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Luminescence Quenching of Tris(2,2′-bipyridine) Complexes of Chromium(III), Ruthenium(II), and Osmium(II) by Cyanide Complexes

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Luminescence quenching of excited $Cr(bpy)_3^{3+}$, $Ru(bpy)_3^{2+}$, and $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) by cyanide complexes has been investigated. Discrimination between energy and (reductive or oxidative) electron-transfer quenching has been obtained on the basis of correlations between the quenching rate constants and the spectroscopic and thermodynamic quantities involved in the processes. For each excited complex the quenching takes place by energy transfer with $Cr(CN)_6^{3-}$; by reductive electron transfer with $Mo(CN)_8^{4-}$, $Fe(CN)_6^{4-}$, and $Ru(CN)_6^{4-}$; and by oxidative electron transfer with $Fe(CN)_6^{3-}$ and $Co(CN)_6^{3-}$. $Ni(CN)_4^{2-}$ apparently quenches $^*Cr(bpy)_3^{3+}$ via reductive electron transfer, $^*Ru(bpy)_3^{2+}$ via energy transfer, and $^*Os(bpy)_3^{2+}$ via oxidative electron transfer.

Introduction

Energy and electron transfer are two efficient quenching mechanisms of electronically excited states of coordination compounds.[2,3] As electron transfer can occur with either reduction (reductive quenching) or oxidation (oxidative quenching) of the excited state, the three expected mechanisms can be schematized as follows:

$$^*A + B \xrightarrow{k_{\text{en.t.}}} A + {}^*B \qquad (1)$$

$$^*A + B \xrightarrow{k_{\text{Red}}} A^- + B^+ \qquad (2)$$

$$^*A + B \xrightarrow{k_{\text{Ox}}} A^+ + B^- \qquad (3)$$

Energy transfer (reaction 1) has been studied for several years,[2,3] while electron transfer has received attention only recently[4-6] owing to its relevance to the energy conversion problem.[7,8]

Discrimination between energy and electron-transfer quenching is often difficult for both practical and theoretical reasons.[2,4] Correlations between the quenching rate constants and the thermodynamic quantities involved in the quenching processes can provide useful information about the nature of the operative quenching mechanism. In the present work we report a systematic study of the bimolecular quenching of the luminescent excited state of $Cr(bpy)_3^{3+}$, $Ru(bpy)_3^{2+}$, and $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) by cyanide complexes. These systems were chosen in order to explore a wide range of excited-state energies and redox potentials, i.e., of the spectroscopic and thermodynamic quantities involved in reactions 1–3. Some of the results reported here have been the object of a preliminary communication.[9]

Experimental Section

Materials. $[Cr(bpy)_3](ClO_4)_3\cdot{}^1/_2H_2O$,[10] $[Ru(bpy)_3]Cl_2\cdot 6H_2O$,[11] and $[Os(bpy)_3](ClO_4)_2\cdot H_2O$[12] were prepared and purified following published procedures. Emission[13] and absorption[14] spectra of the three complexes agreed well with the literature values. Pure samples of the cyanide complexes were available from previous investigations.[9] All other chemicals were of reagent grade quality.

Apparatus. Absorption spectra were recorded with a Perkin-Elmer 323 double-beam spectrophotometer. The emission intensity and the luminescence spectra were measured with a Perkin-Elmer MPF-3 spectrofluorimeter equipped with a 15-W xenon lamp and a Hamamatsu R 446 phototube. Emission lifetimes were determined by means of a modified Applied Photophysics apparatus which is based on the single-photon counting technique. The light source was a thyratron-gated air flash lamp (repetition rate 18 kHz); the pulses had a full-width at half-height of 3.0 ns. Both exciting (337 or 380 nm) and emitted beams were filtered by means of grating monochromators. The performance of the single-photon counting equipment was checked by measuring the emission lifetime of rhodamine B; the value of 3.3 ns measured with this apparatus is in good agreement with the literature value of 3.2 ns.[15]

Procedure. All of the experiments were carried out at room temperature (~20 °C), in air-equilibrated aqueous solution. Measurements were taken on freshly prepared samples in red light using doubly distilled water. $M(bpy)_3^{z+}$ concentration was about 10^{-4} M; the quencher concentration was in the range 10^{-6}–10^{-2} M, and the ionic strength was adjusted to 0.50 M with NaCl. Emission and lifetime experiments were performed using the right-angle geometry at the wavelength corresponding to the emission maximum (728, 610, and 730 nm for $Cr(bpy)_3^{3+}$, $Ru(bpy)_3^{2+}$, and $Os(bpy)_3^{2+}$, respectively). When necessary, the emission intensities were corrected for absorption of the incident light by the quenchers; this correction was never higher than 10%. In all cases, absorption by the quenchers at the emitting wavelength was negligible. For each quenching experiment the absorption spectrum of the sample was essentially equal to the sum of the $M(bpy)_3^{z+}$ and quencher spectra.

Results

Under our experimental conditions, the excited-state lifetimes were 51 μs for $^*Cr(bpy)_3^{3+}$,[16] 0.40 μs for $^*Ru(bpy)_3^{2+}$, and 0.021 μs for $^*Os(bpy)_3^{2+}$. For all but one of the $M(bpy)_3^{z+}$–quencher couples, linear Stern–Volmer plots were obtained from steady-state emission intensity measurements. Lifetime measurements confirmed that no static quenching was present. For the $Os(bpy)_3^{2+}$–$Fe(CN)_6^{3-}$ couple, the intensity Stern–Volmer plot was not linear; a linear plot was obtained with lifetime measurements. The Stern–Volmer quenching constants obtained from the linear plots were divided by the excited-state lifetime in order to get the bimolecular quenching constant, k_q. The k_q values are collected in Table I.

Discussion

The k_q values alone provide no information about the nature of the quenching mechanism. However, inferences on the quenching mechanism can be obtained from relationships between the bimolecular quenching constant and the thermodynamic quantities which determine the driving force of the various processes. Such thermodynamic quantities are (i)

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Table I. Bimolecular Quenching Constants[a]

	$*Cr(bpy)_3^{3+}$		$*Ru(bpy)_3^{2+}$ [b]		$*Os(bpy)_3^{2+}$	
Quencher, B	10^8k_q, $M^{-1}\ s^{-1}$	Reacn[c]	10^8k_q, $M^{-1}\ s^{-1}$	Reacn[c]	10^8k_q, $M^{-1}\ s^{-1}$	Reacn[c]
$Mo(CN)_8^{4-}$	52	2	3.4	2	2.8	2
$Cr(CN)_6^{3-}$	41	1	9.5	1	25	1
$Fe(CN)_6^{4-}$	49	2	33	2	3.8	2
$Fe(CN)_6^{3-}$	2.6	3	65	3	94[d]	3
$Ru(CN)_6^{4-}$	55	2	~0.1[e]	2	1.3	2
$Co(CN)_6^{3-}$	<0.002		<0.01	3	1.3	3
$Ni(CN)_4^{2-}$	14	2	56	1	0.9	3

[a] Aqueous solution, $\mu = 0.50$ M (NaCl), ~20 °C; precision ±10%. [b] From ref 9. [c] Reaction responsible for the quenching (see text). [d] A slightly higher value is reported in ref 17. [e] This work.

Table II. Electronic Energy and Redox Potentials of the Excited States

*A	$E(*A)$,[a] $cm^{-1} \times 10^3$	$E(*A/A^-)$,[b] V	$E(A^+/*A)$,[b] V
$*Cr(bpy)_3^{3+}$	13.8[c]	+1.46[d]	>−0.1[e]
$*Ru(bpy)_3^{2+}$	17.1[f]	+0.89[g]	−0.86[h]
$*Os(bpy)_3^{2+}$	14.9[i]	+0.67[j]	−1.02[k]

[a] Energy for the 0–0 vibrational level transition of the luminescent excited state. [b] Reduction potential vs. NHE (see the text for their calculation). [c] N. A. P. Kane-Maguire, J. Conway, and C. H. Langford, *J. Chem. Soc., Chem. Commun.*, 801 (1974). [d] For $Cr(bpy)_3^{3+,2+}$ $E_{1/2} = -0.25$ V at $\mu = 0.5$ (NaCl): B. R. Baker and D. Mehta, *Inorg. Chem.*, 4, 848 (1965). [e] Electroinactive at the ground state up to +1.6 V vs. SCE at the platinum electrode in DMF (0.1 M TEAP); see ref 20. [f] R. J. Watts and G. A. Crosby, *J. Am. Chem. Soc.*, 93, 3184 (1971). [g] For $Ru(bpy)_3^{2+,+}$ $E_p = -1.33$ V vs. SCE in CH_3CN (0.1 M $TBAPF_4$): N. E. Tokel-Takvoryan, R. E. Hemingway, and A. J. Bard, *J. Am. Chem. Soc.*, 95, 6582 (1973). [h] For $Ru(bpy)_3^{3+,2+}$ $E^{o\prime} = +1.26$ V in 1 M H_2SO_4: D. A. Buckingham and M. M. Sargeson in "Chelating Agents and Metal Chelates", F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N.Y., 1964. [i] J. N. Demas, E. W. Harris, C. M. Flynn Jr., and D. Diemente, *J. Am. Chem. Soc.*, 97, 3838 (1975). [j] For $Os(bpy)_3^{2+,+}$ $E_p = -1.28$ V vs. SCE in CH_3CN (0.1 M TEAP): S. Roffia, M. Ciano, and M. A. Raggi, unpublished results. [k] For $Os(bpy)_3^{3+,2+}$ $E^{\circ\prime} = +0.83$ V in 0.5 M HCl: F. P. Dwyer, N. A. Gibson, and E. C. Gyarfas, *J. Proc. R. Soc. N. S. W.*, 84, 68 (1950).

Table III. Energy of the Lowest Excited State and Formal Redox Potentials of the Cyanide Quenchers

No.	Quencher, B	$E(*B)$,[a] $cm^{-1} \times 10^3$	$E^{\circ\prime}(B^+/B)$,[b] V	$E^{\circ\prime}(B/B^-)$,[b] V
1	$Mo(CN)_8^{4-}$	19.6[c]	+0.79[d]	(<−1.8)[e]
2	$Cr(CN)_6^{3-}$	12.4[f,g]	(>+1.6)[h]	−1.35[i,j]
3	$Fe(CN)_6^{4-}$	23.7[k]	+0.44[l]	(<−1.7)[m]
4	$Fe(CN)_6^{3-}$	23.5[k]	(>+1.0)[n]	+0.44[l]
5	$Ru(CN)_6^{4-}$	>19.0[o]	+0.97[p]	(<−1.5)[e]
6	$Co(CN)_6^{3-}$	20.6[f,q]		−0.90[j,r]
7	$Ni(CN)_4^{2-}$	23[s]	(>+1.0)[n]	−1.12[t]

[a] Lowest energy absorption feature, unless otherwise noted. [b] Formal reduction potential vs. NHE, at 25 °C and $\mu = 0.5$ M (see text). [c] J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, 85, 249 (1963). [d] I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, 40, 247 (1936). [e] Electroinactive up to the indicated potential at the mercury electrode in deaerated 0.50 M NaCl solution, 25 °C; from ref 9. [f] Energy of the lowest excited state from emission spectra. [g] P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, 70, 199 (1970). [h] Electroinactive up to the indicated potential at the platinum electrode in DMF vs. SCE (0.1 M TEAP); from ref 20. [i] $E^\circ = -1.28$ V at $\mu = 0$. [j] D. A. Buckingham and M. M. Sargeson in "Chelating Agents and Metal Chelates", F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N.Y., 1964, p 237. [k] J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, 90, 4260 (1968). [l] I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, 39, 945 (1935). [m] A. N. Frumkin, *Trans. Faraday Soc.*, 55, 156 (1959). [n] Electroinactive up to the indicated potential at the platinum electrode in deaerated 0.50 M NaCl solution, 25 °C; from ref 9. [o] F. Zuloaga and G. Jauregui, *Rev. Latinoam. Quim.*, 2, 97 (1971). [p] D. D. DeFord and A. W. Davidson, *J. Am. Chem. Soc.*, 73, 1469 (1951). [q] A. Woelpl and D. Oelkrug, *Ber. Bunsenges. Phys. Chem.*, 79, 394 (1975). [r] $E^\circ = -0.83$ V at $\mu = 0$. [s] W. R. Mason and H. B. Gray, *J. Am. Chem. Soc.*, 90, 5721 (1968). [t] $E_{1/2}$ from A. A. Vlček, *Collect. Czech. Chem. Commun.*, 22, 948 (1957).

the energies of the excited states of the donor and quencher for the energy-transfer process (reaction 1), (ii) the reduction potential of the excited state and the oxidation potential of the quencher for the reductive electron-transfer process (reaction 2), and (iii) the oxidation potential of the excited state and the reduction potential of the quencher for the oxidative electron-transfer process (reaction 3).

Evidently, the quenching process involves the lowest energy excited state of the $M(bpy)_3^{z+}$ complexes, namely, a doublet metal-centered state for $*Cr(bpy)_3^{3+}$ and a "triplet" metal-to-ligand change-transfer state for $*Ru(bpy)_3^{2+}$ and $*Os(bpy)_3^{2+}$. The spectroscopic and thermodynamic quantities of these excited states are collected in Table II. The energy given is that of the 0–0 transition. The redox potentials have been obtained by adding the excited-state energy (in eV) to the formal potential of the ground state.[17] This assumes that the entropy difference between excited and ground states is negligible, so that all of the spectroscopic energy is available as free energy in the excited-state reactions. As to the formal potential of the ground state, when $E^{o\prime}$ for aqueous solutions was unknown, $E^{o\prime}$ in DMF or CH_3CN was used, after an appropriate correction for the liquid junction potential.[18] Unless otherwise noted, all of the potentials used are vs. NHE. The data reported in Table II indicate that the energy available for the energy-transfer process decreases in the order $*Ru(bpy)_3^{2+} > *Os(bpy)_3^{2+} > *Cr(bpy)_3^{3+}$, the oxidizing ability decreases in the order $*Cr(bpy)_3^{3+} > *Ru(bpy)_3^{2+} > *Os(bpy)_3^{2+}$, and the reducing ability decreases in the order $*Os(bpy)_3^{2+} > *Ru(bpy)_3^{2+} > *Cr(bpy)_3^{3+}$.

The spectroscopic and thermodynamic quantities of the cyanide quenchers are given in Table III. In the case of $Cr(CN)_6^{3-}$, $Ru(CN)_6^{4-}$, and $Co(CN)_6^{3-}$ the reported excited-state energy is the 0–0 energy of the lowest lying excited state. In all the other cases, since the 0–0 excitation energy is difficult to evaluate because of the lack of luminescent emission, the values of the lowest energy absorption feature are reported. It should be noted that these excited states are strongly distorted with respect to the ground state so that the zero-vibrational energy level of the excited state may lie at considerably lower energy than the absorption maximum. The redox potentials listed in Table III are those of aqueous solutions at $\mu = 0.5$ M. When values at this ionic strength were not available in the literature, appropriate corrections were made. It should be noted, however, that these corrections do not substantially affect the discussion below.

It is instructive to correlate the k_q and the thermodynamic data of Tables II and III, in the hope of obtaining information about the nature of the quenching mechanism. Such correlations are meaningful only for homogeneous families which exhibit similar reorganization energies. From this point of view the family of the cyanide quenchers is less homogeneous than that of the bipyridine complexes. Therefore, the discussion below is based on a comparison of the k_q's obtained for the quenching processes by the same cyanide quencher. The most probable quenching reaction (eq 1–3) resulting from the discussion below is indicated in Table I.

$Mo(CN)_8^{4-}$. The values of Tables II and III show that both energy-transfer and oxidative quenching are thermodynamically unfavored in all three cases, while reductive quenching (reaction 2) is thermodynamically favored for $*Cr(bpy)_3^{3+}$ and $*Ru(bpy)_3^{2+}$ and only slightly unfavored for $*Os(bpy)_3^{2+}$. The k_q values increase with increasing driving force of reaction 2, in qualitative agreement with the expectations for an outer-sphere electron-transfer reaction.[19]

$Cr(CN)_6^{3-}$. The energy-transfer mechanism is thermodynamically and spin allowed for all three donors, whereas both electron-transfer mechanisms are thermodynamically unfavored in all cases. The occurrence of an energy-transfer quenching mechanism has also been confirmed by the presence of a sensitized emission from $Cr(CN)_6^{3-}$ when $*Ru(bpy)_3^{2+}$ and $*Cr(bpy)_3^{3+}$ are used as donors.[20] It is evident from Table I that the quenching constant decreases in the order $*Cr(bpy)_3^{3+} > *Os(bpy)_3^{2+} > *Ru(bpy)_3^{2+}$. Whenever energy and spin requirements are satisfied, many other factors can play a role in determining the rate of energy transfer; unfortunately, little is known about their relative importance.[2] Compared to the case of $*Ru(bpy)_3^{2+}$ and $*Os(bpy)_3^{2+}$, energy transfer from $*Cr(bpy)_3^{3+}$ should be more favored by the higher ionic charge and by the absence of excited-state distortion but should not be favored by the metal-centered nature of the excited state, which is expected to cause a less favorable orbital overlap between donor and quencher orbitals.[21] The fact that the rate constant for quenching is higher for $*Cr(bpy)_3^{3+}$ than for $*Ru(bpy)_3^{2+}$ and $*Os(bpy)_3^{2+}$ suggests that ionic charge and/or excited-state distortion play the major role in energy-transfer processes. The higher rate constant for $*Os(bpy)_3^{2+}$ relative to $*Ru(bpy)_3^{2+}$ can be attributed to the more diffuse character of the d metal orbitals in $*Os(bpy)_3^{2+}$.

$Fe(CN)_6^{4-}$. The most favored quenching mechanism is clearly the reductive quenching (reaction 2). The increase of k_q with increase in the driving force for reaction 2 is consistent with this mechanism. Support for the reductive quenching mechanism comes from the $*Ru(bpy)_3^{2+}$–$Fe(CN)_6^{4-}$ system, for which Creutz and Sutin[22] have obtained evidence of $Ru(bpy)_3^{+}$ formation, in agreement with reaction 2. On the other hand, the energy-transfer quenching mechanism proposed by Demas and Addington[23] for the $*Ru(bpy)_3^{2+}$–$Fe(CN)_6^{4-}$ system has no experimental support.

$Fe(CN)_6^{3-}$. From the values of excited-state energies reported in Tables II and III, an energy-transfer mechanism appears to be unlikely. For the $*Ru(bpy)_3^{2+}$–$Fe(CN)_6^{3-}$ system, Demas and Addington[23] have suggested an energy-transfer quenching mechanism on the basis of a band observed by Kiss et al.[24] at 18.2 × 10^3 cm^{-1} in the $Fe(CN)_6^{3-}$ spectrum. Such a band, however, has not been reported in more recent papers[25,26] and is absent in freshly prepared solutions of pure $Fe(CN)_6^{3-}$, although an absorption feature at ~18 × 10^3 cm^{-1} arises under the spectrophotometer light. Thus, energy transfer seems unlikely, unless it involves "nonspectroscopic" excited states of $Fe(CN)_6^{3-}$. With $*Ru(bpy)_3^{2+}$ and $*Os(bpy)_3^{2+}$ a reductive quenching is also unlikely, while oxidative quenching (reaction 3) seems to be allowed. As far as the $*Cr(bpy)_3^{3+}$–$Fe(CN)_6^{3-}$ system is concerned, the uncertainty of the thermodynamic data precludes a distinction between the two electron-transfer mechanisms. However, inasmuch as the k_q values increase with increase in the driving force for reaction 3, we suggest that an oxidative quenching also occurs with $*Cr(bpy)_3^{3+}$.

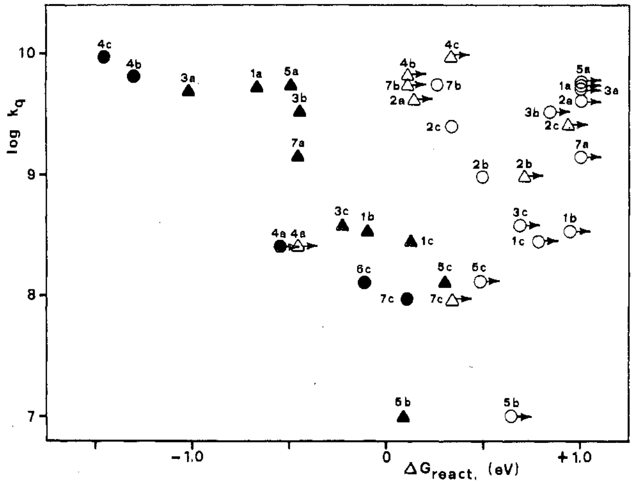

Figure 1. Relation between the quenching rate constant and the free-energy change for reductive (△) and oxidative (○) quenching (reactions 2 and 3). Full points correspond to the quenching mechanism that is thought to be most probable (also indicated in Table I). For each point, the $M(bpy)_3^{z+}$–quencher system is identified by a number indicating the quencher (see Table III) and a letter indicating the excited complex (a, b, and c are for $*Cr(bpy)_3^{3+}$, $*Ru(bpy)_3^{2+}$, and $*Os(bpy)_3^{2+}$, respectively).

$Ru(CN)_6^{4-}$. On the basis of the thermodynamic quantities of Tables II and III, mechanisms 1 and 3 are clearly thermodynamically unfavored. As far as the reaction 2 is concerned, it is thermodynamically allowed with $*Cr(bpy)_3^{3+}$ but slightly endothermic in the other two cases. While the k_q for the quenching of $*Cr(bpy)_3^{3+}$ and $*Ru(bpy)_3^{2+}$ seems to agree with this trend, the k_q for the $*Os(bpy)_3^{2+}$–$Ru(CN)_6^{4-}$ system appears to be surprisingly high.

$Co(CN)_6^{3-}$. From the data of Tables II and III, an energy-transfer mechanism appears to be thermodynamically unfavored. The lack of knowledge of the oxidation potential of $Co(CN)_6^{3-}$ precludes any direct inference on the occurrence of reaction 2. However, such a process seems quite improbable because (i) $Co(CN)_6^{3-}$ is presumably very difficult to oxidize and (ii) $*Cr(bpy)_3^{3+}$ (which would have the highest driving force for reaction 2) is practically unquenched by $Co(CN)_6^{3-}$. Thus, we suggest that quenching of $*Ru(bpy)_3^{2+}$ and $*Os(bpy)_3^{2+}$ by $Co(CN)_6^{3-}$ occurs via an oxidative mechanism (reaction 3); this reaction is thermodynamically allowed for the Os(II) complex and slightly unfavored for the Ru(II) one, in agreement with the trend in the k_q values.

$Ni(CN)_4^{2-}$. For the $*Ru(bpy)_3^{2+}$–$Ni(CN)_4^{2-}$ system, Demas and Addington[23] suggested an energy-transfer quenching mechanism on the basis of an estimate of ~18 × 10^3 cm^{-1} for the lowest (nonspectroscopic) excited state of $Ni(CN)_4^{2-}$. This suggestion is indirectly supported by the fact that an electron transfer seems to be unfavored. However, even with the assumption that the lowest excited state of $Ni(CN)_4^{2-}$ is as low as 18 × 10^3 cm^{-1}, the energy-transfer quenching mechanism is excluded for the two remaining cases. It is also noteworthy that the higher quenching constant for $*Cr(bpy)_3^{3+}$ compared to that for $*Os(bpy)_3^{2+}$ is in contrast with an energy-transfer mechanism. The less unfavored process seems to be oxidative quenching for the $*Os(bpy)_3^{2+}$–$Ni(CN)_4^{2-}$ system, whereas for the $*Cr(bpy)_3^{3+}$–$Ni(CN)_4^{2-}$ system a reductive quenching is probably allowed.

The validity of the inferences made above can also be tested considering the quantitative relationship between quenching constants and free-energy changes for the reaction involved in the quenching mechanism. In Figure 1, the quenching constants for the systems reported herein have been gathered as a function of the free-energy change for reductive and oxidative quenching (eq 2 and 3). It can be seen that the points which correspond to the quenching mechanism that is thought to be the most probable on the basis of the above discussion lie on a Marcus-type "band".[19] The scattering of these points from a common curve is not unexpected, because the excited states, and even more so the quenchers, differ in their inherent barriers to electron transfer.[27] It is noteworthy that in the cases for which an energy-transfer mechanism has been thought to be the most probable, both of the points corresponding to the electron-transfer mechanisms lie far from the Marcus-type curve.

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Registry No. $Cr(bpy)_3^{3+}$, 15276-15-0; $Ru(bpy)_3^{2+}$, 15158-62-0; $Os(bpy)_3^{2+}$, 23648-06-8; $Mo(CN)_8^{4-}$, 17923-49-8; $Cr(CN)_6^{3-}$, 14875-14-0; $Fe(CN)_6^{4-}$, 13408-63-4; $Fe(CN)_6^{3-}$, 13408-62-3; $Ru(CN)_6^{4-}$, 21029-33-4; $Co(CN)_6^{3-}$, 14897-04-2; $Ni(CN)_4^{2-}$, 15453-80-2.

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Stereochemical Activity of s Orbitals

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The dependence of the bond angles of AH_n ($n = 2, 3, 4, 5, 6$) molecules on various energy parameters are studied by extended Hückel theory (EHT). The results suggest that, contrary to the expectations of the valence shell electron pair repulsion (VSEPR) model, the only important Pauli repulsions in "normal" covalent molecules (four or fewer electron pairs) are those between bond pairs. The driving force for bending in a molecule such as H_2O is due primarily to the relative *n*p–*n*s energy separation of the central atom in agreement with our previous ab initio calculations. Thus, H_2O bends not because there are lone pair–lone pair or lone pair–bond pair repulsions but because the 2s orbital is lower in energy and the molecule can maximize its occupation only by bending. The *n*p–*n*s energy separation also controls the degree to which three-center, four-electron (3c-4e) bonds bend toward the two-center, two-electron (2c-2e) bonds in molecules such as ClF_3. In these "hypervalent" molecules the Pauli exclusion principle also contributes to the bending. However, this effect does not arise from lone pair–bond pair repulsions but from bond-pair attractions, i.e., the desire to delocalize the "electron-rich" 3c-4e bond into the "electron poor" 2c-2e bond.

Introduction

In our previous ab initio study of the geometry of H_2O[1] we have shown that the basic tenet of the valence shell electron pair repulsions (VSEPR) model,[2] that the geometry is determined by Pauli repulsion of localized lone pairs, is not viable. Rather, the geometry of H_2O is determined by two competing effects: one, the Pauli repulsions between bond pairs, which tend to increase the bond angle; two, the system's desire to lower the total energy by keeping the more stable oxygen 2s orbital fully occupied, which tends to decrease the bond angle. No Pauli repulsions due to the lone pairs were evident in our analysis. Both of these effects are manifest in extended Hückel theory[3] (EHT) and, as we will show, are the primary reason for its often correct prediction of the geometry.

The exact geometry of any molecule is, of course, a complex balance of forces, and we do not want to suggest that a model as simple as EHT can account for all the subtle effects in the total energy. However, for the gross features of the geometry, EHT appears to incorporate the major effects and has had a long success in describing the major qualitative features of the bonding. Allen and co-workers have studied the relation of EHT to ab initio calculations.[4] An examination of EHT and Walsh diagrams has been presented by Gimarc,[5] and Bartell has compared the results of VSEPR and EHT.[6] However, the dependence of the EHT predictions on parameter choice and how this relates to the qualitative description of the geometry