Inorg. Chem. **1994,** *33,* 5957−5959 **5957**

Diffusion Limited Quenching of the Cluster Centered Excited State of the Copper(I) Cluster $Cu_4I_4(py)_4$ by Ferrocenium Ion in CH_2Cl_2 Solution

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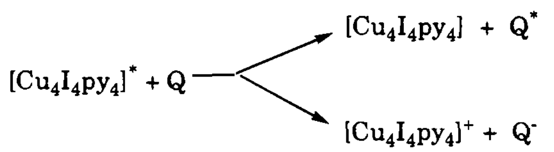
Received June 3, 1994

The rich photophysical properties of the Cu(I) cluster $Cu_4I_4(py)_4$ (**I**) (py = pyridine) have been the subject of recent attention in this laboratory.[1] In room temperature solutions, the luminescence spectrum of **I** displays an intense band at $\lambda_{max} = 690$ nm with a relatively long lifetime ($\tau = 3-10$ μs in different solvents), assigned as emission from a "cluster centered" (CC) excited state (**I***) having mixed iodide-to-copper charge transfer (XMCT) and d−s character.[2] The energy of **I*** has been conservatively estimated as 1.66 μm^{-1} and the potential for the ES half cell $\mathbf{I}^+ + e^- \rightarrow \mathbf{I}^*$ ($E_{1/2}(\mathbf{I}^+/\mathbf{I}^*)$ as −1.78 V.[3] **I*** can be quenched in CH_2Cl_2 solution by nitrobenzenes and by tris(β-dionato)chromium(III) complexes CrL_3.[3] The former quenchers (Q) function by an electron transfer mechanism demonstrated by correspondence of rate constants k_q with the reduction potentials ($E_{1/2}(Q/Q^-)$.[4] The CrL_3 complexes quench by competitive energy transfer and electron transfer mechanisms (eq 1).[3]



A surprising feature of these results was the requirement of very large potentials ($-\Delta G_{el}° = E_{1/2}(Q/Q^-) - E_{1/2}(\mathbf{I}^+/\mathbf{I}^*)$)[6] before electron transfer quenching becomes significantly competitive with radiative and nonradiative deactivation of **I*** and, for the Cr(III) complexes, with energy transfer quenching.[3] The present study was initiated to extend the range of quencher properties and to examine the origin of the above kinetics properties.

Experimental Section

The ferrocenium salts $[Fc]PF_6$, $[Me_2Fc]PF_6$ and $[Me_{10}Fc]PF_6$ (where Fc^+ is ferrocenium ion, i.e., $Fe(\eta^5\text{-}C_5H_5)_2^+$, $Me_2Fc^+ = Fe(\eta^5\text{-}C_5H_4\text{-}CH_3)_2^+$, and $Me_{10}Fe^+ = Fe(\eta^5\text{-}C(CH_3)_5)_2^+$) were synthesized according to literature methods.[8] The $Cu_4I_4(py)_4$ was prepared and recrystallized as described earlier.[2] Solvent CH_2Cl_2 was distilled from CaH_2 and stored under Ar until used. Solutions for quenching studies were prepared as follows. Individual stock solutions of $Cu_4I_4(py)_4$ and of the appropriate quencher in CH_2Cl_2 were prepared at the respective concentrations ~1 and ~3 mM. A small volume of the quencher solution was transferred to a 5 mL volumetric flask by a microsyringe, then the flask was filled to the mark with the $Cu_4I_4(py)_4$ solution. The resulting solution was transferred to a round Pyrex cell fitted with a greaseless Rotoflow stopcock and degassed by three or four freeze−pump−thaw cycles. Quencher concentrations were determined quantitatively from optical absorption spectra; i.e., for Fc^+, $\lambda_{max} = 617$ nm ($\epsilon = 410$ M^{-1} cm^{-1}), for Me_2Fc^+, 650 nm (332), and for $Me_{10}Fc^+$, 778 nm (394).[8]

Emission lifetimes were determined with the Nd/YAG laser system described previously with the exception that the excitation source is now a Continuum Model NY-61 laser plus third harmonic generator (355 nm).[3,9] Photophysical measurements under applied hydrostatic pressure were carried out with solutions prepared and deaerated as above. The high pressure cell and flash photolysis apparatus have been described previously.[3,9] Kaleidagraph software was used for data plotting and to fit rate data to theoretical models.

Results and Discussion

The second order quenching constant (k_q) includes terms from both pathways ($k_q = k_{en} + k_{el}$), and as predicted by theory,[4] the oxidative quenching contribution k_{el} is a function of the driving force for electron transfer, $-\Delta G_{el}°$. In the earlier study, two key points were noted. One was that contributions to quenching by electron transfer were apparent only for substrates for which $-\Delta G_{el}°$ values are larger than 0.4 V. This behavior was attributed to the large reorganization energy (λ) required in the $\mathbf{I}^*/\mathbf{I}^+$ exchange process, owing in part to the distortion of **I*** from the ground state configuration reflected by "Stokes" shifts up to 1.6×10^4 cm^{-1} from excitation to emission maxima.[2] A large λ is also consistent with the sizable activation enthalpies found for certain quenchers, e.g., $\Delta H_q^{\ddagger} = 28 \pm 1$ kJ mol^{-1} for *m*-dinitrobenzene and 40 ± 2 kJ mol^{-1} for *o*-dinitrobenzene as determined in temperature dependence studies of k_q (7.2×10^6 and 4.2×10^6 M^{-1} s^{-1}, respectively, at ambient *T*)[3]. Secondly, even at very negative $\Delta G_{el}°$'s, k_q appeared to level off at values nearly an order of magnitude less than that estimated (1.8×10^{10} M^{-1} s^{-1}) for a diffusion limited bimolecular reaction in 295 K CH_2Cl_2.[7] For example, when Q = $Cr(hfac)_3$ (hfac = hexafluoroacetylacetonate), for which $\Delta G_{el}° = -0.99$ V, the measured k_q was 1.4×10^9 M^{-1} s^{-1}. One explanation of the latter observation might be a requirement of a specialized orientation in the encounter complex before electron transfer can be effected. An alternative, more prosaic, explanation would be that, owing to an exceedingly large reorganization energy, the $\Delta G_{el}°$ values for none of the quenchers explored were sufficiently negative to approach maximum rates of electron transfer.

These quenching studies were extended to examine whether **I*** could be quenched bimolecularly at diffusion-controlled

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(1) (a) Ford, P. C.; Vogler, A. *Acc. Chem. Res.* **1993**, *26*, 220−226. (b) Ford, P. C. *Coord. Chem Rev.* **1994**, *132*, 129−140.

(2) (a) Kyle, K. R.; Ryu, C. K.; DiBenedetto, J. A.; Ford, P. C. *J. Am. Chem. Soc.* **1991**, *113*, 2954−2965. (b)Vitale, M.; Palke, W. E.; Ford, P. C. *J. Phys. Chem.* **1992**, *96*, 8329−8336.

(3) Døssing, A.; Kudo, S.; Ryu, C. K.; Ford, P. C. *J. Am. Chem. Soc.* **1993**, *115*, 5132−5137.

(4) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891−899.

(5) (a) For the CrL_3 compounds $E(Q/Q^-)$ values range from −2.43 to −0.79 V vs ferrocenium/ferrocene, Fc^+/Fc, in CH_2Cl_2,[5b] while the energies of the ligand field excited state ^2E_g (1.22 to 1.28 μm^{-1}) are nearly unaffected by L.[5c] (b) Gamache, R. E., Jr.; Rader, R. A.; McMillin, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 1141−1146. (c) Fatta, A. M.; Lintvedt, R. L. *Inorg. Chem.* **1971**, *10*, 478−481.

(6) The free energy of electron transfer is $\Delta G_{el}° = -\{E_{1/2}(Q/Q^-) - E_{1/2}(\mathbf{I}^+/\mathbf{I}^*)\}$, where $E_{1/2}(Q/Q^-)$ is the quencher reduction potential and $E_{1/2}(\mathbf{I}^+/\mathbf{I}^*)$ is the half cell potential for the CC excited state estimated by subtracting the ES energy E^{00} from the ground state reduction potential, i.e., $E_{1/2}(\mathbf{I}^+/\mathbf{I}^*) = E_{1/2}(\mathbf{I}^+/\mathbf{I}) - E^{00}) = -1.78$ V vs Fc^+/Fc, in CH_2Cl_2.[3] (This calculation is an underestimate since it does not include the work terms for charge creation $w_p - w_r = -0.14$ V which should be added to $\Delta G_{el}°$).

(7) (a) The viscosity of CH_2Cl_2 at 25° C was estimated from data given at 15 and 30 °C ($\eta \approx 0.41$ cp at 25 °C).[7b] From the equation[7c] $k_d = (2RT/3000\eta)(2 + r_D/r_Q + r_Q/r_D)$ a value of 1.8×10^{10} M^{-1} s^{-1} was determined at 25 °C. (b) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 62nd ed.; CRC Press Inc.: Boca Raton, FL, 1981. (c) von Smoluchowski, M. *Z. Phys. Chem.* **1917**, *92*, 129.

(8) Lee, S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 1367−1369.

(9) Crane, D. R.; Ford, P. C. *J. Am. Chem. Soc.* **1991**, *113*, 8510−8516.

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limiting rates by using quenchers with even higher reduction potentials. Ferrocenium and its methylated analogs offer a useful set of Q in this context with reduction potentials, respectively, 0.45. 0.30 and −0.04 V vs Ag/AgCl in CH_2Cl_2/0.1 M [*n*-Bu_4N]PF_6 (i.e., 0.0, −0.15 and −0.49 V vs Fc^+/Fc) for Fc^+, Me_2Fc^+ and $Me_{10}Fc^+$. These give the respective $\Delta G_{el}°$ values −1.78, −1.63 and −1.29 V.[8,10]

The second order rate constants k_q for the dynamic quenching of emission from **I*** were determined from linear Stern−Volmer plots[12] of τ_0/τ vs [Q] (where τ is the lifetime for a particular [Q] and τ_0 is that in the absence of quencher). These gave k_q values of $(1.2 \pm 0.2) \times 10^{10}$ and $(0.81 \pm 0.16) \times 10^{10}$ M^{-1} s^{-1}, respectively, for Q = Fc^+ and $Me_{10}Fc^+$. (The k_q for Me_2Fc^+ was determined for only one concentration and gave a value of $\sim 1.2 \times 10^{10}$ M^{-1} s^{-1}). Notably, these values are significantly higher than the largest k_q noted previously for eq 1[3] and fall close to the estimated diffusion limit under these conditions.[9]

The near-diffusional character of quenching by Fc^+ was further evidenced by examining the effects of hydrostatic pressure. The activation volume of a dynamic process is defined by[12]

$$\Delta V_i^{\ddagger} = -RT\left(\frac{d \ln k_i}{dP}\right)_T \tag{2}$$

and can be determined from the linear plot of $\ln(k_q/k_q^a)$ vs *P* (where k_q is the value at applied pressure *P* and k_q^a that at ambient *P*). Data thus plotted for the effect of *P* (0.1 to 300 MPa) on k_q with Fc^+ as quencher in 297 K CH_2Cl_2 gave a positive $\Delta V^{\ddagger}_q$ value of $+6.2 \pm 0.5$ cm^3 mol^{-1} consistent with the expectation that the diffusion rate will slow under pressure owing to increased viscosity. Nonetheless, it should be noted that a similar value was seen for quenching by $Cr(hfac)_3$ (+6.6 cm^3 mol^{-1}), where k_q^a is somewhat smaller (1.4×10^9 M^{-1} s^{-1}).[3]

According to electron transfer theory,[13] the rate should maximize when the driving force approaches the sum of the inner and outer sphere reorganization energies (i.e., when $-\Delta G_{el}° = \lambda = \lambda_{is} + \lambda_{os}$). The present results indicate that a driving force >1 V is required in order for k_q to approach k_d. Therefore, the anomalous behavior observed earlier[3], where the highest k_q was substantially less than k_d, was simply due to insufficient reaction potential. This can be attributed to a very large λ required by the **I***/**I**$^+$ exchange process. One major contribution to reorganization energy would be structural differences between **I*** and **I**$^+$ owing in part to the major distortion of the cluster centered excited state from the corresponding ground state structure. This distortion is experimentally manifested in the large "Stokes" shift between excitation and emission maxima noted above, which has been interpreted by *ab initio* calculations[14] in terms of enhanced Cu−Cu bonding and decreased Cu−I bonding in the ES.

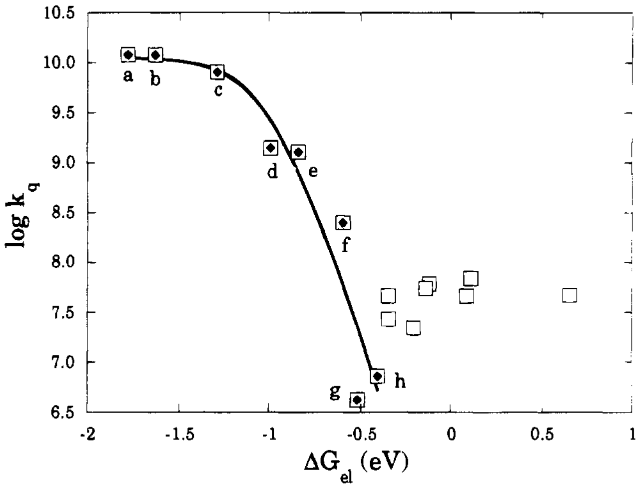

Figure 1. Plot of log k_q vs $\Delta G_{el}°$ for the quenching of emission from **I*** by ferrocenium derivatives (this work) and by nitroaromatic and chromium (*β*-dionato) quenchers (ref 3). The solid curve represents the best fit according to eqs 3 and 4 for electron transfer quenching (see text) for the following substrates: (a) Fc^+, (b) Me_2Fc^+, (c) $Me_{10}Fc^+$, (d) $Cr(hfac)_3$, (e) 1,4-benzoquinone, (f) *p*-dinitrobenzene, (g) *o*-dinitrobenzene, (h) *m*-dinitrobenzene. Open squares represent experimental data for the other CrL_3 complexes which were studied in ref 3.

Figure 1 is a plot of log(k_q) as the function of $\Delta G_{el}°$. The curve shown represents the best least-squares fit of selected data, i.e., the k_q's for the ferrocenium derivatives,[15] the nitroaromatics and $Cr(hfac)_3$, to the equation

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

In eq 3, k_{el}' is the rate constant for electron transfer in an outer sphere precursor complex and K_a is the "equilibrium constant" (k_d/k_{-d}) for precursor complex formation (~1 M^{-1}, if one or both of the participants is uncharged). According to electron transfer theory,[13] k_{el}' can be expressed by

$$k_{el'} = \nu_n \kappa_e \exp\left[\frac{-(\Delta G_{el}° + \lambda)^2}{4\lambda RT}\right] \tag{4}$$

in which ν_n is the frequency factor and κ_e is adiabaticity factor.[13] The best fit (*R* = 0.96) was obtained by allowing the product $K_a\nu_n\kappa_e$ and reorganization energy λ to iterate until optimum values were obtained. The fit indicated in Figure 1 gave a typical value[16] of 1.5×10^{11} M^{-1} s^{-1} for $K_a\nu_n\kappa_e$ and a large value of 1.89 eV (183 kJ mol^{-1}) for λ.[17] For comparison, a similar treatment of the kinetic data[18] for the redox quenching of the metal-to-ligand charge transfer emission from the Cu(I) complex

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(10) (a) The estimated doublet excited state energies of the ferrocenium ions[10b] are 1.48 μm^{-1} for Fc^+, 1.36 μm^{-1} for Me_2Fc^+, and ~1.2 μm^{-1} for $Me_{10}Fe^+$. (b) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955−970.

(11) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings; Menlo Park, CA, 1978; pp 243−264.

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

(13) (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441−497. (b) Marcus, R. A.; Sutin, N. *Biochem. Biophys. Acta* **1986**, *811*, 265.

(14) Vitale, M.; Palke, W. E.; Ford, P. C. *J. Phys. Chem.* **1992**, *96*, 8329−8336.

(15) (a) Although it was assumed in this treatment that the principal contribution to the quenching mechanism is electron transfer, it should be noted that the ligand field ES of the ferrocenium derivatives are sufficiently low in energy to quench **I*** by energy transfer as well.[10] Although our current results cannot directly differentiate between the energy and electron transfer quenching, the well behaved fit of k_q values to the Marcus model would argue for a pathway dominated by an electron transfer mechanism. In this context, energy transfer quenching of **I*** by various CrL_3,has previously been shown[3] to be much slower than k_d, an observation which may indicate significant Franck−Condon contribution to this mechanism as well. Ferrocene itself, which is unlikely to participate in electron transfer quenching of **I*** but has a triplet ES of 1.5 μm^{-1},[15b] quenches the emission from **I*** by an apparent energy transfer mechanism with a k_q of 3×10^9 M^{-1} s^{-1} (determined from a linear Stern−Volmer plot), a factor of four less than that seen for quenching by Fc^+. (b) Farmilo, A.; Wilkinson, F. *Chem. Phys. Lett.* **1975**, *34*, 575−580.

(16) Fox, L. S.; Kozik, M. Winkler, J. R.; Gray, H. B. *Science* **1990**, *247*, 1069.

$Cu(dpp)_2^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) by a series of nitrobenzenes gives a reorganization energy of 0.62 eV).

The outer sphere contribution to the reorganization energy λ_{os} for quenching of **I*** by Fc^+can be estimated from the classical model to be about 0.5 eV.[19] This leaves about 1.4 eV to be accounted for as the contribution from the inner sphere contribution. Furthermore, given that the self exchange rates of the Q/Q^- pairs in each case are quite facile, this leads one to conclude (as was done previously in a more qualitative fashion) that the intrinsic barrier to electron transfer quenching of **I*** lies largely in the $\mathbf{I^*} \rightarrow \mathbf{I^+}$ transformation and is one result of the distortion of the cluster centered excited state reflected by the extremely large separation of excitation and emission bands.

In summary, quenching of the cluster center excited state of $Cu_4I_4(py)_4$ follows a Marcus type kinetics behavior with quenching rates approaching the diffusion limits for the more strongly oxidizing ferrocenium ion derivatives. The requirement of a substantial reaction potential ($-\Delta G_{el}°$) before electron transfer quenching becomes competitive with radiative and nonradiative decay of **I*** can be attributed to the sizable reorganization energy accompanying electron transfer. This is apparently the result of large inner sphere effects owing to the distortion of the excited state cluster relative to the the analogous ground state structures.

Acknowledgment. This research was supported by the U.S. National Science Foundation (Grant No. CHE-9024845). Laser flash photolysis experiments were carried out on a system constructed in part support from a U.S. Department of Energy University Research Instrumentation Grant (No. DE-FG05-91ER79039). We thank Drs. Marcello Vitale and Jerald Simon for their assistance.

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(17) As noted above, the Cr(β-dionato)$_3$ complexes also quench **I*** by an energy transfer mechanism, e.g., k_q of 4.7×10^7 M^{-1} s^{-1} for Q = tris(acetylacetonato)chromium(III) although $\Delta G_{el}° = +\ 0.65$ V. An attempt was made to fit more of the data plotted in Figure 1 by assuming identical CrL_3 energy transfer rate constants with $k_{en} = 5.4 \times 10^7$ M^{-1} s^{-1} (average for the three CrL_3 quenchers with positive $\Delta G_{el}°$'s). This was subtracted from the k_q's for the CrL_3 complexes (except those three) and the residual was estimated as the k_{el} component. These data, plus the k_q's for the ferrocenium ions and the nitroaromatics were fit to eqs 3 and 4. A large λ was thus obtained, but the fit (both by eye and by correlation, $R = 0.85$) was poor, no doubt because the assumed k_{en} independence of L is questionable.

(18) Gamache, R. E., Jr.; Rader, R. A.; McMillin, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 1141−1146.

(19) (a) The value of λ_{os} can be estimated from the equation[13]

$$\lambda_{os} = \left(\frac{\Delta e^2}{4\pi\epsilon_0}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r_{12}}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)$$

where Δe is the charge transferred, a_1 and a_2 are the radii of the reactants ($a_1 \sim 11$ Å, $a_2 \sim 4.0$ Å),[18b,c] $r_{12} = a_1 + a_2$ and D_{op} and D_s are the optical and static dielectric constants of CH_2Cl_2, 8.93 and 2.02, respectively.[18d] (b) Raston, C. L.; White, A. H. *J. Chem. Soc. Dalton Trans.* **1985**, 2153. (c) Tran, D.; Hunt, J. P.; Wherland, S. *Inorg. Chem.* **1992**, *31*, 2460−2464. (d) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; J. Wiley and Sons: 1986; p 490.