron transfer may be followed by a rapid reverse reaction which leads to no net chemical change. To explore this possibility, a number of flash photolysis experiments were carried out. Ethanol solutions, 10^{-5}M in $Ru(bipy)_3^{2+}$ and 2 x 10^{-4}M in $Co(tfac)_3$, were degassed by three freeze-thaw cycles and exposed to 250-J unfiltered flashes. The flashed solutions were analyzed at 675-nm, the absorption maximum of $Ru(bipy)_3^{3+}$,[45a] and in the 480 to 550-nm region where $Co(acac)_2$ absorbs.[46]

B. Quenching of Organic Triplets by Beta-diketonenate Isomers

The general procedure in studying the quenching of various triplets by these isomers was to prepare benzene stock solutions containing ca. 2 x 10^{-3}M of the various donors. In this work, the donors used were anthracene, 9-methylanthracene, 9-phenylanthracene, pyrene and phenanthrene. These stock solutions were kept in dark and refrigerated. The absorption spectra were checked periodically, but no change was detected. Solutions of beta-diketonate complexes were always freshly prepared. In a typical flash experiment, solutions containing 4 x 10^{-5}M of the donor and 10^{-6}M to 10^{-5}M of the quencher were prepared by dilution of the stock solutions and transferred to the degassing bulb of the flash cell. The flash cell was then connected to the vacuum line and the solution degassed by nine freeze-thaw cycles.

Since the triplet states of these donors are efficiently and rapidly quenched by molecular oxygen,[1,47] a number of tests of the cell were carried out to ensure that O_2 could not leak into the degassed sample. In these tests, the empty cell and degassing bulb were attached to the vacuum line and evacuated to a pressure of 5 x 10^{-6}mm of Hg. The cell was closed off and allowed to stand for approximately 4 hours. After which the cell and degassing bulb were returned to the vacuum line and the pressure within the cell was remeasured. Within experimental error, however, no increase in pressure was found within the cell or degassing arm.

Following the freeze-thaw cycles, the cell was closed off, removed from the vacuum line, and placed in the flash apparatus. Various parameters, such as photomultiplier voltage, slit width, and alignment of the analyzing beam, were optimized to obtain a full scale deflection on the oscilloscope graticle. The flash was then triggered and the oscilloscope trace was photographed with a Polaroid oscilloscope camera. The kinetic data, i.e. the absorbance of the triplet state as a function of time, were taken from the Polaroid photograph.

CHAPTER 3

RESULTS

(I) Quenching of $Ru(bipy)_3^{2+}$ and $Ru(bipic)_3^{2+}$

(a) Absorption and Emission Spectra

As previously mentioned, the unsymmetrical substituted beta-diketonate complexes of Co(III) and Cr(III) can be separated into their geometric isomers. The chromatographic separation is based on slight differences in the dipole moments of the isomers. Although the difference in the dipole moments of the isomers is due to differences in the molecular structure, the electronic absorption spectra of the isomers are essentially identical. The absorption spectra of the cis- and trans- isomeric forms of $Co(tfac)_3$, $Co(bzac)_3$, $Cr(tfac)_3$ and $Cr(bzac)_3$ are shown in Figures 5 through 12. These spectra show that the energies of transitions, and to a first approximation, the energies of the various excited states are identical. It is not readily apparent from the absorption spectra, however, that there are slight differences in the molar extinction coefficients. Thus, the molar extinction coefficients of the various pairs of cis- and trans- isomers are listed in Table I.

Since the band maxima in the absorption spectra reflect the vertical Franck-Condon transitions, the

Figure 5

Absorption Spectrum of Trans-Co(tfac)$_3$ in Ethanol

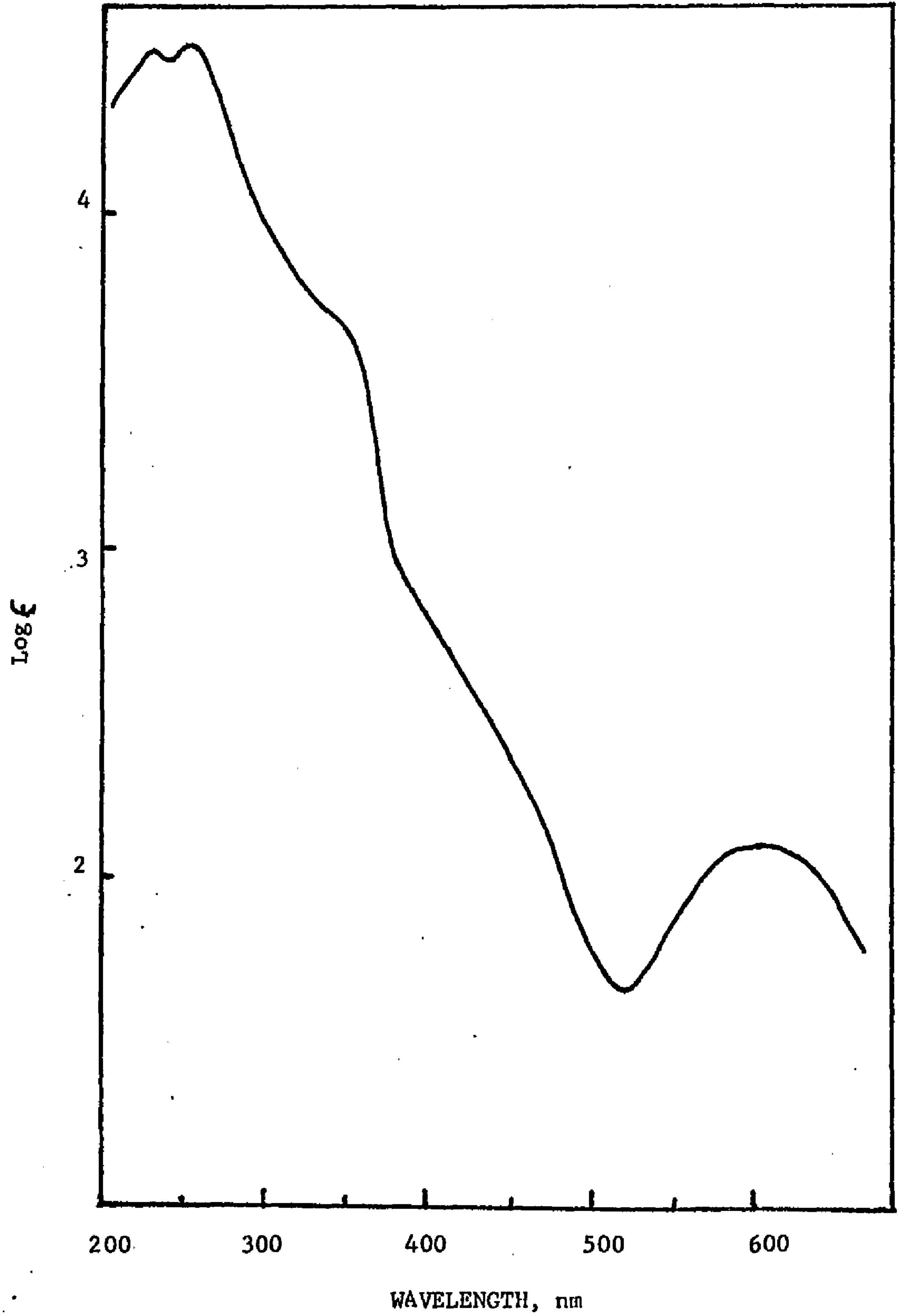


Figure 6

Absorption Spectrum of Cis-Co(tfac)$_3$ in Ethanol

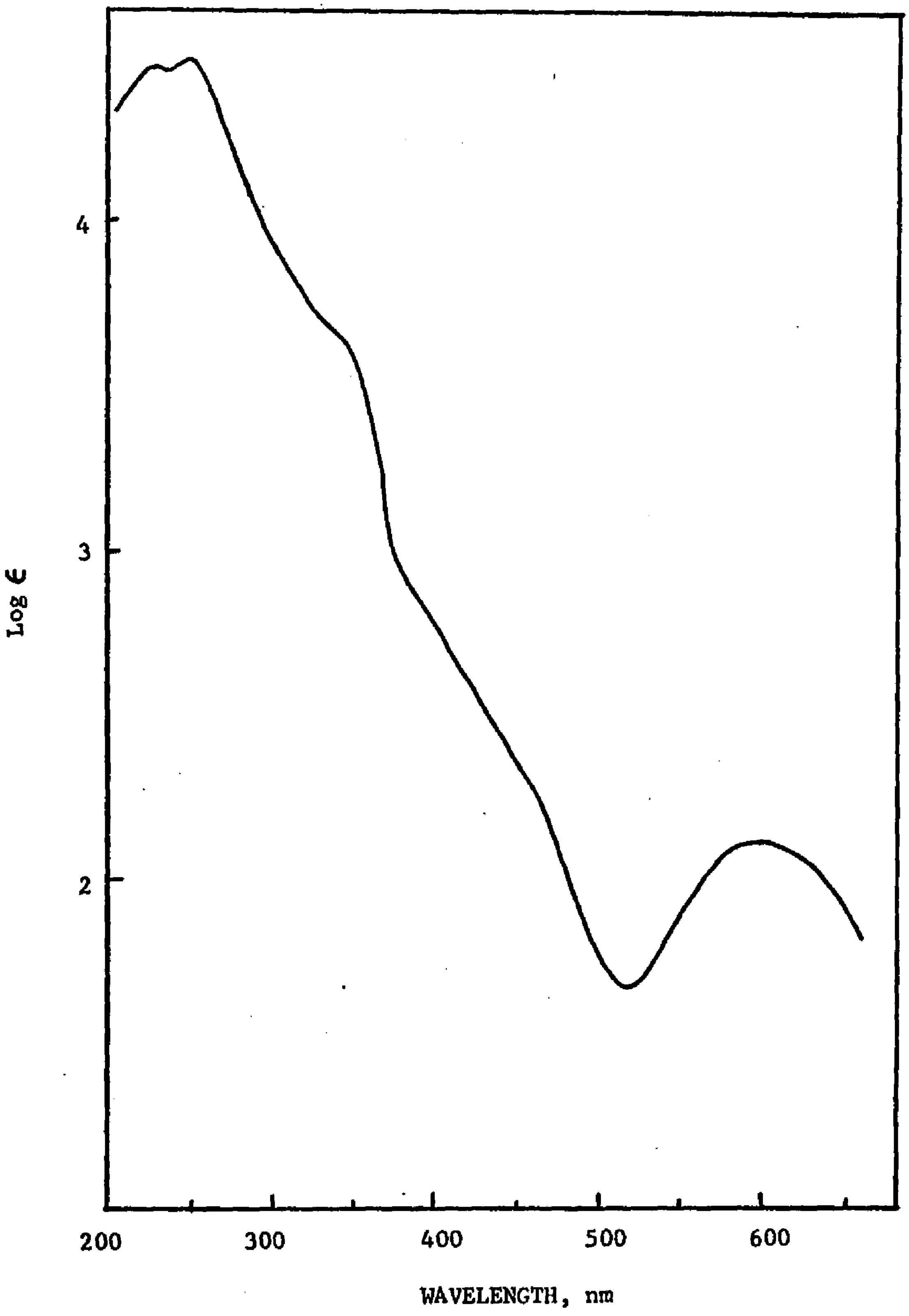


Figure 7

Absorption Spectrum of Trans-Co(bzac)$_3$ in Chloroform

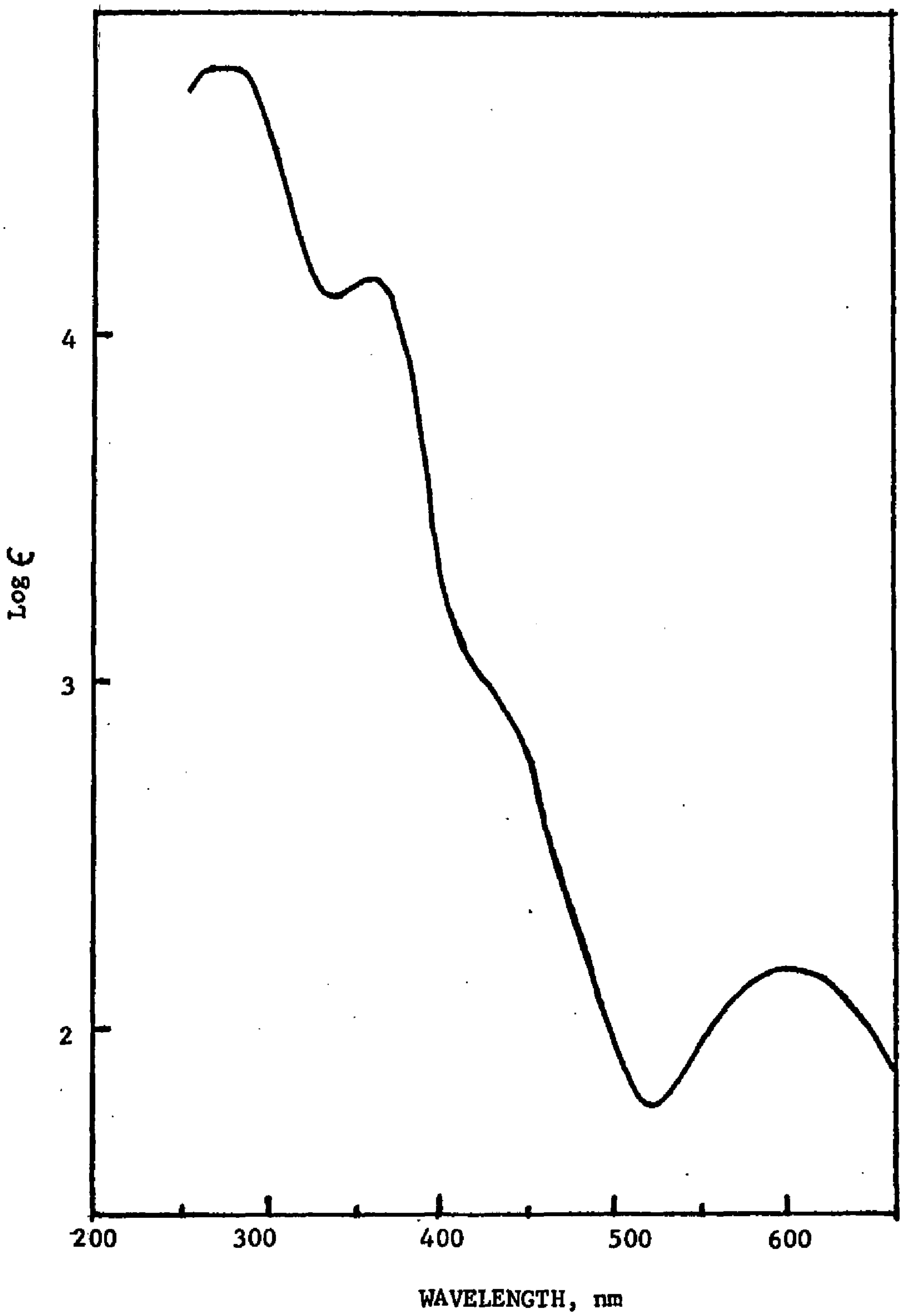


Figure 8

Absorption Spectrum of Cis-Co(bzac)$_3$ in Chloroform

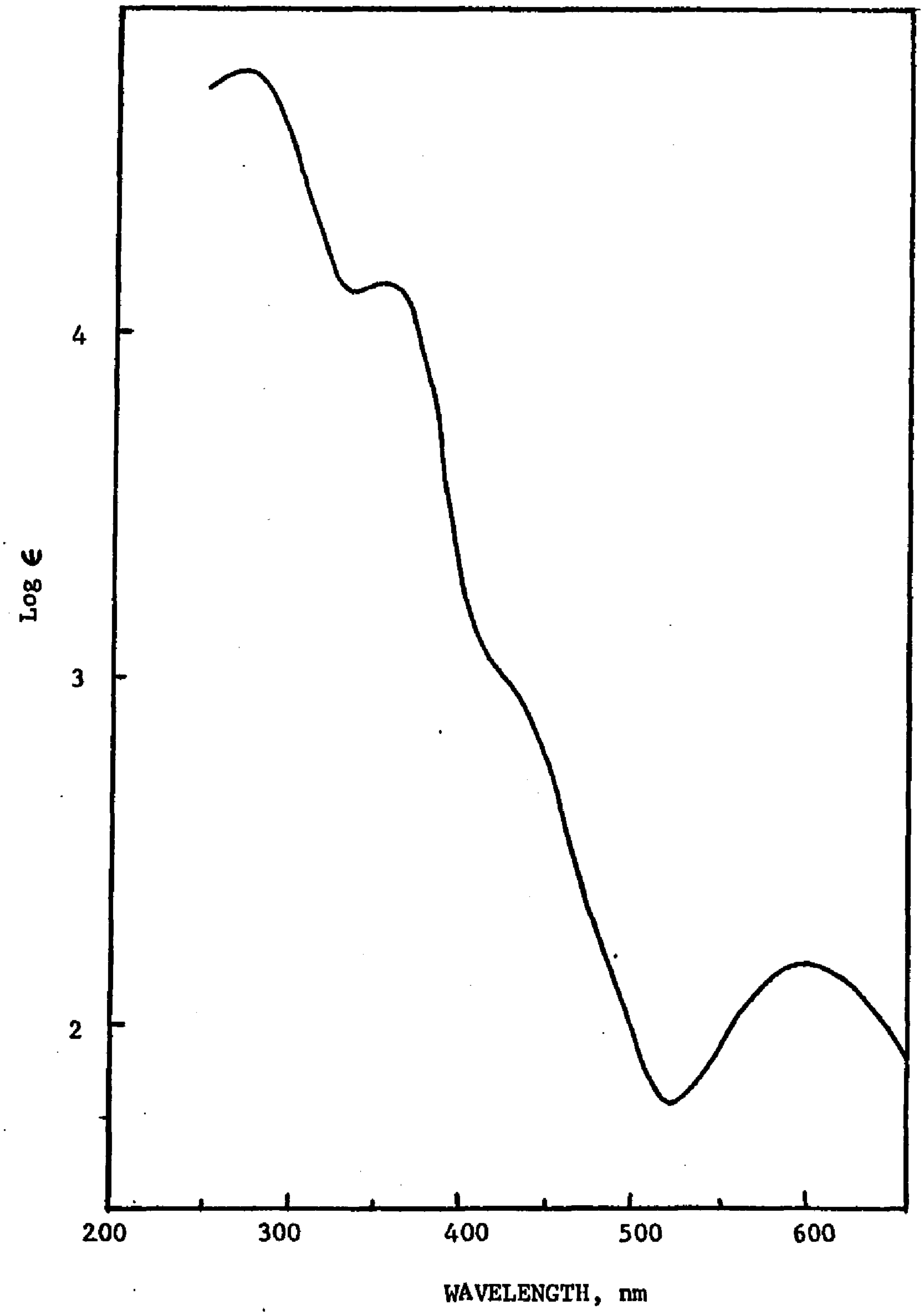


Figure 9

Absorption Spectrum of Trans-$Cr(tfac)_3$ in Ethanol

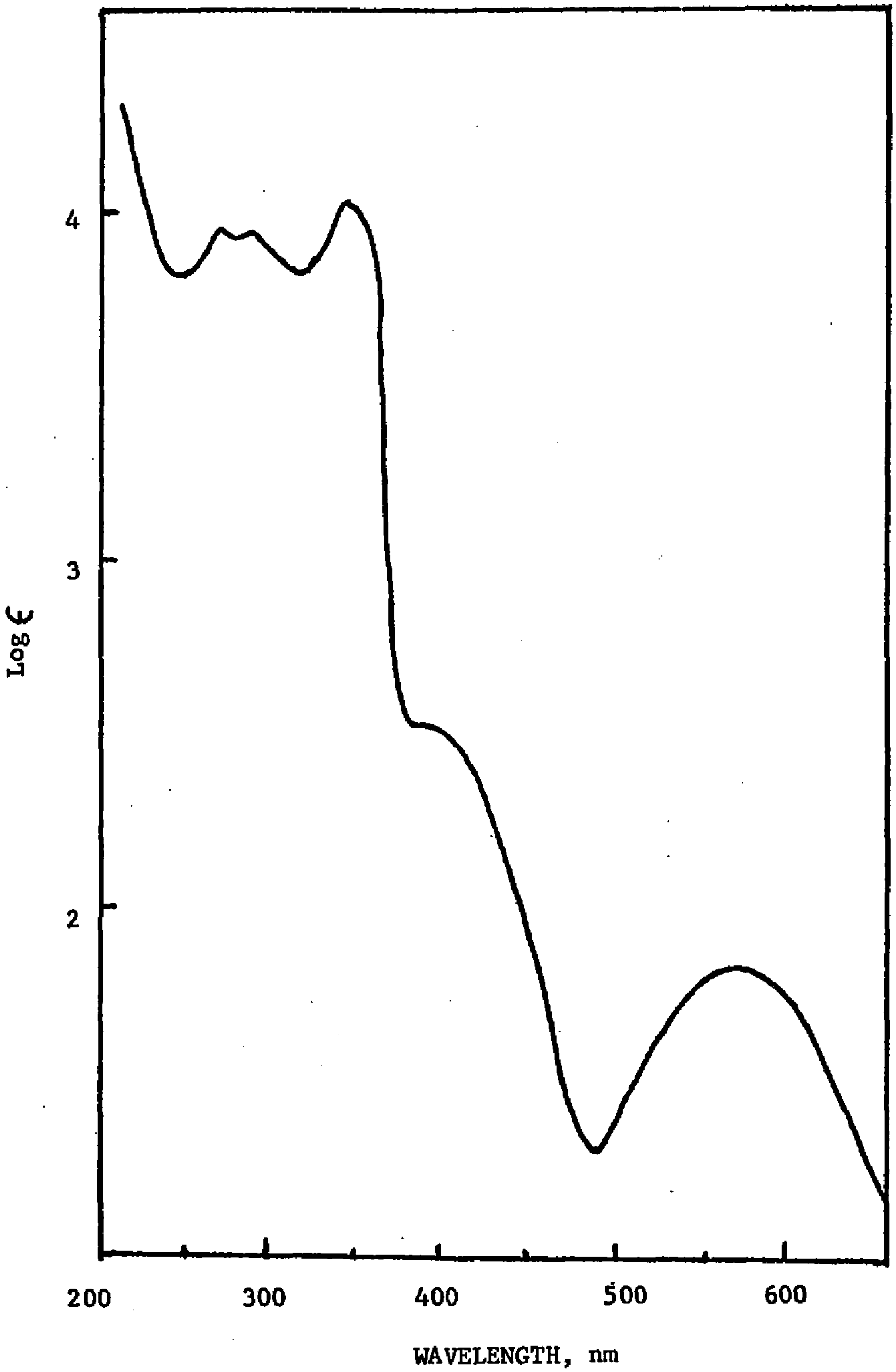


Figure 10

Absorption Spectrum of Cis-$Cr(tfac)_3$ in Ethanol

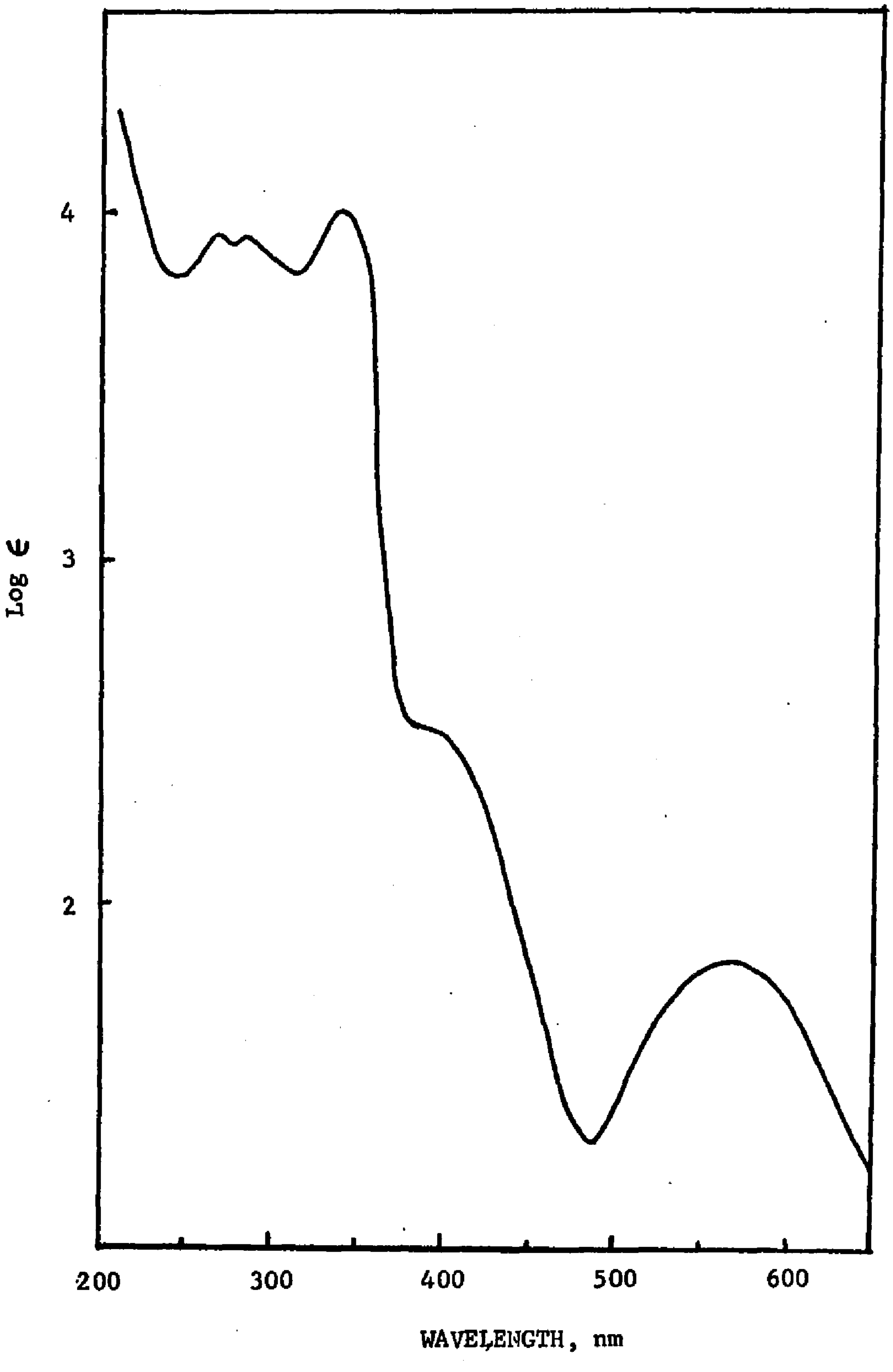


Figure 11

Absorption Spectrum of Trans-$Cr(bzac)_3$ in Chloroform

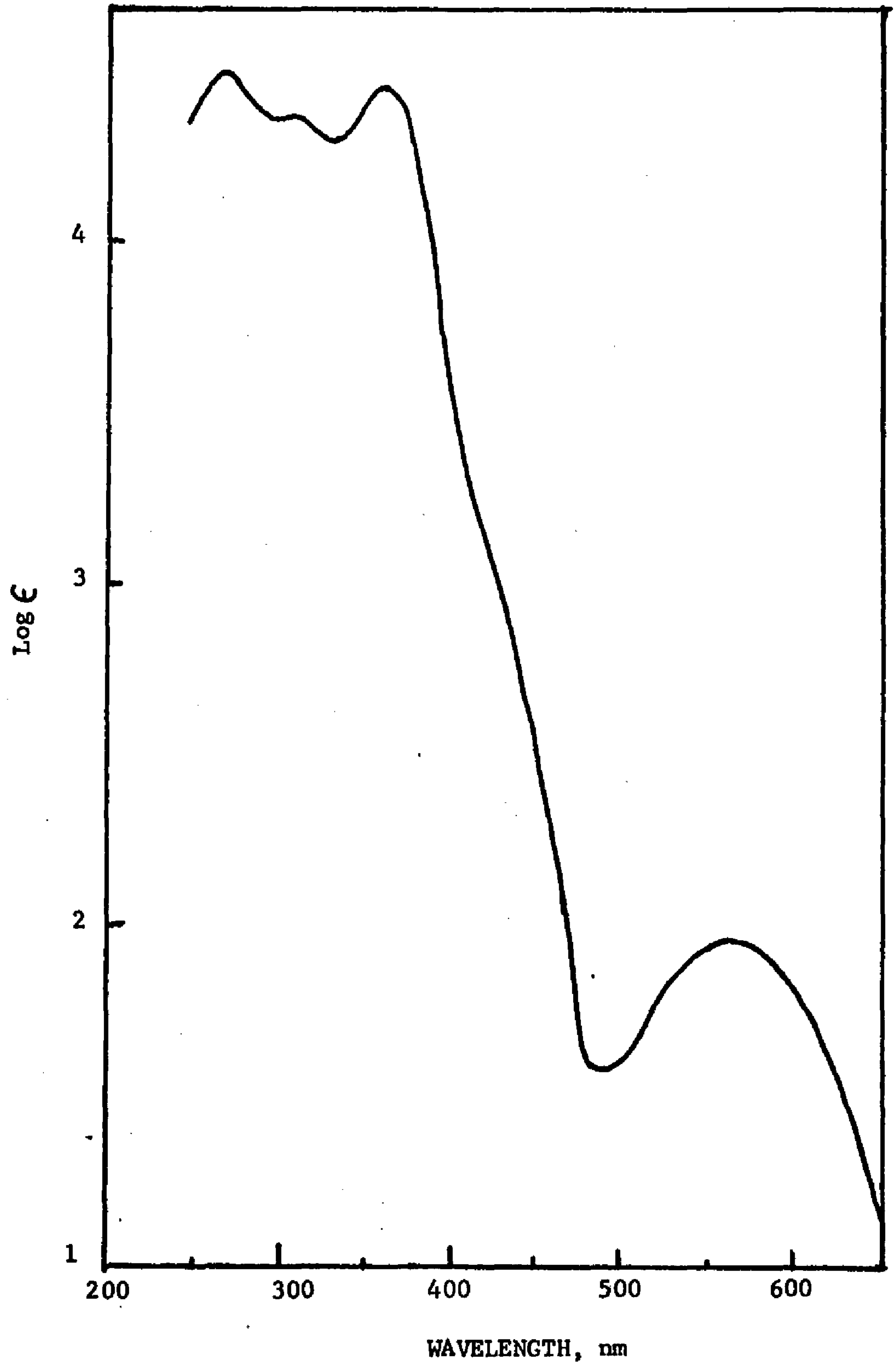


Figure 12

Absorption Spectrum of Cis-Cr(bzac)$_3$ in Chloroform

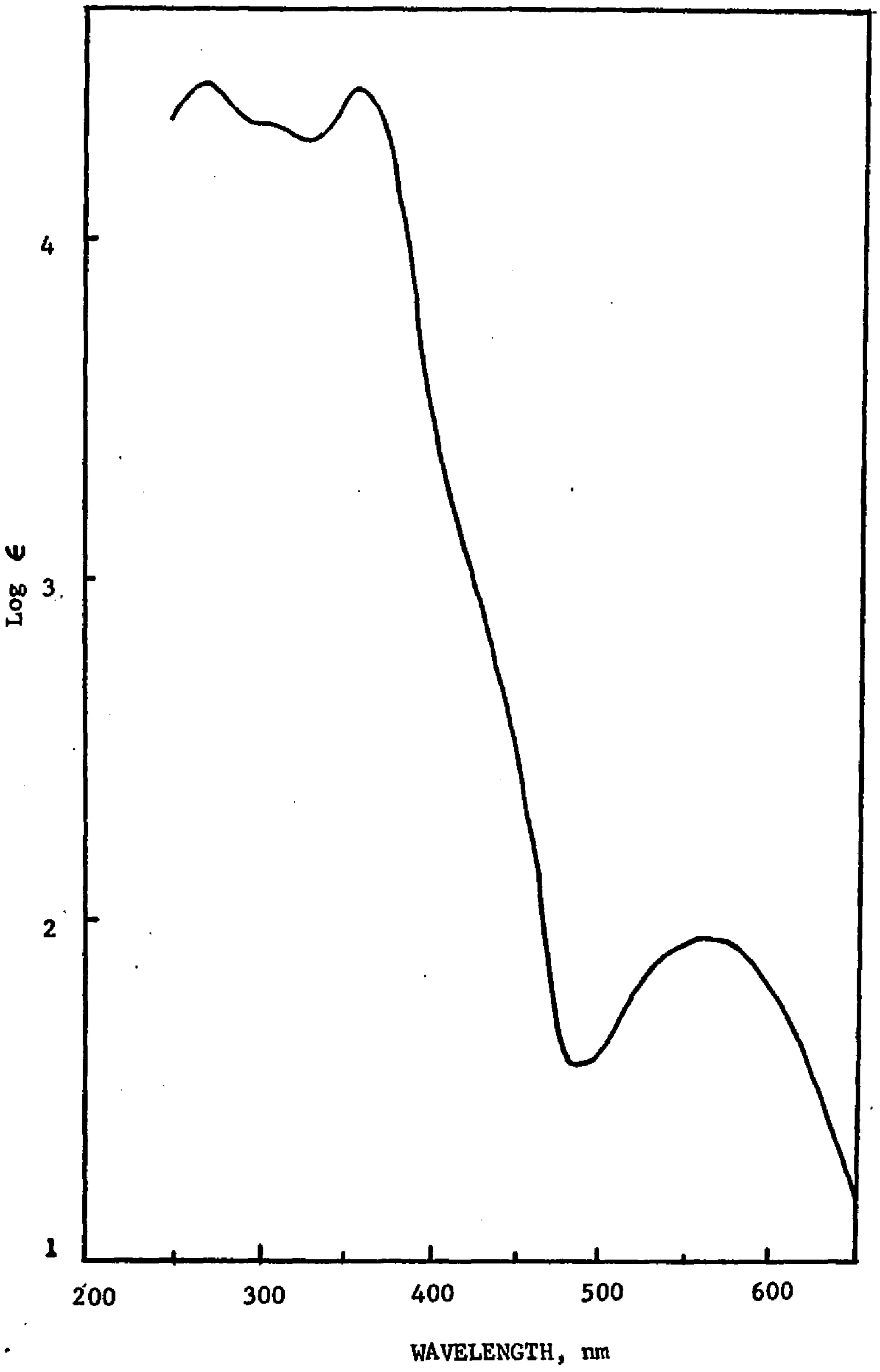


Table I

Molar Extinction Coefficients of the Ultraviolet and Visible Absorption Bands of Beta-diketonate Isomers

Compound	λ, nm	ϵ, $M^{-1}cm^{-1}$
cis-$Co(tfac)_3$[a]	597	131
	332	5,760
	253	31,000
	235	30,900
trans-$Co(tfac)_3$[a]	597	130
	332	6,000
	252	33,000
	232	31,800
cis-$Co(bzac)_3$[b]	598	150
	356	11,600
	262	54,400
trans-$Co(bzac)_3$[b]	598	153
	355	13,800
	267	60,100

a. in ethanol.

b. in chloroform.

Table I (continued)

Compound	λ, nm	ϵ, $M^{-1}cm^{-1}$
cis-Cr(tfac)$_3^a$	563	69.0
	386	345
	338	12,000
	277	9,680
	264	10,100
trans-Cr(tfac)$_3^a$	564	68.3
	386	390
	340	12,000
	278	10,000
	264	10,200
cis-Cr(bzac)$_3^b$	563	88.0
	358	22,500
	292(sh)	20,100
	256	27,000
trans-Cr(bzac)$_3^b$	563	91.2
	358	22,400
	292(sh)	22,400
	260	30,300

a. in ethanol.

b. in chloroform

(sh): shoulder.

energies of the thermally equilibrated ligand-field excited states are estimated by the Fleischauer-Adamson criteria.[48] This technique was used to estimate the energy of the $^4T_2$ state of the Cr(III) complexes and $^1T_1$ state of the Co(III) complexes. It could not be applied to higher energy transitions, however, since the absorption bands overlap. For these higher energy excited states, energies were estimated from the absorption maxima or data available in the literature. The energies of the ^2E states of the Cr(III) complexes were obtained from low temperature emission spectra.[49] Since the visible absorption spectra of $Co(tfac)_3$ and $Co(bzac)_3$ are similar to that of $Co(acac)_3$(acac denotes acetylacetone), the energies of spin forbidden states, such as $^3T_1$ and $^3T_2$ states were assumed to be equal to those found in $Co(acac)_3$.[50] The energies of the various excited states of these isomers as well as the spectral assignments of the transitions are summarized in Table II.

The visible absorption spectra of $Ru(bipy)_3^{2+}$ and $Ru(bipic)_3^{2+}$, Figure 13 and 14, are dominated by intense metal to ligand charge transfer transitions[36] at 452-nm and 460-nm, respectively. Also shown in Figure 15 and 16 are the room temperature, 22-23°C, emission spectra of these Ru(II) complexes. Recent studies have interpreted the luminescence as

Table II

Energies of the Excited States of Beta-diketonate Complexes

Compound	Energy, kK	Assignment
$Co(tfac)_3$	9.1[a]	$^3T_1$
	12.5[a]	$^3T_2$
	13.7[b]	$^1T_1$
	20.41-23.53[c]	$^3L(\pi\rightarrow\pi^*)$
	30.1[d]	CT
	39.5[d]	CT
	42.6[d]	$^1L(\pi\rightarrow\pi^*)$
$Co(bzac)_3$	9.1[a]	$^3T_1$
	12.5[a]	$^3T_2$
	13.7[b]	$^1T_1$
	21.5[e]	$^3L(\pi\rightarrow\pi^*)$
	28.1[d]	CT
	38.2[d]	CT
	43.7[d]	$^1L(\pi\rightarrow\pi^*)$

a. From absorption spectrum of $Co(acac)_3$.

b. Estimated from Fleischauer-Adamson criterion.

c. Values obtained from emission spectra of $La(tfac)_3$.

d. From absorption maxima.

e. ^3L of bzac.

Table II (continued)

Compound	Energy, kK	Assignment
$Cr(tfac)_3$	12.34^a	^2E
	14.4^b	$^4T_2$
	$20.41\text{-}23.53^c$	$^3L(\pi \rightarrow \pi^*)$
	29.6^d	CT
	36.1^d	CT + $L(\pi \rightarrow \pi^*)$
	37.9^d	$L(\pi \rightarrow \pi^*)$ + CT
$Cr(bzac)_3$	12.42^a	^2E
	14.2^b	$^4T_2$
	21.5^e	$^3L(\pi \rightarrow \pi^*)$
	27.9^d	CT
	34.2^d	CT + $L(\pi \rightarrow \pi^*)$
	38.7^d	$L(\pi \rightarrow \pi^*)$ + CT

a. From low temperature emission spectrum.

b. Estimated from Fleischauer-Adamson criterion.

c. Values obtained from emission spectra of $La(tfac)_3$.

d. From absorption maxima.

e. ^3L of bzac.

Figure 13

Absorption Spectrum of $Ru(bipy)_3Cl_2 \cdot 6H_2O$ in Ethanol

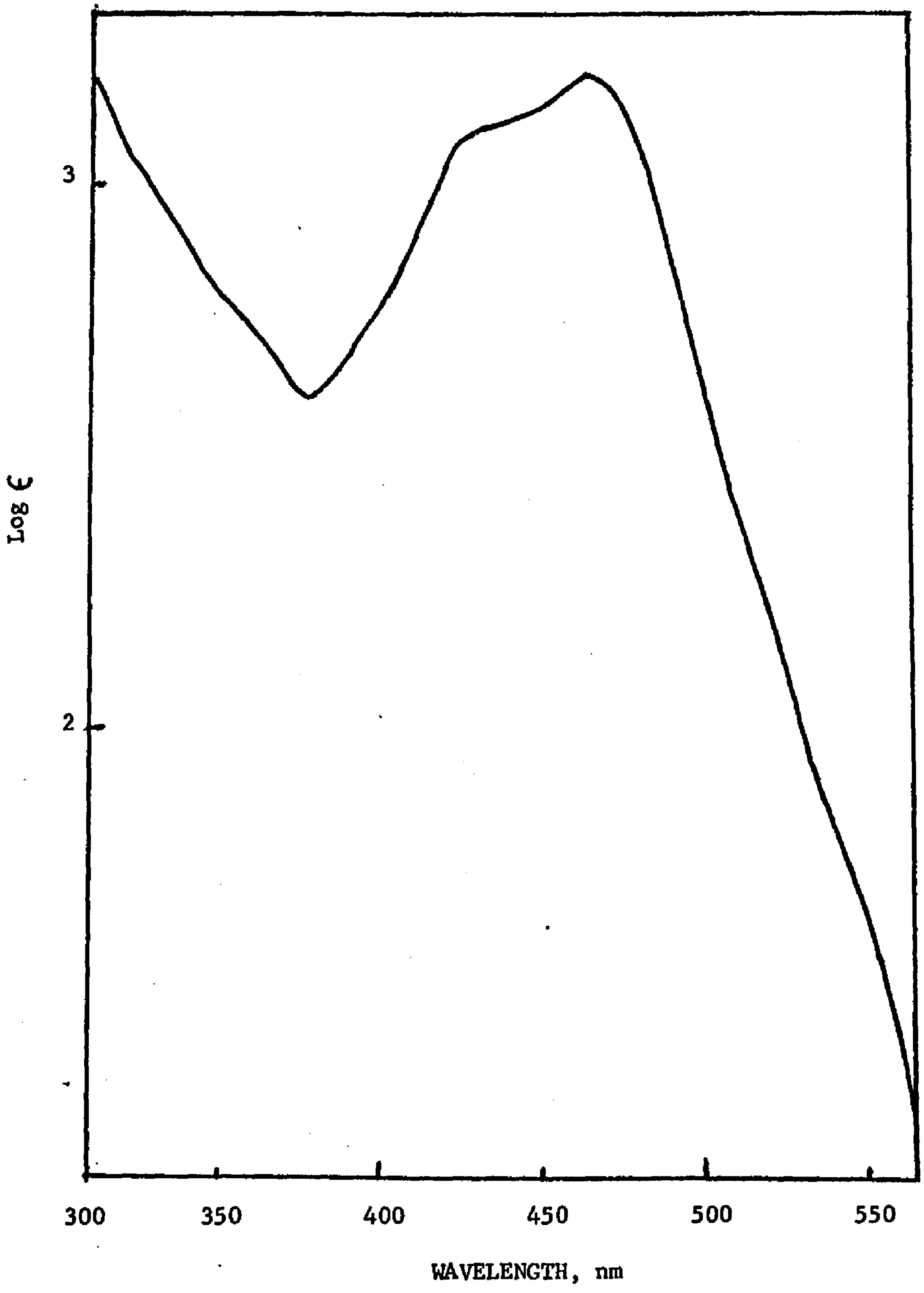
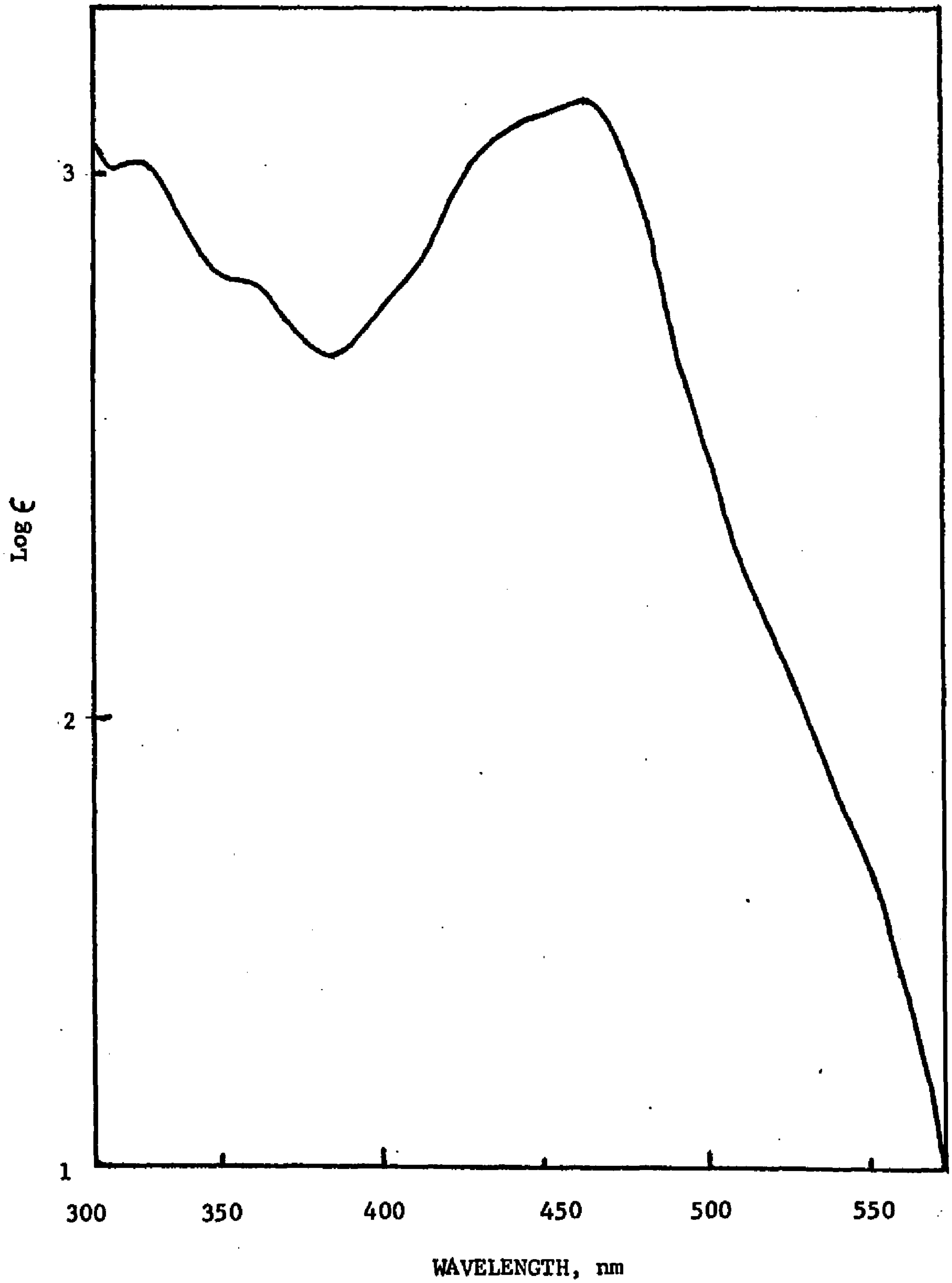


Figure 14

Absorption Spectrum of $Ru(bipic)_3Cl_2 \cdot 4H_2O$ in Ethanol



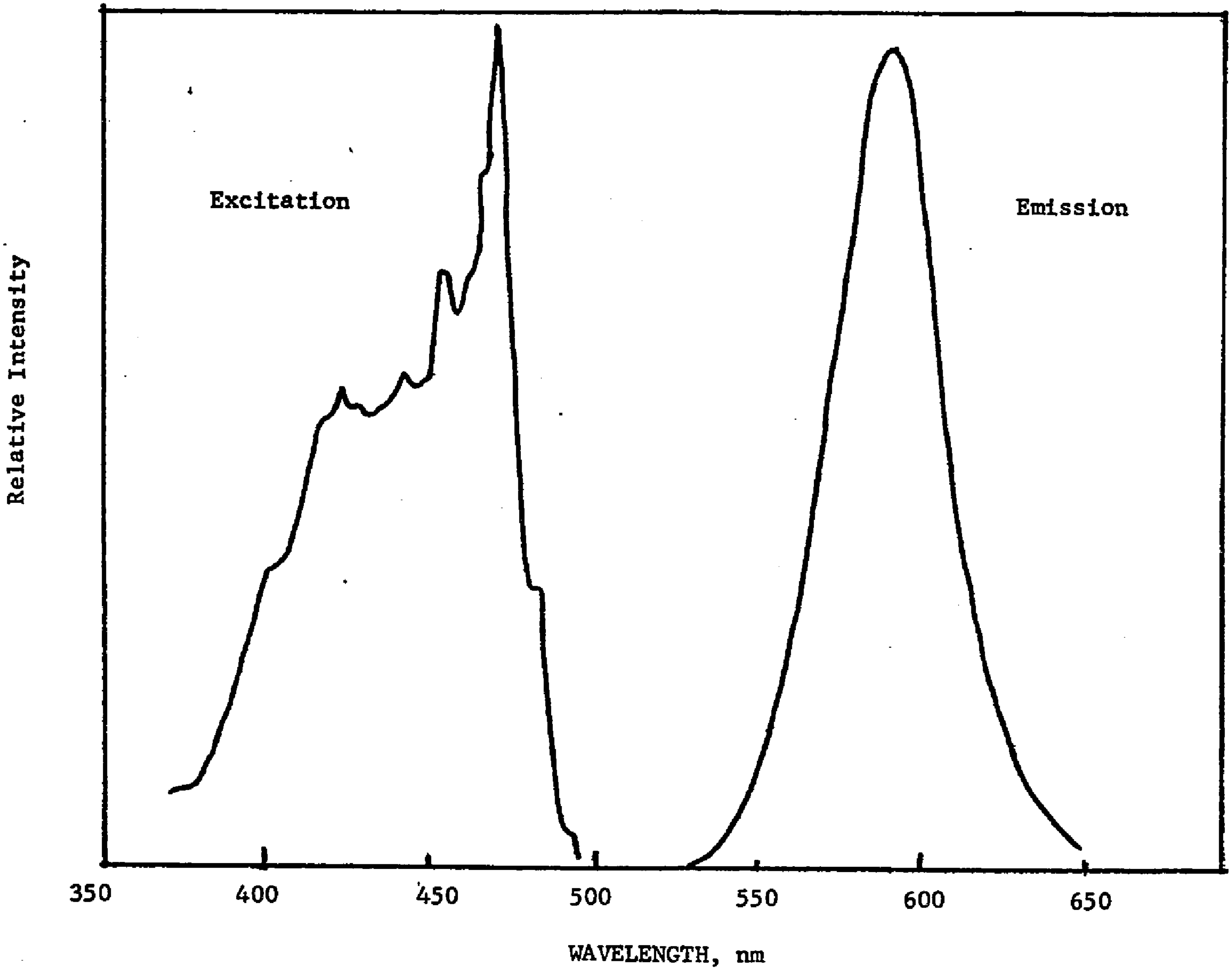


Figure 15

Emission Spectrum of $Ru(bipy)_3Cl_2 \cdot 6H_2O$ in Ethanol

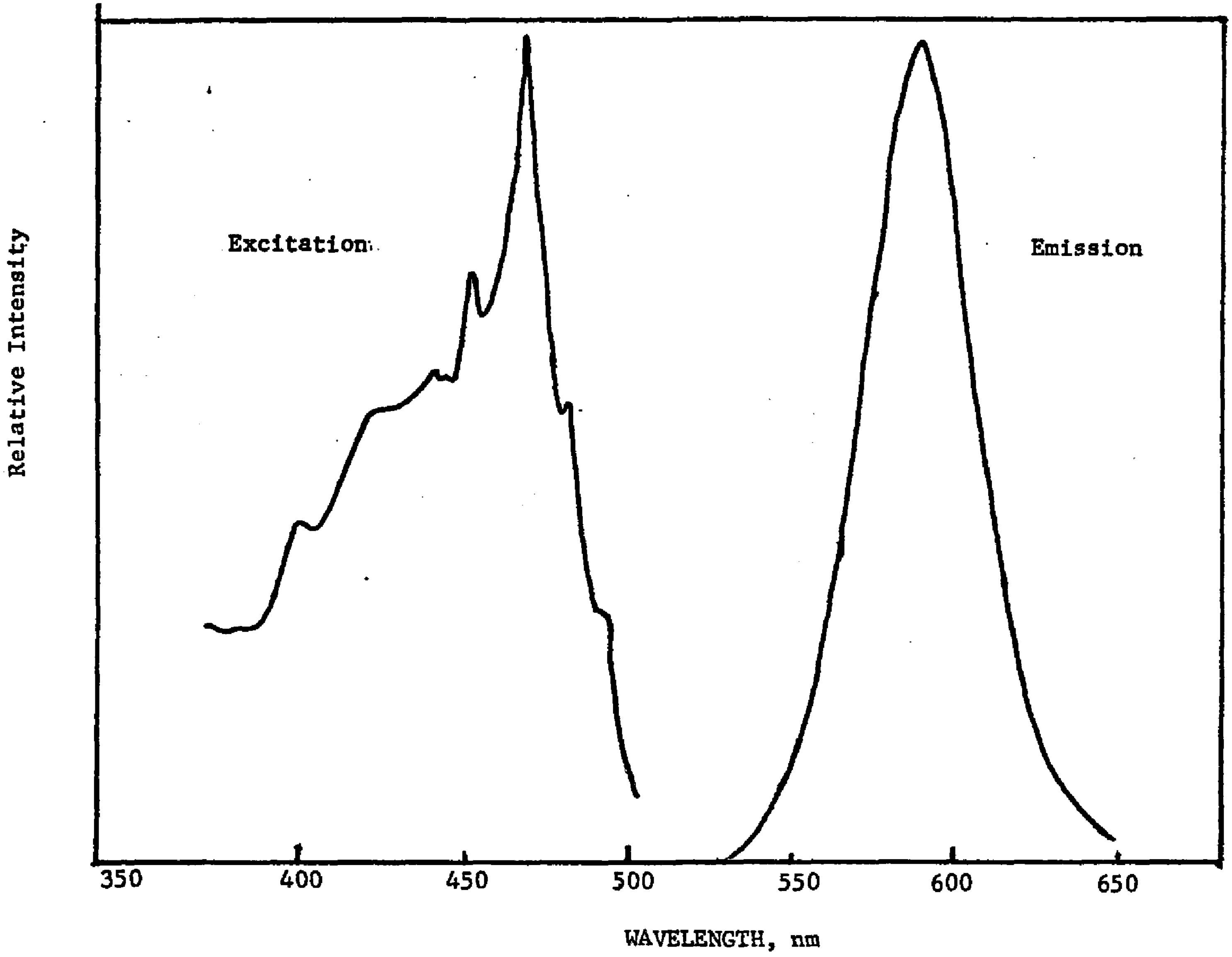


Figure 16

Emission Spectrum of Ru(bipic)$_3$Cl$_2$·4H$_2$O in Ethanol arising from three closely spaced electronic states (A_1, E, and A_2 in D_3 symmetry).[37] The energy spacing between these states is 1 symmetry). 3700 cm^{-1}.[37] Therefore at room temperature, the states are in rapid thermal equilibrium. Furthermore, due to the high atomic number of the metal ion, Z=44, the spin-orbit coupling is sufficiently large to render meaningless a singlet or triplet classification.[51] For convenience, however, we will refer to these states as a triplet state which contains some singlet character. The above reservations, however, should be kept in mind.

To quantitatively study a donor-quencher interaction, a necessary piece of information is the thermally equilibrated energy of the excited state of the donor. This energy can be obtained from emission spectra where the transition between the zero vibrational level of the excited state and the zero vibrational level of the ground state can be assigned. At 77°K, the emission spectra of these Ru(II) complexes in ethanol-methanol (4:1, v/v) glass consists of a broad band between 10- and 18-kK with a 1.3 kK vibrational progression.[37] From these low temperature spectra, the energy of the luminescent state is calculated to be 18.3 kK for $Ru(bipy)_3^{2+}$ and 18.0 kK for $Ru(bipic)_3^{2+}$. At room temperature, of course, the energies may be somewhat different. Unfortunately, the vibrational fine structure is not observed in the emission spectra recorded at room temperature, Figures 15 and 16. Thus, the energies of the thermally equilibrated luminescent states were estimated by applying the Fleischauer-Adamson criteria to the short wavelength tail of the emission band.[48] Under the conditions of these quenching experiments, the thermally equilibrated energies are estimated to be 18.0 kK for $Ru(bipy)_3^{2+}$ and 18.0 kK for $Ru(bipic)_3^{2+}$. These estimates, however, are in good agreement with the values reported by Demas and Addington[13] and others[10] determined at room temperature in aqueous solution.

(b) Intensity Quenching of $Ru(bipy)_3^{2+}$ and $Ru(bipic)_3^{2+}$ by Beta-diketonate Complexes

In a simplified form, a bimolecular quenching reaction can be written as

$$D^* + Q \xrightarrow{k_b} D + Q \qquad (26)$$

where D* represents a luminescent donor and Q the quencher. Steady state analysis of a reaction sequence including excitation, radiative and nonradiative relaxation, and bimolecular quenching, equation 26, leads to the Stern-Volmer expression.[52]

$$\frac{I_o}{I} = 1 + K_{sv}[Q] \qquad (27)$$

K_{sv} represents the Stern-Volmer quenching constant and is related to k_b by

$$K_{sv} = k_b\tau_o \qquad (28)$$

where τ_o is the radiative lifetime measured in the absence of the quencher. The absorption spectra of the isomeric forms of these Co(III) and Cr(III) complexes overlap the absorption and emission spectra of these Ru(II) complexes and standard equations (see experimental section) were used to correct for trivial effects. The values of K_{sv} summarized in Table III were obtained from least squares analysis of plots of $(I_o/I)_{corrected}$ versus the concentration of the quencher, [Q]. These plots for the various isomers, Figures 17 through 30 were found to be linear through ca. 70% quenching. Since a static mechanism, i.e. a thermal equilibrium to form a nonluminescent donor-quencher pair, generally causes a distinct upward curvature to the plots, the linearity of the plots indicates that quenching occurs by a dynamic mechanism. The bimolecular rate constant, k_b , for the quenching of $^*Ru(bipy)_3^{2+}$, listed in Table III, were calculated from equation 28 , where τ_o

Table III

Stern-Volmer Quenching Constants and Bimolecular Rate Constants for the Quenching of $Ru(bipy)_3^{2+}$ and $Ru(bipic)_3^{2+}$ by Beta-Diketonate Complexes

Complex	$K_{sv}^{a} \times 10^{-3}$, M^{-1}	$k_b^{b} \times 10^{-9}$, M^{-1} sec^{-1}	$K_{sv}^{c} \times 10^{-3}$, M^{-1}
cis-$Co(tfac)_3$	1.43 ± 0.26	1.8	1.58 ± 0.18
trans-$Co(tfac)_3$	1.39 ± 0.22	1.8	1.41 ± 0.13
cis-$Co(bzac)_3$	0.89 ± 0.11	1.1	0.79 ± 0.10
trans-$Co(bzac)_3$	0.87 ± 0.11	1.1	0.80 ± 0.10
cis-$Cr(tfac)_3$	0.28 ± 0.03 (0.20 ± 0.06)[d]	0.36	0.24 ± 0.02
trans-$Cr(tfac)_3$	0.20 ± 0.02 (0.20 ± 0.05)[d]	0.25	0.18 ± 0.02
cis-$Cr(bzac)_3$	0.70 ± 0.15	0.85	0.49 ± 0.05
trans-$Cr(bzac)_3$	0.50 ± 0.06	0.63	0.54 ± 0.05

a. Obtained for the quenching of $Ru(bipy)_3^{2+}$.

b. Obtained from the average K_{sv} for the quenching of $Ru(bipy)_3^{2+}$ and the lifetime of $Ru(bipy)_3^{2+}$ in absolute ethanol, 790nsec.

c. Obtained for the quenching of $Ru(bipic)_3^{2+}$.

d. Measured in a 40% (by volume) formamide-ethanol solution.

Figure 17

Stern-Volmer plot for the Quenching of $Ru(bipy)_3^{2+}$ by

<u>Trans</u>-Co(tfac)$_3$ in Ethanol

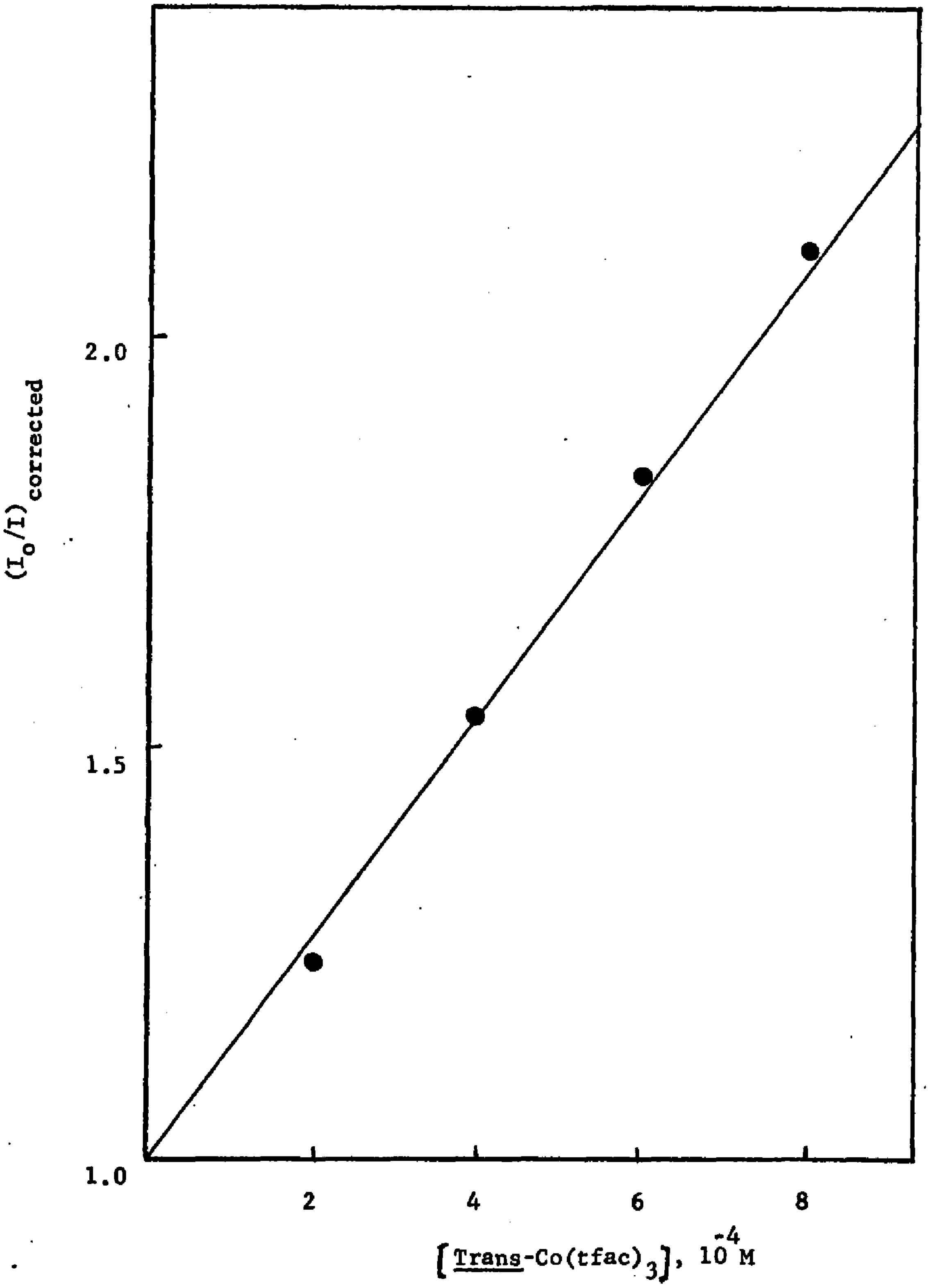


Figure 18

Stern-Volmer Plot for the Quenching of $Ru(bipy)_3^{2+}$ by

<u>Cis</u>-$Co(tfac)_3$ in Ethanol

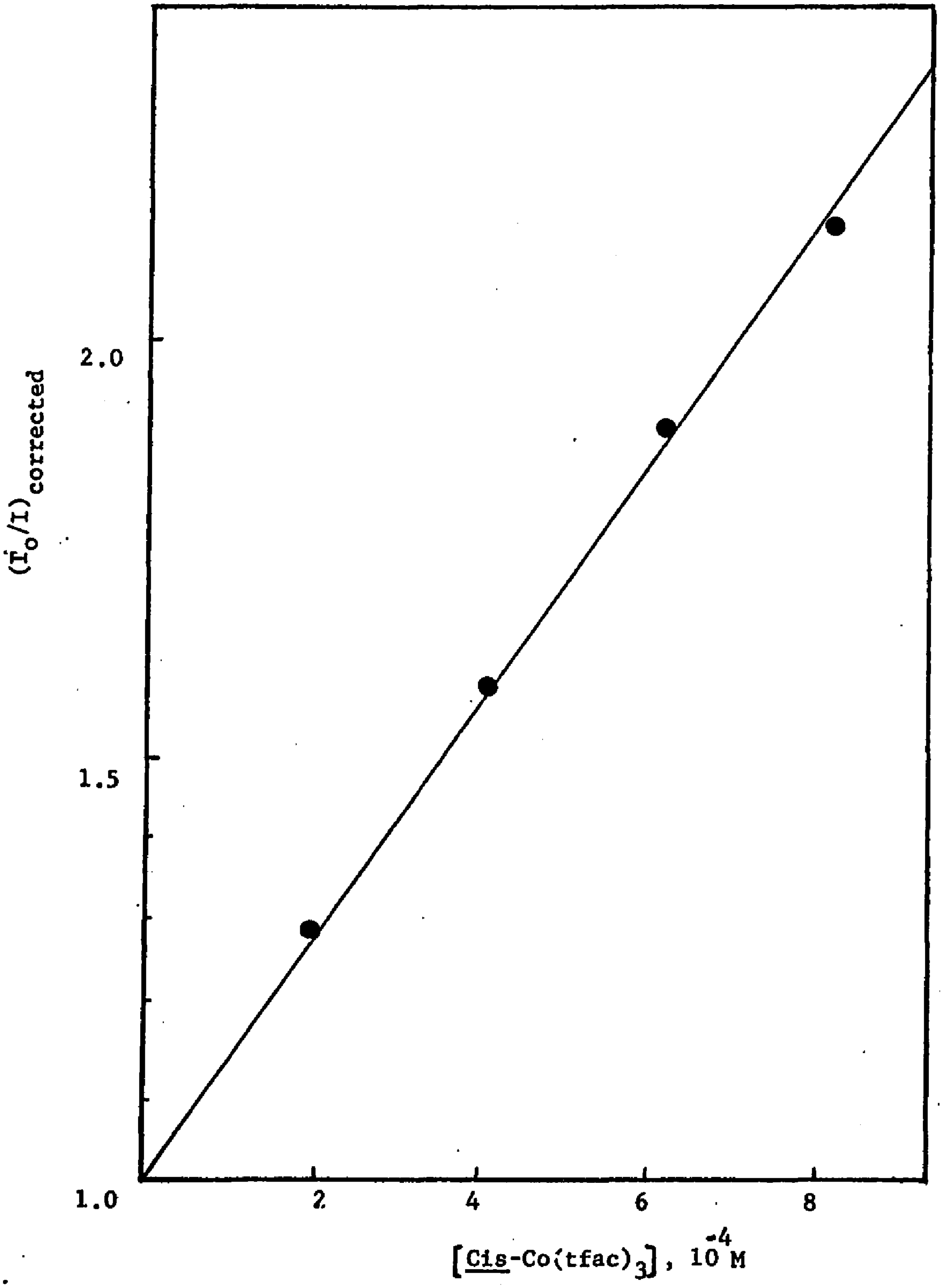


Figure 19

Stern-Volmer Plot for the Quenching of $Ru(bipy)_3^{2+}$ by Trans-$Co(bzac)_3$ in 10% (by volume) Chloroform-Ethanol

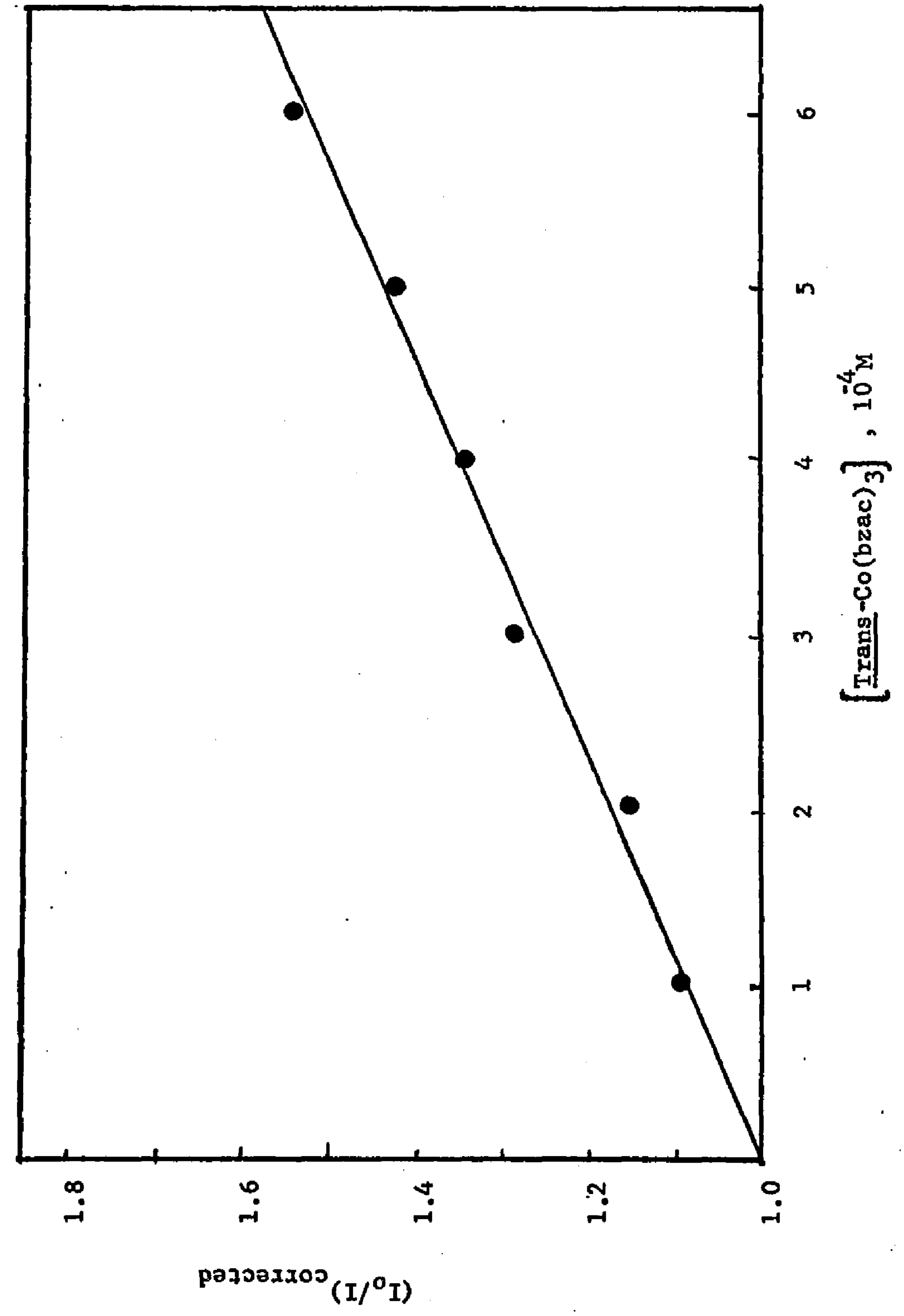


Figure 20

Stern-Volmer Plot for the Quenching of $Ru(bipy)_3^{2+}$ by <u>Cis</u>-$Co(bzac)_3$ in 10% (by volume) Chloroform-Ethanol

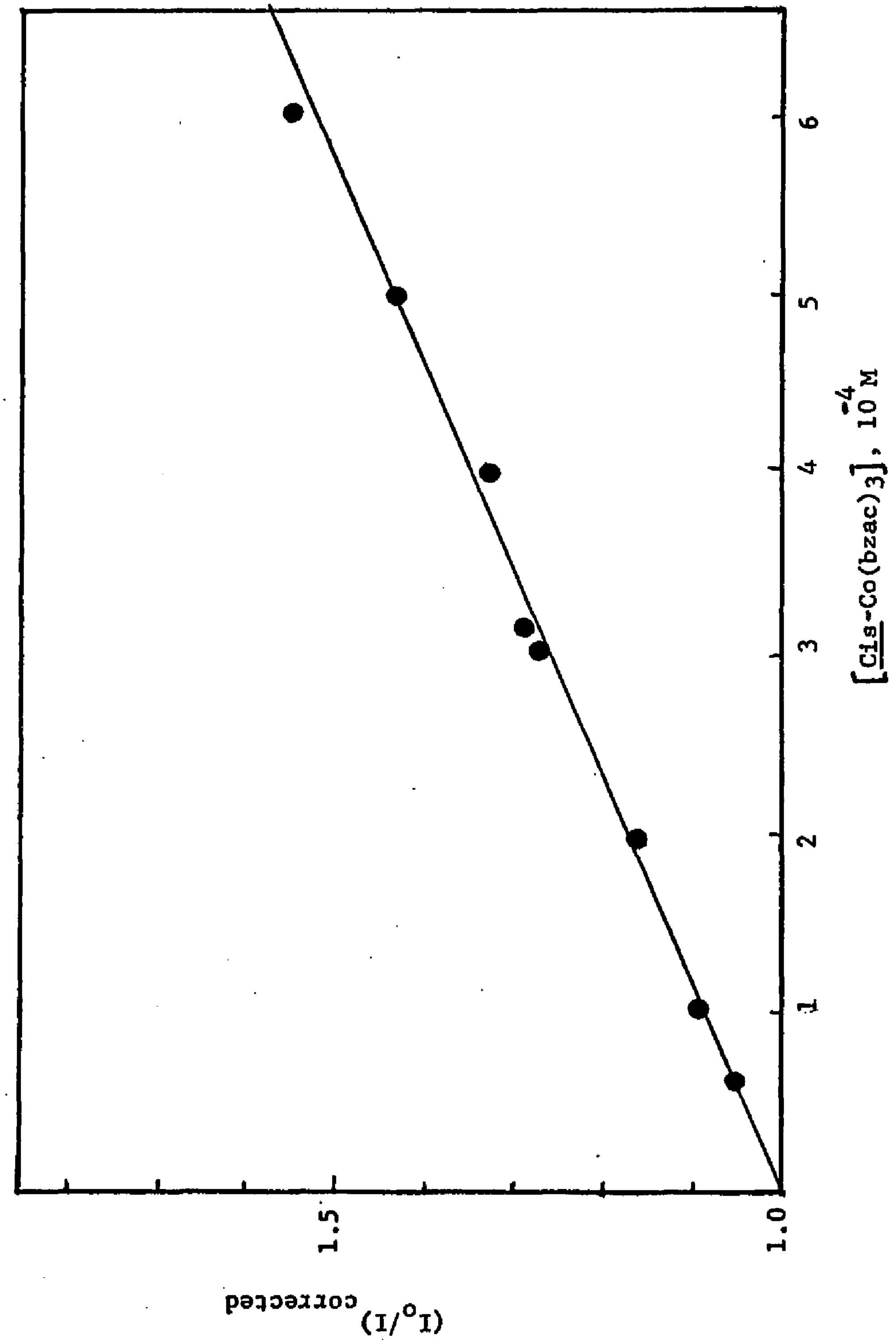


Figure 21

Stern-Volmer Plot for the Quenching of $Ru(bipic)_3^{2+}$ by Trans-$Co(tfac)_3$ in Ethanol

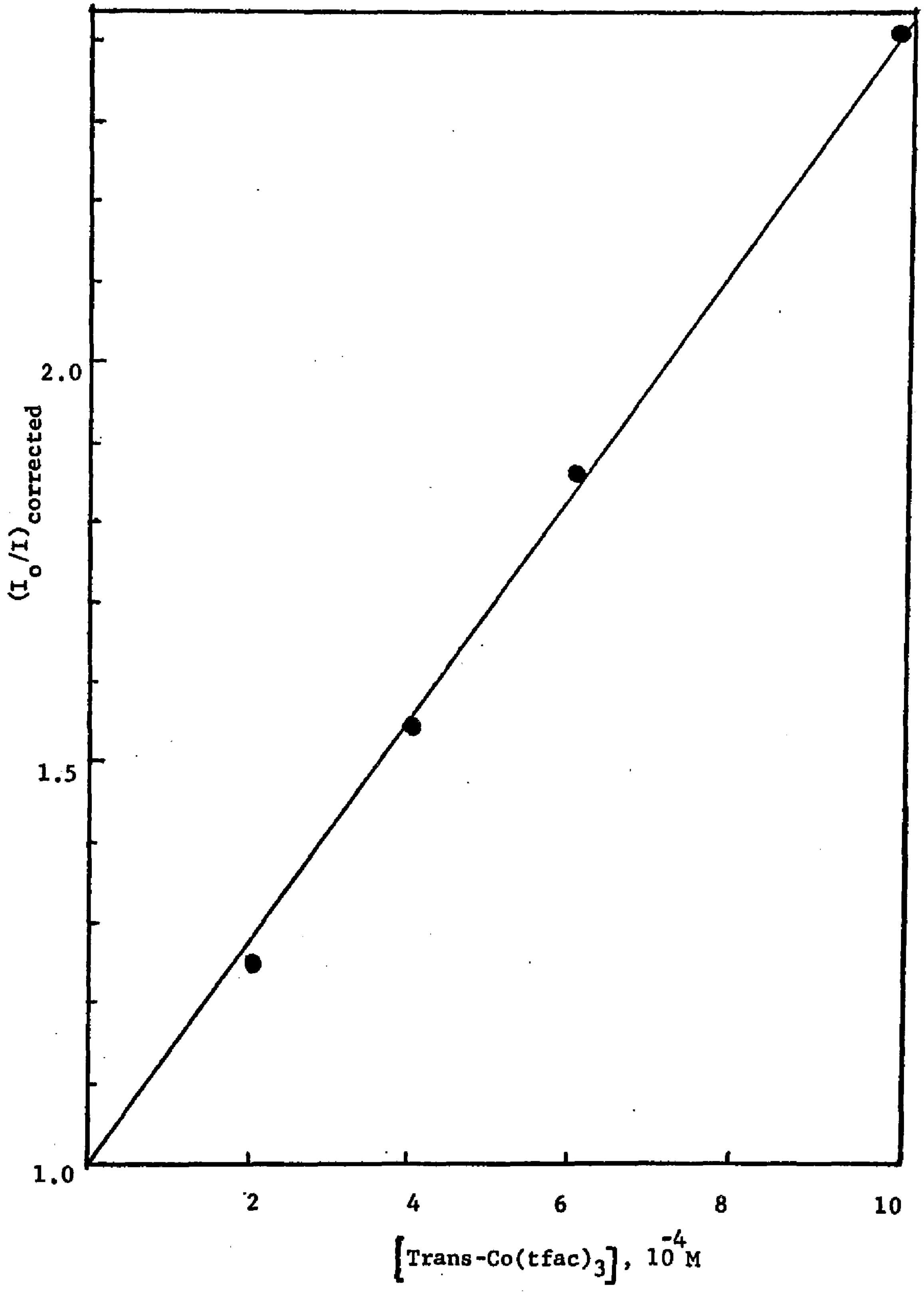


Figure 22

Stern-Volmer Plot for the Quenching of $Ru(bipic)_3^{2+}$ by Cis-$Co(tfac)_3$ in Ethanol

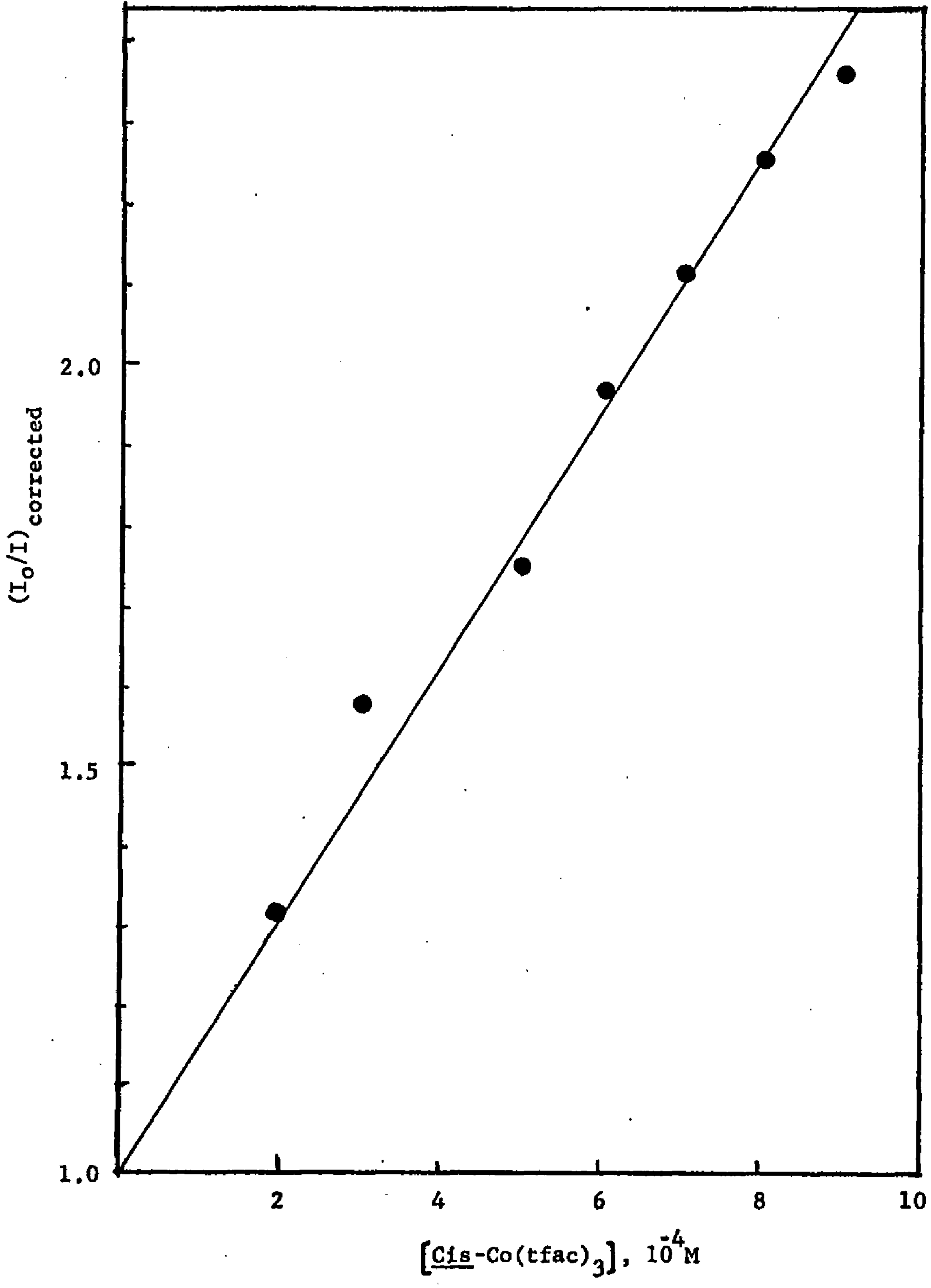


Figure 23

Stern-Volmer Plot for the Quenching of $Ru(bipic)_3^{2+}$ by

Trans-$Co(bzac)_3$ in 10% (by volume) Chloroform-Ethanol

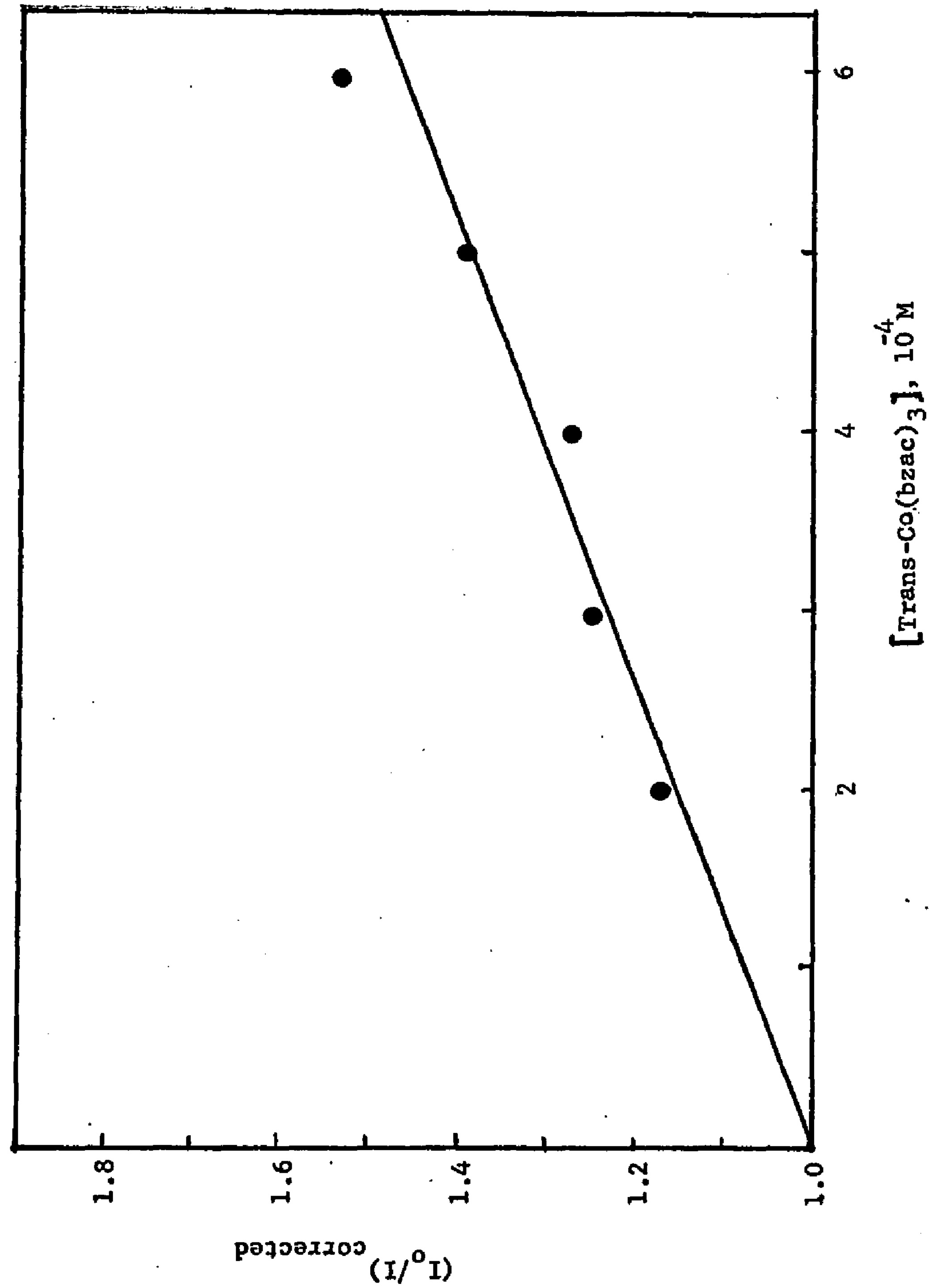


Figure 24

Stern-Volmer Plot for the Quenching of $Ru(bipic)_3^{2+}$ by Cis-$Co(bzac)_3$ in 10% (by volume) Chloroform-Ethanol

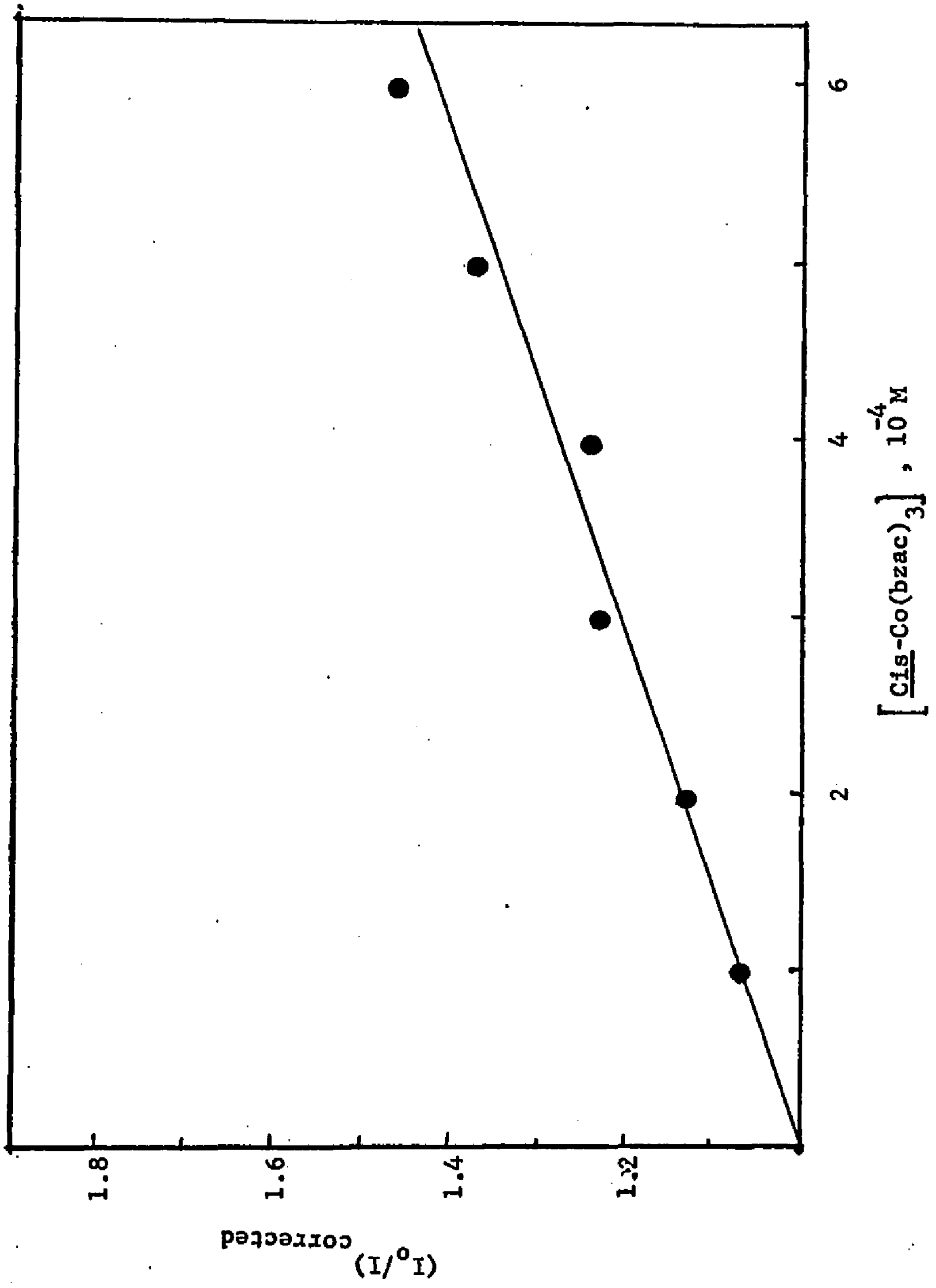


Figure 25

Stern-Volmer Plots for the Quenching of $Ru(bipy)_3^{2+}$ by Trans- and Cis-$Cr(tfac)_3$ in Ethanol

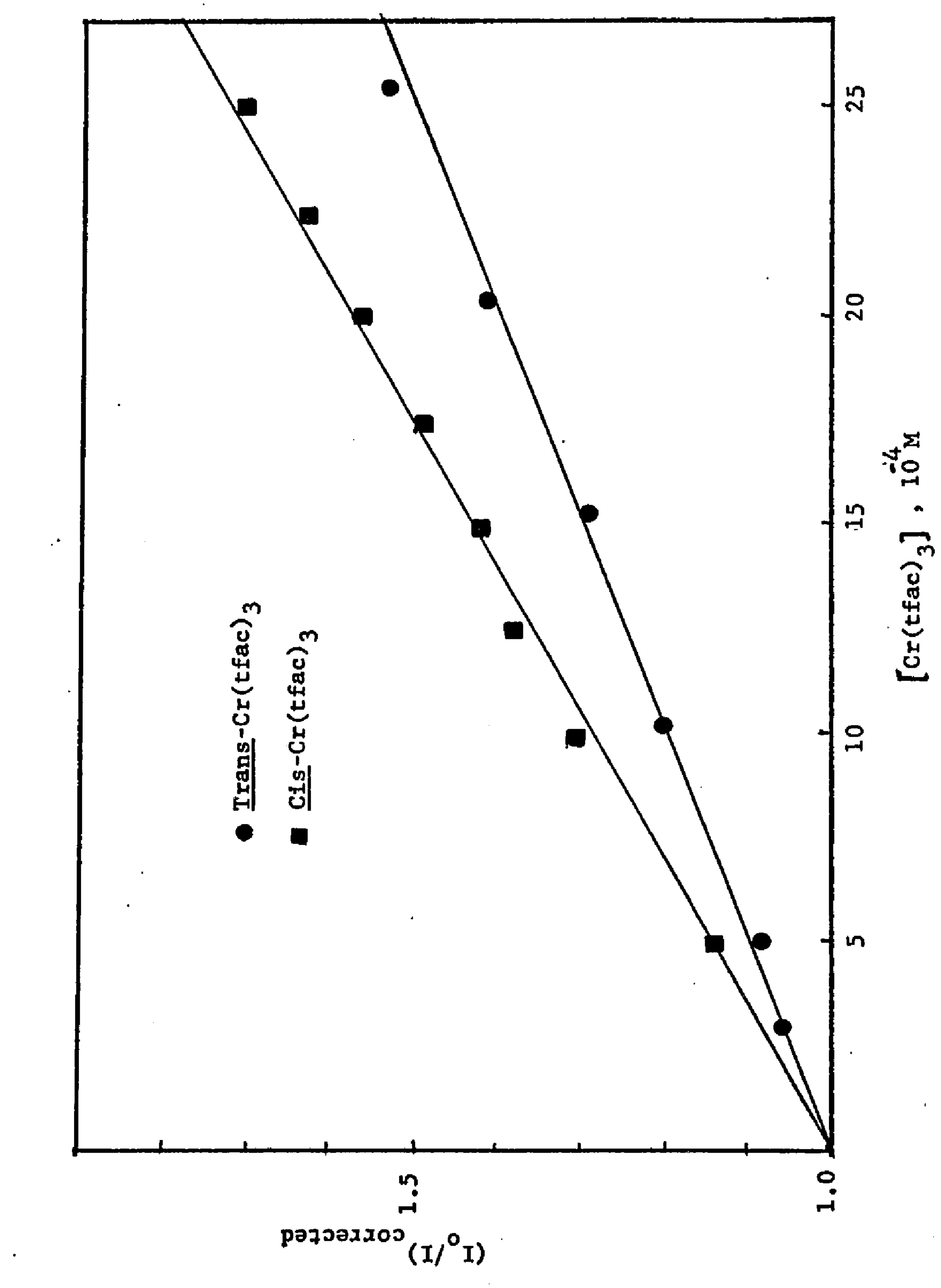


Figure 26

Stern-Volmer Plots for the Quenching of $Ru(bipic)_3^{2+}$ by

<u>Trans</u>- and <u>Cis</u>-$Cr(tfac)_3$ in Ethanol

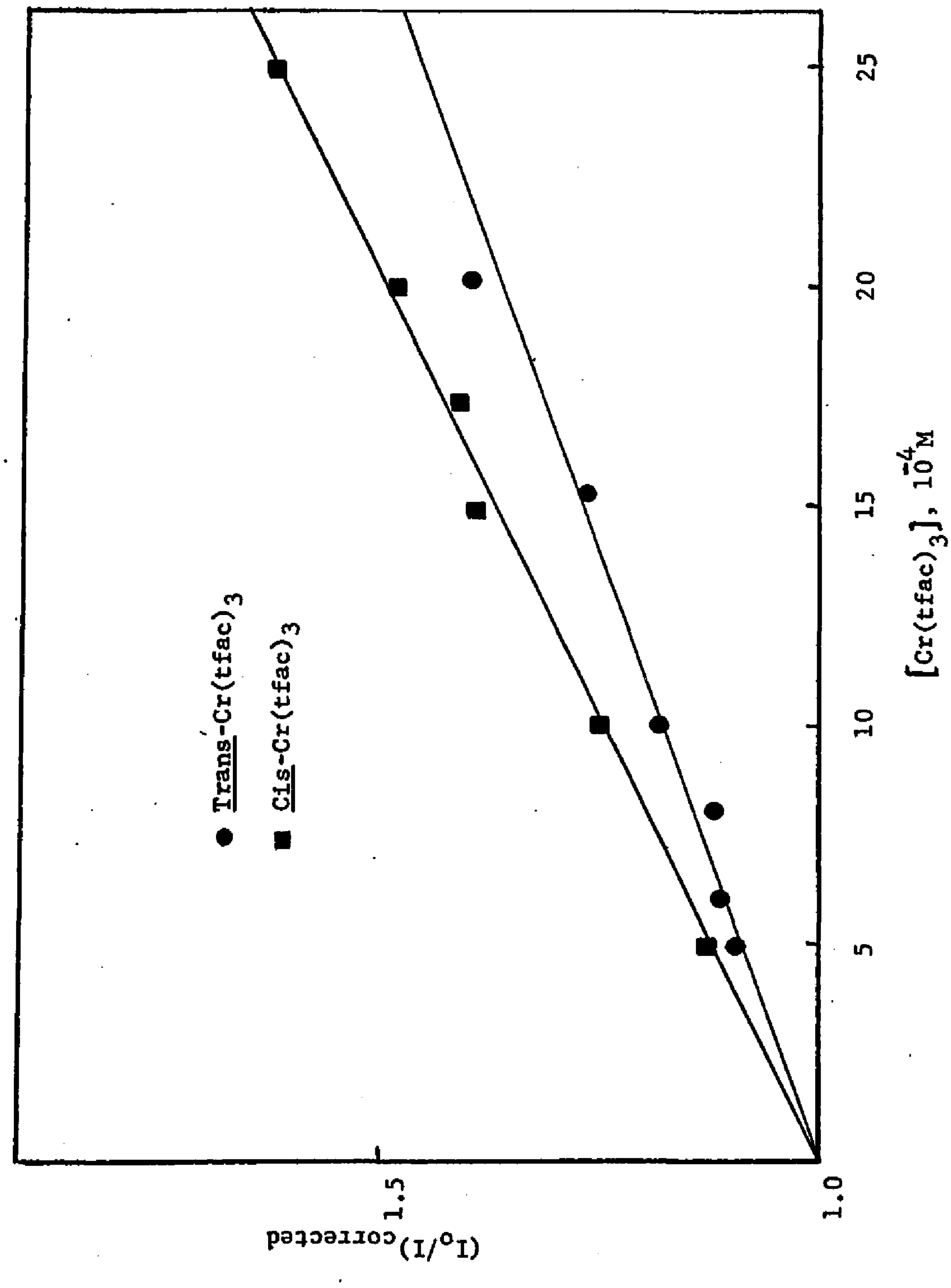


Figure 27

Stern-Volmer Plot for the Quenching of $Ru(bipy)_3^{2+}$ by

Trans-$Cr(bzac)_3$ in 10% (by volume) Chloroform-Ethanol

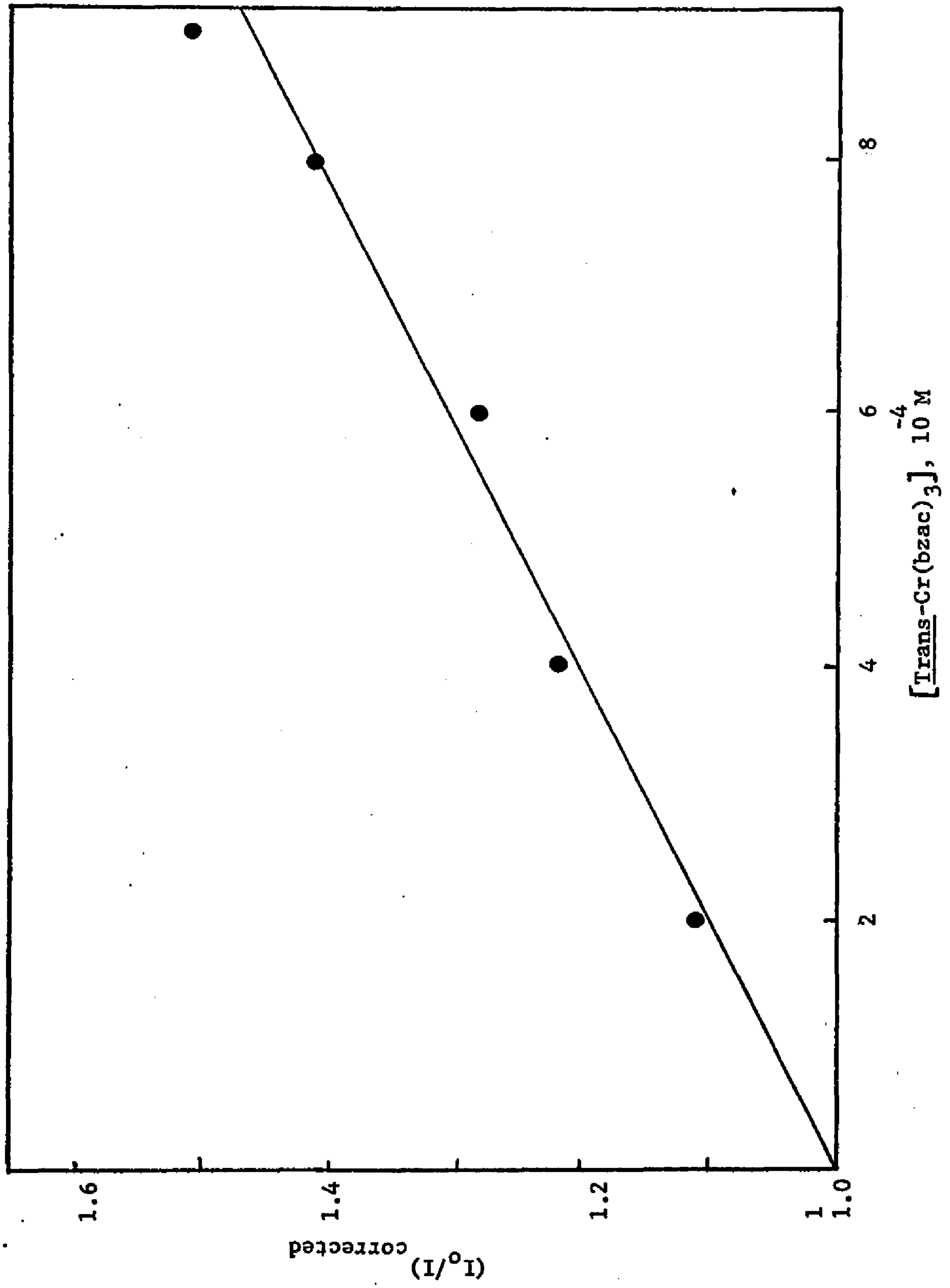


Figure 28

Stern-Volmer Plot for the Quenching of $Ru(bipy)_3^{2+}$ by

Cis-$Cr(bzac)_3$ in 10% (by volume) Chloroform-Ethanol

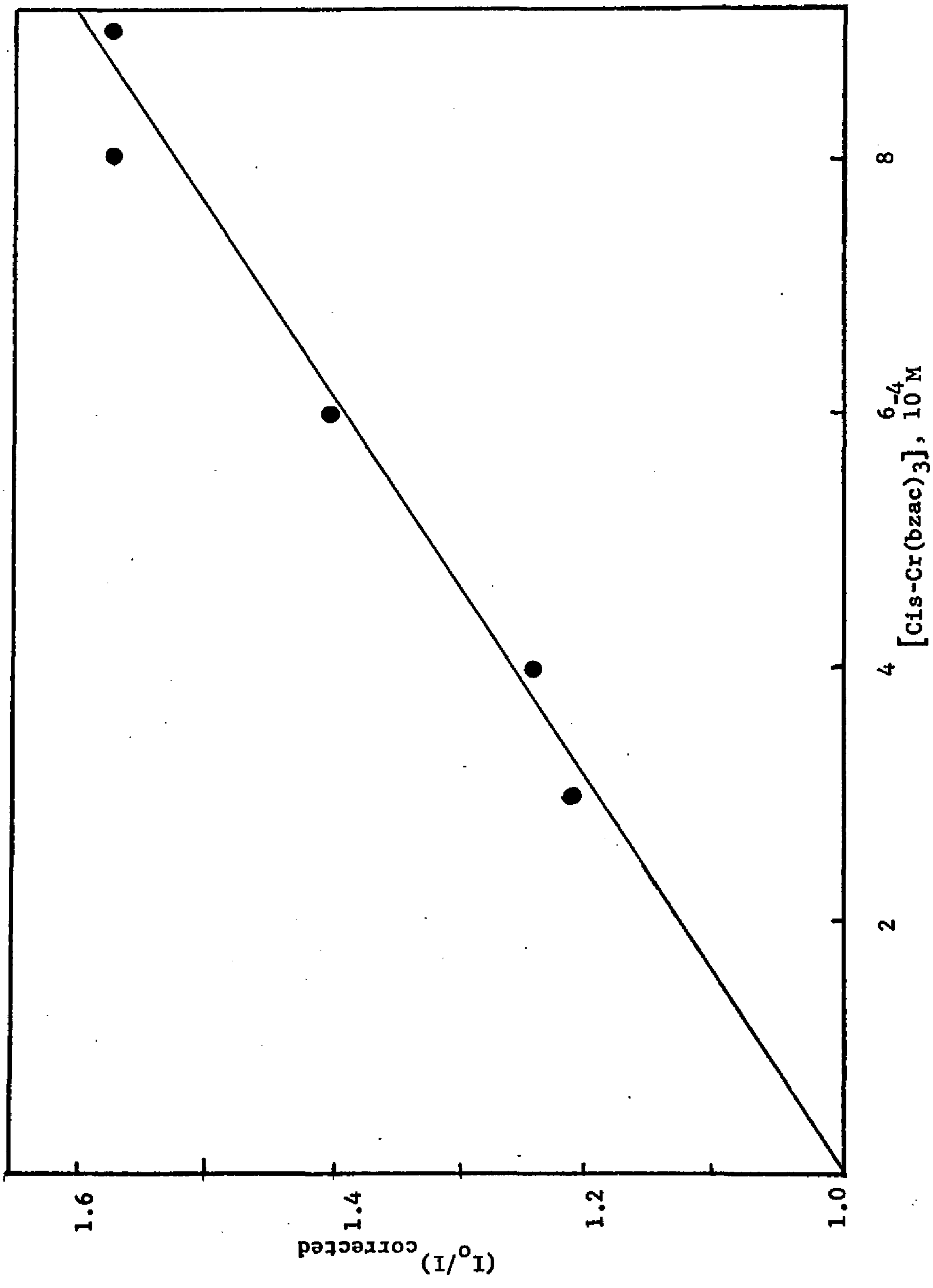


Figure 29

Stern-Volmer Plot for the Quenching of $Ru(bipic)_3^{2+}$ by <u>Trans</u>-$Cr(bzac)_3$ in 10% (by volume) Chloroform-Ethanol

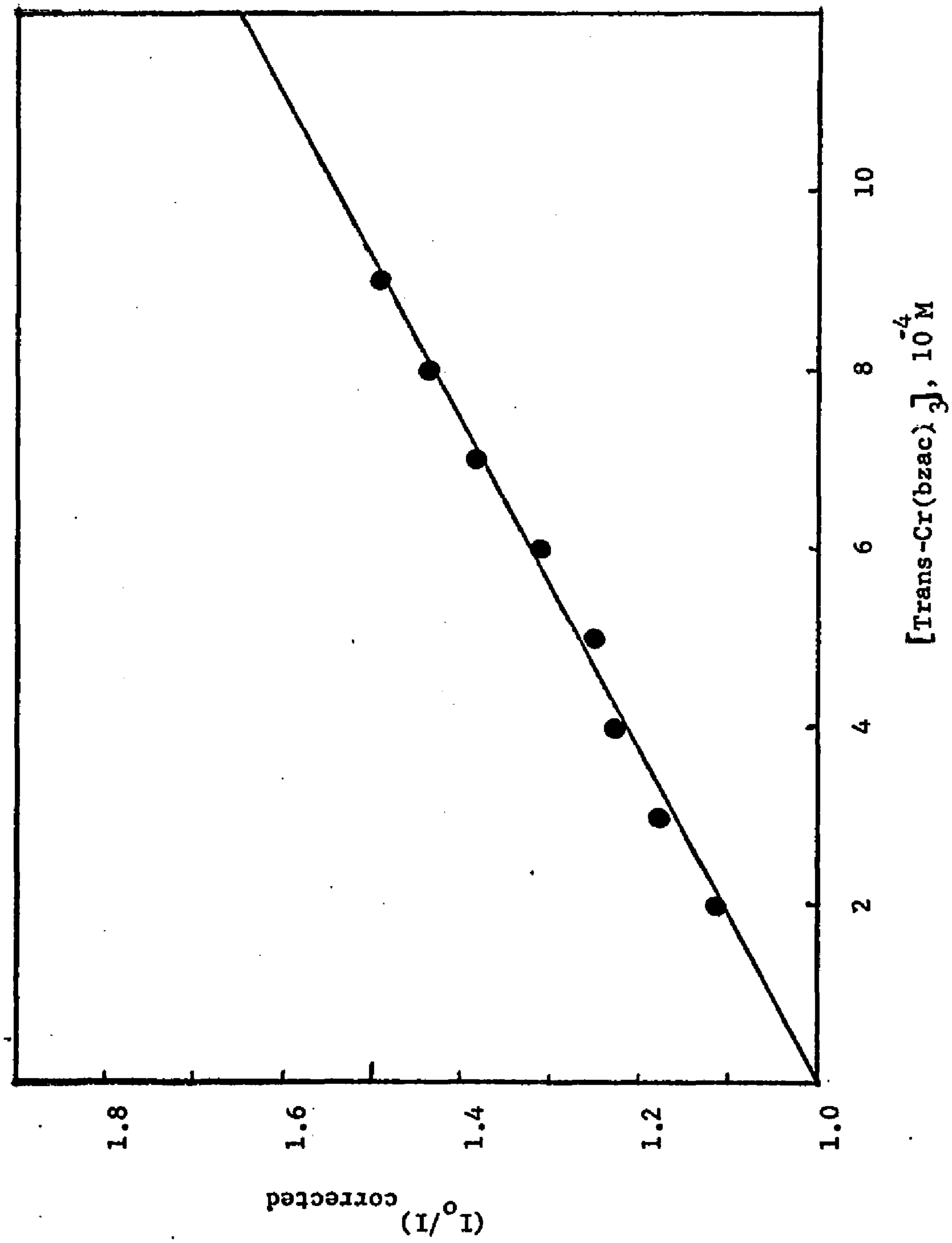
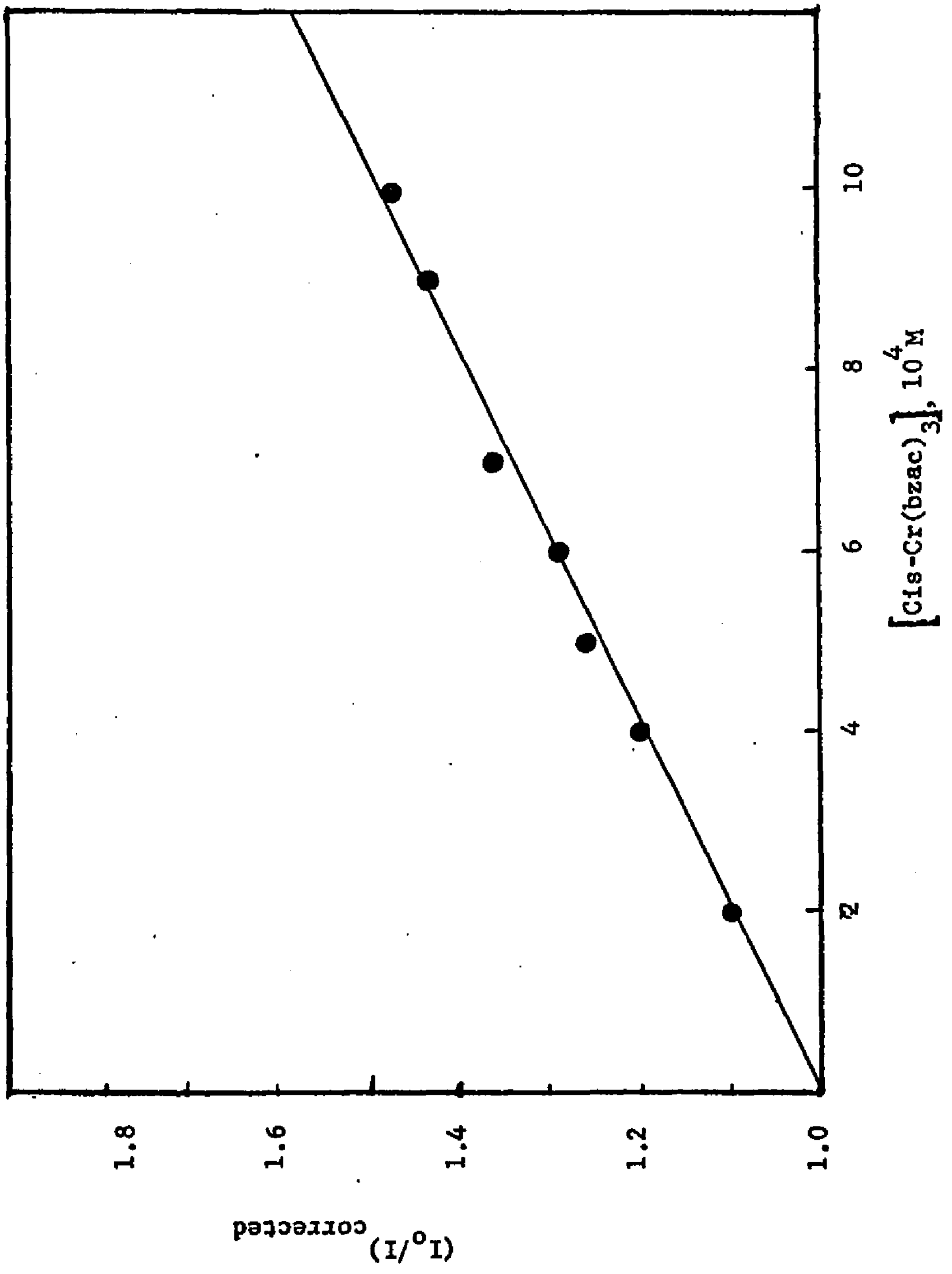


Figure 30

Stern-Volmer Plot for the Quenching of $Ru(bipic)_3^{2+}$ by

Cis-$Cr(bzac)_3$ in 10% (by volume) Chloroform-Ethanol



is the radiative lifetime of $Ru(bipy)_3^{2+}$ in de-areated absolute ethanol, 790 nsec.[53]

(c) Continuous and Flash Photolysis Experiment

Often quenching experiments *per se* do not distinguish various quenching mechanisms. Because of this, a number of continuous and flash photolysis experiments were carried out in an attempt to elucidate the quenching mechanism. Degassed ethanol solutions, 10^{-4}M in $Ru(bipy)_3^{2+}$ and 10^{-3}M in $Co(tfac)_3$ or degassed chloroform-ethanol solutions (10% chloroform by volume), 10^{-4}M in $Ru(bipy)_3^{2+}$ and 5×10^{-4}M in $Co(bzac)_3$ were photolyzed at 452-nm. Under these conditions, greater than 86% of the radiation is absorbed by $Ru(bipy)_3^{2+}$. Spectra recorded periodically during the photolysis did not indicate any net chemical change. After photolysis, analyses of the photolytes for Co(II) by the thiocyanate method were also negative. The upper limits of the quantum yields determined in these photochemical experiments are summarized in Table IV.

Table IV

Quantum Yields of Co(II) on Photolysis of $Ru(bipy)_3^{2+}$ in the Presence of Beta-diketone Complexes of Co(III)

Quencher, conc. x 10^4 M	$Ru(bipy)_3^{2+}$ conc. x 10^4 M	$\lambda_{excitation}$	$\phi_{Co(II)}$
trans-$Co(tfac)_3$, 10.0	0.996	452-nm	$\leq 1.16 \times 10^{-3}$
cis-$Co(tfac)_3$, 9.80	0.996	452-nm	$\leq 1.94 \times 10^{-3}$
trans-$Co(bzac)_3$, 5.25	0.996	452-nm	$\leq 1.29 \times 10^{-3}$
cis-$Co(bzac)_3$, 5.07	0.996	452-nm	$\leq 1.10 \times 10^{-3}$

These steady state photolysis experiments are inconclusive, however, since quenching via an electron transfer mechanism, equation 29

$$*Ru(bipy)_3^{2+} + CoL_3 \longrightarrow Ru(bipy)_3^{3+} + CoL_3^- \qquad (29)$$

could be followed by rapid reverse reaction

$$CoL_3^- + Ru(bipy)_3^{3+} \longrightarrow Ru(bipy)_3^{2+} + CoL_3 \qquad (30)$$

For this reason a number of flash photolysis experiments were carried out. Degassed ethanol solution, 10^{-5}M in $Ru(bipy)_3^{2+}$ and 2 x 10^{-4}M in $Co(tfac)_3$, were exposed to 250-J flashes, but transients lasting longer than 60 μsec were not detected at 675-nm, the absorption maximum of $Ru(bipy)_3^{2+}$ ($\epsilon = 420\ M^{-1} cm^{-1}$).[45] Nor were any transients detected in the 480-nm to 550-nm region, where Co(acac)$_2$ absorbs.[46] The absence of a transient absorbance indicates that if quenching occurs by electron transfer, the rate constant of the reverse reaction must be $> 5 \times 10^8$ M^{-1}sec^{-1}.[54]

(II) Quenching of the Triplet States of Various Organic Donors

In view of the possibility of using the triplet state of organic molecules to sensitize a reaction within a metal complex,[55] the quenching of organic triplets by metal complexes is a topic of current interest. Although interesting, the experiments are difficult because the majority of organic donors do not phosphoresce in fluid solution.[56] However, the triplet-triplet absorption spectra of a large number of organic molecules are known and the quenching reactions can be followed by monitoring the decay of the triplet formed in a flash photolysis experiment.[38] Typical oscilloscope traces monitoring the decay of the triplet states of organic donors studied are shown in Figures 31 through 35. The absorption maxima of the triplet-triplet transitions of the donors used in these experiments are listed in Table V.

Table V

Absorption Maxima of the Triplet-Triplet Transitions of The Donors and the Analysis Wavelength

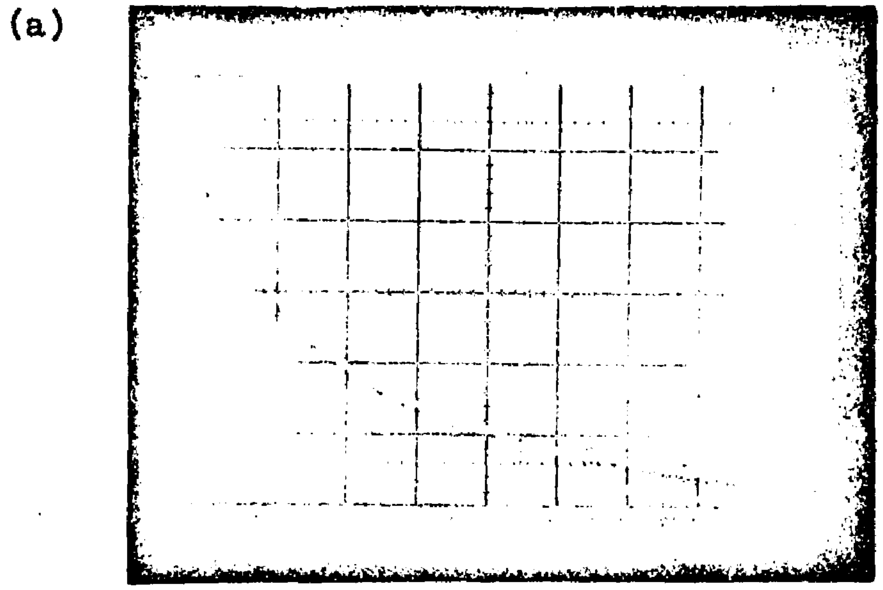
Donor	Triplet-Triplet Absorption Maxima,[a] nm	$\lambda_{\text{analyzed}}$, nm
Anthracene	420	420
	398	
Pyrene	520	
	411	408
	387	
	369	
Phenanthrene	520	
	508	
	481	482
	453	
	425	
9-methylanthracene	-[b]	420
9-phenylanthracene	-[b]	420

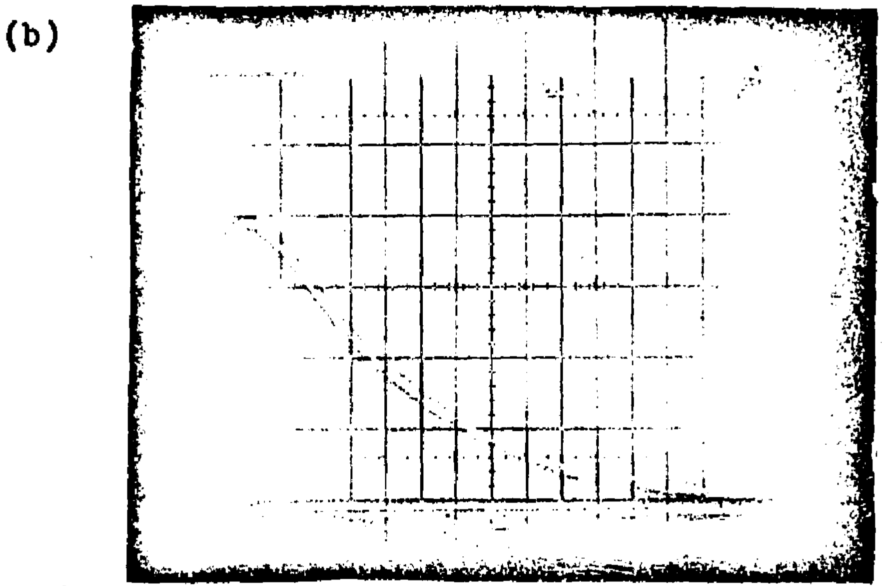
a. Values reported in hexane at 20°C.[1]

b. No spectroscopic data on the triplet state of these donors is currently available in literature.

Figure 31

The Decay Trace of the Triplet State of Anthracene





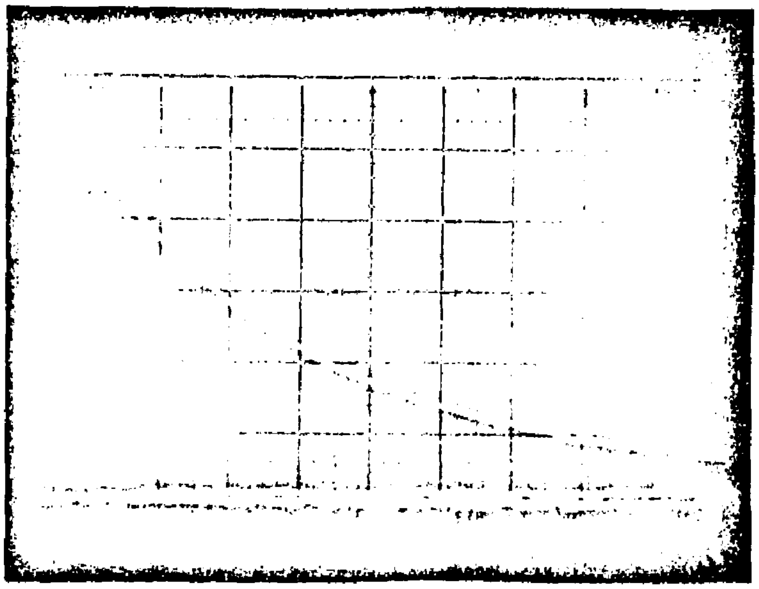
(a) 4.00 x 10^{-5}M anthracene, 0.1 msec per division.

(b) 4.00 x 10^{-5}M anthracene and 9.36 x 10^{-6}M trans-Co(bzac)$_3$, 50 μsec per division.

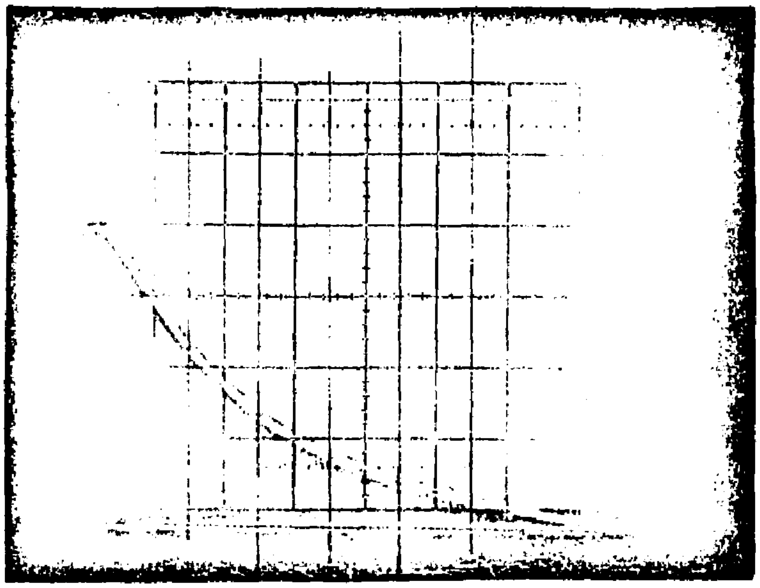
Figure 32

The Decay Trace of the Triplet State of 9-Phenylanthracene

(a)



(b)

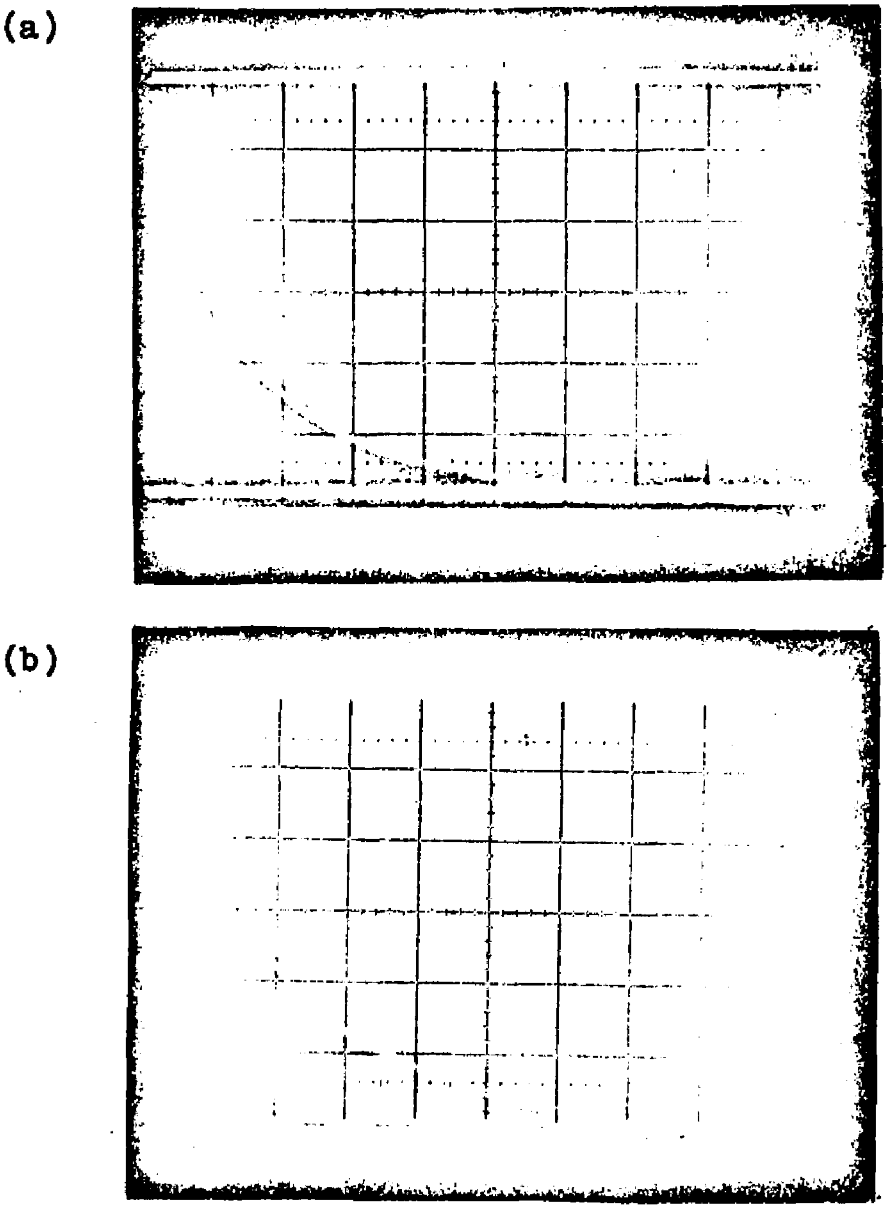


(a) 4.00 x 10^{-5}M 9-phenylanthracene, 0.1 msec per division.

(b) 4.00 x 10^{-5}M 9-phenylanthracene and 8.88 x 10^{-6}M cis-Co(bzac)$_3$, 0.1 msec per division.

Figure 33

The Decay Trace of the Triplet State of 9-Methylanthracene

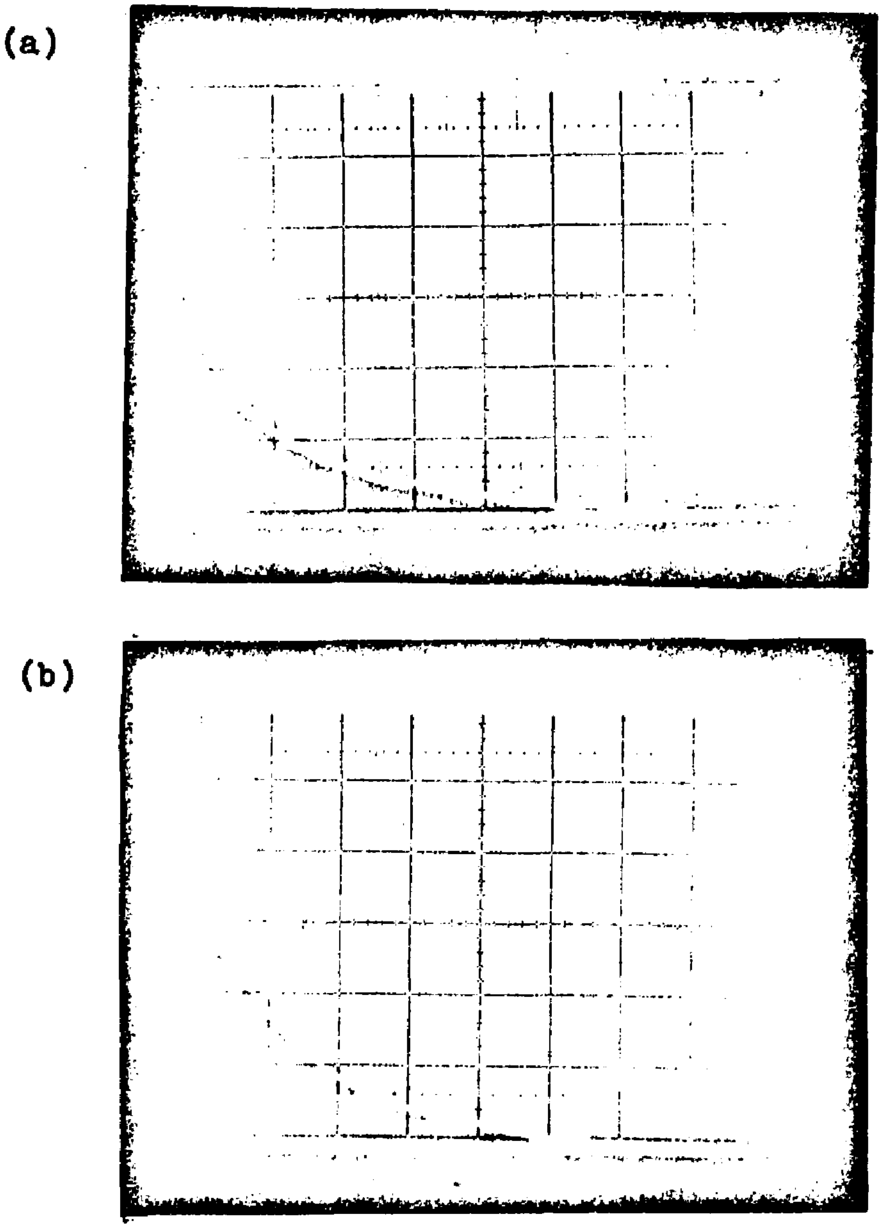


(a) 4.06×10^{-5}M 9-methylanthracene, 0.2 msec per division.

(b) 4.06×10^{-5}M 9-methylanthracene and 2.86×10^{-6}M cis-Cr(bzac)$_3$, 0.1 msec per division.

Figure 34

The Decay Trace of the Triplet State of Pyrene

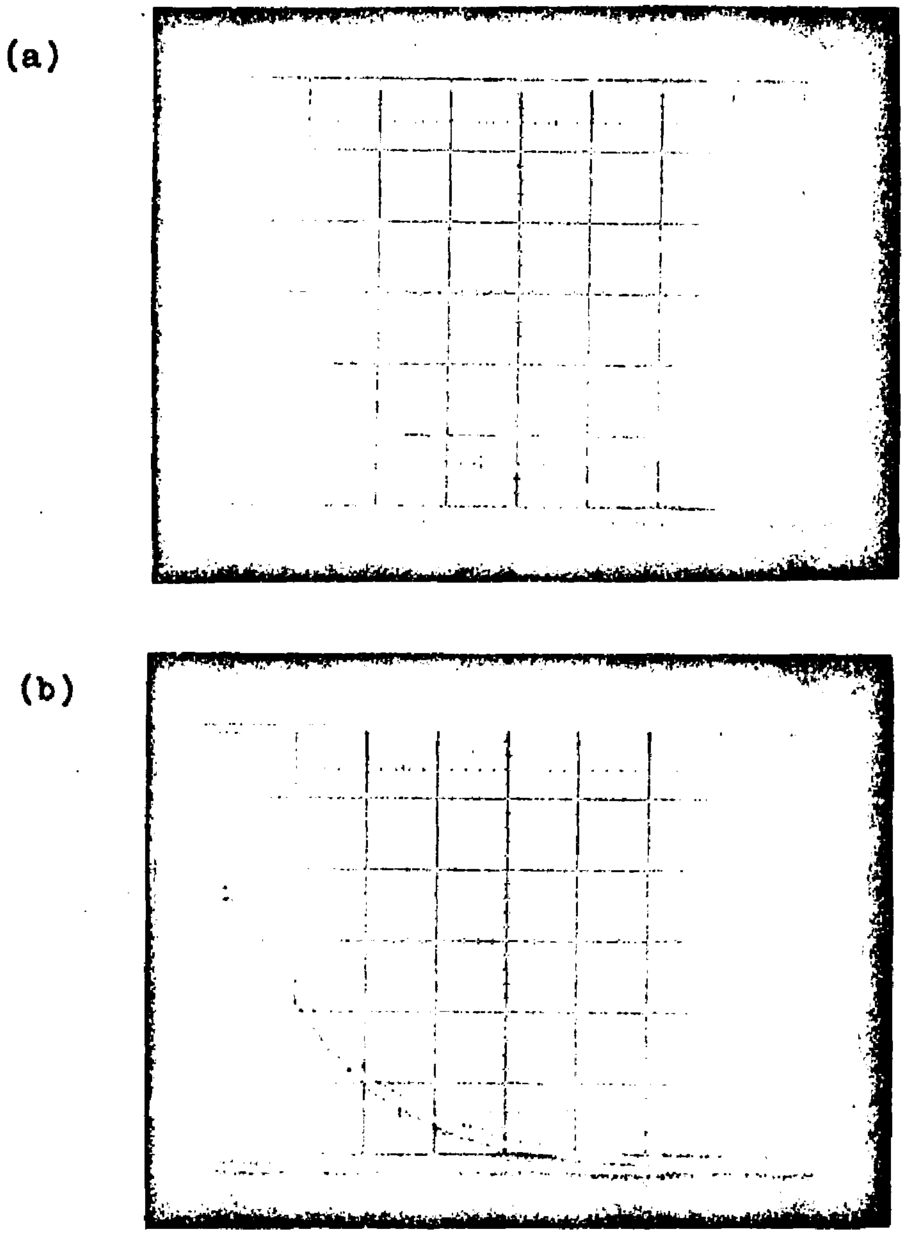


(a) 3.98×10^{-5}M pyrene, 0.2 msec per division

(b) 3.98×10^{-5}M pyrene and 1.56×10^{-6}M trans-Co(tfac)$_3$, 0.1 msec per division.

Figure 35

The Decay Trace of the Triplet State of Phenanthrene



(a) 3.97 x 10^{-5}M phenanthrene, 50 μsec per division.

(b) 3.97 x 10^{-5}M phenanthrene and 1.15 x 10^{-6}M trans-Co(tfac)$_3$, 50 μsec per division.

From previous experiments, the decay of the triplet state in fluid solution can be described by the kinetic expression.[12, 16a, 57]

$$-\frac{d[^3D]}{dt} = k_1[^3D] + k_2[^3D]^2 \qquad (31)$$

where $[^3D]$ is the concentration of donor molecules in the triplet state. The first order term, k_1, is the sum of at least two terms,[58]

$$k_1 = k_1^o + k_1^* \qquad (32)$$

where k_1^o is the true radiative and nonradiative unimolecular decay rate constant. Unlike k_1^o, k_1^* varies with temperature and viscosity and appears to be due to interaction with adventitious quenchers, such as oxygen. A small contribution to triplet decay may also arise from a self-quenching reaction, equation 33.

$$^3D + {}^1D \xrightarrow{k_{33}} 2\,{}^1D \qquad (33)$$

where ^1D represent the singlet ground state of the donor. The kinetic expression describing equation 33 is given by

$$-\frac{d[^3D]}{dt} = k_{33}[^3D][^1D] \qquad (34)$$

The concentration of singlet states, $[^1D]$, can be expressed in terms of the total concentration, $[D_o]$ and the concentration of triplet states, $[^3D]$, i.e.

$$[^1D] = [D_o] - [^3D] \tag{35}$$

Substituting this expression into equation 34 yields

$$-\frac{d[^3D]}{dt} = k_{33}[D_o][^3D] - k_{33}[^3D]^2 \tag{36}$$

Although self-quenching gives rise to a second order term, it is small in comparison to triplet-triplet annihilation reactions. In a triplet-triplet annihilation reaction,[59] equation 37

$$2\,^3D \xrightarrow{k_{37}} {}^1D* + {}^1D \tag{37}$$

energy transfer occurs from one triplet donor to another triplet donor to form a ground singlet state and an excited singlet state. This excited singlet may then return to the ground state either directly or through the lowest triplet state. The annihilation is second order and described by the expression

$$-\frac{d[^3D]}{dt} = k_{37}[^3D]^2 \tag{38}$$

Combining equations 31, 32, 36, and 38 yields

$$-\frac{d[^3D]}{dt} = (k_1^o + k_1^* + k_{33}[D_o])[^3D] + (k_{37}-k_{33})[^3D]^2 \qquad (39)$$

which is the general expression for the decay of a triplet state, equation 31, where

$$k_1 = k_1^o + k_1^* + k_{33}[D_o] \qquad (40)$$

and

$$k_2 = k_{37} - k_{33} \qquad (41)$$

In the presence of quencher, however, an additional term arises from the quenching reaction 42

$$^3D + Q \xrightarrow{k_b} D + Q \qquad (42)$$

Since $[Q_o] >> [^3D]$, the $[Q]$ remains constant during the experiment and the expression describing the decay of the triplet in the presence of a quencher can be written as

$$-\frac{d[^3D]_Q}{dt} = (k_1^o + k_1^* + k_{33}[D_o] + k_b[Q_o])[^3D] + (k_{37}-k_{33})[^3D]^2 \qquad (43)$$

Letting $k_1' = k_1^o + k_1^* + k_{33}[D_o] + k_b[Q_o]$ (44)

and $k_2 = k_{37} - k_{33}$ (45)

equation 43 assumes the form

$$-\frac{d[^3D]_Q}{dt} = k_1'[^3D] + k_2[^3D]^2 \qquad (46)$$

The bimolecular rate constant for quenching, k_b, can then be obtained from the difference in the first order constants, i.e.

$$k_b = \frac{k_1' - k_1}{[Q_o]} \qquad (47)$$

In the absence of the quencher the values of k_1 were obtained by computer analysis of the decay curves. The integrated rate law, obtained by integration of equation 31, is

$$\frac{1}{k_1} x \frac{[^3D]_o(k_1 + k_2[^3D])}{[^3D](k_1 + k_2[^3D_o)} = t \qquad (48)$$

where $[^3D]_o$ represents the triplet state concentration at a chosen time, $t_o = 150\,\mu$sec, after the flash. Substituting

$$[^3D]_o = A_o/\epsilon l \qquad \text{and} \qquad [^3D] = A_t/\epsilon l$$

into equation 48 yields

$$\frac{1}{k_1} x \frac{A_o(k_1 + (k_2/\epsilon l) x A_t)}{A_t(k_1 + (k_2/\epsilon l) x A_o)} = t \qquad (49)$$

where A_o and A_t represent the absorbance at time t_o and t, ϵ is the extinction coefficient of the triplet-triplet absorption and l is the pathlength of the flash cell, 17 cm. A computer program which used searching techniques involving the simplex then obtains k_1 and $k_2/\epsilon l$ by minimizing the quantity

$$\sum\left[\frac{1}{k_1} x \frac{A_o(k_1 + (k_2/\epsilon l)A_t)}{A_t(k_1 + (k_2/\epsilon l)A_o)} - t\right]^2$$

according to the criterion of least squares. A copy of the program is given in Appendix 1.

In the presence of an excess of the quencher, the second order term is negligible and equation 43 reduces to

$$-\frac{d[^3D]}{dt} = k_1'[^3D] \qquad (50)$$

Under these conditions, k_1' was obtained directly from the slope of plots of the $Log(A_o/A_t)$ versus time. Representative plots for each of the donors studied are shown in Figure 36 through 40. The bimolecular quenching rate constants, k_b, calculated from equation 47 are listed in Table VI.

When anthracene and 9-methylanthracene were used as the donors, an decrease in the absorbance of the solution was found after the flash experiment. Since

Figure 36

The First Order Plot of the Decay of the Triplet State of Anthracene in the Presence of 5.08×10^{-6} M <u>Trans</u>-$Cr(tfac)_3$

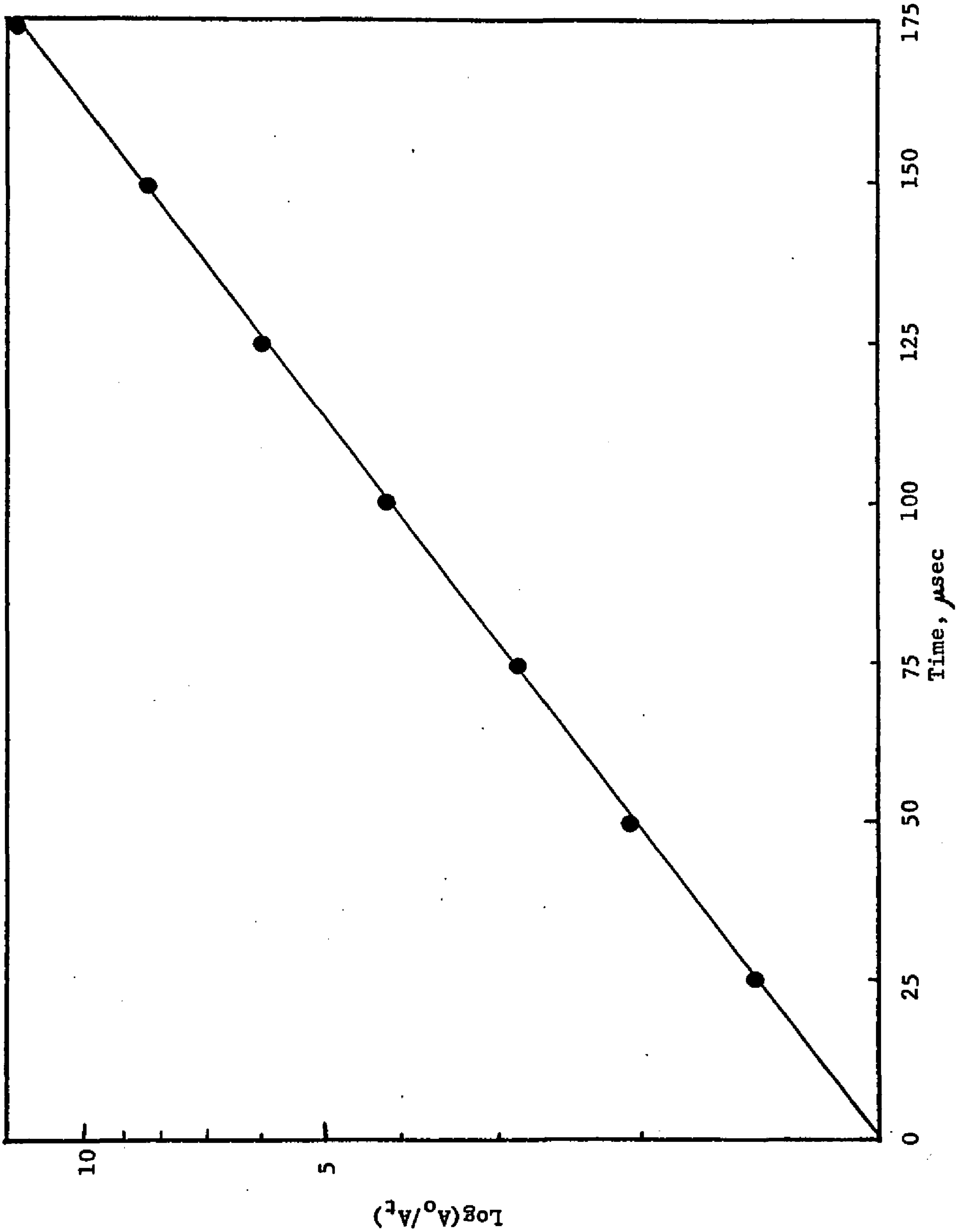


Figure 37

The First Order Plot of the Decay of the Triplet State of 9-phenylanthracene in the Presence of 5.08×10^{-6} M <u>Trans</u>-Cr(tfac)$_3$

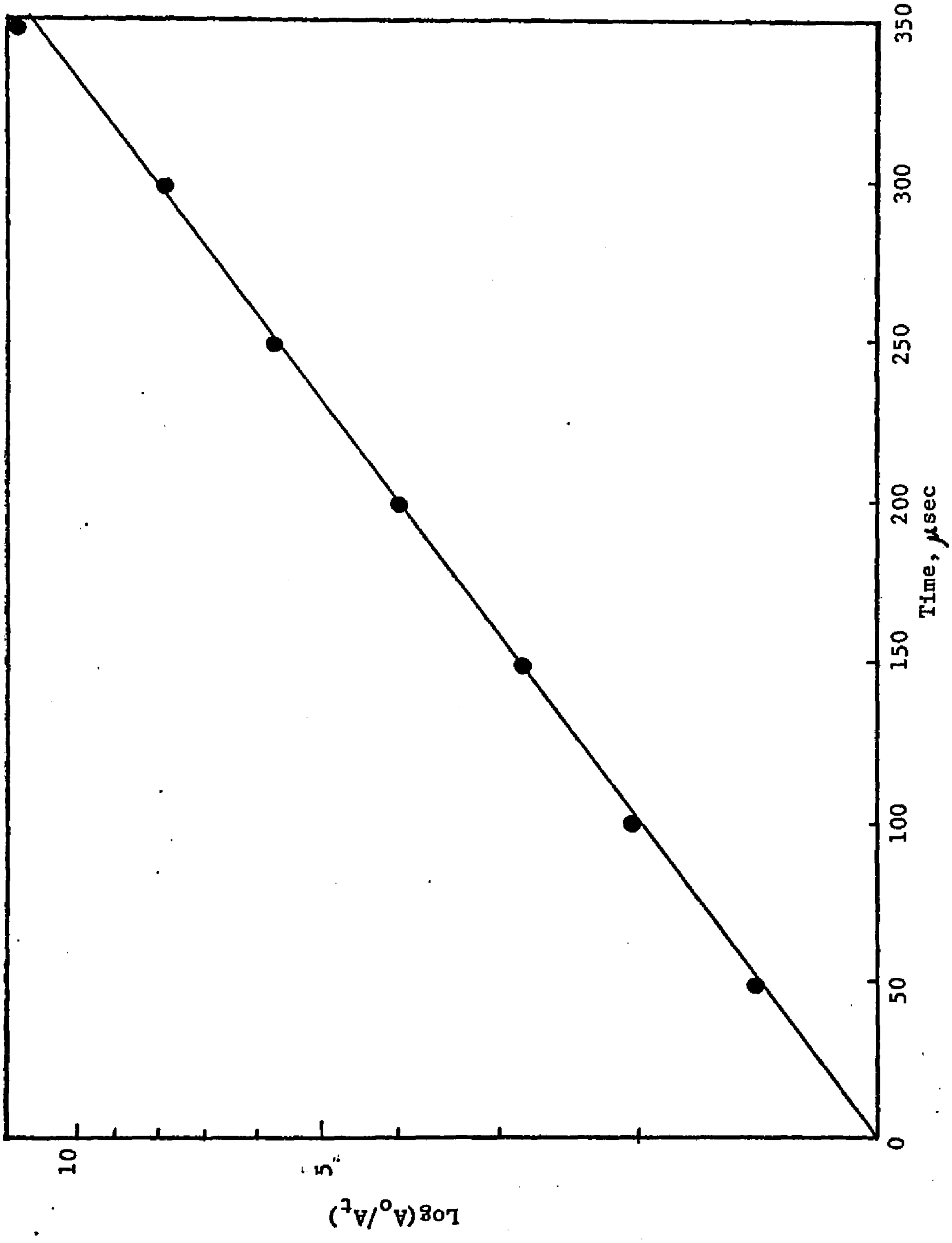


Figure 38

The First Order Plot of the Decay of the Triplet State of 9-Methylanthracene in the Presence of 5.13×10^{-6} M *Trans*-Co(tfac)$_3$

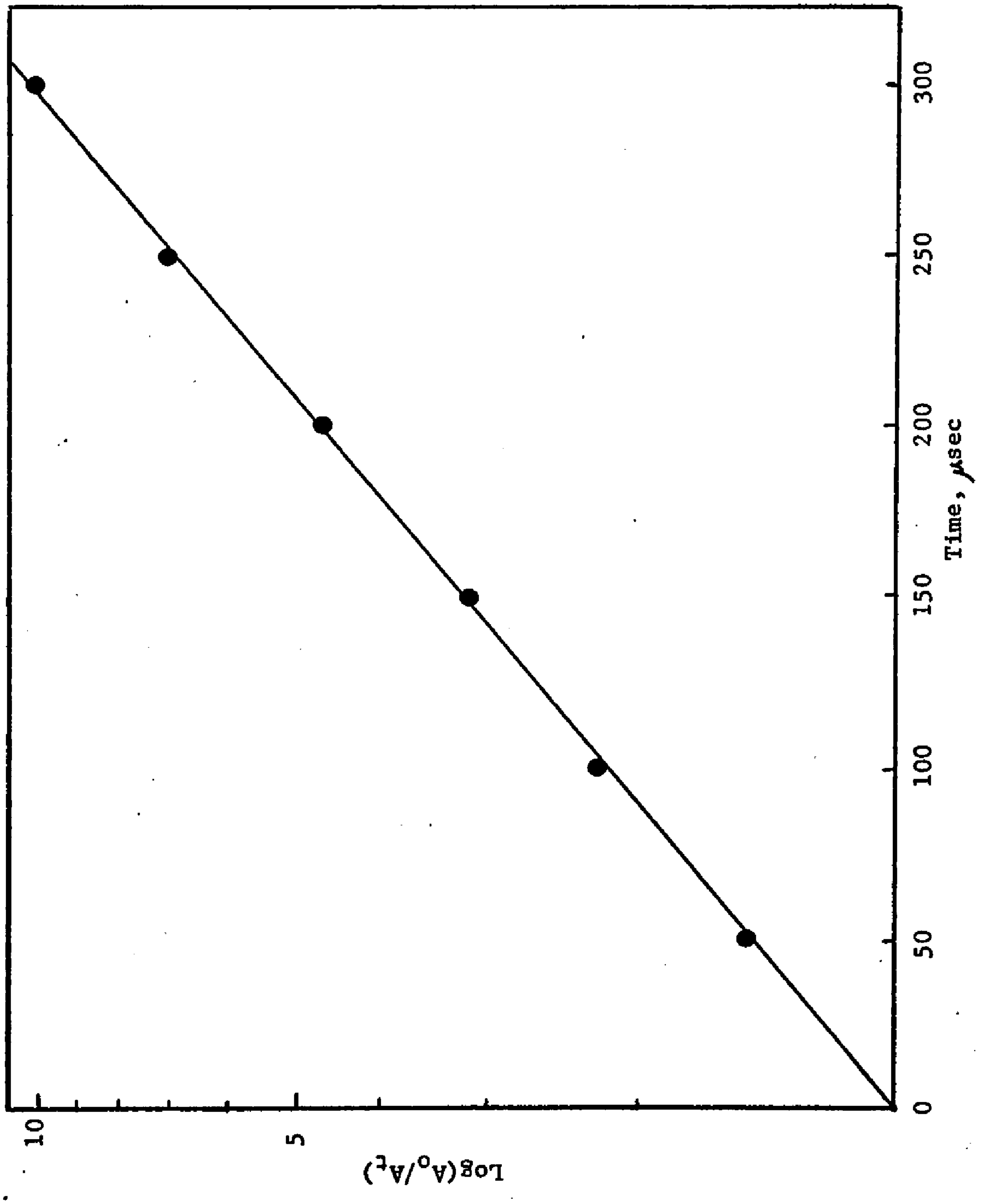


Figure 39

The First Order Plot of the Decay of the Triplet State of Pyrene in the Presence of 1.16×10^{-6} M Cis-Cr(tfac)$_3$

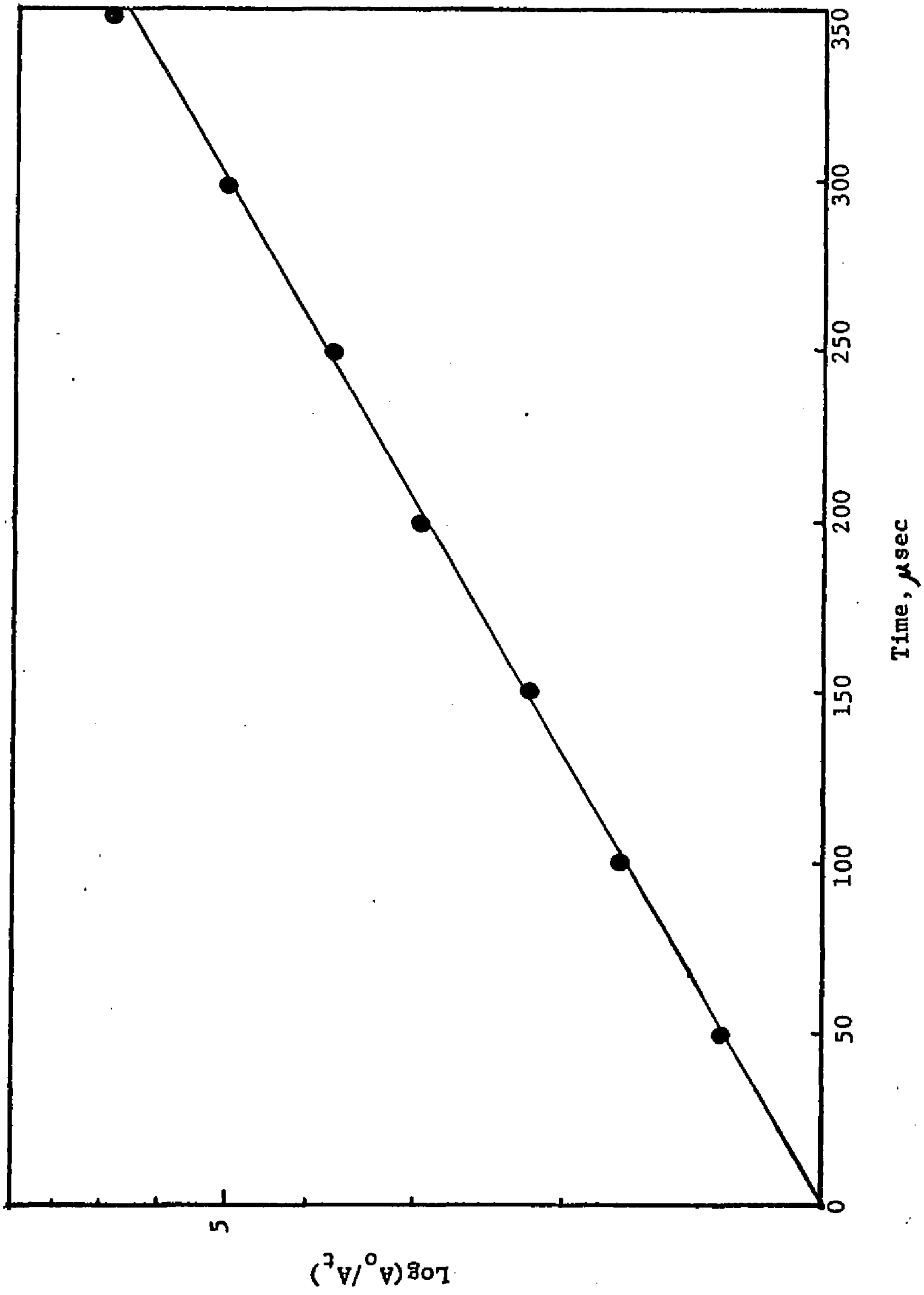


Figure 40

The First Order Plot of the Decay of the Triplet State of Phenanthrene in the Presence of 1.15×10^{-6} M *Trans*- Co(tfac)$_3$

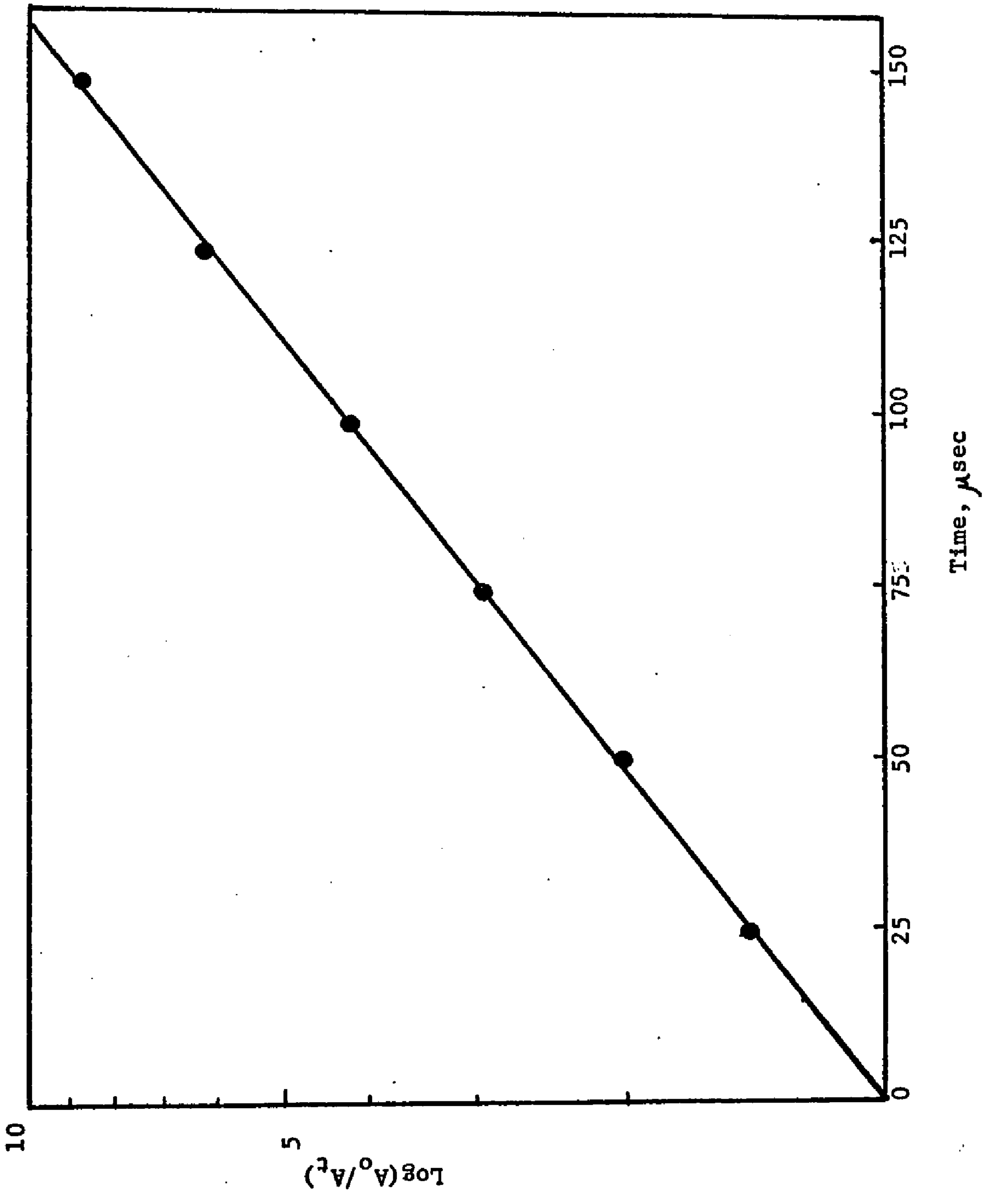


Table VI

Bimolecular Quenching Rate Constants[a] for the Quenching of the Triplet State of Organic Donors

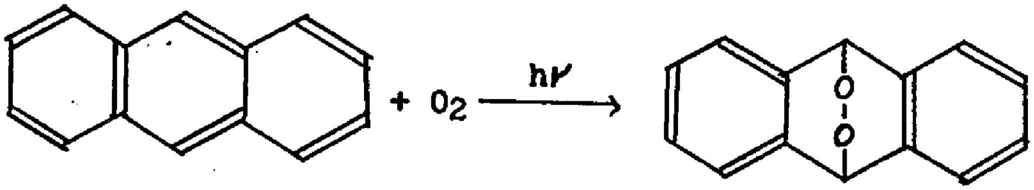
Donors	9-phenylanthracene	9-methylanthracene	anthracene	pyrene	phenanthrene
E_T	14.7 kK[b]	14.7 kK[b]	14.9 kK[c]	16.8 kK[c]	21.6 kK[c]
trans-Co(tfac)$_3$	0.47 ± 0.05	1.02 ± 0.09	0.90 ± 0.09	2.88 ± 0.29	5.26 ± 0.53
cis-Co(tfac)$_3$	0.49 ± 0.05	1.03 ± 0.09	0.95 ± 0.09	3.00 ± 0.30	4.35 ± 0.44
trans-Co(bzac)$_3$	0.21 ± 0.02	1.20 ± 0.11	0.95 ± 0.09	2.46 ± 0.25	4.57 ± 0.46
cis-Co(bzac)$_3$	0.25 ± 0.03	1.03 ± 0.09	0.89 ± 0.09	2.36 ± 0.24	4.02 ± 0.40
trans-Cr(tfac)$_3$	0.70 ± 0.07	1.39 ± 0.13	1.90 ± 0.19	2.79 ± 0.28	4.75 ± 0.47
cis-Cr(tfac)$_3$	0.82 ± 0.08	1.21 ± 0.11	1.93 ± 0.19	2.94 ± 0.29	4.82 ± 0.48
trans-Cr(bzac)$_3$	0.67 ± 0.07	1.33 ± 0.12	1.82 ± 0.18	3.58 ± 0.71	5.66 ± 0.60
cis-Cr(bzac)$_3$	0.85 ± 0.08	1.22 ± 0.11	1.77 ± 0.17	2.75 ± 0.55	5.08 ± 0.51

a. Bimolecular rate constant x 10^{-9} M^{-1} sec^{-1}.

b. Values obtained from sensitization experiments, see ref. 73.

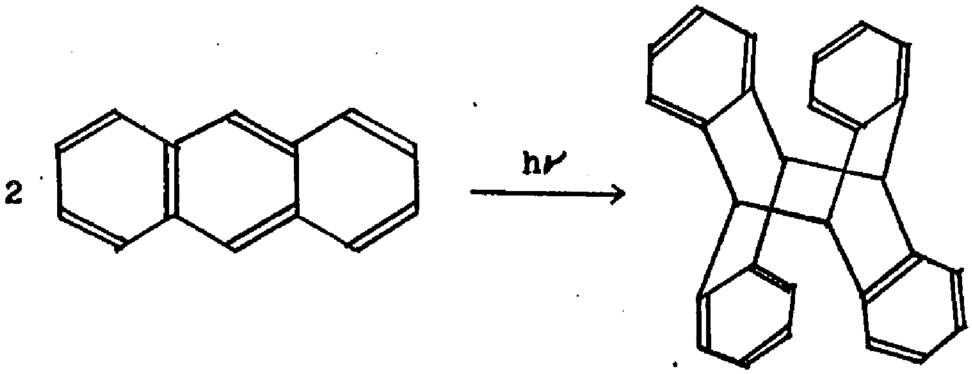
c. Ref. 1.

a similar decrease in absorbance was observed in the absence of the quencher, it was apparent that anthracene and 9-methlyanthracene underwent a photochemical reaction which was unaffected by the metal complexes. Previous studies have shown that anthracene and 9-methylanthracene can undergo either a photoperoxidation,



(51)

or dimerization.[60]



(52)

Since the flash experiments were carried out under conditions which involved an exhaustive removal of dissolved O_2, the photochemical reaction appears to be a dimerization. This reaction, which occurs through the singlet state of the molecule, would be unaffected by these beta-diketonate complexes, but it is questionable whether it could occur at the concentrations of anthracene and 9-methylanthracene used in these experiments, 4×10^{-5}M.

CHAPTER 4

Discussion

(I) Spectrum Assignment of Energy Levels

The absorption spectra of beta-diketonate complexes of Cr(III) and Co(III) have been investigated by a number of workers. The assignments, however, are often based on the parent complex; the metal acetylacetonate complex. The spectral assignments of the transitions observed in these complexes are listed in Table VII.

Barnum assigns the intense bands, $\epsilon \sim 10^4$ $M^{-1}cm^{-1}$, at 270-nm and 255-nm in the spectrum of Cr(acac)$_3$ to a $\pi - \pi^*$ transition within the enolate ring.[50] Similarly, the bands at 256-nm and 228-nm in the spectrum of Co(acac)$_3$ are also assigned to ligand-centered $\pi - \pi^*$ transitions. The assignment is based on the intensity of the bands, the absence of a blue shift in polar solvents, and the presence of a small red shift on going from the acetylacetonates to the corresponding benzoylacetonates.[32a] The latter is thought to arise from an increase in the delocalization of the π- system due to the C_6H_5 substituent.

More recent analyses of the spectra involving extensive molecular orbital calculations, however, assign the 228-nm band in the spectrum of $Co(acac)_3$ to a $\pi-\pi^*$ transition, but assign the 256-nm band to a charge-transfer transition.[61] These assignments seem more reasonable since 254-nm photolysis of $Co(acac)_3$ leads to photo-reduction and the formation of Co(II).[62] With $Cr(acac)_3$, the assignments are less distinct. The transition at 270-nm is assigned to a ligand $\pi-\pi^*$ transition with some charge-transfer character while the transition at 255-nm is assigned to a charge-transfer transition with ligand $\pi-\pi^*$ character.

The absorption band at 332-nm in the spectrum of $Cr(acac)_3$ is assigned as charge-transfer transition. In the spectrum of $Co(acac)_3$, this charge-transfer transition is assigned to the band at 323-nm.[55]

Since the energies of the donors used in these experiments are < 22 kK, quenching processes involving these excited states would be very endothermic and can be ruled out. The quenching reaction must then involve the lower energy excited states of these complexes. There are three states which must be considered: the lowest triplet π^* state of the ligand, designated ^3L, and the spin-allowed and spin-forbidden ligand-field states of the complexes. It should be noted, however, that a charge-transfer state of triplet multiplicity may also lie at relatively low energy. For example, molecular orbital calculations and sensitization of the reduction of a number of acidopentaamminecobalt(III) complexes suggest such a low energy state.[55a] In many cases, the results are contradictory, however, and there is no general agreement as to the energies of these states. Thus, the subsequent discussion is limited to those spin forbidden states where the energy of the state can be determined from available spectral data.

Previous studies of the phosphorescence of europium beta-diketone complexes have shown that excitation of ligand-centered transitions gave rise to a phosphorescence characteristic of the Eu^{3+} ion.[63] These results were interpreted in terms of an intramolecular energy transfer mechanism where the lower energy ligand triplet state was an essential link in the transfer of energy from the ligand to the metal ion. It seems reasonable to assume then that the ^3L state might be involved in these quenching reactions.

An exact determination of the energy of the ^3L state in these Cr(III) and Co(III) complexes, however, is not possible. The Co(III) complexes do not emit and the low temperature emission of the Cr(III) complexes is a metal-centered $^2E \rightarrow {}^4A_2$ transition.[49] The phosphorescence from Na(tfac) has a maximum at *ca.* 450-nm

22.2 kK, but the emission intensity is weak and it is difficult to determine the energy with certainty.[62] The energy has been determined with good accuracy, however, from the emission spectra of La(tfac)$_3$.[64] In an 3:1 methanol-ethanol glass, Brinen and coworkers report that the broad structured emission characteristic of the trifluoroacetylacetonate ligand spans the energy range 23.53 kK to 20.41 kK. Thus, in the energy level diagram, Figure 41, the energy of the ^3L state of trifluoroacetylacetone is presented as a range of energies as opposed to a specific energy.

The energy of the ^3L state of benzoylacetone is reported to be 21.5 kK.[65] The phosphorescent emission is broad, however, and the energy of this state is also presented as a range in Figure 41 .

The other lower energy excited states which could be involved in these quenching reactions are the spin allowed and spin forbidden ligand-field states. The band which has a maximum at 597-nm in the spectra of these Co(III) complexes is assigned to a $^1A_1 \rightarrow {}^1T_1$ transition.[50] The maximum, however, reflects the vertical Franck-Condon transition. Thus the energy of the thermally equilibrated excited ligand-field state, shown in Figure 41, was estimated by the Fleischauer-Adamson criteria applied to the long wavelength side of the absorption band.[48] Two weak absorption bands have been reported in the absorption spectrum of $Co(acac)_3$ in chloroform solution. These bands, which occur at 1100-nm and 800-nm are assigned to the $^1A_1 \rightarrow {}^3T_1$ and $^1A_1 \rightarrow {}^3T_2$ transitions, respectively.[50] Since the ligand-field strength of tfac and bzac are slightly less than that of acac,[32] upper limits of the energies of the $^3T_1$ and $^3T_2$ states of $Co(bzac)_3$ and $Co(tfac)_3$, shown in Figure 41, are taken from the transitions found in the spectrum of $Co(acac)_3$.

In the ligand-field spectra of $Cr(bzac)_3$ and $Cr(tfac)_3$, the spin allowed $^4A_2 \rightarrow {}^4T_2$ transition occurs at 563-nm.[50] The energy of the thermally equilibrated $^4T_2$ state is less than that indicated by the band maximum and was estimated by the Fleischauer-Adamson criteria.[48] The energies of the spin forbidden ^2E states were obtained from low temperature phosphorescence spectra and are also shown in Figure 41.

(II) Quenching of $Ru(bipy)_3^{2+}$ and $Ru(bipic)_3^{2+}$

A. Quenching Mechanism

Noting that Ag^+ (Z=47) and I^- (Z=53) were inefficient quenchers, whereas Co(III) and Cr(III) complexes were efficient quenchers, Demas and Addington have pointed out that quenching of these Ru(II) complexes (Z=44) by an external heavy atom mechanism is unlikely.[13]

Table VII

Spectrum Assignment of Beta-diketonate Complexes

$Cr(acac)_3^a$		$Cr(tfac)_3^b$		$Cr(bzac)_3^c$		Assignment
λ_{max}, nm	$\epsilon, M^{-1}cm^{-1}$	λ_{max}, nm	$\epsilon, M^{-1}cm^{-1}$	λ_{max}, nm	$\epsilon, M^{-1}cm^{-1}$	
255	$1.12x10^4$	264	$1.02x10^4$	260	$3.03x10^4$	CT + $L(\pi\rightarrow\pi^*)$
270	$1.05x10^4$	278	$1.00x10^4$			$L(\pi\rightarrow\pi^*)$ + CT
(295)	$6.31x10^3$					
332	$1.51x10^4$	340	$1.20x10^4$	358	$2.24x10^4$	CT
380	$4.26x10^2$	386	$3.90x10^2$			
388	$4.26x10^2$					
(410)	1.58x10					
435	50					
560	66	563	68.3	563	91.2	$^4A_2\rightarrow{}^4T_2$

a. in ethanol, ref 50.

b. in ethanol

c. in chloroform.

Table VII (continued)

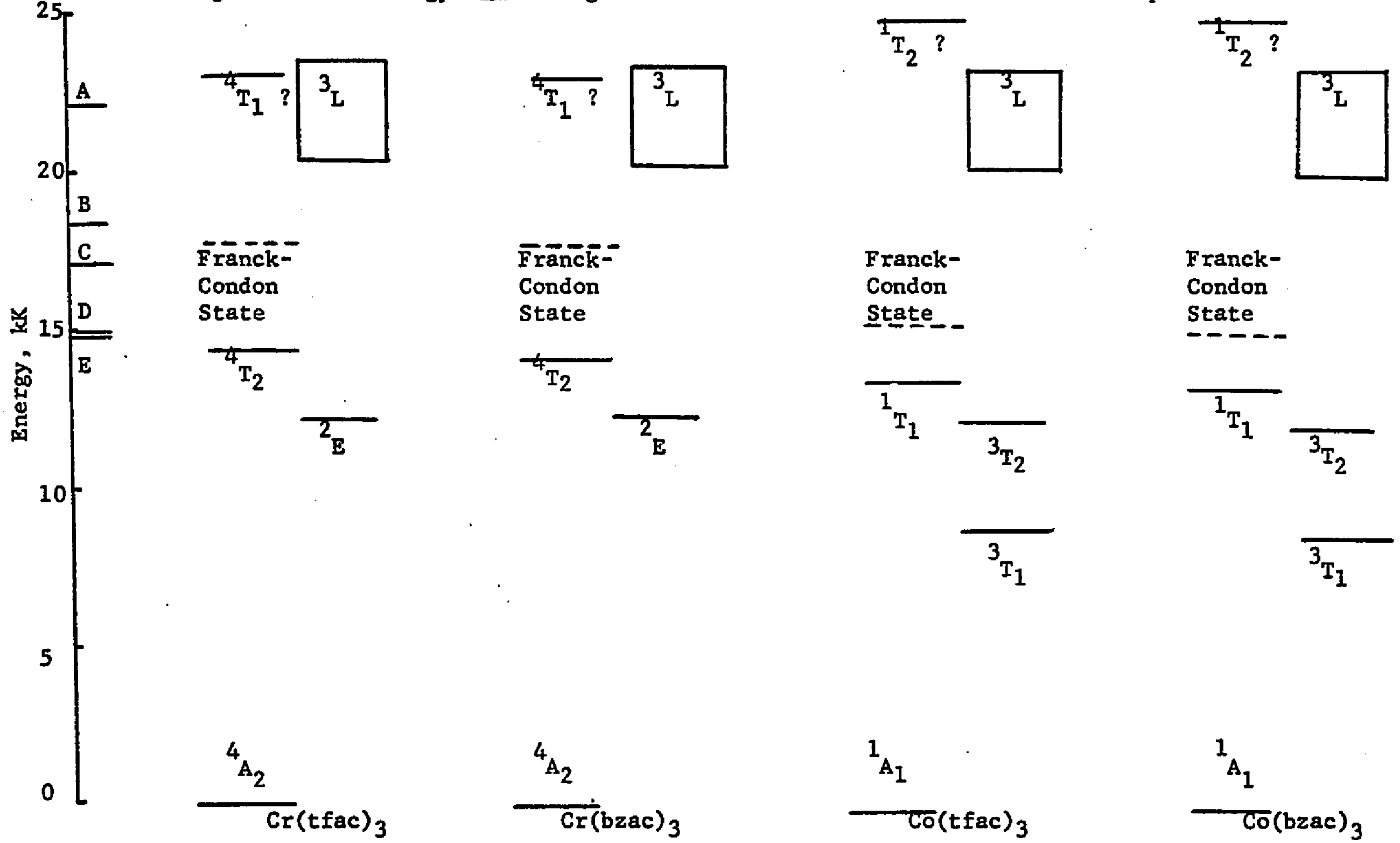
$Co(acac)_3$[a]		$Co(tfac)_3$[b]		$Co(bzac)_3$[c]		Assignment
λ_{max}, nm	ϵ, $M^{-1}cm^{-1}$	λ_{max}, nm	ϵ, $M^{-1}cm^{-1}$	λ_{max}, nm	ϵ, $M^{-1}cm^{-1}$	
228	3.98×10^4	232	3.18×10^4			$L(\pi \rightarrow \pi^*)$
256	3.39×10^4	252	3.30×10^4	267	6.01×10^4	CT
(295)	1.00×10^4					
323	7.76×10^3	332	6.00×10^3	355	1.38×10^4	CT
(400)	3.16×10^2					
595	1.26×10^2	597	1.31×10^2	598	1.53×10^2	${}^1A_1 \rightarrow {}^1T_1$
800	3					${}^1A_1 \rightarrow {}^3T_2$
1100	1.9					${}^1A_1 \rightarrow {}^3T_1$

a. in ethanol, ref. 50.

b. in ethanol

c. in chloroform

Figure 41 Energy Level Diagram of the Donors and Beta-diketonate Complexes



The lowest triplet state energies of donors are represented by A. Phenanthrene, C. Pyrene, D. Anthracene and E. 9-methylanthracene or 9-phenylanthracene. B is the charge-transfer luminescent state of RuB_3^{2+}.

These authors also point out that there is no correlation between the magnetic moment of a wide variety of quenchers and their quenching efficiency. This lack of correlation as well as the high atomic number of Ru(II) rule out a spin-catalyzed deactivation induced by either the paramagnetism or spin-orbit coupling of the quencher. Since these donors and quenchers are hindered, steric considerations indicate that formation of a π-complex is unlikely. Since the quenchers are neutral, ion-pair exciplexes are also ruled out. A charge-transfer stabilized exciplex is possible, but there is no evidence currently available for such species involving transition metal complexes. Thus, quenching by either an energy transfer or a donor-acceptor chemical reaction remain as the most reasonable mechanisms for the quenching reaction.

There are numerous precedents to justify the assumption of energy transfer. For example, in fluid system at -113°C, the quenching of benzil phosphorescence by $Cr(NCS)_6^{3-}$, $Cr(acac)_3$ and $Cr(en)_3$ is accompanied by the sensitization of Cr(III) $^2E \rightarrow {}^4A_2$ emission.[6b] Similarly, the quenching of $Ru(bipy)_3^{2+}$ by $Cr(NCS)_6^{3-}$ causes a sensitized emission from the Cr(III) complex.[6a] Although the latter establishes an energy transfer mechanism, these beta-diketone complexes do not emit at room temperature and the choice of a quenching mechanism is based on indirect evidence.

Previous studies of the quenching of the organic triplets by beta-diketonate complexes have shown that the quenching efficiency increases as the π system of the quencher becomes more exposed and delocalized.[16c] Furthermore, Wilkinson and Farmilo have shown that the quenching of various organic triplets by beta-diketone complexes occurs by an energy transfer mechanism.[30] In view of these results, it seems reasonable to expect, if quenching occurs by an energy transfer mechanism, a similar pattern in the quenching of $Ru(bipy)_3^{2+}$. Although the data obtained in these experiments are more limited, the Stern-Volmer constants listed in Table III do follow this pattern; the quenching efficiency of $Cr(bzac)_3$ is larger than that of $Cr(tfac)_3$. Thus, consider first quenching via an energy transfer mechanism.

Since the luminescent state of these Ru(II) complexes possess some triplet character,[37] energy transfer to both the ^2E and $^4T_2$ states of the Cr(III) complexes satisfy Wigner's rules of spin conservation. The energies of the ^2E state, obtained from low temperature emission spectra, are 12.34 kK and 12.42 kK for $Cr(tfac)_3$ and $Cr(bzac)_3$, respectively.[49] Although the absorption maxima of the $^4A_2 \rightarrow {}^4T_2$ transitions occur at 17.8 kK, the energies of the thermally equilibrated $^4T_2$ states, estimated by the Fleischauer-Adamson criteria are 14.4 kK and 14.2 kK for $Cr(tfac)_3$ and $Cr(bzac)_3$, respectively.[48] Thus energy transfer to either state satisfies both spin and energy requirements and the quenching reaction may be written as

$$RuB_3^{2+} \xrightarrow[\Phi_{IC}]{h\nu} {}^*RuB_3^{2+} \qquad (53)$$

$$^*RuB_3^{2+} \longrightarrow RuB_3^{2+} + h\nu \qquad (54)$$

$$^*RuB_3^{2+} \longrightarrow RuB_3^{2+} \qquad (55)$$

$$^*RuB_3^{2+} + CrL_3(^4A_2) \longrightarrow RuB_3^{2+} + {}^*CrL_3(^4T_2) \qquad (56)$$

$$^*RuB_3^{2+} + CrL_3(^4A_2) \longrightarrow RuB_3^{2+} + {}^*CrL_3(^2E) \qquad (57)$$

$$^*CrL_3\ (^4T_2) \longrightarrow CrL_3(^4A_2) \qquad (58)$$

$$^*CrL_3\ (^2E) \longrightarrow CrL_3(^4A_2) \qquad (59)$$

where B represents bipyridine or bipicoline and Φ_{IC} , the intersystem crossing yield, is taken to be unity.[36]

The oxidative and reductive properties of these Ru(II) complexes are now firmly established.[9,16] The potentials of the half reactions are

$$^*RuB_3^{2+} \longrightarrow RuB_3^{3+} + e^- \qquad E^o = 0.84V \quad (60)$$

$$^*RuB_3^{2+} + e^- \longrightarrow RuB_3^{+} \qquad E^o = 0.84V \quad (61)$$

On energetic grounds, reductive quenching by these Cr(III) complexes, forming RuB_3^+ and $Cr(tfac)_3^+$, is unlikely. On the other hand, oxidative quenching by some Cr(III) complexes has been established.[67] Thus, the most likely chemical quenching mechanism would involve oxidative quenching and would be written as

$$RuB_3^{2+} \xrightarrow[\Phi_{IC}]{h\nu} {}^*RuB_3^{2+} \qquad (62)$$

$${}^*RuB_3^{2+} + CrL_3 \longrightarrow RuB_3^{3+} + CrL_3^- \qquad (63)$$

$$RuB_3^{3+} + CrL_3^- \longrightarrow RuB_3^{2+} + CrL_3 \qquad (64)$$

The data gathered in these experiments do not conclusively establish either mechanism. Our preference, however, is an energy transfer mechanism. This is based on the irreversibility of the reduction of the Cr(III) complexes.[68] Assuming reduction of the Cr(III) complex did occur during the quenching encounter, equation 63, the lability of Cr(II) complexes suggests that some ligand dissociation would occur and a net photochemical reaction would result. Of course, if the back reaction, equation 64, is rapid, no net chemical change would occur. We find it difficult to accept, however, that the latter would be 100% efficient. Rather we would expect to see some net reaction, yet the results obtained in these experiments gave no indication of a net reaction. Although there are reservations, our preference is an energy transfer mechanism.

As was the case with the Cr(III) isomers, quenching of the Co(III) isomers could also occur by either an electron transfer or energy transfer mechanism. Due to the low energy of the Ru(II) donors, however, energy transfer would be limited to the lower energy ligand-field state of the complexes. Although Wigner's rules of spin conservation limit energy transfer to the triplet states of the Co(III) complexes, the rules are based on a formal assignment of spin multiplicity. In view of the spin-orbit coupling within these metal complexes the mechanism, equations 65 through 71 , is written to indicate energy transfer to both singlet and triplet states of the Co(III) complex.

$$\mathrm{RuB_3^{2+}} \xrightarrow[\Phi_{IC}]{h\nu} {}^*\mathrm{RuB_3^{2+}} \qquad (65)$$

$$^*\mathrm{RuB_3^{2+}} + \mathrm{CoL_3(^1A_1)} \longrightarrow \mathrm{RuB_3^{2+}} + {}^*\mathrm{CoL_3(^3T_1)} \qquad (66)$$

$$^*\mathrm{RuB_3{}^{2+}} + \mathrm{CoL_3(^1A_1)} \longrightarrow \mathrm{RuB_3^{2+}} + {}^*\mathrm{CoL_3(^3T_2)} \qquad (67)$$

$$^*\mathrm{RuB_3^{2+}} + \mathrm{CoL_3(^1A_1)} \longrightarrow \mathrm{RuB_3^{2+}} + {}^*\mathrm{CoL_3(^1T_1)} \qquad (68)$$

$$^*\mathrm{CoL_3(^3T_1)} \longrightarrow \mathrm{CoL_3(^1A_1)} \qquad (69)$$

$$^*\mathrm{CoL_3(^3T_2)} \longrightarrow \mathrm{CoL_3(^1A_1)} \qquad (70)$$

$$^*\mathrm{CoL_3(^1T_1)} \longrightarrow \mathrm{CoL_3(^1A_1)} \qquad (71)$$

As mentioned above, quenching by electron transfer is also possible. On energetic grounds, reductive quenching by these Co(III) complexes, forming RuB_3^+ and $Co(tfac)_3^+$, is unlikely. On the other hand, oxidative quenching by a number of Co(III) complexes has been established.[41, 42] Thus, the most likely chemical quenching mechanism would involve oxidative quenching and would be written as

$$RuB_3^{2+} \xrightarrow[\Phi_{IC}]{h\nu} {}^*RuB_3^{2+} \tag{72}$$

$$^*RuB_3^{2+} + CoL_3 \longrightarrow RuB_3^{3+} + CoL_3^- \tag{73}$$

$$RuB_3^{3+} + CoL_3^- \longrightarrow RuB_3^{2+} + CoL_3 \tag{74}$$

A clear distinction between an energy transfer and electron transfer mechanism can not be made in these quenching reactions. There is, however, indirect evidence which leads us to suggest the latter mechanism. As mentioned above, the quenching efficiency of these beta-diketone complexes increases, in an energy transfer mechanism, as the π system of the quencher becomes more exposed and delocalized. With the Cr(III) isomers, the order of quenching efficiency is $Cr(bzac)_3 > Cr(tfac)_3$. With the Co(III) isomers, the order is inverted and leads us to suspect an electron transfer mechanism. This suspicion, however, must be judged with caution since steady state and flash photolysis experiments gave no indication of a redox reaction. Steady state photolysis experiments indicated that $\Phi_{Co(II)} \leq 10^{-3}$ and, in flash photolysis experiments, no transient absorbance lasting longer than 60 μsec was detected at 675-nm, the absorption maximum of $Ru(bipy)_3^{3+}$, or in the 480-nm to 550-nm region, an absorption band of $Co(acac)_2$.

The point of these experiments, however, was to explore the role of structure within the quenching encounter. Regardless of the quenching mechanism, the initial reaction, in the energy transfer schemes

$$^{*}RuB_3^{2+} + ML_3 \longrightarrow RuB_3^{2+} + {}^{*}ML_3 \qquad (75)$$

or in the electron transfer scheme,

$$^{*}RuB_3^{2+} + ML_3 \longrightarrow RuB_3^{3+} + ML_3^{-} \qquad (76)$$

involves a bimolecular reaction between the donor and acceptor. The linearity of the Stern-Volmer plots establishes a dynamic quenching mechanism.[2] Thus the K_{SV}'s can be used to probe the role of structure within the quenching encounter.

B. Structural Effect

Stern-Volmer constants for the quenching of $Ru(bipy)_3^{2+}$ by the Co(III) isomers are identical within experimental error. This equality is also observed with the slightly more hindered $Ru(bipic)_3^{2+}$. There are two possibilities to account for the results: (1) the bimolecular quenching rate is diffusion controlled, and (2) little or no discrimination occurs on the basis of molecular structure or dipole moment during the quenching encounter. Assuming the Stokes' radii and interaction radii are equal, the Einstein-Smoluchowski theory yields a theoretical diffusion controlled limit of $5.5 \times 10^{9} M^{-1} sec^{-1}$ for k_b in ethanol at 25°C.[1] The values of k_b, listed in Table III, indicate that the Co(III) isomers quench at slightly less than the theoretical diffusion controlled rate. Thus, it is possible that diffusion has a leveling effect on quenching efficiency, and no differences between the isomers can be detected. Similarly, no discrimination of these isomers is found in the quenching of the slightly more hindered $Ru(bipic)_3^{2+}$.

With the Cr(III) isomers, however, the values of k_b are less than the theoretical limit suggesting that barriers exist and a number of collisions are requisite to achieve a set of requirements for quenching to occur. The K_{SV} of <u>cis</u>-$Cr(tfac)_3$ is 1.4 ± .3 times larger than that of the trans-isomer. This difference, which is found with both donors is frustratingly small, but is similar to that previously reported for the cis- and trans- isomers of $Cr(en)_2Cl_2^+$.[17] The difference in the K_{sv}'s was not affected by the addition of an electrolyte, 0.01M LiCl, but appears to be dependent on the solvent medium. The solubilities of the complexes, however, limit the solvents which could be used , but a number of measurements were made in mixed solvents. Although the experimental error is large, increasing the solvent dielectric constant by the addition of formamide, 40% by volume, led to an elimination of the difference. The K_{sv}'s of the cis- and trans- isomers were then identical within experimental error.

Concealment of a potential difference in the quenching efficiency by either a thermal[35] or photochemical[70] isomerization during the preparation or measurement of the samples appears unlikely. The K_{sv}'s obtained from degassed samples stored in the dark for one hour prior to measurement were within experimental error of the K_{sv}'s obtained from equivalent samples measured immediately after preparation and de-areation. The emission intensity of samples 10^{-3}M in the isomers and 10^{-4}M in $Ru(bipy)_3^{2+}$ (ca. 80% of the light is absorbed by $Ru(bipy)_3^{2+}$) was also found to be independent of the time of exposure, 10 min, to the exciting light of the emission spectrophotometer.

We find these results somewhat surprising since a bimolecular collision which involves ligand-field states might be expected, a priori, to be susceptible to structural differences. For example, the rate constant for quenching of a triplet donor by $Fe(acac)_3$ is 6.1 times larger than that of $Fe(dpm)_3$ when energy transfer to a ligand-field state occurs, but the ratio decreases to 3.2 when energy transfer to an internal ligand state occurs.[30] Also, the difference in the quenching efficiency of the <u>cis</u>- and <u>trans</u>- isomers of $Cr(en)_2X_2^+$ and $Cr(en)_2XY^+$ led to the suggestion that geometric factors play some role in determining quenching efficiency.[17] Although this suggested structural dependence is somewhat clouded due to the differences in the electronic structure of the isomers, the importance of steric hindrance is indicated in the quenching of organic triplets by the higher efficiency of acetylacetonate complexes as compared to dipivaloylmethanate complexes. The difference in the quenching efficiency with the $Fe(acac)_3$ and $Fe(dpm)_3$ complexes is substantially larger than that found in these experiments. Since the oscillator strengths of the $^6A_{1g} \longrightarrow {}^4T_{1g}$ and $^6A_{1g} \longrightarrow {}^4T_{2g}$ transitions in these Fe(III) complexes are identical, the difference in the quenching efficiency is attributed to differences in the distance between the Fe(III) complex and the donor during the quenching encounter.[30] The t-butyl groups prevent the $Fe(dpm)_3$ complex from approaching the donor as closely as the $Fe(acac)_3$ complex. With these geometric isomers, however, the molecular size is essentially identical and the structural difference arises from the complex as a whole. If the quenching encounter were sensitive to only a specific part of the molecule, such as a metal ligand pair, the structural differences between these geometric isomers would be negated. Within this hypothesis of specificity to a given part of the quencher, the lack of any apparent discrimination of the $Cr(bzac)_3$ isomers may reflect an extension of the "conducting ability" of the ligand through the phenyl substituent. Although not formally resonant, the phenyl group is inductively coupled to the chelate ring and metal ion and may extend the "conducting ability" beyond the structural difference in the isomers. With the $Cr(tfac)_3$ isomers, the "conducting" region is not as extensive. A more intimate encounter would be required and the difference in the K_{sv}'s may reflect the difference in the molecular structure of the isomers. We doubt that the difference is due to differences in their diffusion rates. If this were the case, the similarity in the formal charge and size of the Co(tfac)$_3$ and Cr(tfac)$_3$ would suggest similar differences in the quenching efficiencies of the Co(III) isomers, yet none is observed.

Alternatively, the elimination of the difference in the mixed solvents may indicate that solvation of the isomers may be the cause of the differences in their quenching efficiencies. Although the isomers have identical electronic spectra, there are differences in their dipole moments--the basis for their separation by chromatography. In the chromatographic separation of the isomeric forms of these complexes, the separation between the bands of <u>cis</u>- and <u>trans</u>-Cr(tfac)$_3$ is larger than that between <u>cis</u>- and <u>trans</u>-Cr(bzac)$_3$.[35] This suggests that the difference in the dipole moments of the <u>cis</u>- and <u>trans</u>- isomers of Cr(tfac)$_3$ may be larger than that between the <u>cis</u>- and <u>trans</u>- isomers of Cr(bzac)$_3$. The larger difference in the isomeric forms of Cr(tfac)$_3$ may induce differences in the size and shape of the solvation shells. Also, H-bonding to the CF$_3$ group of Cr(tfac)$_3$ might also induce a preferential solvation of the isomers. This difference in solvation may then give rise to the observed difference in the quenching efficiencies of the isomers. With the Cr(bzac)$_3$ isomers, however, the difference in the dipole moments is apparently smaller and the difference in the solvation of the isomers may not be sufficiently pronounced to induce a difference in the quenching efficiency.

Prior to discussing the results obtained in the quenching of various organic triplet donors, it seems worthwhile to summarize the results of these experiments. Intuitively a structural dependence is expected, yet these results, at least with these Co(III) isomers and the $Cr(bzac)_3$ isomers, indicate that such a dependence can be small or nonexistant. These results, however, are quite different from those of Wilkinson and Farmilo where a pronounced structural dependence was found.[30] Although the uncertainty in the quenching mechanism with these Ru(II) complexes precludes a quantitative comparison, the results do suggest two distinct structural effects: one which depends on molecular size of the quencher and one which depends on orientational factors. These ideas will be more fully discussed in next section.

(III) Quenching of the Triplet State of Organic Compound

A. Quenching Mechanism

In the quenching of organic triplet donors by coordination compounds, definitive experimental evidence which distinguishes between the possible quenching mechanisms is rare. With the majority of metal complexes which have been used as quenchers, the dearth of conclusive experimental data arises from the absence of a sensitized emission or transient absorbance. Thus, it might be assumed that the evidence for a specific quenching mechanism would hardly be convincing. Over the past twenty years, however, a considerable amount of information has been amassed which indicates that the principle mechanism for the quenching of the donors used in this study by the beta-diketone complexes occurs by an energy transfer process.[6b, 70]

Hammond and coworkers have shown that the quenching efficiency of beta-diketone compexes of a number of metal ions does not correlate with the paramagnetism or spin-orbit coupling parameter of the complex.[29] For example, the diamagnetic complex $Ni(dpm)_2$ is a more efficient quencher than the paramagnetic $Cr(dpm)_3$ and the rare earth complexes $Er(dpm)_3$, $Gd(dpm)_3$ and $La(dpm)_3$ are less efficient quenchers than the corresponding Fe(III), Co(III) and Cr(III) complexes.

Thus quenching via a magnetic or spin-orbit coupling process does not appear to be the principle mechanism. The absence of a net chemical change in the donor or quencher also relegates a chemical mechanism to a minor role. On the other hand, the sensitization of the $^2E \longrightarrow {}^4A_2$ phosphorescence in $Cr(acac)_3$ by benzil and anthracene at low temperatures establishes an energy transfer mechanism.[6b] In a recent extensive study, Wilkinson and Farmilo have shown that the quenching efficiency of $Fe(acac)_3$, $Fe(dpm)_3$, $Ru(acac)_3$, and $Al(acac)_3$ depends on the energies of the excited states of these complexes.[30] This characteristic dependence on the energy of the triplet state being quenched and on the spectroscopically determined energy levels of the complexes established energy transfer as the quenching mechanism.

The quenching behavior of these Cr(III) and Co(III) isomers parallels that found with other beta-diketone complexes. For example, the quenching efficiency of these diamagnetic Co(III) isomers is essentially the same as the paramagnetic Cr(III) isomers. Thus quenching via a magnetic mechanism can be ruled out. With the exception of 9-methylanthracene and anthracene which underwent a photochemical reaction, no net chemical change was detected in these experiments and quenching via a chemical mechanism is ruled out. Although more limited, the data summarized in Table VI and Figure 41, parallel the results of Wilkinson and Farmilo; the quenching efficiency depends on the triplet state energy of the donor and the energy levels of the quencher. Thus it seems reasonable to limit the subsequent discussion to a quenching mechanism which involves energy transfer.

As indicated by Figure 41, the majority of the triplet donors used in these experiments are of sufficient energy to populate only the ligand-field states of these isomers. This was deliberately chosen to be the case since our initial idea, which was subsequently verified by Wilkinson and Farmilo, was that energy transfer to these ligand-field states would be most susceptible to structural differences of these isomers.

Consider first, the quenching of the lower energy donors: 9-phenylanthracene, 9-methylanthracene, anthracene, and pyrene by the isomers of Cr(III). These triplet donors have energies within the range 14.7 kK to 16.8 kK. Thus, energy transfer to the thermally equilibrated $^4T_2$, ca. 14.4 kK, and ^2E, ca. 12.4 kK, states of the isomers is an allowed exothermic process. A distinction between these states as to which is the acceptor level can not be made, since energy transfer to either state satisfies the conservation of spin momenta. Thus the quenching reactions are written as

$$^{3}D^{*} + CrL_3(^{4}A_2) \longrightarrow {}^{*}CrL_3(^{4}T_2) + D \qquad (77)$$

$$^{3}D^{*} + CrL_3(^{4}A_2) \longrightarrow {}^{*}CrL_3(^{2}E) + D \qquad (78)$$

where $^{3}D^{*}$ and D represent the donor in the triplet state and in the ground state, respectively.

With the Co(III) complexes, however, a distinction between the acceptor levels is possible. Energy transfer processes to either the thermally equilibrated $^{1}T_1$, $^{3}T_2$, or $^{3}T_1$ states of the Co(III) isomers satisfy the required exothermicity. Since the ground state of these complexes is a $^{1}A_1$, conservation of spin momenta requires energy transfer to the triplet ligand-field states. Thus, using the same notation as in equations 77 and 78, the quenching reactions can be written as

$$^{3}D^{*} + CoL_3(^{1}A_1) \longrightarrow {}^{*}CoL_3(^{3}T_2) + D \qquad (79)$$

and

$$^{3}D^{*} + CoL_3(^{1}A_1) \longrightarrow {}^{*}CoL_3(^{3}T_1) + D \qquad (80)$$

The latter distinction, however, must be judged with caution, since it is based on the assignment of formal spin states. If the spin-orbit coupling within the Co(III) complex is sufficient, such an assignment is dubious.

The required exothermicity of an energy transfer process from either pyrene or anthracene demands population of lower energy ligand-field states. Yet, it is also apparent from Table VI that the bimolecular rate constants for the quenching of pyrene are larger than those of anthracene or its substituted analogues. Clearly, factors other than energetic and spin conservation are important in these quenching processes. It might be postulated that pyrene is of sufficient energy to populate higher energy ligand-field, charge-transfer, or ligand centered states. Such a postulate, however, is not borne by the spectroscopic data. For example, molecular orbital calculations indicate that the $^4T_1$ state of $Cr(acac)_3$ or $^1T_2$ state of $Co(acac)_3$ lie at energies of 23 kK and 25 kK respectively.[50] Although the ligand-field strengths of bzac and tfac are slightly less than that of acac,[32a] the difference would be a small fraction of ca. 8 kK necessary to decrease the energies of these states such that energy transfer from pyrene can occur. Similarly, the ligand localized triplet states are far too energetic, $E > 20$ kK, to be involved in the quenching of pyrene. The remaining possibility, a low energy charge transfer transition, is found in the absorption spectra of $Cr(tfac)_3$ and $Cr(bzac)_3$ at 29.6 kK and 27.9 kK, respectively. In the spectra of $Co(tfac)_3$ and $Co(bzac)_3$, the transitions occur at 30.1 kK and 28.1 kK respectively. The absorption bands overlap and the energy of the thermally equilibrated charge-transfer state can not be placed with any degree of certainty. Generally, however, the difference between the band maximum and the thermally equilibrated energy is ≤ 5 kK (see Figure 41). Thus the lowest energy spin allowed charge-transfer state, that of $Cr(bzac)_3$, would be expected to lie at an energy ≥ 22.9 kK. Since this is substantially larger than the 16.8 kK energy of the triplet state of pyrene, energy transfer to this state is endothermic and unlikely.

Associated with these spin allowed charge-transfer transitions are the corresponding spin forbidden transitions. The transitions, which produce a charge-transfer state of triplet multiplicity, are weak and have not been characterized in the absorption spectra of the complexes. The energies of these triplet states are lower than the corresponding singlet states by essentially twice the exchange integral.[71] Thus an estimate of the energy of these states can be made. Navon and Sutin have pointed out that the singlet-triplet separation of a charge-transfer state will be less than the separation between ligand-field states of singlet and triplet multiplicity.[41] From Figure 41, the $^1T_1-^3T_1$ separation in these Co(III) complexes is 7.6 kK. Comparing this value to the $^1CT-^3CT$ splitting of $Ru(bipy)_3^{2+}$, ca. 4.0 kK, indicates that the estimate is an upper limit. Substracting this value, 7.6 kK, from the energies of singlet charge-transfer states yields triplet state energies of 22.0 kK, 20.3 kK, 22.5 kK, and 20.5 kK for $Cr(tfac)_3$, $Cr(bzac)_3$, $Co(tfac)_3$, and $Co(bzac)_3$, respectively. The latter, however, are estimates of the vertical Franck-Condon transitions and must be further corrected for vibrational relaxation. As mentioned above, this correction is <5 kK and applied to the above estimates indicates that lower limits of the ^3CT states energies would lie in the range 15.3 kK to 17.5 kK. Thus energy transfer from pyrene to a ^3CT state is possible. We doubt, however, that this is an adequate explanation of the increase in the quenching rate constant.

Previous studies have indicated that if quenching involves spin-allowed energy transfer to a charge-transfer or ligand state the rate is diffusion limited.[70a] In benzene at 22°C, the Debye expression yields $1 \times 10^{10} M^{-1} sec^{-1}$ and $1.5 \times 10^{10} M^{-1} sec^{-1}$ for a diffusion controlled process.[72] The rate constants for the quenching of pyrene, $2.36 \times 10^9 M^{-1} sec^{-1}$ to $3.58 \times 10^9 M^{-1} sec^{-1}$, are somewhat less than the diffusion controlled limit, but the difference is small and it is difficult to come to a firm conclusion.

In our opinion, the difference may be in the quantum mechanical constraints placed on the probability of energy transfer during the quenching encounter. Wilkinson and Farmilo have assigned the quenching of organic triplets by metal acetylacetonate complexes to energy transfer by an exchange mechanism.[30] If we assume the same mechanism in these quenching experiments, the probability of energy transfer, as derived by Dexter, is proportional to $\int_0^\infty P_D(\bar{\nu})\epsilon_A(\bar{\nu})d\bar{\nu}$ where $P_D(\bar{\nu})$ is the donor emission spectrum and $\epsilon_A(\bar{\nu})$ is the acceptor absorption spectrum[1]. As the triplet energy of the donor increases, the phosphorescence spectrum overlaps a progressively larger fraction of the first ligand-field band of these isomers. Applying this integral quantitatively is difficult, however, since the phosphorescence spectra of the donors in fluid solution are not known. At least with the Cr(III) isomers, the increase in the quenching rate constant with the energy of the donor is in qualitative agreement with the predicted behavior. With the Co(III) isomers, however, there is a discontinuity found with 9-methylanthracene. There does not appear to be any apparent explanation for this discontinuity, but it should be noted that this donor, unlike the others, did undergo a photochemical reaction.

The largest rate constants for quenching were found with the highest energy donor, phenanthrene. From the above discussion and Figure 41, it is quite likely that quenching of this donor may involve energy transfer to higher energy states. The energy of phenanthrene $E_T = 21.6$ kK, is sufficient to populate not only the triplet charge-transfer states, but is also similar in energy to the ligand triplets. The absence of ligand phosphorescence in the emission spectra of these Cr(III) and Co(III) complexes, however, negates the exact determination of the ligand triplet energy. As discussed above, the energies shown in Figure 41 are estimates obtained from the emission spectra of the sodium salts and the Al(III) and La(III) complexes. Within the range to which we were able to estimate the energy of the ligand triplet state, energy transfer from phenanthrene to this state is possible and could explain the increase in rate constant.

It is apparent from the above discussion that the acceptor level of the complex involved in quenching of pyrene and phenanthrene can not be firmly established. The point of the discussion, however, was to establish that, at least with anthracene and its substituted analogues, energy transfer must occur to the ligand-field states of the isomers to satisfy the required exothermicity of an energy transfer process. This is an important point since previous studies have indicated that these states would be most sensitive to the structural differences in these isomers.

B. Structural Effects

The role of molecular structure in determining the course and efficiency of a chemical reaction has been recognized for some time. Although these same ideas have often been involved in the quenching of various donors by coordination compounds, a hiatus exists between that which is intuitively expected and that which is based on experimental fact. During the course of this study, however, a number of studies, principally those of Wilkinson and coworkers,[70a] have significantly closed the gap. It is worthwhile then to summarize the available results prior to discussing the results of these experiments. Wilkinson's experiments which were carried out with beta-diketone complexes and organic donors and are directly applicable to the results obtained in these experiments have established the following:

(1) Spin-allowed exothermic energy transfer from triplet states of organic molecules which results in the

production of excited internal ligand or charge-transfer states of a coordination compound should be diffusion controlled (subject to spin restrictions).

(2) Spin allowed exothermic energy transfer to ligand-field states will depend critically on the spatial overlap between d orbital and the π orbitals of the organic donor during the collision.

In view of these results, it is apparent that the role of structure in the quenching encounter will depend on the acceptor level of the quencher; the ligand-field states being most susceptible. Thus, the results obtained in these experiments are separated in terms of which levels of the complexes are the acceptors.

With the higher energy donors, pyrene and phenanthrene, energy transfer to the internal ligand states or charge-transfer states of the isomers can occur. Energy transfer to a ligand localized triplet state is essentially identical to energy transfer between organic compounds and can be represented by the formal equation

$$^3D^* + L\text{-}ML_2 \longrightarrow {}^3L^*\text{-}ML_2 + {}^1D \qquad (81)$$

Intermolecular energy transfer, equation 81 , is then followed by an intramolecular energy transfer to the metal ion and radiative or nonradiative decay to the ground state.

$$^{3}L^{*}\text{-}ML_2 \longrightarrow L\text{-}M^{*}L_2 \longrightarrow L\text{-}ML_2 \qquad (82)$$

Since the intervening species $L^{*}\text{-}ML_2$ is specific to a given ligand, the structural difference between these cis- and trans- isomers is negated. The structural difference in these geometric isomers arises from the arrangement of the asymmetric ligands about the metal ion (see Figure 1). The ligands per se are identical. Thus no structural effect is expected and the lack of any discrimination above experimental error between the isomeric forms of these isomers supports this expectation. A slight structural effect, however, is present if a bulky substituent prevents a close approach between the donor and the acceptor. For example, the quenching of the triplet state of benzophenone, $E_T = 24.0$ kK, by $Fe(acac)_3$ or $Fe(dpm)_3$ results in population of a ligand centered state, yet the quenching rate constant of the former, $3.2 \pm 0.3 \times 10^{9} M^{-1}sec^{-1}$ is somewhat larger than that of the latter, $0.87 \pm 0.08 \times 10^{9} M^{-1}sec^{-1}$.[30]

The ligand localized triplet states are too energetic to be involved in the quenching of pyrene. Thus, quenching must involve energy transfer to either a triplet charge transfer state or the ligand-field state. The increase in the rate constant found on going from anthracene to pyrene, however, suggests energy transfer to a triplet charge-transfer state of these isomers. Irrespective of the assumptions made regarding the acceptor level, the rate constants listed in Table VI clearly indicate that no discrimination of the isomers beyond experimental error occurs. Although various rationalizations, such as those given above, might be put forth to explain the lack of discrimination, these results are quite different from previous results where the steric difference was induced by replacing a methyl group by a t-butyl group.[29, 30]

With the lower energy donors, anthracene, 9-methylanthracene, and 9-phenylanthracene, the energies of the triplet states of the donors demand that energy transfer produce ligand-field excited states. Energy transfer to these states, localized at the metal ion, requires a more intimate encounter between the triplet donor and the complex to achieve an orbital overlap. Under such conditions, a structural effect is expected and has been experimentally observed. In energy transfer to the $^4T_{1g}$ or $^4T_{2g}$ states of $Fe(dpm)_3$ and $Fe(acac)_3$, the rate constant for the quenching of anthracene by $Fe(acac)_3$ is 7.6 ± 0.5 x $10^8 M^{-1}sec^{-1}$[30] while that of $Fe(dpm)_3$ is 1.5 ± 0.2 x $10^8 M^{-1}sec^{-1}$. This difference shows how critical a close approach is for transfer to a ligand-field state. Quite different results were found in these experiments. The rate constants for quenching by the various pairs of isomers (Table VI) were identical within experimental error. Thus, during the energy transfer process to the ligand-field states of these geometric isomers, no discrimination occurred.

The lack of any difference in the quenching efficiency of these isomers can not be attributed to the leveling effect of diffusion. The rate constants listed in Table VI are less than the theoretical diffusion limit which in benzene at 22°C is $1 \times 10^{10} M^{-1} sec^{-1}$. Furthermore, the rate constants for the quenching of anthracene found in these experiments are similar to those found for $Fe(acac)_3$ and $Fe(dpm)_3$ where the rate constants differed by a factor of five.

The rate constants listed in Table VI show that energy transfer efficiency does depend on the substituents attached to the parent anthracene chromophore. Since the energies of anthracene and its substituted analogues are more than adequate to populate the lower energy ligand-field state of the isomers (Figure 41), the difference in the quenching rates is not due to energetics. Rather, the difference is thought to arise from some steric hindrance during the quenching encounter. The small size of the methyl substituent in 9-methylanthracene would be expected to cause only slight perturbation on the quenching encounter. Consistent with this expectation, there is very little difference in the rate constants found with anthracene and 9-methylanthracene.

The smaller rate constants found for the quenching of 9-phenylanthracene as compared to anthracene or 9-methylanthracene indicate that the phenyl substituent causes additional steric hindrance to the energy transfer process. The absorption spectrum of 9-phenylanthracene is slightly red shifted as compared to that of anthracene. Although this suggests some conjugation with the parent chromophore, inspection of molecular models indicates that the phenyl group is not planar with the parent chromophore. In the similar molecule 9,10-diphenylanthracene, the angle between the plane of the phenyl group and the plane of anthracene has been reported to be 60°[1]. Thus, an extension of the anthracene π system through conjugation of the phenyl substituent is unlikely or inefficient and the effect of this substituent is principally steric hindrance. A number of flash experiments were carried out with 9,10-diphenylanthracene, but the intersystem crossing yield in this molecule is small[1,56] and reliable flash data could not be obtained.

We find it surprising that even with the substituted donors where the decrease in the rate constant indicates a necessity of additional collisions for energy transfer to occur that <u>no</u> discrimination of the isomers occurred.

Regardless of which excited state of the complex is the final acceptor level in the energy transfer step, these results are quite different from those found with acetylacetonate and dipivaloylmethanate complexes.[30] In these complexes, however, the steric difference is due only to the size of the substituent; the larger substituent, a t-butyl group, appears to prevent a close approach of the quencher to the donor. These geometric isomers, however, are essentially identical in size, but differ only in the arrangement of the asymmetric ligands about the metal ion. There are two possible explanations to account for the difference found with acetylacetonate and dipivaloylmethanate complexes and the results found in these experiments.

The first explanation arises from the theory of exchange energy transfer. As mentioned in the introduction, the equation has the form

$$k_{et} \propto \exp(-2R/L) \qquad (83)$$

Assuming the Bohr radius, L, of the initial and final electronic states of the donor and acceptor are the same, 1 Å; and the separation distance, R, is that given by the Van der Waals radii of a methyl group, 2.0 Å ,[68] and a t-butyl group, 3.15 Å; the ratio $k_{et}^{acac}/k_{et}^{dpm} = 10$. Considering the approximations made, this is in reasonable agreement with the value of 5.1 calculated from rate constants for the quenching of triplet anthracene by $Fe(acac)_3$ and $Fe(dpm)_3$. The geometric isomers of Co(III) and Cr(III) are essentially the same, and according to the equation no difference is expected. This explanation, however, implies that a distinction between structural effects exists. Provided the structural variation *per se* is not involved in accepting the donor energy, those structural variations which change the distance of separation between the donor and acceptor will introduce to the efficiency of energy transfer a structural dependence. Those structural variations which do not change the distance of separation, i.e., differences due to the orientation of the ligands about the metal ion, will not introduce a steric dependence.

The alternative explanation arises from the concept of the "conducting ability" of a ligand. Previous studies of the quenching of various organic and inorganic donors have shown that quenching efficiency can be significantly increased by changing one or more of the ligands in the coordination sphere of the quencher.[70b] Although not conclusive, it does suggest that quenching may be specific to a given metal-ligand pair or a specific part of the quencher. With these geometric isomers, however, structural difference arises from the complex as a whole, but is negated if quenching reflects a specific part of the complex such as a metal-ligand pair. Within this hypothesis then, no difference is expected, yet the difference in the quenching efficiency of $Fe(acac)_3$ and $Fe(dpm)_3$ would still reflect differences in the distances of separation.

Intuitively, a structural dependence is expected, yet these results suggest that a dependence will be found only when the structural difference between two quenchers is sufficient to change the distance of separation between the donor and the acceptor.

CHAPTER 5

Conclusion

It is worthwhile to summarize the results of these experiments. The initial premise of the work was to determine whether the quenching of an excited donor would be dependent on the structure of the quencher. To do so, however, it is necessary to ensure that the structural modification does not induce a concurrent change in the electronic structure of the quencher. Since the cis- and trans- isomers of the unsymmetrically substituted beta-diketonate complexes of Co(III) and Cr(III) have identical electronic spectra, these isomers were chosen to probe the role of structure in a quenching encounter.

Quenching studies of the luminescent charge-transfer state of $Ru(bipy)_3^{2+}$ or $Ru(bipic)_3^{2+}$ by geometric isomers of $Co(tfac)_3$, $Co(bzac)_3$, and $Cr(bzac)_3$ yield identical Stern-Volmer constants. This equality then implies that little or no structural discrimination occurs during the quenching encounter. In the quenching of these Ru(II) complexes by cis- and trans-$Cr(tfac)_3$, however, cis-$Cr(tfac)_3$ is a more efficient quencher than trans-$Cr(tfac)_3$. The difference is just slightly above experimental error, and may be due to differences in the solvation of the isomers.

The same geometric isomers were used to quench five organic triplet donors. These experiments, which were carried out by flash photolysis techniques, yield identical bimolecular quenching rate constants for each pair of isomers. These results also suggest little or no discrimination during the quenching encounter.

Comparing these results with previous results which showed that the acetylacetonate complexes were more efficient quenchers than the dipivaloylmethanate complexes suggests two types of structural effects. Those which change the distance between the donor and the quencher give rise a structural dependence, whereas those which involve the orientation of the donor and the quencher do not appear to be important. An alternative explanation can also account for these results: if quenching is specific to a given part of the molecule, these geometric isomers lose their structural differences and no discrimination would be expected.

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original concentration of $Ru(bipy)_3^{2+}$.

APPENDIX I

Computer program used to obtain first- and second-order rate constants for triplet decays

```
      IMPLICIT REAL 8(A-H,O-Z)
      DIMENSION X(50),Y(50),G(10,2),XC(50)
      DATA G/20*0.0D0/
      COMMON/SHARE/X,Y,DEL,NP,M,N
      EXTERNAL FUNC
    7 READ(5,1)NP,M,N
    1 FORMAT (3I4)
      IF(NP)8,8,9
    9 READ(5,2)(X(I),Y(I),I=1,NP)
      READ(5,2) DEL
    2 FORMAT(8F10.6)
      WRITE(6,1)NP,M,N
      WRITE(6,2) DEL
      WRITE(6,14)(X(I),Y(I),I=1,NP)
   14 FORMAT(5X,F10.6,F10.6)
      READ(5,2)((G(I,J),J=1,N,I=1,M)
      CRITE=1.0D-06
      WRITE(6,14)((G(I,J),J=1,N)I=1,M)
      CALL NELDE(M,N,G,10,CRITE,-1,L,FUNC,VAL)
      WRITE(6,4)VAL
    4 FORMAT(D25.16)
      WRITE(6,6) G(L,1),G(L,2)
    6 FORMAT(5X20HRATE CONSTANTS   K1=E14.5,5X3HK2=E14.5)
      WRITE(6,102)
  102 FORMAT(5X,4HTIME,8X,9HCLAC TIME,8X,4HDIFF)
      DO 100 II=1,NP
      XC(II)=LOG(DEL*(G(L,1)+G(L,2)*Y(II))/(Y(II)*(G(L,1)+
     1G(L,2)*DEL)))/G(L,1)
      DELL=XC(II)-X(II)
      WRITE(6,101) X(II),XC(II),DELL
  101 FORMAT(3F15.2)
  100 CONTINUE
      GO TO 7
    8 STOP
      END


      DOUBLE PRECISION FUNCTION FUNC(B)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION B(2),X(50),Y(50)
      COMMON/SHARE/X,Y,DEL,NP,M,N
      WRITE(6,4) B(1),B(2)
      DUM=1.0D0
      WRITE(6,3) DEL
    3 FORMAT (2X4HDEL=F12.6)
      SUM=0.0D0
```

```
      DO 1 I=1,NP
      T=(LOG(DEL*(B(1)+B(2)*Y(I))/(Y(I)*(B(1)+B(2)*DEL))))
     1/B(1)=X(I)
      IF(DUM)1,1,6
    6 CONTINUE
    4 FORMAT (5X,2F12.6)
    1 SUM=SUM+T**2
      FUNC=SUM
      DUM=-1.0D0
      RETURN
      END


      SUBROUTINE NELDE(M,N,P,NP,CRIT,K1,L,FUNC,BOT)
      DOUBLE PRECISION P(1),S,Y(50),X(50),M1,YB,PB(50),PS(50),
     1TOP,BOT
      DOUBLE PRECISION PSS(50),CRIT
      DOUBLE PRECISION FUNC
      INTEGER H,L
      K=K1
      M1=M-1
    1 TOP=-1.0D30
      BOT=1.0D30
      L=1
      DO 2 J=1,M
      DO 3 I=1,N
      KK=(I-1)*NP+J
    3 X(I)=P(KK)
      Z=FUNC(X)
      Y(J)=Z
      IF(Z-TOP)5,5,4
    4 TOP=Z
      H=J
    5 IF(Z-TOP)6,2,2
    6 BOT=Z
      L=J
    2 CONTINUE
      IF(K)7,7,97
   97 CALL OUT(CRIT,M,Y,N,P,NP,TOP,BOT,H,L)
    7 IF(CRIT-DABS(TOP-BOT))10,10,9
    9 IF(K)11,12,11
   11 CALL OUT(CRIT,M,Y,N,P,NP,TOP,BOT,H,L)
   12 RETURN
   10 YB=0.0D0
      IF(BOT=1.E30)14,13,14
   13 BOT=Y(1)
   14 DO 15 I=1,N
      KK=(I-1)*NP
      Z=0.0D0
      DO 16 J=1,M
```

```
      IF(J-H)17,16,17
   17 KKK=KK+J
      Z=Z+P(KKK)
   16 CONTINUE
      Z=Z/M1
      PB(I)=Z
      KKK=KK+H
      PS(1)=2.0D0*Z-P(KKK)
   15 X(I)=PS(I)
      Z=FUNC(X)
      IF(Z-BOT)18,18,19
   18 BOT=Z
      DO 20 I=1,N
      X(I)=2.*PS(I)-PB(I)
   20 PSS(I)=X(I)
      Z=FUNC(X)
      IF(Z-BOT)21,21,22
   21 BOT=Z
   23 DO 24 I=1,N
      KK=(I-1)*NP+H
   24 P(KK)=PSS(I)
      GO TO 25
   22 Z=BOT
   26 DO 27 I=1,N
      KK=(I-1)*NP+H
   27 P(KK)=PS(I)
   25 Y(H)=Z
      GO TO 28
   19 DO 29 J=1,M
      IF(J-H)30,29,30
   30 IF(Z-Y(J))26,29,29
   29 CONTINUE
      IF(Z-BOT)32,32,31
   32 DO 33 I=1,N
      KK=(I-1)*NP+H
   33 P(KK)=PS(I)
      TOP=Z
   31 DO 34 I=1,N
      KK=(I-1)*NP+H
      X(I)=0.5*(P(KK)+PB(I))
   34 PSS(I)=X(I)
      Z=FUNC(X)
      IF(Z-TOP)35,35,36
   35 TOP=Z
      GO TO 23
   36 DO 37 I=1,N
      KK=(I-1)*NP
      KKK=KK+L
      DO 37 J=1,M
      K2=KK+J
   37 P(K2)=(P(K2)+P(KKK))*0.5
      GO TO 1
```

```
      YB=Y(1)
      TOP=YB
      BOT=YB
      H=1
      L=1
      DO 41 J=2,M
      Z=Y(J)
      IF(Z-TOP)40,39,39
   39 TOP=Z
      H=J
      GO TO 41
   40 IF(Z-BOT)42,41,41
   42 BOT=Z
      L=J
   41 CONTINUE
      IF(K)7,7,98
   98 CALL OUT(CRIT,M,Y,N,P,NP,TOP,BOT,H,L)
      GO TO 7
      END


      SUBROUTINE OUT(CRIT,M,Y,N,P,NP,TOP,BOT,H,L)
      DOUBLE PRECISION P(1),Y(1),TOP,BOT,CRIT
      INTEGER H,L
      WRITE(6,101)CRIT
  101 FORMAT(////' THIS IS NELDER AND MEAD OUTPUT.'///'
     1CRIT =',D25.16)
      DO 3 J=1,M
      WRITE(6,102)J,Y(J)
      WRITE(6,104)N
      DO 3 I=1,N
      KK=(I-1)*NP+J
    3 WRITE(6,105)P(KK)
  105 FORMAT(/20XD25.16)
  102 FORMAT(///' Y(',I3,')=',D25.16)
      WRITE(6,103)TOP,BOT,H,L
  104 FORMAT(' THE VALUES, IN ORDER, OF THE',I3,' INDEPENDENT
     1VARIABLES ARE AS FOLLOWS')
  103 FORMAT(//' TOP = ',D25.26,3X,'BOT = ',D25.16,3X,'H = ',
     1I3,3X,'L =',I3/////)
      RETURN
      END
```