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Inorganic Exciplexes Revealed by Temperature-Dependent Quenching Studies

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Temperature-dependent quenching studies of CT (charge-transfer) excited states of copper(I) complexes have been carried out in methylene chloride solution by a lifetime method. Activation parameters have been determined for both electron-transfer and energy-transfer quenching of *Cu(dpp)$_2^+$ as well as for quenching of *Cu(dmp)$_2^+$ by a series of Lewis bases (dpp denotes 2,9-diphenyl-1,10-phenanthroline and dmp denotes 2,9-dimethyl-1,10-phenanthroline). For those reactions involving Lewis bases, the apparent enthalpy of activation ranges from 0 to ca. −15 kJ mol^{-1} with a bell-shaped dependence on the donor strength. At 25 °C the quenching rates vary from 1.4×10^6 M^{-1} s^{-1} for the weak donor CH$_3$CN to 5.7×10^8 M^{-1} s^{-1} for the relatively strong donor DMF. The results establish that a reversible complex is formed between the excited state and Lewis bases prior to quenching, and the adduct is interpreted to be a five-coordinate exciplex. Finally, reasons that so few examples of exciplexes of transition-metal complexes have been identified are discussed.

Introduction

Exciplex, or excited-state complex, formation is an extremely common phenomenon with the excited states of organic molecules.[1-3] In contrast, corresponding adducts involving the excited states of transition-metal complexes are seldom invoked, although some examples have been reported recently.[4-7] To the extent that the d orbitals of the metal are involved, this dichotomy arises partly from the heavy-atom effect and partly from the fact that the frontier orbitals tend to be much less exposed in transition-metal complexes than in typical organic molecules. The forces responsible for exciplex formation include dipole–dipole interactions,[1,2] exchange interactions,[8] and charge-transfer phenomena.[1,2] The dipole strength associated with a thermally equilibrated excited state of a metal complex is usually weak because efficient intersystem crossing ensures that the transition to the ground state is spin forbidden. The problem is compounded if a metal-centered excited state is involved, and radiative decay is orbitally forbidden as well. Exchange interactions would be possible, but access to the d orbitals of the metal center is usually blocked by ligands in its primary coordination shell. A charge-transfer interaction with the quencher can, of course, occur, but the most common means of detecting exciplexes, namely luminescence spectroscopy, is compromised because the restricted orbital overlap inhibits radiative decay. For these various reasons, exciplex interactions are more favored with excited states of coordinatively unsaturated systems, where direct access to the d orbitals is possible.[4,7,9,10]

Some of these constraints are removed if one or more of the orbitals involved in the excitation is a ligand orbital; consequently, there are likely to be more examples of "inorganic" exciplexes of this type.[5,6,11] Even if exciplex formation occurs, direct detection of the exciplex by luminescence spectroscopy will not always be possible. Hence it is important to establish other means of characterization. In the following we show how studies of the temperature dependence of emission quenching can be used to detect exciplex formation. This approach has previously proven fruitful in studies involving singlet oxygen.[12,13]

As has been shown previously, the charge-transfer (CT) luminescence of Cu(NN)$_2^+$ systems, where NN denotes a heteroaromatic chelating ligand derived from 1,10-phenanthroline (phen), can be quenched by a variety of substrates.[4,9,10,14] To a good approximation, the quenching constants obtained pertain to the lowest energy triplet excited state.[14] Ordinary energy-transfer and electron-transfer quenching has been observed,[14] but exciplex quenching is proposed to occur in the presence of Lewis bases.[4,9] In particular, studies of steric effects[15] and volume of activation data[16] reveal that quenching by Lewis bases entails expansion of the coordination number of the copper center. Detailed studies of the enthalpy of activation as a function of donor strength are described below, and they strongly suggest that the five-coordinate adduct is a true reaction intermediate that can properly be described as an exciplex.

Experimental Section

Materials. [Cu(dmp)$_2$]BPh$_4$ and [Cu(dpp)$_2$]BPh$_4$ were prepared by a previously reported method.[17] The dmp ligand was purchased from Aldrich and used without further purification. The dpp ligand was synthesized by Dr. Dan Lee of Purdue University by a literature method.[18] The ligands 2,4-pentanedione (Aldrich) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Eastman Chemical Co.) are abbreviated as acac and hfac, respectively, when deprotonated. The complexes Cr(acac)$_3$ and Cr(hfac)$_3$ were prepared by published procedures.[19,20]

High-purity distilled-in-glass methylene chloride, ethyl acetate, and dimethylformamide were obtained from Burdick and Jackson and used without further purification. Dimethyl sulfoxide and tetrahydrofuran were obtained from Fisher Scientific. DMSO was used without further purification, and THF was freshly distilled from sodium/benzophenone and stored over sodium before use.

Apparatus. Absorbance measurements were taken on a Perkin-Elmer Lambda 4C UV/vis spectrophotometer. Lifetime measurements were obtained with an EG&G Princeton Applied Research Model 2100 N$_2$-pumped dye laser with a pulse width of approximately 8 ns as previously described.[14] Temperature control was achieved (±0.1 °C) with a Lauda K-2/RD water bath.

Methods. All samples were deoxygenated by multiple freeze/pump/thaw cycles and placed under an inert atmosphere of nitrogen. Solutions of Cu(dmp)$_2^+$ and Cu(dpp)$_2^+$ in methylene chloride were prepared such that the absorbance at the exciting wavelength was 0.4. Samples were equilibrated in a cell holder for 20–30 min at each tem-

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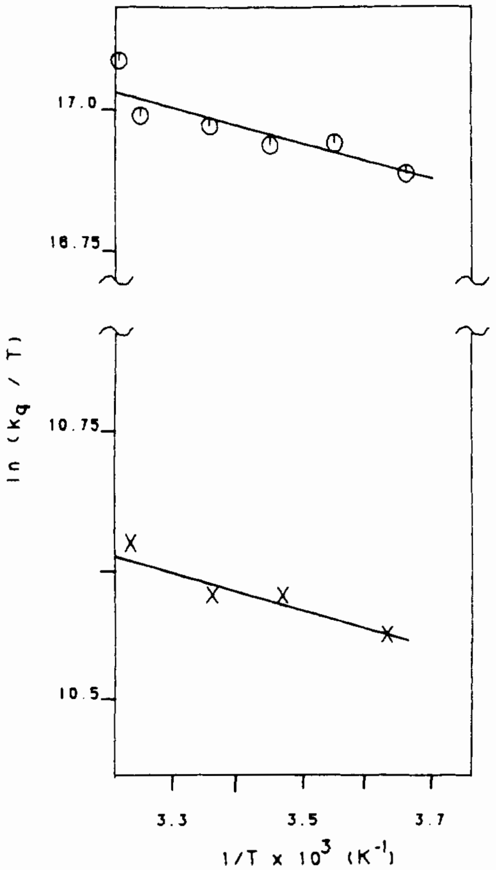

Figure 1. Eyring plots for the quenching of $^*Cu(dpp)_2^+$ by $Cr(acac)_3$ (X) and $Cr(hfac)_3$ (O) in methylene chloride.

perature prior to measurement. Emission decay curves were monitored with a 15-ns gate for $Cu(dpp)_2^+$ solutions and a 10-ns gate for $Cu(dmp)_2^+$ solutions. Coumarin 460, 480, and 485 laser dyes from Exciton were chosen to give maximum emission intensities. A 600-nm long-pass filter was placed before the detector to minimize scattering. Lifetimes were calculated as before.[4]

The second-order quenching rate constant, k_q, was estimated by the Stern–Volmer method[21] via least-squares fits of lifetime data to eq 1,

$$1/\tau = 1/\tau^\circ + k_q[Q] \tag{1}$$

where τ° is the lifetime in the absence of quencher and [Q] is the molar concentration of quencher. When ethyl acetate was used as the quencher, the data were fit to eq 2, where k_{q2} is a third-order rate constant. Since

$$1/\tau = 1/\tau^\circ + k_{q1}[Q] + k_{q2}[Q]^2 \tag{2}$$

the effect of temperature on sample volume over the range of temperatures studied was negligible, no adjustments of the quencher concentrations were necessary.

Results

Cr(III) Quenchers. The temperature dependences of the quenchings of the CT emission from $Cu(dpp)_2^+$ by $Cr(hfac)_3$ and $Cr(acac)_3$ were studied as representative examples of electron-transfer and energy-transfer quenching processes, respectively.[14] In both cases the quenching rate increased with temperature. Pertinent data are presented in Figure 1, and the indicated activation parameters obtained are compiled in Table I.

Lewis Base Quenchers. The temperature dependence of emission quenching by a series of Lewis bases was the focus of this investigation, and the results are presented in Table I. In all cases, except ethyl acetate, the quenching conformed to simple Stern–Volmer kinetics. As illustrated in Figure 2, the Stern–Volmer plots with ethyl acetate were nonlinear and displayed distinct upward curvature. In order to model these data, we had to invoke parallel quenching paths described by k_{q1} and k_{q2}, where k_{q2} represents a pathway that depends on the second power of the quencher concentration. The fastest quenching rates were found with DMF and DMSO, while the quenching rate constant varied by more than 2 orders of magnitude over the series. In general, relatively high quencher concentrations—upward of 1 M solutions—were required, except for DMF and DMSO, where millimolar levels of quencher sufficed. In every case except the k_{q1} pathway with ethyl acetate, the quenching rate decreased with increasing temperature; hence, negative apparent enthalpies of activation were obtained (Table I). Representative Eyring plots are presented in Figure 3.

Table I. Activation Parameters for Quenching

quencher	donor no.[a]	k_q(298 K), $M^{-1}\,s^{-1}$	ΔH_q^*, kJ mol^{-1} [b]	ΔS_q^*, J $mol^{-1}\,K^{-1}$ [c]
		Quenching of $^*Cu(dpp)_2^+$		
$Cr(acac)_3$		1.2×10^7	+18.0	−170
$Cr(hfac)_3$		7.0×10^9	+2.8	−47
		Quenching of $^*Cu(dmp)_2^+$		
acetonitrile[d]	14.3	1.4×10^6	−2.0	−110
dioxane[d]	14.8	7.5×10^6	−5.0	−145
acetone[d]	17.0	1.9×10^6	−12.0	−150
ethyl acetate	17.1	0.6×10^6 [e]	+38.1	−1.1
		1.4×10^6 [f]	−15.0	−177
THF	20.0	8.4×10^6	−7.7	−139
DMF	24.0	5.7×10^8	−1.7	−84
DMSO	29.0	4.7×10^8	−0.3	−80

[a] Gutmann, V. *Chimia* **1977**, *31*, 1–7. [b] Estimated error in ΔH^* is ±2 kJ mol^{-1}. [c] Estimated error in ΔS^* is ±20 J mol^{-1}. [d] From ref 4. [e] k_{q1} path. [f] k_{q2} path; units are $M^{-2}\,s^{-1}$.

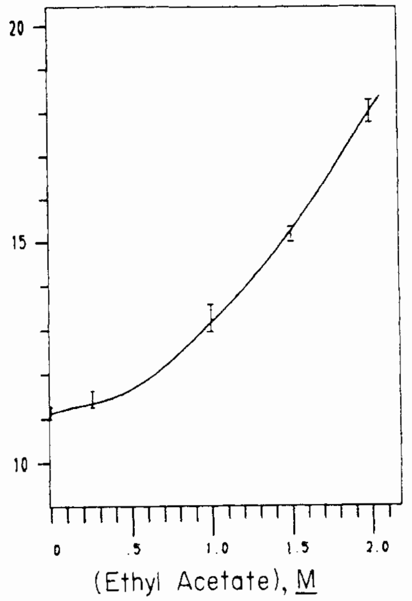

Figure 2. Stern–Volmer plot for the quenching of $^*Cu(dmp)_2^+$ by ethyl acetate at 25 °C.

Discussion

Cr(III) Quenchers. In previous work, Cr(III) complexes involving acetylacetonate ligands have been shown to quench the CT states of $Cu(dpp)_2^+$ by parallel energy-transfer and electron-transfer mechanisms.[14] Note that bulky phenyl substituents of $Cu(dpp)_2^+$ severely retard exciplex quenching.[15] The quenching rate constants are therefore modeled by eq 3, where k_d is the rate

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{k_{el} + k_{en}} \tag{3}$$

constant appropriate for a diffusionally controlled process and where k_{el} and k_{en} represent the rate constants for electron-transfer and energy-transfer quenching, respectively.[14] Of the two Cr(III) complexes studied here, the driving force for electron-transfer quenching is only favorable for $Cr(hfac)_3$. Since in this system $k_{el} \gg k_d$,[14] it follows from eq 3 that $k_q \simeq k_d$. Consistent with a diffusion-limit rate, quenching by $Cr(hfac)_3$ is characterized

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(21) Reference 3, pp 246–248.

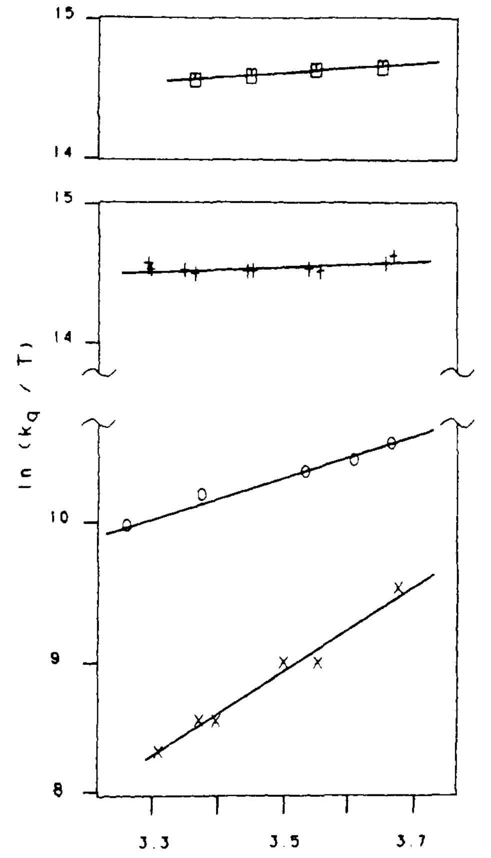

Figure 3. Eyring plots for the quenching of *Cu(dmp)$_2^+$ by Lewis bases in methylene chloride: (×) k_{q2} path for ethyl acetate; (○) THF; (+) DMSO; (□) DMF.

by a small positive enthalpy of activation and a moderately negative entropy of activation (Table I).

In contrast, oxidative quenching of *Cu(dpp)$_2^+$ by Cr(acac)$_3$ is a highly endoergic process, and $k_q \simeq k_{en}$.[14] A much higher enthalpy of activation and a much more negative entropy of activation are therefore observed. The strongly negative entropy of activation probably reflects the stringent orbital overlap requirements for energy-transfer quenching.[22,23] The enthalpy of activation can be rationalized in terms of the theory proposed by Balzani and co-workers, who have argued that the barrier to energy transfer is determined by the reorganizational energies of the donor and the acceptor molecules, as well as the driving force for energy transfer.[24,25] The main enthalpic barrier to energy transfer can probably be traced to structural reorganization required within the copper complex. Conversion to the ground state formally requires depopulation of a ligand π-antibonding orbital and conversion of copper(II) to copper(I),[26,27] two oxidation states with distinct stereochemical preferences. In line with the anticipated structural reorganization, the CT emission is broad-band and unstructured as well as strongly Stokes-shifted.[26] Other factors influencing the energy-transfer rate are more favorable. Thus, energy transfer to the doublet states of the Cr(III) systems has been shown to be exothermic,[14] and the reorganizational energy at Cr(III) should be minimal since conversion to the doublet state formally requires only a spin flip of a d electron in a nonbonding orbital.

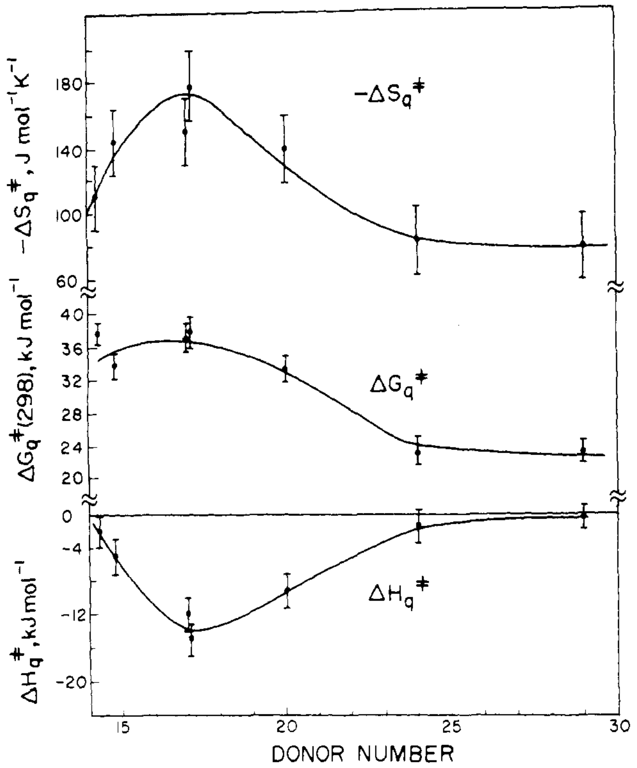

Figure 4. Activation parameters as a function of donor number in methylene chloride. The curved lines drawn through the $\Delta H_q^\ddagger$, $\Delta S_q^\ddagger$, and $\Delta G_q^\ddagger$(298) data are simply visual aids. See Table I for the key to the donors. The k_{q2} data are plotted for ethyl acetate.

Lewis Bases and Exciplex Quenching. There is no strong correlation between the quenching rate constant and the base strength as measured by the Gutmann donor number; however, the data in Table I suggest that there is a tendency for the quenching rate to increase the donor strength. In stark contrast with the case of Cr(III) quenchers, negative activation enthalpies are obtained for quenching by Lewis bases. Figure 4 shows that the activation enthalpy also varies in a complicated way with a change in base strength. For the weaker donors, $\Delta H_q^\ddagger$ becomes increasingly exothermic as the base strength increases, while, for bases stronger than ethyl acetate, $\Delta H_q^\ddagger$ shifts to less and less exothermic values. As will be shown, the negative enthalpies of activation can be explained by a simple exciplex-quenching mechanism as can the variation with base strength. A simplified kinetic scheme is presented in eqs 4 and 5, where *Cu and Cu

$$^*\mathrm{Cu} + \mathrm{Q} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} {}^*\mathrm{Cu}\cdots\mathrm{Q} \tag{4}$$

$$^*\mathrm{Cu}\cdots\mathrm{Q} \xrightarrow{k_Q} \mathrm{Cu} + \mathrm{Q} \tag{5}$$

respectively denote the emissive CT excited state and the ground state of Cu(dmp)$_2^+$, Q represents the quencher, and *Cu···Q denotes a complex formed between *Cu and Q. The importance of eqs 4 and 5 is that the observed k_q cannot be viewed as an elementary rate constant but must be regarded as a composite quantity. As we shall see, the existence of the k_{-a} step is the root cause of the negative apparent activation energies.

In the above scheme *Cu···Q is not a simple encounter complex; it must be regarded as an exciplex with a significant dissociation energy. As before, *Cu···Q is regarded as a five-coordinate adduct with a coordinate-covalent bond connecting the copper center and the Lewis base.[4,9,10,16] In no case is there evidence for the buildup of spectroscopically detectable amounts of *Cu···Q, and we have previously shown that *Cu···Q can be treated as a steady-state intermediate.[4] Within this approximation, k_q is given as

$$k_q = \frac{k_a k_Q}{k_Q + k_{-a}} \tag{6}$$

Two limiting forms of eq 6 exist, and they depend on the relative

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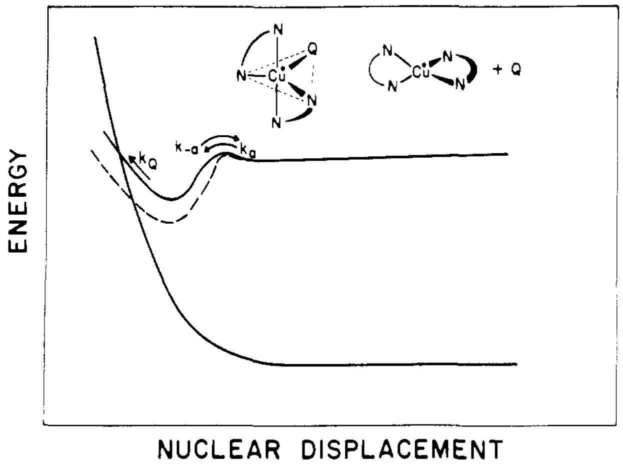

Figure 5. Schematic enthalpy profile for the reaction of $^*Cu(dmp)_2^+$ with a Lewis base. The ground-state surface is assumed to be repulsive, but the excited state forms a five-coordinate adduct. The dashed curve corresponds to a stronger donor. See text for the definition of the rate constants.

magnitudes of k_Q and k_{-a}. When relatively weak bases are employed, dissociation of the adduct should be most facile, whence $k_{-a} \gg k_Q$. In this event $k_q \simeq k_a k_Q / k_{-a}$ and

$$\Delta H_q^* = \Delta H_a + \Delta H_Q^* \tag{7}$$

or

$$\Delta H_q^* = \Delta H_a^* - \Delta H_{-a}^* + \Delta H_Q^* \tag{8}$$

In eqs 7 and 8, ΔH_q^* represents the observed activation enthalpy, while ΔH_a^*, ΔH_{-a}^*, and ΔH_Q^* represent activation enthalpies for the individual steps in the reaction sequence. These steps are shown schematically in Figure 5, where conversion to the ground state is assumed to occur at the intersection of the two surfaces. Of course, ΔH_a is the enthalpy of formation of the complex $^*Cu \cdots Q$. When this term dominates in eq 7, the observed enthalpy of activation is negative and becomes more negative as the bond between $^*Cu$ and Q strengthens. This limit for eq 6, therefore, accounts for the initial correlation between ΔH_q^* and donor number as depicted in Figure 4.

However, this correlation necessarily breaks down when strong enough adducts are formed. As depicted in Figure 5, when the minimum in the excited-state surface shifts to lower energy, radiationless decay to the ground state becomes more facile. At the same time, the enthalpic barrier to dissociation increases so that the k_{-a} step is less competitive. In the limit where $k_Q \gg k_{-a}$, $k_q \simeq k_a$ and a nonnegative enthalpy of activation should be observed.[28] In our system, the measured value of ΔH_q^* appears to be negative even for the strongest donors DMSO and DMF; however, the deviation from zero is within experimental error. When the magnitudes of k_Q and k_{-a} are comparable to each other, k_q must be described by eq 6. A strictly linear Eyring plot is not expected,[13] although deviations from linearity may not be resolvable in the temperature range that is accessible. In this event the k_Q and the k_{-a} terms combine to determine the magnitude of the negative contribution to ΔH_q^*, and the contribution from k_Q probably moderates the overall exothermicity. Thus, the increase in ΔH_q^* that occurs with the stronger donors can be explained in terms of the increasing importance of the k_Q term.

Figure 4 reveals that the changes in the enthalpy and entropy of activation tend to compensate each other. Thus when ΔH_q^* shifts negatively so as to favor quenching, this is countered by a negative shift in ΔS_q^*. A detailed treatment of the entropy data is not warranted because of the inherently large errors in the measurements; however, the fact that ΔS_q^* tends to level off at ca. -80 J mol^{-1} K^{-1} for the stronger donors is in keeping with the proposal that k_q tends toward the k_a limit.

Entropy considerations are obviously important in dictating the reaction kinetics; otherwise, the five-coordinate adducts would accumulate in solution because their formation is exothermic. Indeed, an alternative interpretation of the data could be constructed on the assumption that the kinetic barrier to quenching is entirely entropy controlled. In this view, quenching could be envisaged as a single-step reaction with an *intrinsically* negative activation enthalpy. Negative activation energies have previously been proposed to occur in reactions between carbenes and olefins.[29-31] Although a similar interpretation could conceivably be imposed on our data because a new bond is formed during the approach to the transition state, this model does not account for the fact that the least negative activation energies occur when the strongest coordinate-covalent bonds form.

Finally, the possibility that Lewis bases may affect the lifetime by more than one mechanism should be acknowledged. Since relatively high concentrations of the Lewis bases are required, "outer-sphere" interactions may also be important. Thus the local environment of the complex may be enriched with quencher due to specific solvation interactions; similarly, the extent of ion-pairing may vary from solution to solution. In the case of ethyl acetate, effects of this type may be responsible for the k_{q1} process that has the anomalous activation parameters. Even here, however, rate comparisons reveal that this mechanism represents only a minor contribution to the quenching. Exciplex quenching is clearly the dominant pathway.

Conclusions

Exciplex interactions involving the d orbitals are difficult to characterize for the excited states of transition-metal complexes because ligands in the primary coordination shell tend to screen out the substrate. As is evident from studies of organic molecules,[32,33] orbital contact is often a prerequisite for effective complex formation. Coordinatively unsaturated excited states such as $^*Cu(dmp)_2^+$ are, however, susceptible to exciplex formation via coordinate-covalent bond formation. As shown by this work and other recent studies,[13,34] even if direct spectroscopic detection of the excited state is not possible, exciplex formation can be established from the temperature dependence of the reaction kinetics, if the activation enthalpy reflects the enthalpy of adduct formation. This method of analysis is most reliable when the results from a series of quenching reactions can be correlated with known thermodynamic parameters. Thus, in the case of $^*Cu(dmp)_2^+$, the enthalpy of activation becomes more negative when stronger Lewis bases are employed until there is a shift in the rate-determining step of the reaction mechanism. Quenching interactions involving very weak bases may also be difficult to study because the enthalpy of activation is likely to remain positive, as when steric forces inhibit adduct formation.[35]

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