and A. Electronic energy donors and acceptors which show large Stokes shifts would be expected to show large values for $\Delta G^{\ddagger}{}_{D}$ and $\Delta G^{\ddagger}{}_{A}$, respectively, and vice versa. For a discussion of this parameter and some typical values, see ref 2 and 4.

The second adjustable parameter for each accepting state is the transmission coefficient κ which from activated complex theory occurs in equations for k_{en}, i.e.

$$k_{en} = (\kappa kT/h) \exp\left(\frac{-\Delta G^{\ominus \ddagger}}{RT} \right) \qquad (7)$$

Values of κ less than unity arise in these cases because the overlap of wave functions on the donor and the acceptor for the well-shielded metal-centered states is often low; hence, the probability of energy transfer is correspondingly low. For low-energy donors with $\tilde{\nu}_{00}(^3D^*) < 1.7$ μm^{-1}, only the one state, i.e., $^2E_g, ^2T_{1g}$, needs to be considered, and thus eq 3 becomes

$$k_q = \frac{k_d}{6} \left[1 + \frac{1}{^2k_{en_1}/(^2k_{-en_1} + k_{-d})} \right]^{-1} \qquad (8)$$

Note that

$$k_{en_1}/k_{-en_1} = \exp\left(\frac{-\Delta G^{\ominus}{}_{en_1}}{RT} \right) \qquad (9)$$

when $\tilde{\nu}_{00}(^3D^*) \gg \tilde{\nu}(A_1^*)$, $\Delta G^{\ominus \ddagger} \rightarrow 0$ (see eq 5) and $^2k_{-en_1} \rightarrow 0$ (from eq 7 and 9) and thus eq 8 becomes

$$k_q \text{ (plateau)} = sk_d k_{en}^0/(k_{en}^0 + k_{-d}) \qquad (10)$$

where $k_{en}^0 = \kappa kT/h$ and s, the spin statistical factor, is in this case $^1/_6$.

The fact that the rate contants for quenching by Cr-(dpm)$_3$ of the triplet states of anthracene, acridine, pyrene, and coronene are within experimental error the same despite being well below diffusion controlled is confirmation that k_{en}^0 and therefore κ are sensibly constant for the production of the $^2E_g, ^2T_{1g}$ state in Cr(dpm)$_3$ from all of these organic triplet states. If k_d and k_{-d} are taken as 1.0 $\times 10^{10}$ dm^3 mol^{-1} s^{-1} and 1.2 $\times 10^{10}$ s^{-1}, respectively,[2] then $\kappa(^2E_g, ^2T_{1g})$ from this plateau value is 1.0 $\times 10^{-4}$ (cf. κ-$(^2E_g, ^2T_{1g})$ for Cr(acac)$_3$ which is 6.2 $\times 10^{-3}$); i.e., replacing the methyl groups in the ligand by *tert*-butyl groups causes a steric reduction in the transmission coefficient by a factor of 62 for energy transfer to the $^2E_g, ^2T_{1g}$ state of the com-

plex. For donors with $\tilde{\nu}_{00}(^3D^*) > 1.9$ μm^{-1}, we need to combine eq 2 and 3 in order to explain the observed variations in rate constants with the energy of the triplet state being quenched. Fleischauer et al.[14] estimate $\tilde{\nu}_{00}(^4T_{2g}) = 1.623$ μm^{-1} for Cr(acac)$_3$, and, using their relationship for $\tilde{\nu}_{00}$ in terms of $\tilde{\nu}(5\%)$, the wavenumber at which the absorbance is 5% that at the band maximum, we estimate $\tilde{\nu}(^4T_{2g}) = 1.650$ μm^{-1} in the case of Cr(dpm)$_3$. The curve shown drawn through the data for Cr(dpm)$_3$ in Figure 2 uses $\tilde{\nu}(^2T_{2g}) = 2.0$ μm^{-1} and $^2\Delta G^{\ddagger}(0) = 250$ cm^{-1} for both $^2E_g, ^2T_{1g}$ and $^2T_{2g}$ and $^4\Delta G^{\ddagger}(0) = 2000$ cm^{-1} for $^4T_{2g}$. These values for the reorganizational free energies are equal to those found[4] and expected[2] for the analogous states in the case of quenching by Cr(acac)$_3$. The best fit to the experimental data was found with $\kappa(^2T_{2g})$ and $\kappa(^4T_{2g}) = 6.4$ $\times 10^{-4}$ and 1.0 $\times 10^{-3}$, respectively. In the case of Cr(acac)$_3$, $\kappa(^4T_{2g}) = 7.2 \times 10^{-3}$; i.e., for this state the steric factor is 7.2 in contrast to the figure of 62 in the case of the steric effect on the transmission coefficient for transfer to produce the $^2E_g, ^2T_{1g}$ state. Of course, in the case of Cr(acac)$_3$ no information is available from energy transfer experiments concerning the $^2T_{2g}$ state because, as explained earlier, quenching to lower-lying doublet states almost equals the spin statistically modified diffusion-controlled limit.

These results confirm the expectation that modification of the ligands in β-diketonatochromium(III) complexes in such a way as to hardly affect the energies, bandwidths, or Stokes shifts does not affect the free energies of activation for energy transfer ($\Delta G^{\ddagger}(0)$ values) but that steric blocking by the *tert*-butyl groups on Cr(dpm)$_3$ has a major effect on transmission coefficients for energy transfer especially for the highly shielded, innermost energy levels.

Summary

Variations in the rate constants for quenching of triplet states of organic molecules by Cr(dpm)$_3$ have been shown (i) to allow the experimental determination of the energy of the $^2T_{2g}$ state in this complex, (ii) to confirm the existence of plateau regions for exothermic electronic energy transfer which have not reached diffusion-controlled limits, and (iii) to give transmission coefficients for energy transfer which decrease with increased steric hindrance and with increased shielding by the ligand of the metal-centered states.

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COMMENTS

Determination of the Magnitude and Sign of $^1J_{CN}$ in Hydrogen Cyanide

Sir: Sometime ago Binsch and Roberts[1] reported in this Journal the magnitudes of the NMR spin–spin coupling constants $^1J_{CH}$ and $^2J_{NH}$ of ^{15}N-enriched hydrogen cyanide. More recently, Friesen and Wasylishen[2] determined the magnitude of $^1J_{CN}$ for this system. Because of our interest

in the coupling constants involving nitrogen[3,4] we have now measured the sign of $^1J_{CN}$, using doubly enriched hydrogen cyanide.

Doubly enriched H^{13}C^{15}N was prepared from K^{13}C^{15}N (Prochem) in a manner similar to that described by Binsch and Roberts.[1] After final drying over P$_2$O$_5$, the gas was condensed and sealed in a 5-mm coaxial NMR tube. The

(1) G. Binsch and J. D. Roberts, *J. Phys. Chem.*, **72**, 4310 (1968).
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(3) J. M. Schulman and T. Venanzi, *J. Am. Chem. Soc.*, **98**, 4701, 6739 (1976).
(4) J. M. Schulman, J. Ruggio, and T. J. Venanzi, *J. Am. Chem. Soc.*, **99**, 2045 (1977).

proton-coupled ^{15}N spectrum at 10.09 MHz displayed a quartet centered at 251.9 ppm (with respect to anhydrous liquid ammonia[5]), $J_{CN} = 18.6 \pm 0.1$ Hz, $J_{NH} = 8.6 \pm 0.1$ Hz.

Single-frequency lower-power irradiation of the proton N–H doublet at higher shielding collapsed the more highly shielded N–H doublet in the ^{15}N spectrum. Similarly, irradiation of the deshielded protons collapsed the deshielded N–H doublet. When the negative magnetogyric ratio of ^{15}N is considered, these results mean that J_{CN} and J_{CH} are of *opposite* sign.[6] Since the latter value is always positive, J_{CN} is negative, in accord with the experimental result for CH_3CN, −17.5 Hz.[7] The magnitudes of J_{CN} and J_{NH} obtained here are in very good agreement with those reported previously, 18.5 ± 0.1[2] and 8.7 ± 0.1 Hz[1], respectively.

The observed isotropic coupling constant $^1J_{CN}$ is the sum of four terms: diamagnetic, orbital, spin dipolar, and Fermi contact (see Table I). Lee et al.[8] showed that the diamagnetic term has a magnitude of less than 0.1 Hz, through Monte-Carlo integration of the expectation value of $\vec{r}_C \cdot \vec{r}_N / r_C^3 r_N^3$ using a double-zeta wave function. The orbital term has been calculated by coupled Hartree–Fock perturbation theory as −9.4 Hz (INDO, semiempirical)[3] and −6.0 Hz (ab initio, in a $10s^56p^3/5s^3$ contracted Gaussian basis set).[9] Thus, the spin-dipolar and Fermi-contact terms account for −9.2 to −12.6 Hz, half or more of the total −18.6 Hz of $^1J_{CN}$.

Semiempirical calculations suggest that the remainder is due to a very large negative spin-dipolar term and a small positive contact term arising from a positive contribution from the nitrogen lone pair.[3] This is supported by the case of mesitonitrile oxide which lacks the lone pair and in which $^1J_{CN} = 77.5$ Hz,[10] presumably negative.

(5) G. Levy and R. L. Lichter, "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy", Wiley-Interscience, New York, 1979, p 32.
(6) R. Johannesen, *J. Chem. Phys.*, 48, 1414 (1968).
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(9) W. S. Lee and J. M. Schulman, *J. Am. Chem. Soc.*, 101, 3182 (1979).

TABLE I: Calculated Coupling Constants of HCN[a]

	$^1J_{CN}$
Fermi contact	3.3[b]
orbital $^1J^a$	0.1[c]
orbital $^1J^b$	−9.4,[b] −6.0[d]
dipolar	−12.7,[b] −2.8[d]
expt	−18.6 ± 0.1

[a] The bond lengths employed were $R_{CH} = 1.063$ Å and $R_{CN} = 1.155$ Å. [b] Semiempirical, INDO. [c] Monte-Carlo numerical integration. [d] Ab initio, contracted Gaussian basis.

There are at present no accurate ab initio calculations of either the Fermi contact or spin-dipolar terms in nitriles due, in part, to triplet instabilities in the coupled Hartree–Fock method. With the negative sign of $^1J_{CN}$ now established, the accounting for the spin-dipolar and Fermi-contact terms represents an important challenge to ab initio theorists studying coupling constants. This is particularly so since the spin-dipolar term can be estimated to be ca. −2.8 Hz in a $10s^56p^3/5s^3$ basis set,[11] which implies that the Fermi-contact term is negative, contrary to the semiempirical prediction.

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