Activation Volumes (ΔV^*_q) for Energy- and Electron-Transfer Quenching of [Cu(dpp)$_2^+$]*
(dpp = 2,9-Diphenyl-1,10-phenanthroline)

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The quenching of emission from the metal to ligand charge-transfer (MLCT) state of the copper(I) complex Cu-(dpp)$_2^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) by the uncharged chromium(III) complexes CrL$_3$ (L = acetylacetonate, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, 1,1,1-trifluoro-2,4-pentanedionate) and several nitrobenzene derivatives has been investigated in dichloromethane, chloroform, and tetrahydrofuran solutions as a function of hydrostatic pressure (0.1–250 MPa). The patterns in all three solvents were similar. For those quenchers having reduction potentials $E_{1/2}$(Q) < –1.6 V (vs the ferrocenium/ferrocene, Fc$^+$/Fc, couple in dichloromethane), the principal bimolecular deactivation mode is energy transfer. In such cases, there is little effect of pressure on the quenching rate constant k_q ($\Delta V^*_q = \sim 0$ cm^3 mol^{-1}). In contrast, substantially more positive $E_{1/2}$(Q) values lead to k_q's approaching diffusion limits and significantly positive ΔV^*_q values (up to +8 cm^3 mol^{-1}), reflecting the pressure-induced increases in solution viscosity. For $E_{1/2}$(Q) $\sim$ –1.6 V, the dominant pressure-dependent term is electron transfer within the outer-sphere precursor complex, and the resulting charge creation in the transition state leads to substantially negative ΔV^*_q values approaching –20 cm^3 mol^{-1}.

Introduction

The value of pressure studies in gaining insight into the mechanisms of the unimolecular excited-state processes of transition metal complexes has been amply demonstrated.[2] One advantage is that pressure can be varied continuously over large ranges, thus providing a systematic perturbation of the medium.[3] Recently, we exploited this advantage by using pressure studies to probe the mechanisms of bimolecular reactions of metal complex excited states (ES).[4-6] One system of interest has been the quenching of the metal to ligand charge-transfer (MLCT) ES of Cu(dpp)$_2^+$ (I, dpp = 2,9-diphenyl-1,10-phenanthroline) by different tris(β-dionato)chromium(III) complexes via competitive energy-transfer and electron-transfer pathways.[7] The pressure effects on the quenching kinetics for various members of this series in CH$_2$Cl$_2$ are quite varied and depend on the free energy change ($\Delta G_{el}°$) of the excited-state electron-transfer process.[6] The impetus of the present study was to probe the generality of this behavior in other solvents and to verify whether other examples could be found of the dramatically negative activation volumes ($\Delta V^*_q = $ –20.6 cm^{-1} mol^{-1}) demonstrated for the electron-transfer quenching of I* by *p*-chloronitrobenzene.

$$^3[\text{Cu(dpp)}_2^{*+}]^. + Q \begin{array}{c} \text{(a)} \nearrow k_{el} \\ \\ \text{(b)} \searrow k_{en} \end{array} \begin{array}{c} \text{Cu(dpp)}_2^{2+} + Q^. \\ \\ \text{Cu(dpp)}_2^+ + Q^. \end{array} \quad (1)$$

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(2) (a) Ford, P. C. In *Inorganic High Pressure Chemistry, Kinetics and Mechanisms*; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986; Chapter 6, pp 295–338. (b) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* 1989, *89*, 549–688.
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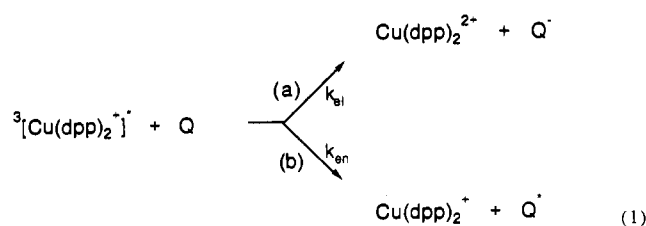## Experimental Section

Materials. The salt [Cu(dpp)$_2$][BPh$_4$] was a gift from D. R. McMillin and R. M. Everly of Purdue University. The reagent grade solvents chloroform (Burdick & Jackson), tetrahydrofuran (Fisher), and dichloromethane (Fisher) were used without purification. THF was taken only from freshly opened bottles. The solid organic quenchers (*p*-dinitrobenzene, *p*-chloronitrobenzene, and methyl 3-nitrobenzoate) were purchased from Aldrich. The *p*-dinitrobenzene and methyl 3-nitrobenzoate were recrystallized from acetone and used immediately. The *p*-chloronitrobenzene was recrystallized from absolute ethanol/water and acetone/water mixtures and used immediately. Nitrobenzene was purchased from Mallinckrodt and was distilled before use. CrL$_3$ compounds were prepared by literature methods[8] with the exception of Cr(acac)$_3$, which was purchased from Aldrich. These compounds were recrystallized from either absolute ethanol/*n*-hexane or benzene/*n*-hexane mixtures.

Preparation of Samples for Spectroscopic Measurements. Sample solutions were prepared by first adding sufficient [Cu(dpp)$_2$][BPh$_4$] to a 1 cm path length fluorimetry cell sealed with a serum cap to give a 0.10 mM solution in 3–4 mL of the appropriate solvent. (This concentration is an order of magnitude lower than the onset of ion-pairing effects on the emission lifetime of this salt.[7]) After the addition of a weighed sample of solid or measured volume of liquid quencher to the fluorimetry cell, solvent ($\sim$4–5 mL) was added, and the solution was purged vigorously with nitrogen. The cell and solution were weighed after deaeration to determine the solvent mass and hence the solution concentrations.

Some of the solution from the fluorimetry cell was transferred to a quartz optical capsule (8 mm in diameter and 25 mm in length) and purged again briefly with N$_2$ to ensure the absence of O$_2$. The capsule was then sealed with a Teflon piston fitted with two Viton O-rings. (The capsule/piston design transmits the applied hydrostatic pressure without exchange between the sample solution and the surrounding medium.) Since THF attacks Viton quickly, the O-rings were replaced after every experiment involving that solvent. The quartz capsule was placed into a modified Nova-Swiss four-window, 400-MPa high-pressure spectroscopic cell, which was filled with pressure-transmitting fluid (neat solvent) and sealed.

High-Pressure Experiments. The apparatus for lifetime measurements under pressure has been described previously.[4-6] The high-pressure cell was connected to an Enerpac hand pump and a Heise gauge, which were used to generate and measure, respectively, the applied hydrostatic pressure. The excitation source for the emission lifetime measurements was a Quanta-Ray DCR-1A Nd:YAG pulse laser operating at 532 nm. The emission was monitored at 675 nm at right angles through a Spex

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Table I. Emission Lifetimes and Volumes of Activation for Nonradiative Decay for $Cu(dpp)_2{}^+$ in Different Solvents

solvent	$\tau_0{}^a$ (ns)^a	$\tau_0{}^{250}$ (ns)^a	$\Delta V^{\ddagger}{}_d$ (cm^3 mol^{-1})^b
CH$_2$Cl$_2$	265	225	−1.6
CH$_3$CN	115	102	−1.2
CHCl$_3$	205	232	+1.2
THF	160	155	−0.3

^{a} Experimental uncertainties of ±5% are typical for these lifetime measurements. $\tau_0{}^a$ is the lifetime measured at ambient pressure; $\tau_0{}^{250}$ is the lifetime measured at 250 MPa. ^{b} Estimated experimental uncertainties ±0.5 cm^{-1} mol^{-1}.

single monochromator with an RCA 8852 photomultiplier tube. The signal from the PMT was processed by a Tektronix 8912AD transient digitizer interfaced to a Zenith Z-158 computer. Four to six luminescence lifetime measurements, each a signal average of sixty-four emission decay traces, were made at each pressure. For at least one elevated pressure two independent series of four to six lifetime measurements were acquired at different times during the process of the experiment. This procedure provides a check for possible hysteresis or reactions affecting the lifetime under these conditions. All experiments were conducted at room temperature (20 ± 1 °C).

Results and Discussion

In an earlier study[9] the ambient pressure lifetime (τ^a) of I* was determined to be 265 ns in pure dichloromethane. Chloroform and THF were found to be suitable solvents for high-pressure studies, and in these the emission lifetimes are 205 and 160 ns, respectively. The emission decay curves were exponential in all cases for these three solvents. Some nonexponential decays were observed for acetonitrile solutions.

The reciprocal of the measured lifetime, τ^{-1}, equals the ES emission decay rate constant k_e, which is the sum of several contributions

$$k_e = k_n + k_r + k_p + k_q[Q] \qquad (2)$$

where k_n, k_r, k_p, and k_q represent the rate constants for nonradiative deactivation, radiative deactivation, net photochemical reaction, and bimolecular quenching by quencher Q, respectively. For $Cu(dpp)_2{}^+$ in pure CH$_2$Cl$_2$, CHCl$_3$, or THF without added quencher, no net photochemistry was observed; thus, $k_p \ll k_n + k_r$ and $k_e = k_n + k_r$. Under these conditions, τ decreased at elevated pressures for THF, CH$_2$Cl$_2$, and CH$_3$CN solutions of $Cu(dpp)_2{}^+$ but increased slightly for CHCl$_3$ solution (Table I).

The change of a rate constant with pressure can be expressed conveniently by the volume of activation $\Delta V^{\ddagger}$, which is defined by

$$\Delta V_i{}^{\ddagger} = -RT(\partial \ln k_i/\partial P)_T \qquad (3)$$

Thus, the activation volume for emission decay in the absence of quencher can be calculated from the slope of a plot of $\ln(\tau_0{}^a/\tau_0)$ vs P, where the superscript "a" denotes ambient pressure and the subscript "0" indicates the absence of added quencher. The resulting $\Delta V_e{}^{\ddagger}$ values for the various solutions are summarized in Table I. Since the emission quantum yields were small ($\sim 10^{-3}$ in CH$_2$Cl$_2$),[9] $k_n \gg k_r$ and $k_e \sim k_n$; thus $\Delta V_e{}^{\ddagger}$ reflects the pressure sensitivity of the nonradiative deactivation pathway ($\Delta V_d{}^{\ddagger}$). These values fall in line with those small $\Delta V_d{}^{\ddagger}$ values determined previously for complexes which deactivate nonradiatively via a weak coupling mechanism.[10]

Emission from I* is susceptible to dynamic quenching by both energy transfer and electron transfer.[7] In no case was emission from the quencher itself observed in the region 350–800 nm.

Rate constants for bimolecular quenching (k_q) were calculated from

$$k_q = (\tau_q{}^{-1} - \tau_0{}^{-1})[Q]^{-1} \qquad (4)$$

where τ_q and τ_0 denote the measured emission lifetimes of I* in the presence and absence of quencher, respectively, under otherwise identical conditions. Inspection of the resulting k_q values (Table II) shows that these do not differ dramatically among the three solvents for any one quencher. For each pressure, the quencher concentration (in molarity) was corrected for solvent compressibility using data compiled by Bridgman.[6,11] Values of k_q were then calculated from the measured lifetimes τ_q and τ_0 and the corrected [Q] values for different P according to eq 4. The volumes of activation $\Delta V_q{}^{\ddagger}$ for the quenching process were then determined from the slopes of $\ln(k_q/k_q{}^a)$ vs P plots at constant T. The markedly different responses of k_q to pressure are illustrated in Figure 1 for different quenchers in THF solution.

Organic Quenchers. Electron transfer is the only energetically accessible pathway for the quenching of I* by the nitroaromatic compounds studied here, since triplet energies of these species are significantly higher than the ES energy of the Cu(I) emitter ($\sim 14.5 \times 10^3$ cm^{-1}).[7] The reduction potential $E_{1/2}(I^+/I^*)$ has been estimated to be about −1.41 V, so, when the quencher reduction potential $E_{1/2}(Q)$ is comparable, the free energy change $\Delta G_{el}{}^\circ$ for the electron transfer from I* to Q is sufficiently favorable for quenching to be observable under our conditions. (This generally requires a k_q of $>10^6$ mol^{-1} s^{-1}, since the lifetimes are sub-microseconds.) The calculated $\Delta V_q{}^{\ddagger}$ values for these nitro-aromatics span the remarkable range from −20.4 cm^3 mol^{-1} for p-chloronitrobenzene to +6.9 cm^3 mol^{-1} for p-dinitrobenzene.

Quenching by p-dinitrobenzene approaches the diffusion limit k_D in all three solvents. Under such conditions, the quenching rate would be largely determined by the solvent viscosity,[12] which increases with increasing pressure. This effect is reflected in the substantially positive $\Delta V_q{}^{\ddagger}$ values calculated for this reaction in all three solvents; these $\Delta V_q{}^{\ddagger}$ values are comparable to the results of earlier experiments which have probed pressure effects on diffusion-limited bimolecular processes in acetonitrile and ethanol.[13] In contrast, the slower quenching by p-chloronitrobenzene, methyl m-nitrobenzoate, or nitrobenzene leads in each case to large, negative $\Delta V_q{}^{\ddagger}$ values in each solvent. Electron transfer from I* to the uncharged Q (eq 1a) engenders significant charge separation and hence increased solvation in the transition state. The more negative values ($\sim$−20 cm^3/mol) were observed for CH$_2$Cl$_2$ solutions, while smaller but still substantially negative values ($\sim$−11 cm^3 mol^{-1}) were found in CHCl$_3$ and THF.

CrL$_3$ Quenchers. Interpretation of the $\Delta V_q{}^{\ddagger}$ values determined for quenching of I* by the tris(β-dionato)chromium(III) compounds is complicated by competitive energy-transfer quenching (eq 1b). The low-lying doublet ligand field (^{2}LF) states of these CrL$_3$ complexes are nearly isoergic, each with an electronic energy (($12.5 \pm 0.4) \times 10^3$ cm^{-1})[13] less than that of I*. In contrast, the CrL$_3$ reduction potentials are dramatically dependent on L and range from −0.79 V for Cr(hfac)$_3$ to −2.43 V for Cu(acac)$_3$ (vs Fc$^+$/Fc in dichloromethane). Thus, energy transfer (eq 1b) should always contribute to the total ES quenching, and the rate constants k_{en} ($\sim 10^{7.6\pm0.3}$ M^{-1} s^{-1}) have been shown to be relatively independent of the nature of L.[6,7] Whether electron-transfer quenching will be competitive depends on the reduction potential of the Cr(III) quencher. If reduction of CrL$_3$ by I* is highly exoergic, then electron transfer will much faster than energy

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Table II. Rate Constants and Activation Volumes for the Quenching of [Cu(dpp)2]* in Different Solvents

		solvent					
		CH_2Cl_2[b]		$CHCl_3$		THF	
quencher	$-E_{1/2}$ (V)[a]	$10^7 k_q$ (s⁻¹)	$\Delta V_q{}^*$ (cm³ mol⁻¹)	$10^7 k_q$ (s⁻¹)	$\Delta V_q{}^*$ (cm³ mol⁻¹)	$10^7 k_q$ (s⁻¹)	$\Delta V_q{}^*$ (cm³ mol⁻¹)
Cr(hfac)₃	0.79	940	+8.0	530	+7.5	460	+8.3
Cr(tfac)₃	1.64	4.2	−8.1	5.1	−3.6	3.1	−4.6
Cr(acac)₃	2.43	1.5	−0.1	2.8	+0.2	1.8	−0.7
p-dinitrobenzene	1.18	1050	+6.9	1000	+6.0		
p-chloronitrobenzene	1.58	3.0	−20.4	5.5	−7.3	0.82	−12.4
methyl *m*-nitrobenzoate	1.57[c]	4.8[d]	−21.0[d]	4.6	−11	1.4	−11.6
nitrobenzene	1.76	0.30[d]	−19.6[d]	0.31	−18.2	<0.1	

[a] Ligand reduction potentials vs Fc⁺/Fc in dichloromethane; ref 7. [b] Data from ref 6 except where noted. [c] In acetonitrile. From: Maki, A. H.; Geske, D. H. *J. Am. Chem. Soc.* **1961**, *83*, 1852. [d] This work.
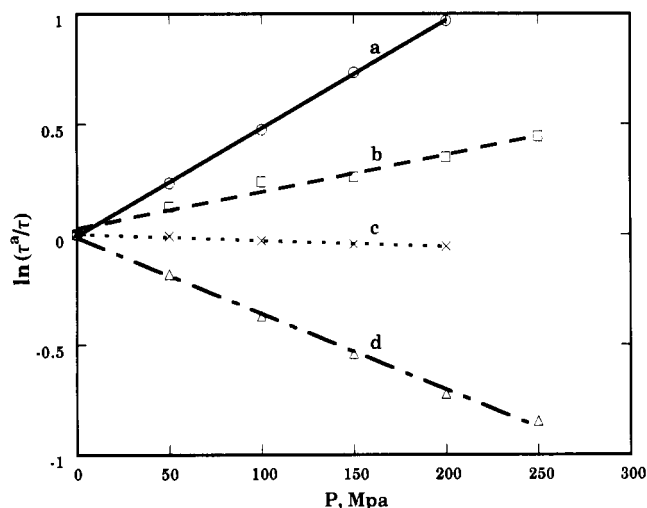

Figure 1. Plots of $\ln(\tau^a/\tau)$ for various quenchers in dichloromethane: (a) *p*-chloronitrobenzene; (b) Cr(tfac)₃; (c) Cr(acac)₃; (d) Cr(hfac)₃.

transfer and k_q will approach the diffusion limit k_D. This situation exists for quenching of I* by Cr(hfac)₃; for which k_q approaches k_D in all three solvents. As for *p*-dinitrobenzene, the reaction rate is governed by the solvent viscosity, and the response to pressure gives a large, positive $\Delta V_q{}^*$ in each solvent.

For Q = Cr(acac)₃ electron transfer from I* is decidedly endergonic, and the operative quenching mechanism is energy transfer. Correspondingly, the pressure dependence of this pathway is small. Unlike electron transfer, there is no net movement of charge from one metal center to another, and solvation changes are likely to be small. The ES volumes of both the donor and accepter chromophores are likely to have slightly larger volumes than the corresponding ground states, but neither the MLCT ES of I nor the ²LF state of CrL₃ should be significantly distorted from the respective ground states. The expected net result of energy transfer would then be small opposing contributions to give a $\Delta V_q{}^*$ of nearly zero, as observed for quenching by Cr(acac)₃ in all solvents (see Table II).

When $\Delta G_{el}{}^\circ$ for electron transfer is approximately zero or slightly negative, such as for Cr(tfac)₃, the rates for electron-transfer and energy-transfer quenching of I* are comparable,

and the total rate for quenching is several orders of magnitude slower than the diffusion limit; therefore it is little affected by viscosity changes. The contribution from energy transfer to $\Delta V_q{}^*$ is still expected to be small, but electron transfer from [Cu-(dpp)₂⁺]* to Cr(tfac)₃ leads to a charge separation in the transition state. The $\Delta V_q{}^*$ values −8.1, −3.6 and −4.6 cm³ mol⁻¹, respectively, in CH_2Cl_2, $CHCl_3$, and THF are significantly smaller than those observed for those nitroaromatics having comparable reduction potentials $E_{1/2}$(Q). This would be expected, however, since the measured $\Delta V_q{}^*$ reflects the pressure sensitivity of both the energy- and electron-transfer pathways and would be attenuated by the pressure-independent energy-transfer pathway. In addition, since the negative change on a CrL₃⁻ moiety should be delocalized over a larger surface area than on the nitroaromatic anion, it is likely that the volume changes due to electron-transfer-induced solvent electrostriction would be smaller in the former case.

Summary

The present data illustrate the greater generality of expected pressure effects on bimolecular quenching of a metal complex ES by competitive energy and electron transfer. When $k_q \sim k_D$, pressure-induced changes in solvent viscosity are responsible for the observed positive $\Delta V_q{}^*$ values, regardless of the actual quenching mechanism. When $k_q < k_D$ and when either the luminactive complex or (as in the present case) Q is uncharged, energy-transfer rates are likely to be little affected by pressure while electron-transfer rates will be much more responsive to P owing to solvation changes as charges are moving in the transition state. For electon transfer between [Cu(dpp)₂⁺]* and Cr(tfa)₃ or, more dramatically, *p*-chloronitrobenzene, methyl *m*-nitrobenzoate, or nitrobenzene, this is reflected by quite negative $\Delta V_q{}^*$ values. (Of course, a different pressure response would be predicted if charge neutralization were the result of electron transfer.) Notably, such behavior was found for all three solvents investigated here and has been recently demonstrated as well for the quenching of the cluster-centered LMCT/ds excited state of the copper(I) cluster $Cu_4I_4(py)_4$ in dichloromethane solution.[15]

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