Pressure Effects on the Competitive Energy and Electron Transfer Quenching of the MLCT Excited State of $Cu(dpp)_2^+$ (dpp = 2,9-Diphenyl-1,10-phenanthroline) by CrL_3 (L = β-Dionato Ligands) and Other Quenchers in Solution

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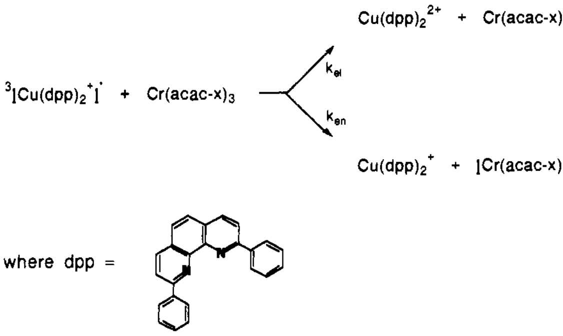
Abstract: The quenching of emission from the metal-to-ligand charge transfer (MLCT) state of the copper(I) complex $Cu(dpp)_2^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) by tris(β-dionato)chromium(III) complexes CrL_3 and several organic substrates has been investigated in dichloromethane solution as a function of hydrostatic pressure (0.1–250 MPa). For those quenchers having reduction potentials $E_{1/2}(Q) < -1.6$ V, the principal bimolecular deactivation mode is energy transfer, and 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 values approaching diffusion control 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 substantially negative ΔV^*_q's were noted. These results are interpreted in terms of the McMillin proposal (*J. Am. Chem. Soc.* **1985**, *107*, 1141–1146) of competitive energy and electron transfer quenching for these complexes.

Introduction

The studies described here are concerned with the use of hydrostatic pressure[2-4] to probe bimolecular mechanisms for the deactivation of transition metal complex excited states (ES). Notably, variation of pressure allows for the systematic and continuous variation of solution properties,[5] and the resulting effects on ES energies and dynamics have provided valuable insight into photochemical and photophysical mechanisms.[6-8] The bulk of the earlier work has been concerned with the effects of pressure on the unimolecular deactivation pathways of metal complex ES. However, recent reports from this laboratory have described investigations of the Lewis base quenching of the metal-to-ligand charge transfer (^{3}MLCT) excited state of $Cu(dmp)_2^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline)[2] and of reactive quenching[3] by various organic substrates of the long-lived $\sigma^* \rightarrow \sigma^b$ ES of the platinum dimer $Pt_2(\mu\text{-}\eta^2\text{-}H_2P_2O_5)_4^{4-}$. The present studies are concerned with pressure effects on the competitive electron transfer and energy transfer quenching of the MLCT excited state of the copper(I) complex $Cu(dpp)_2^+$ (I, dpp = 2,9-diphenyl-1,10-phenanthroline) by various substates.

McMillin and co-workers have established that, while $Cu(dmp)_2^+$ undergoes Lewis base quenching of its triplet MLCT state, the ES of the more sterically crowded diphenyl analogue $Cu(dpp)_2^+$ is much less susceptible to quenching via a similar mechanism.[9] They also demonstrated that $^3[Cu(dpp)_2^+]^*$ (^{3}**I***) *is* susceptible to quenching by various electron and energy acceptors[10] such as the chromium(III) β-dionato derivatives CrL_3. These Cr(III) complexes display a remarkable range of reduction potentials (−0.79 to −2.43 V referenced to the ferrocenium/ferrocene couple in dichloromethane)[10,11] dependent on the nature of L, but their doublet ligand field ES energies are relatively invariant (12.5 ± 0.4 × 10^3 cm^{-1}).[12] For these quenchers, electron and energy transfer processes have been shown to be competitive, e.g.,



(1)

and where k_{el} is the rate constant for electron transfer and k_{en} is that for energy transfer.

The Cr(III) β-dionato complexes make up a particularly attractive series of quenchers to study given the absence of ground state (GS) ion pairing interactions between the $^3[Cu(dpp)_2^+]^*$ donor and the uncharged energy or electron acceptors CrL_3. The electron transfer process leads to the creation of charge, i.e., the formation of a dication $Cu(dpp)_2^{2+}$ and of anions CrL_3^-, while energy transfer does not. Therefore, the electron transfer kinetics should be the more susceptible to perturbations of the solvent medium, and the partitioning between energy and electron transfer may be tunable by pressure. Furthermore, examination of the energy transfer pathway will allow evaluation of the pressure effects on the formation of the precursor complex, independent of the charge creating electron transfer process. Another attractive feature is that the use of a luminescent probe allows investigation

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Table I. Formulas, Ligand Names, and Synthetic Methods or Sources of Tris(β-dionato)chromium(III) Complexes Used in the Present Study

complex	neutral ligand	ref for synthesis/ source
$Cr(acac)_3$	acetylacetone (2,4-pentanedione)	*a*, *b*
$Cr(dbm)_3$	dibenzoylmethane (1,3-diphenyl-1,3-propanedione)	*c*
$Cr(hfac)_3$	1,1,1,5,5,5-hexafluoro-2,4-pentanedione	*d*
$Cr(tfbzac)_3$	4,4,4-trifluorobenzoylacetone (4,4,4-trifluoro-1-phenyl-1,3-butanedione)	*e*
$Cr(tta)_3$	thenoyltrifluoroacetone (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione)	*e*
$Cr(tc\text{-}bzac)_3$	2-thiocyanato-1-phenyl-1,3-butanedione	*f*, *g*
$Cr(br\text{-}dbm)_3$	2-bromo-1,3-diphenyl-1,3-propanedione	*c*
$Cr(tfac)_3$	1,1,1-trifluoro-2,4-pentanedione	*e*
$Cr(n\text{-}acac)_3$	3-nitro-2,4-pentanedione	*h*
$Cr(tc\text{-}acac)_3$	3-thiocyanato-2,4-pentanedione	*f*, *g*
$Cr(br\text{-}acac)_3$	3-bromo-2,4-pentanedione	*c*

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of very fast kinetics at low concentrations ($\sim 10^{-4}$ mol L^{-1}) to avoid the ion pairing complications that have plagued previous pressure effect studies of bimolecular electron transfer dynamics.[13]

Experimental Section

Materials. The salt $[Cu(dpp)_2](BPh_4)$ was a gift from D. R. McMillin and R. M. Everly of Purdue University. High-purity dichloromethane was purchased from Burdick & Jackson and used without further purification. The organic quenchers were purchased from Aldrich. The tris(β-dionato)chromium(III) compounds were prepared by literature methods (Table I) with the exception of $Cr(bzac)_3$ (bzac = benzoylacetonate), which was purchased directly from Eastman Kodak. These were recrystallized repeatedly, typically from absolute ethanol–*n*-hexane or benzene–*n*-hexane mixtures. The aromatic organic quenching agents were recrystallized prior to use. The *p*-dinitrobenzene was recrystallized twice from acetone and used immediately. The recrystallized compound remained noticeably colored, a pale orange. A few weeks later it had become dark orange. The *p*-chloronitrobenzene was recrystallized from absolute ethanol–water and acetone–water mixtures several times and used immediately. The 9,10-dichloroanthracene was recrystallized twice from ethyl acetate to give long yellow needles.

Dichloromethane solutions of I and the appropriate quencher were prepared as follows. Enough $[Cu(dpp)_2](BPh_4)$ (0.3 mg) was added to a 1.0 cm path length fluorimetry cell closed with a serum cap to give a 0.10 mM solution once the CH_2Cl_2 ($\sim$3 mL) was later added. (This concentration is an order of magnitude lower than the onset of ion pairing effects on the emission lifetime of this salt described by Everly and McMillin.[9c]) Solid quencher was then added to give a concentration sufficient to reduce the emission lifetime (τ_e) to a value about half that observed in the absence of quencher (τ_0). Since the effect of the quencher is a function of both the concentration and the quenching rate constant, the amount of quencher required ranged from $\sim$4 mg for $Cr(tta)_3$ to $\sim$70 mg for $Cr(acac)_3$. The cell with its solid contents was weighed, dichloromethane (3 mL) was added, and the resulting solution was bubbled vigorously with N_2 to remove O_2. After the deaeration procedure, the cell and solution were again weighed and the exact concentrations determined from the calculated volume of the CH_2Cl_2 in the cell.

Solutions for Stern–Volmer experiments were produced in a similar manner. After each successive addition of solid quencher, a small volume of CH_2Cl_2 was added, and the solution was bubbled with nitrogen until the approximate original total volume was attained. The cell was then weighed to determine the exact amount of solvent present.

A different procedure was used for preparing $Cr(hfac)_3$ samples since the large k_q value ($\sim 10^{10}$ M^{-1} s^{-1}) necessitated very low quencher concentrations. About 0.01 g of this compound was dissolved in some CH_2Cl_2, and the solution was diluted to 25 mL in a volumetric flask. A measured volume of the $Cr(hfac)_3$ solution (about 6×10^{-4} M) was added to the fluorimetry cell containing the approximate quantity of $[Cu(dpp)_2](BPh_4)$, and the weight of the cell plus contents was determined before and after the solution was bubbled with N_2. The exact quencher concentration was calculated from these weights and the original volume of quencher solution.

For high-pressure experiments, standard glovebox techniques were used to transfer the sample solution under N_2 from the fluorimetry cell to a quartz optical capsule (8 mm in diameter, 25 mm in length) that was subsequently capped with a Teflon piston fitted with two Viton O-rings. (The capsule/piston combination was designed to transmit the applied hydrostatic pressure without exchange of the sample solution with the surrounding medium.) The quartz capsule was then placed into a modified Nova-Swiss four-window 400-MPa high-pressure spectroscopic cell. This high-pressure cell was then filled with deaerated dichloromethane (which served as the pressure-transmitting fluid) and sealed.

Apparatus. The Nova-Swiss cell loaded as described was attached to an Enerpac hand pump and gauge which were used to generate and measure the applied pressure. The apparatus used for lifetime measurements employed a Quanta-Ray DCR-1A Nd:YAG pulse laser with harmonic generator operating at 532 nm (second harmonic) as the excitation source. The $Cu(dpp)_2^+$ chromophore absorbs very strongly at this wavelength. Laser power was typically 20–50 mJ/pulse. The emission was monitored at right angles through a Spex single monochromator with an RCA 8852 photomultiplier tube. The monitoring wavelength was 670 nm, except in the case of solutions containing 9,10-dichloroanthacene (a strong blue emitter) for which a λ_{mon} of 775 nm (plus two red filters) was used. The signal from the PMT was processed by a Tektronix 8912AD transient digitizer coupled to a Zenith Model Z-158 computer.

Lifetime Measurement Procedures. Experiments were carried out at room temperature (20 ± 1 °C). Four to six luminescence lifetime measurements, each a signal average of 64 emission decay traces, were made at each pressure *P*. For at least one pressure, usually 100 MPa, the ES lifetime was independently measured at least twice at different times during the pressure/lifetime run in order to check for possible hysteresis or reaction affecting the lifetime under these conditions.

Results

The decay of the MLCT phosphorescence from $^3[Cu(dpp)_2^+]^*$ proved to be exponential for all conditions studied here. The ambient pressure emission in neat dichloromethane (293 K) was measured to be 265 ns in agreement with our previous report.[2] In the presence of the CrL_3 complexes as well as several organic quenchers, this emission was quenched dynamically to give much shorter lifetimes. The bimolecular quenching constants k_q were determined according to

$$k_q = (\tau_e^{-1} - \tau_0^{-1})[Q]^{-1} \qquad (2)$$

where τ_e and τ_0 are the measured lifetimes of $^3\mathbf{I}^*$ in the presence or absence of quencher, Q, respectively, under otherwise identical conditions. Values of [Q] were corrected for solvent compressibility, a valid correction given the first-order decay kinetics.[8] Although the k_q values were measured in most cases by using a single quencher concentration (*the present interest is in the change in the rate with P not the absolute value of* k_q), the ambient pressure k_q values measured were in reasonably good agreement with those reported earlier[10] with the exception of Q = $Cr(tfac)_3$ (Table II). Consequently, k_q was redetermined for $Cr(tfac)_3$ via the Stern–Volmer method (τ_0/τ_e vs $[Cr(tfac)_3]$) for five evenly spaced concentrations over the range 0–0.050 M. The resulting linear plot gave the k_q value $(4.2 \pm 0.7) \times 10^7$ M^{-1} s^{-1} (experimental uncertainty based on 2σ), in good agreement with that determined for a single concentration.

Owing to the wide range of k_q's, it was necessary to use quencher concentrations from 1.1×10^{-4} M for the fast quencher $Cr(hfac)_3$ to 5.8×10^{-2} M for the much slower quencher $Cr(acac)_3$ in order to obtain the desirable condition of 50% luminescence quenching at ambient pressure. Detection of the $^3\mathbf{I}^*$ emission from solutions with low [Q] presented little difficulty; however, emission from solutions having higher [Q] was more difficult to detect owing to interfering absorption by the solution at the excitation and/or

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Table II. Rate Constants at Ambient Pressure (k_q) and at 250 MPa (k_q^{250}) and Volumes of Activation ($\Delta V^{\ddagger}_q$) for Quenching of Luminescence from $^3[Cu(dpp)_2^+]^*$ by Various Substrates in Dichloromethane Solution

quencher	k_q, 10^7 M^{-1} s^{-1}	k_q^{250},[a] 10^7 M^{-1} s^{-1}	$\Delta V^{\ddagger}_q$,[b] cm^3 mol^{-1}
$Cr(hfac)_3$	940 ± 240 [770][c]	420 (4)[d]	+8.0 ± 0.8
$Cr(tfbzac)_3$	200 ± 30 [130]	183 (4)	+0.8 ± 1.8
$Cr(tta)_3$	220 ± 40 [200]	179 (5)	+2.1 ± 1.8
$Cr(tc\text{-}bzac)_3$	60 ± 7	41 (3)	+3.8 ± 0.4
$Cr(br\text{-}dbm)_3$	4.2 ± 0.4	6.0 (3)	−3.5 ± 0.4
$Cr(tfac)_3$	4.2 ± 0.7 [9.5]	9.5 (6)	−8.1 ± 1.0
$Cr(n\text{-}acac)_3$	6.3 ± 0.8	9.3 (3)	−3.8 ± 1.0
$Cr(tc\text{-}acac)_3$	3.4 ± 0.3	3.9 (4)	−1.4 ± 0.7
$Cr(br\text{-}acac)_3$	6.7 ± 0.6	8.6 (4)	−2.4 ± 0.5
$Cr(dbm)_3$	6.8 ± 2.2 [6.5]	7.0 (4)	−0.3 ± 1.0
$Cr(acac)_3$	1.5 ± 0.3 [1.0]	1.5 (3)	−0.1 ± 0.8
p-dinitrobenzene	1050 ± 140 [1100]	521 (2)	+6.9 ± 1.3
p-chloronitrobenzene	3.0 ± 0.6 [2.9]	24 (3)	−20.4 ± 4.8
9,10-dichloroanthracene	60 ± 4	53 (2)	+1.2 ± 0.4
O_2	120 ± 14	160 (2)	−2.4 ± 1.0

[a] Experimental uncertainty was comparable (in percentage) to that recorded for k_q. [b] $\Delta V^{\ddagger}_q$ values determined from plots of ln k_q vs pressure at a single [Q]. [c] k_q values reported by ref 10. [d] Number of independent determinations in parentheses.

emission wavelength. In no case was any emission attributable to the quencher itself observed in the region from 350 to 800 nm nor was emission observed from an ambient pressure CH_2Cl_2 solution of $Cr(acac)_3$ (0.10 M) when excited directly with full laser power.

The volume of activation for any dynamic excited state process is defined by

$$\Delta V^{\ddagger}_i = -RT\left(\frac{\mathrm{d}\ln k_i}{\mathrm{d}P}\right)_T \tag{3}$$

where k_i is the rate constant at a particular pressure. The activation volume can be determined from the slope ($-\Delta V^{\ddagger}_i/RT$) of the ln ($k_i$) vs P plot at constant temperature. In the present case, such plots had the form ln (k_q/k_q^a) vs P, where k_q^a is the quenching constant at ambient P, and were linear within experimental uncertainty for the pressure range (0.1–250 MPa) investigated. (It should be noted that second-order effects may indeed lead to nonlinear behavior,[8] and furthermore that the term "volume" of activation is a convenient representation of pressure effects but should not be over-interpreted as solely indicating actual volume changes along a reaction coordinate.)

In the absence of added quencher, increasing the hydrostatic pressure of a dichloromethane solution of **I** from 0.1 MPa (ambient pressure) to 250 MPa caused a small, but reproducible, reduction in the ^{3}**I*** lifetime from 265 to 225 ns. The emission decay was strictly exponential at all pressures. The linear plot of ln (τ_0^a/τ_0)) versus P for six pressures from 0.1 to 250 MPa gave an apparent activation volume $\Delta V^{\ddagger}_0 = -1.6$ cm^3 mol^{-1} for the overall deactivation rate ($k_0 = \tau_0^{-1}$) in the absence of quenchers.[2] In the absence of unimolecular photoreaction or bimolecular quenching, the overall deactivation (k_0) would be largely the result of nonradiative processes ($k_n = 3.8 \times 10^6$ s^{-1} at ambient pressure) since the contribution of radiative deactivation ($k_r = 5 \times 10^3$ s^{-1}) is minor.[14] Thus, since k_0 (i.e., $k_n + k_r$) is relatively insensitive to pressure, the same may be stated for k_n.

When quencher is present, the magnitude of the pressure effect on the measured lifetime τ_e depends on the values of k_q and [Q] owing to the relationship $k_e = k_0 + k_q[Q]$. Under such conditions, the individual k_q's were calculated at different pressures to determine the response of the quenching rate to P. This was done by measuring τ_e of $Cu(dpp)_2^+$ solutions containing the appropriate [Q] at different pressures in 50-MPa intervals from 0.1 (ambient pressure) to 250 MPa. For each P, the value k_q was calculated according to eq 2, after correcting for changes in [Q] resulting from the compressibility of the solvent using data compiled by Bridgman.[15] Plots of ln (k_q/k_q^a) vs P were linear (e.g., Figure 1) and gave the calculated $\Delta V^{\ddagger}_q$ values summarized in Table II for quenching by 11 different $Cr(\beta\text{-dionato})_3$ complexes. Figure 1 displays such plots for the quenchers $Cr(acac)_3$, $Cr(tfac)_3$, and $Cr(hfac)_3$, which illustrate three markedly different responses of k_q to pressure, the respective $\Delta V^{\ddagger}_q$ values being −0.1 ± 0.8, −8.1 ± 1.0, and +8.0 ± 0.1 cm^3 mol^{-1} (see below).

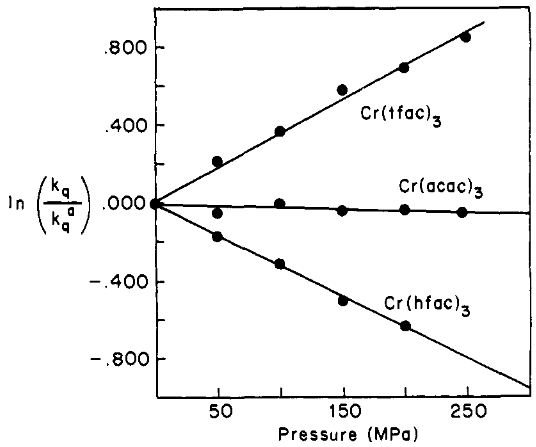

Figure 1. Plots of ln (k_q/k_q^a) vs pressure (MPa) for the quenching of $^3[Cu(dpp)_2^+]^*$ by $Cr(tfac)_3$, (upper line), $Cr(acac)_3$ (middle), and $Cr(hfac)_3$ (lower) in dichloromethane solution at 23 °C.

Table II also includes k_q and $\Delta V^{\ddagger}_q$ values determined for *p*-dinitrobenzene, *p*-chloronitrobenzene, oxygen, and 9,10-dichloroanthracene. The nitrobenzenes were investigated because their low reduction potentials ($E_{1/2} = -1.18$ and -1.58 V vs $Fe(cp)_2^+/Fe(cp)_2$ in CH_2Cl_2 for *p*-dinitrobenzene and *p*-chloronitrobenzene, respectively)[10] combined with high triplet state energies[16] limit their quenching of ^{3}**I*** to electron transfer pathways. In contrast, 9,10-dichloroanthracene has a triplet energy (14.0×10^3 cm^{-1})[17] sufficiently low to undergo energy transfer quenching of ^{3}**I*** (see below) yet a reduction potential[18] unfavorable for competitive electron transfer quenching. Oxygen, of course, is a possible contaminant in all such studies and might undergo either electron or energy transfer quenching (lowest ES is $^1\Delta_g$ at 8.05×10^3 cm^{-1}, $E_{1/2} \sim 0.3$ V for the O_2/O_2^- couple in aqueous solution).[17,19] Quenching of ^{3}**I*** by *p*-dinitrobenzene was slowed significantly by increasing pressure while the rate at which *p*-chloronitrobenzene quenches was accelerated tremendously by increased pressure. In contrast, k_q values for oxygen and 9,10-dichloroanthracene displayed but a modest increase and a modest decrease, respectively, with increasing pressure.

Discussion

McMillin and co-workers have shown that the rate constant for the quenching of the MLCT emission from ^{3}**I*** by a collection of Cr(III) tris(β-dionato) complexes is a marked function of the reduction potential of the CrL_3 species. Energy transfer quenching (e.g., eq 4) is favorable in every case since the E^{00} energy for ^{3}**I***

$$^3[Cu(dpp)_2^+]^* + CrL_3 \rightarrow Cu(dpp)_2^+ + {}^2[CrL_3]^* \tag{4}$$

($\sim 14.5 \times 10^3$ cm^{-1})[10] is higher than the lowest ES of the Cr(β-

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(14) Calculated from $k_n = k_o - k_r$, $k_r = \Phi_r(\tau)^{-1}$, and the value $\Phi_r = 1.3 \times 10^{-3}$ s^{-1}.[9]

(15) (a) Bridgman, P. W. *Collected Experimental Papers of P. W. Bridgman*; Harvard University Press: Cambridge, MA, 1964. (b) The compression of CH_2Cl_2 as a function of pressure was calculated from the polynomial function[15a] $\Delta V/V_0 = (2.522 \times 10^{-5}) + (9.543 \times 10^{-5}) - (3.678 \times 10^{-8})(P^2) + (1.18043 \times 10^{-11})(P^3) - (2.183 \times 10^{-15})(P^4) + (1.662 \times 10^{-19})(P^5)$ by the Asystant software on an IBM AT computer, where P is the pressure in atmospheres.

(16) Lewis, G. N.; Kasha, M. *J. Am. Chem. Soc.* **1944**, *66*, 2100–2116.

(17) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co., Inc.: Menlo Park, CA, 1978; p 352.

(18) The reduction potential for 9,10-dichloroanthracene is −1.7 V vs Ag wire, i.e., about −2.2 vs $Fe(cp)_2^+/Fe(cp)_2$ in dichloromethane.

(19) Bard, A. J.; Parsons, R.; Jordon, J. *Standard Potentials in Aqueous Solutions*; Marcel Dekker, Inc.: New York, 1985; pp 63–64.

Table III. Comparison of Quenching Rate Constants and Activation Volumes to the Reduction Potentials of Various Quenchers

Q^g	$E_{1/2}$,^{a} V	$E_{1/2}$(calc),^{b} V	$\Delta G_{el}°$,^{c} V	k_q, 10^7 M^{-1} s^{-1}	$\Delta V_q^‡$, cm^3 mol^{-1}
Cr(hfac)$_3$	−0.79	−0.83	−0.62 (−0.58)	940	+8.0
Cr(hfac)(tfbac)$_2$	−1.12		−0.29	[470]^d	
p-dinitrobenzene	−1.18		−0.23	1050	+6.9
Cr(tfbzac)$_3$	−1.43	−1.38	0.02 (−0.03)	200	+0.8
Cr(tta)$_3$	−1.43	*e*	0.02	220	+2.1
Cr(tc-bzac)$_3$	*f*	−1.48	(0.07)	60	+3.8
Cr(br-dbm)$_3$	*f*	−1.53	(0.12)	4.2	−3.5
Cr(n-acac)$_3$	*f*	−1.57	(0.16)	6.3	−3.8
p-chloronitrobenzene	−1.58		0.17	3.0	−20.4
Cr(tfac)$_3$	−1.64	−1.60	0.23 (0.19)	4.2	−8.1
Cr(tc-acac)$_3$	*f*	−1.66	(0.25)	3.4	−1.4
Cr(br-acac)$_3$	*f*	−1.89	(0.48)	6.7	−2.4
Cr(dbm)$_3$	−1.87	−1.92	0.46 (0.51)	6.8	−0.3
Cr(pdo)$_3$	−1.91		0.50	[3.9]^d	
c-Cr(bzac)$_3$	−2.09		0.68	[1.6]^d	
t-Cr(bzac)$_3$	−2.11		0.70	[2.8]^d	
Cr(acac)$_3$	−2.43	−2.35	1.02 (0.94)	1.5	−0.1

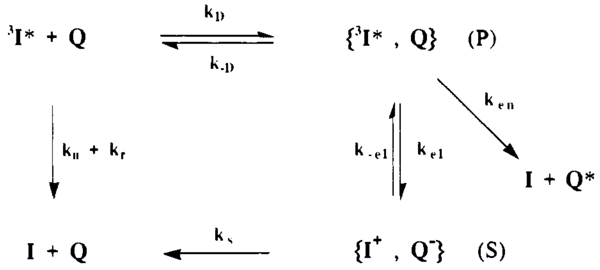
^{a} Measured $E_{1/2}$ values vs the $Fe(cp)_2^+/Fe(cp)_2$ couple in CH_2Cl_2 (ref 10). ^{b} Estimated from the summation of $\sum\sigma_x$ parameters according to ref 20. ^{c} $\Delta G_{el}° = -\{E_{1/2}(Cr^{III}/Cr^{II}) - E_{1/2}(Cu^{II}/{}^*Cu^{I})\}$; values in parentheses were calculated with use of the estimated $E_{1/2}(Cr^{III}/Cr^{II})$. ^{d} k_q data from ref 10. ^{e} $\sum\sigma_x$ parameter unavailable. ^{f} Not known. ^{g} pdo = 1,3-propanediol, bzac = 1-phenyl-1,3-butanedione.

dionato)$_3$ complexes (~12.5 × 10^3 cm^{-1}, a doublet ligand field excited state). However, for those CrL$_3$ complexes with more favorable reduction potentials, the electron transfer channel (eq 5) also becomes available and quenching rates increase dramatically.

$$^3[Cu(dpp)_2^+]^* + CrL_3 \rightarrow Cu(dpp)_2^{2+} + CrL_3^- \qquad (5)$$

Table III organizes the k_q and $\Delta V^‡_q$ values for the CrL$_3$ quenchers in terms of the CrL$_3$/CrL$_3^-$ reduction potentials. The $E_{1/2}$ values are from experimental data reported by McMillin et al.[10] or were estimated from a linear free energy relationship according to the method described in ref 20. Notably, the k_q's of those CrL$_3$ such as Cr(acac)$_3$, for which the reported or estimated $E_{1/2}$ values are −1.55 V or more negative, all fall in the range (1.5–6) × 10^7 M^{-1} s^{-1}, substantially less than the approximate diffusion limit in dichloromethane solution. For $E_{1/2}$ values more positive than −1.55 V, k_q's rise precipitously. The potential for the $Cu(dpp)_2^{2+}/{}^3[Cu(dpp)_2^+]^*$ couple has been estimated[10] as −1.41 V (vs $Fe(cp)_2^+/Fe(cp)_2$) by subtracting the energy of the MLCT excited state energy (1.8 V) from the standard potential determined for the ground state. Thus, the sharp upturn in the k_q values comes when the free energy change for eq 5 ($\Delta G_{el}° = -\{E_{1/2}(Cr^{III}/Cr^{II}) - E_{1/2}(Cu^{II}/{}^*Cu^{I})\}$, where $E_{1/2}(Cu^{II}/{}^*Cu^{I}) = -1.41$ V) is more negative than about 0.14 V, such behavior being consistent with theoretical treatments of the relationship between the free energies and the rates of outer-sphere electron transfer reactions (see below).

Scheme I



Scheme I illustrates a model for the processes described above, similar to the proposals of McMillin et al.[10] The k_q data recorded here for CrL$_3$ quenchers at ambient temperature are in good agreement with this model. In Scheme I it is assumed that quenching involves first the diffusion of the two species $^3I^*$ and Q together to form a precursor complex (P) from which energy and electron transfer are competitive processes. This is likely to be an oversimplification given that the center-to-center distance and orientation requirements of the two mechanisms may be different. (However, the distance requirements for the exchange mechanism for energy transfer should be similar to those for electron transfer.) In the absence of any specific information in this regard, it is not clear how to represent such differences in the scheme; however, this simplification should not have any serious consequence in analyzing the pressure effects on the deactivation kinetics. The decay of $^3I^*$ proved to be exponential at all conditions studied, therefore

$$d[^3I^*]/dt = -k_e[^3I^*] \qquad (6)$$

Use of the steady state approximation allows one to derive the following expression for the observed rate constant for the emission decay $k_e (=\tau_e^{-1})$

$$k_e = (k_n + k_r) + \frac{(k_s\varphi_{el}k_D + k_{en}k_D)[Q]}{(k_{-D} + k_{en} + k_{el} - \varphi_{el}k_{-el})} \qquad (7)$$

where k_n and k_r are the rate constants for decay in the absence of added Q ($=\tau_0^{-1}$), k_D is the rate constant for diffusion of the two reactants together, k_{-D} is the rate constant for diffusion of the components apart before quenching occurs, k_{en} is the rate constant for energy transfer (treated as being irreversible) within the precursor complex P, i.e., $\{^3I^*,Q\}$, k_{el} is the rate constant for electron transfer in the precursor complex to form the successor complex S, i.e., $\{I^+,Q^-\}$, k_{-el} is the rate constant for back electron transfer within S to reform the excited state precursor complex P, k_s is the rate constant for electron transfer within S to form the ground state species I and Q (followed by separation of this pair), and φ_{el} is the ratio $k_{el}/(k_{-el} + k_s)$. Back electron transfer within S without diffusion apart to I^+ and Q^- is assumed here as before,[10] because the huge driving force should make this reaction very fast while separation of these charged species in the relatively nonpolar solvent dichloromethane would not be expected to be particularly favorable. However, from the perspective of the quenching kinetics, the specifics of the process or processes rep-

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[20] (a) It has been shown[20b] that the reduction potentials for a series of Cr(β-dionato)$_3$ compounds in dimethyl sulfoxide or dioxane–water mixtures follow a linear free energy relationship to the sum of the ligand polar substituent constants σ_x. It was assumed that this relationship is also applicable in dichloromethane solution, and the following equation was calculated from the $\sum\sigma_x$ functions tabulated for an extensive series of Cr(β-dionato)$_3$ compounds[11] and the reported[10] $E_{1/2}$ values for five Cr(β-dionato)$_3$ compounds

$$E_{1/2} = -1.95\text{ V} + 1.02\sum\sigma_x$$

(referenced against the $Fe(cp)_2^+/Fe(cp)_2$ couple in CH_2Cl_2, which has been estimated as being 0.29 V more positive than the SCE reference electrode in this solvent[10]). The $E_{1/2}$ values calculated from this relationship for the eleven Cr(β-dionato)$_3$ compounds used in the present study are listed in Table III. No $\sum\sigma_x$ value is available for the ligand thenoyltrifluoroacetonate. It is noteworthy that even the measured $E_{1/2}$ values for the CrL$_3$ complexes are subject to significant experimental uncertainties (estimated ±0.1 V) given their measurement under only quasireversible conditions.[10] (b) Handy, R. F.; Lintvedt, R. L. *Inorg. Chem.* **1974**, *13*, 893–896.

resented by k_s are not relevant if they are irreversible. The quenching rate constant may then be rewritten as

$$k_q = \frac{(k_s\varphi_{el}k_D + k_{en}k_D)}{(k_{-D} + k_{en} + k_{el} - \varphi_{el}k_{-el})} \tag{8}$$

In terms of analyzing the effect of pressure on k_q according to Scheme I, it is useful to consider certain limiting cases. *Case 1* will be that when energy transfer is the only viable quenching pathway. Such would be the case for $Cr(acac)_3$, 9,10-dichloroanthracene, and several other CrL_3. *Case 2* will be that when electron transfer is the dominant quenching pathway owing to the very favorable $\Delta G_{el}°$ for eq 5, as for Q = $Cr(hfac)_3$ or *p*-dinitrobenzene.

Case 1: $k_{en} \gg k_{el}$. For this condition, eq 8 can be rewritten as

$$k_q = \frac{k_{en}k_D}{k_{en} + k_{-D}} \tag{9}$$

Calculation of activation volume according to eq 3 then leads to

$$\begin{aligned}\Delta V^{\ddagger}_{q} &= -RT\left(\frac{d \ln k_q}{dP}\right)_T \\ &= -RT\left\{\left(\frac{d \ln k_D}{dP}\right)_T + \left(\frac{d \ln k_{en}}{dP}\right)_T - \left(\frac{d \ln (k_{en} + k_{-d})}{dP}\right)_T\right\}\end{aligned} \tag{10}$$

i.e.,

$$\Delta V^{\ddagger}_{q} = \Delta V^{\ddagger}_{D} + \Delta V^{\ddagger}_{en} + RT\left(\frac{d \ln (k_{en} + k_{-D})}{dP}\right)_T \tag{11}$$

For $Cr(acac)_3$ and other CrL_3 which apparently quench only via energy transfer, the quenching rates are significantly less than diffusion limited (see below). For that situation, k_{-D} must be much larger than k_{en}; thus, $\Delta V^{\ddagger}_{q} = \Delta V^{\ddagger}_{D} + \Delta V^{\ddagger}_{en} - \Delta V^{\ddagger}_{-D}$. No charge is created in the energy transfer step, so solvation changes should be minimal. Hence, one may estimate the magnitude of the $\Delta V^{\ddagger}_{en}$ contribution to $\Delta V^{\ddagger}_{q}$ from the unimolecular changes in the inner-coordination spheres of the donor and acceptor species. The nonradiative deactivation of $^3I^*$ has been shown to display a small, negative value for $\Delta V^{\ddagger}_{n}$ (−1.6 $cm^3\ mol^{-1}$),[2] and one might expect a similar, if not smaller, contribution to $\Delta V^{\ddagger}_{q}$ from this quarter. In contrast, excitation of CrL_3 to the metal-centered doublet ES might be expected to make a positive contribution, since the excited state should be marginally larger. However, the orbital parentage of this transition is $t_{2g} \rightarrow t_{2g}$ (O_h symmetry approximated) with both orbitals being nonbonding,[21] and the change should be small. As a result, $\Delta V^{\ddagger}_{en}$ can be estimated as the sum of two contributions, small in magnitude and opposite in sign, thus an estimate of 0 ± 1 $cm^3\ mol^{-1}$ appears reasonable.

Quenching of $^3I^*$ by $Cr(acac)_3$ in dichloromethane, which gave a $\Delta V^{\ddagger}_{q}$ value of −0.1 $cm^3\ mol^{-1}$, is a representative example of the *case 1* limit. Since in this limit $\Delta V^{\ddagger}_{q} = \Delta V^{\ddagger}_{D} + \Delta V^{\ddagger}_{en} - \Delta V^{\ddagger}_{-D}$, the above considerations lead to the conclusion that the difference $\Delta V^{\ddagger}_{D} - \Delta V^{\ddagger}_{-D}$ is approximately zero in this case. Notably, in the context of the model described in Scheme I, $\Delta V^{\ddagger}_{D} - \Delta V^{\ddagger}_{-D}$ would represent the change in partial molar volume $\Delta \bar{V}$ upon forming the precursor complex **P** from $^3I^*$ plus $Cr(acac)_3$. The various Q are uncharged, and there would be little or no charge neutralization upon forming the **P**. Thus, a value near zero does not appear unreasonable, and it is likely that this result extends throughout the series of Q investigated in the present case, especially the analogous series of CrL_3 complexes.

Case 2: $k_{el} \gg k_{en}$. Another assumption will also be made, i.e., $k_s \gg k_{-el}$; therefore $\varphi_{el} = k_{el}/k_s$. If this is so, then eq 8 can be rewritten as

$$k_q = \frac{(k_{el}k_D)}{(k_{-D} + k_{el})} \tag{12}$$

since this assumption also dictates that $k_{el} \gg \varphi_{el}k_{-el}$. As $\Delta G_{el}°$ becomes increasingly more favorable, diffusion becomes rate limiting, and k_q should approach k_D, which can be estimated as ~$1.4 \times 10^{10}\ M^{-1}\ s^{-1}$ in ambient pressure dichloromethane.[22] Indeed this appears to be the case for Q = $Cr(hfac)_3$ and *p*-dinitrobenzene for which the measured k_q's are 0.94×10^{10} and $1.05 \times 10^{10}\ M^{-1}\ s^{-1}$, respectively, at ambient pressure (Table II). Calculation of activation volume according to eq 3 then leads to

$$\Delta V^{\ddagger}_{q} = -RT\left\{\left(\frac{d \ln k_D}{dP}\right)_T + \left(\frac{d\ln k_{el}}{dP}\right)_T - \left(\frac{d \ln (k_{el} + k_{-D})}{dP}\right)_T\right\} \tag{13}$$

$$= \Delta V^{\ddagger}_{D} + \Delta V^{\ddagger}_{el} + RT\left(\frac{d \ln (k_{el} + k_{-D})}{dP}\right)_T \tag{14}$$

The diffusion limit is reached when $k_{el} \gg k_{-D}$, under which condition $\Delta V^{\ddagger}_{q} \cong \Delta V^{\ddagger}_{D}$, which should be positive owing to the increased solvent viscosity at elevated pressures. Notably, the $\Delta V^{\ddagger}_{q}$ values measured for Q = $Cr(hfac)_3$ and *p*-dinitrobenzene are +8.0 ± 0.8 and +6.8 ± 1.3 $cm^3\ mol^{-1}$, respectively (Table II). Although $\Delta V^{\ddagger}_{D}$ values for dichloromethane are apparently unknown, values of +7.5 and +9.5 $cm^3\ mol^{-1}$ have been reported for the organic solvents acetonitrile and ethanol, respectively.[23]

Case 3. An intermediate case would be when only a small fraction of intermolecular encounters result in electron transfer. In that situation, the condition $k_{-D} \gg k_{el} + k_{en}$ exists, and (assuming $k_s \gg k_{-el}$) eq 8 can be rewritten as

$$k_q = \frac{(k_{el} + k_{en})k_D}{k_{-D}} \tag{15}$$

which leads to

$$\Delta V^{\ddagger}_{q} = \Delta V^{\ddagger}_{D} - \Delta V^{\ddagger}_{-D} - RT\left(\frac{d \ln (k_{el} + k_{en})}{dP}\right)_T \cong -RT\left(\frac{d \ln (k_{el} + k_{en})}{dP}\right)_T \tag{16}$$

since the conclusion that $\Delta V^{\ddagger}_{D} - \Delta V^{\ddagger}_{-D} \sim 0$ should remain valid. For such a condition, $\Delta V^{\ddagger}_{q} \sim \Delta V^{\ddagger}_{el}$ *if* $k_{el} \gg k_{en}$; however, at least for the CrL_3 quenchers, the simultaneous operation of the ubiquitous energy transfer pathway, although approximately pressure independent, complicates interpretation of these intermediates cases.

The effect of solvent on electron transfer within the precursor complex of an outer-sphere mechanism has been subject to considerable theoretical discussion and experimental evaluation.[24-28] The electron transfer rate constant at a specific distance *r* has

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[21] The absence of major distortions on forming the doublet ES of CrL_3 can be inferred from the independence of this state's energy with respect to the nature of the various L.[12]

[22] (a) Calculation of k_D is from the formula[22b] k_D ($M^{-1}\ s^{-1}$) = $(2 \times 10^5)T/\eta$, where *T* is the temperature (Kelvin) and η is the viscosity in poise (0.41 cP for CH_2Cl_2).[22c] (b) Reference 16, p 314. (c) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Purification*, 4th ed.; Wiley-Interscience: New York, 1986; p 490. The value for 25 °C was interpolated from values listed for 15 °C (0.449 cP) and 30 °C (0.393 cP).

[23] Turley, W. D.; Offen, H. W. *J. Phys. Chem.* **1984**, *88*, 3605–3607.

[24] (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966, 979; **1957**, *26*, 867. (b) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213.

[25] Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557; *Prog. Inorg. Chem.* **1967**, *8*, 391.

[26] (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441–498. (b) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275–282. (c) Sutin, N.; Brunschwig, B. S.; Creutz, C.; Winkler, J. R. *Pure Appl. Chem.* **1988**, *60*, 1817–1830 and references therein.

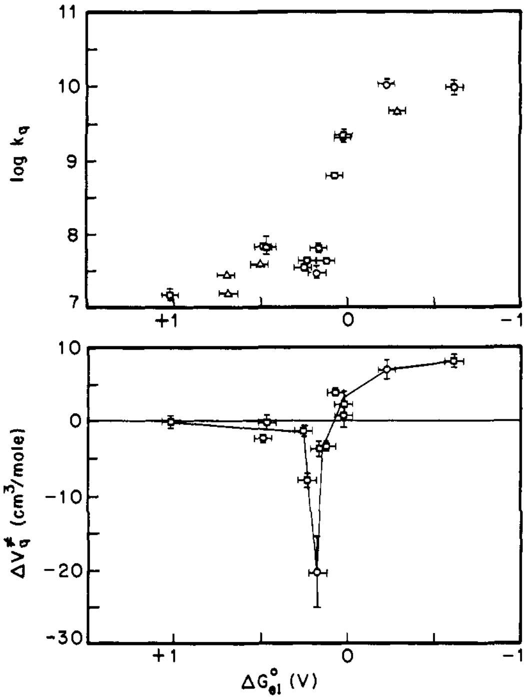

Figure 2. Upper: Plot of log k_q (at ambient pressure) vs the ΔG_{el}° (V) for the reaction $^3[Cu(dpp)_2^{+}]^* + Q \rightarrow [Cu(dpp)_2^{2+}] + Q^-$ in dichloromethane. ΔG_{el}° was calculated from $\Delta G_{el}^{\circ} = -\{E_{1/2}(Cr^{III}/Cr^{II}) - E_{1/2}(Cu^{II}/{}^*Cu^{I})\}$ where the value −1.41 V was used for $E_{1/2}(Cu^{II}/{}^*Cu^{I})$ according to ref 10. (Vertical error bars represent experimental uncertainties in the experimental measurements; horizontal error bars represent estimated uncertainties in the $E_{1/2}(Cr^{III}/Cr^{II})$ values. Squares indicate CrL_3 data from the present work; triangles indicate CrL_3 data from ref 10; circles indicate organic quencher data from the present work.) Lower: Plot of ΔV^{*}_{q} vs ΔG_{el}°.

been described[26] as

$$k_{el}(r) = \nu_n(r)\kappa_{el}(r)\kappa_n(r) \qquad (17)$$

where $\nu_n(r)$ is the effective nuclear frequency, $\kappa_{el}(r)$ is the electronic factor (~1 for an adiabatic electron transfer), and $\kappa_n(r)$ is the nuclear factor, which in the high-temperature (classical) limit is given by

$$\kappa_n(r) = \exp(-\Delta G^*/RT) \qquad (18)$$

where

$$\Delta G^* = \frac{\lambda}{4}\left(1 + \frac{\Delta G_{PS}^{\circ}}{\lambda}\right)^2 \qquad (19)$$

In eq 19, λ is the reorganization parameter, the sum of inner-sphere (λ_{is}) and outersphere (λ_{os}) contributions, and ΔG_{PS}° is the free energy change for the electron transfer reaction at the distance r and equals ($\Delta G_{el}^{\circ} - \Delta G_P^{\circ} + \Delta G_S^{\circ}$), where ΔG_{el}° is the free energy change for the overall reaction and ΔG_P° and ΔG_S° are the respective free energies for formation of the precursor and successor complexes. Therefore in the "normal" Marcus region, the electron transfer contribution to k_q for a series of analogous quenchers should increase dramatically as ΔG_{el}° becomes more negative. As McMillin et al. demonstrated for the quenching of I^* by the tris(β-dionato)chromium(III) complexes,[10] this contribution apparently becomes competitive with energy transfer when ΔG_{el}° approaches +0.2 V (based on the estimate of −1.41 V vs ferrocene for the $Cu(dpp)_2^{2+}/{}^*Cu(dpp)_2^{+}$ couple in dichloromethane).[10] Notably, it is at approximately this potential that the sharp discontinuity occurs in the plot of ΔV^{*}_{q} vs ΔG_{el}° (Figure 2).

The combination of eqs 3, 17, and 18 and the assumption that $\nu_n(r)$ and $\kappa_{el}(r)$ are pressure insensitive[29,30] leads to the relationship

$$\Delta V^{*}_{el} = -(\mathrm{d}\Delta G^*/\mathrm{d}P)_T \qquad (20)$$

According to eq 19, ΔG^* is composed of five terms, λ_{os}, λ_{is}, ΔG_{el}°, ΔG_S°, and ΔG_P°, the first four of which may be pressure dependent (the above discussion has concluded that $\Delta \bar{V}_P$ is ~0). First, electron transfer from the unipositive copper complex to a neutral Q leads to substantial charge separation, hence increased solvation in the transition state and a negative value of ΔV^{*}_{os}. In addition, the formation of a copper(II) from a copper(I) might be expected to be accompanied by significant distortion of the coordination sphere, including the possible addition of at least one solvent molecule to the coordination sphere. Such an effect would be reflected in similarly negative values of ΔV^{*}_{is}, $\Delta \bar{V}_{el}$, and $\Delta \bar{V}_S$. However, factors that may substantially decrease the magnitude of these terms would be the steric bulk of the dpp ligands, which may inhibit further coordination, and the nature of the MLCT excited state of $^3I^*$, which has (at least formally) an oxidized metal center (i.e. Cu(II)) and may already be substantially distorted toward the product configuration. For this reason, it appears likely that of the five components of ΔG^*, λ_{os} is the most sensitive to perturbation of the hydrostatic pressure.

For the case where $\Delta G_{PS}^{\circ}/\lambda \ll 1$, eq 20 would simplify to $\Delta V^{*}_{el} = \Delta V^{*}_{os} + \Delta V^{*}_{is}$. This situation would appear to prevail at the ΔG_{el}° values where the sharp discontinuity in the ΔV^{*}_{q} vs ΔG_{el}° plot appears in Figure 2. Thus, one may conclude that the negative values of ΔV^{*}_{q} observed at that point are reflective of pressure effects on the inner- and outer-sphere rearrangement terms. It is the view of the authors that the predominant term under these conditions is a large, negative ΔV^{*}_{os}, reflecting electron transfer induced solvent electrostriction coupled to the resulting separation of charge. Notably, negative $\Delta V^{*}_{apparent}$ values have been observed in nonaqueous solvents for examples of thermal outer-sphere electron transfer between metal complexes where both partners have electrostatic charges of the same sign or one of the pair is neutral, and this property has also been largely attributed to solvent-rearrangement contributions.[30,31] For the present case, the diminishing impact of this pressure effect as ΔG_{el}° becomes more positive and k_q increases can be attributed to two possible factors, one being the breakdown of the case 3 assumption that $k_{el} \ll k_{-D}$ so that diffusion rates become increasingly more important and the second being the decreasing impact of outer- or inner-sphere rearrangement terms on the ΔG^* of an early transition state.[32]

In summary, the plot of ΔV^{*}_{q} vs quencher reduction potential displays three regimes for the quenching of the MLCT state of $Cu(dpp)_2^{+}$. At $E_{1/2}$ values substantially more negative than −1.6 V, k_q is relatively insensitive to $E_{1/2}$ as expected for quenching dominated by the competing energy transfer pathway. This regime is also characterized by ΔV^{*}_{q} values near zero. The latter observation is also interpreted in terms of precursor complex formation between $^3I^*$ and Q having a $\Delta \bar{V}_P \sim 0$. At much less negative $E_{1/2}(Q)$ values, k_q approaches the diffusion limit as expected for electron transfer quenching with an overall ΔG_{el}° substantially less than zero. The ΔV^{*}_{q} in this regime is strongly positive as the pressure effect is now expressed in terms of the

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(27) (a) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 389–440. (b) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94–100.

(28) Rips, I.; Klafter, J.; Jortner, J. *J. Phys. Chem.* **1990**, *94*, 8557–8561 and references therein.

(29) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303.

(30) (a) Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 5017–5025. (b) Swaddle, T. W. In *Inorganic High Pressure Chemistry*; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986; Chapter 5.

(31) (a) For example, a series of electron transfer reactions between cobalt(III) clathrochelate monocations and ferrocenes in acetonitrile solution studied by stopped flow kinetics gave $\Delta V^{*}_{apparent}$ values ranging from −6 to −14 cm^3 mol^{-1}, and $\Delta V^{*}_{apparent}$ values as negative as −20 cm^3 mol^{-1} have been recorded for the self-exchange reactions of the manganese isonitrile complexes $Mn(CNR)_6^{+/2+}$ in organic solvents (ref 31b). (b) Murguia, M.; Wherland, S. *Inorg. Chem.* **1991**, *30*, 139–144 and references therein.

(32) The term "early transition state" is used here in the context of the Hammond postulate, namely, the greater the driving force of a reaction, the more closely the transition state will resemble the reactants (rather than the products). For such a case, the solvent rearrangement contribution to ΔV^{*}_{q}, especially solvent electrostriction due to charge creation, would be attenuated.

increased solvent viscosity and correspondingly reduced limiting diffusion rates in solution. The third regime is that where $E_{1/2}(Q)$ is ca. −1.6 V (i.e., where $\Delta G_{el}°$ is slightly positive according to the reported $Cu(dpp)_2^{2+}/^3[Cu(dpp)_2^+]^*$ reduction potential[10]). In this regime, electron transfer quenching is competitive with energy transfer and the other deactivation mechanisms, and the pressure effect is expressed as a negative ΔV^*_q. The dominant pressure-dependent factor in this regime is concluded to be the outer-sphere rearrangement energy λ_{os},[33] the negative contribution to ΔV^*_q reflecting solvent electrostriction coupled to the charge separation accompanying electron transfer in this case.

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[33] McMillin et al. (ref 10) have proposed (based on calculated self-exchange rates) that Cr(II) product formed in the electron transfer may be a low-spin d^4 species, either the ground or a low-lying excited state of the unknown tris(β-dionato) Cr(II) intermediate. One might speculate that, if a high-spin d^4 Cr(II) were formed, the expected tetragonal distortion would make a strongly positive contribution to the ΔV^*_{el}. However, under conditions where ΔV^*_{el} appears to be the predominate contributor to ΔV^*_q, the latter is strongly negative. This observation is consistent with but certainly does not substantiate the proposed low-spin Cr(II) intermediate.

Communications to the Editor

Reductive Aromatization of Quinol Ketals: A New Synthesis of *C*-Aryl Glycosides†

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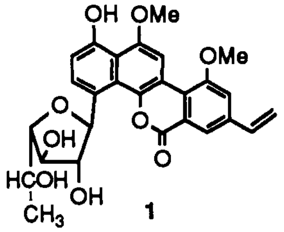
The polyketide-derived *C*-aryl glycosides[1] are a rapidly growing class of natural products with a variety of interesting biological activities. For example, gilvocarcin V (**1**)[2] exhibits significant antitumor activity.



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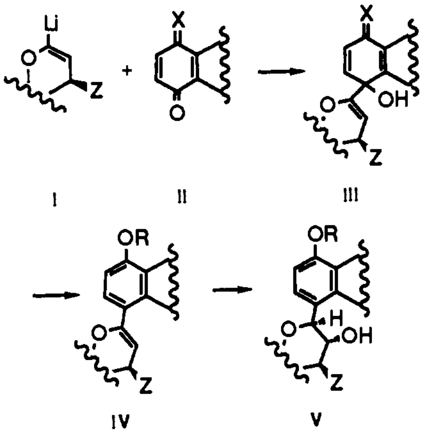
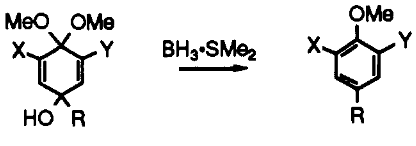
While several of the aromatic "aglycons" of the polyketide *C*-aryl glycosides have been prepared,[3] the problem of regiospecifically attaching sugar moieties to complex substrates has generally been avoided.[4] Most known methods for direct formation of *C*-aryl glycosides[5] rely on the reaction of an electron-rich aromatic with a carbohydrate-derived electrophile;[5b] some recent methods utilize palladium-mediated coupling.[5c–e]

Scheme I



Scheme II. Reductive Aromatization of Simple Quinol Ketals[a]



[a] (**a**) X = H, Y = H, R = CH_3, 96%; (**b**) X = H, Y = H, R = *n*-Bu, 88%; (**c**) X = H, Y = H, R = Ph, 83%; (**d**) X = H, Y = Br, R = CH_3, 85%; (**e**) X = OCH_3, Y = OCH_3, R = CH_3, 82%.

We now report an efficient *C*-aryl glycoside synthesis which is based on a novel "reverse polarity" strategy (Scheme I) and which requires no unusually hazardous or esoteric reagents. The key step is the reductive aromatization of quinol ketals, **III**, the

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* Author to whom correspondence should be sent.

† Portions of this work were described at the 199th National Meeting of the American Chemical Society, Boston, MA, April 1990; paper ORGN 165.

(1) For an excellent review, see: Hacksell, U.; Daves, G. D., Jr. *Prog. Med. Chem.* **1985**, *22*, 1–65.

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