cyclopentanone to lower fields by as much as 6 ppm, reinforcing the conclusion that the keto carbon resonance is exceedingly sensitive to coordination or hydrogen-bonding interactions when the keto group acts as electron donor.

Both chlorophyll *b* and bacteriochlorophyll possess two electron donor groups available for coordination to Mg. ^{13}C nmr should have particular value for determining the relative electron donor strengths of the two donors in the self-interactions of these two chlorophylls. Such experiments are in progress.[15]

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Trapping of Valence States in a Ruthenium(II,III)-Pyrazine Complex

Sir:

Creutz and Taube[1] have measured the electronic spectra of the ions I in which valence states of the ruthenium atoms may be written as (II,II), (II,III), and (III,III). They concluded that an absorption band at 6.5 kK in the (II,III) complex, which is not present in either of the other two complexes, arises from a specific interaction between the mixed-valence Ru atoms. A band about 17.5 kK observed in the (II,II) and, with approximately half the intensity, in the (II,III) complex, but not present in the (III,III) complex, was ascribed to Ru(II) → pyrazine π^* charge transfer. That this band should be present in both the single valence (II,II) and mixed valence (II,III) complexes indicates that in the latter the valences are "trapped," *i.e.*, that the complex belongs to class II in the classification of Robin and Day.[2]

I (n = 4-6)

Since identical ligands surround each Ru atom in the (II,III) complex, it seems surprising at first sight that the two Ru valences should be firmly localized. In this note, we wish to indicate a general condition for valence trapping in a mixed valence system and also to show that the condition is indeed satisfied by the ruthenium complex I. Figure 1 shows the reaction coordinates for a valence interchange M(X,Y) $\rightleftharpoons$ M(Y,X). Electron transfer by a Frank-Condon process at the points x = 0, 1 produces a Y$^+$ ion in the environment of an X$^+$ ion, and *vice versa*. If the coordination spheres about the mixed-valence atoms A and B are distorted by Δq_A and Δq_B

$$E_{FC} = k(\Delta q_A{}^2 + \Delta q_B{}^2) \qquad (1)$$

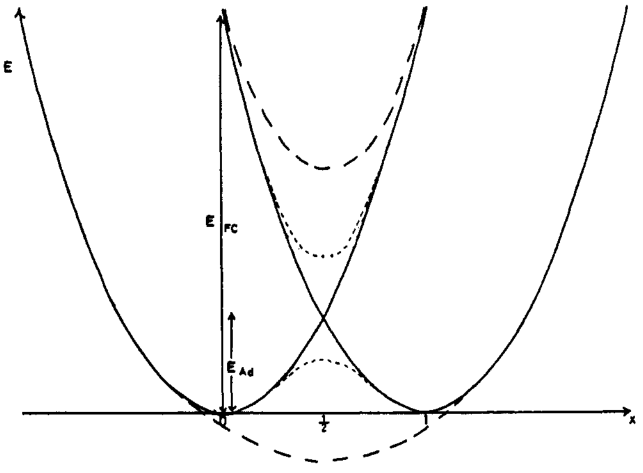

Figure 1. Reaction coordinates for valence interchange (X,Y) $\rightleftharpoons$ (Y,X): (a) (——) energy surface for (X,Y), (Y,X) in the absence of resonance interaction between the sites; (b) (— — —) energy surface with $H_{res} > E_{Ad}$; (c) (------) energy surface with $H_{res} < E_{Ad}$.

On the other hand, if the electron transfer is adiabatic, at $x = {}^1/_2$ the distortions of the coordination spheres about atoms A and B are $\Delta q_A/2$, $\Delta q_B/2$ $(= -\Delta q_A/2)$. Now $E_{Ad} = k[(\Delta q_A/2)^2 + (\Delta q_B/2)^2]$ and with eq 1

$$E_{Ad} = E_{FC}/4 \qquad (2)$$

a relationship originally demonstrated by Hush.[3] At the point $x = {}^1/_2$ the complex is in a delocalized state formed by an equal combination of states (X,Y) and (Y,X). If the resonance interaction between (X,Y) and (Y,X) is H_{res}, the energy of this point is given by

$$E(x = {}^1/_2) = E_{Ad} - H_{res} = E_{FC}/4 - H_{res} \qquad (3)$$

and the energy of any point between x = 0 and x = 1 by the solution of a secular determinant. Then it is clear that if $H_{res} > E_{Ad}$ we have complete delocalization and hence class III[2] behavior, but if $H_{res} < E_{Ad}$ we have valence trapping and class II behavior. This criterion is analogous to the one which determines whether a small polaron or band model is most appropriate to describe the conduction properties of a crystal.[4]

In principle an *a priori* calculation of the class of a mixed-valence complex is therefore possible. The trapping energy E_{Ad} depends upon the relaxation of the metal coordination spheres upon the valence change X $\rightleftharpoons$ Y. E_{Ad} is then calculable in terms of metal-ligand force constants and the differences in metal-ligand stretching frequencies and bond lengths between the valence states X and Y. The resonance stabilization energy of the delocalized state ($x = {}^1/_2$) might also be estimated by a molecular orbital calculation for the complex.

Unfortunately, for the particular case of the diruthenium(II,III)-pyrazine complex the only relevant ir data relate to the difference in Ru-N stretching frequencies in Ru(II) and Ru(III) hexaammine complexes[5,6] so that *a priori* calculation of the mixed-valence class is not yet possible. However, for the special case of a binuclear complex in which the ligands sur-

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(1) C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, **91**, 3988 (1969).
(2) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967).
(3) N. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967).
(4) I. G. Austin and N. F. Mott, *Science*, **168**, 71 (1970).
(5) W. P. Griffiths, *J. Chem. Soc. A*, 899 (1966).
(6) M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, **22**, 359 (1966).

rounding each metal ion are identical, one may demonstrate that there is a definite maximum limit to the valence delocalization which is compatible with the existence of two sites with differing nuclear configurations. Using the spectral data of Creutz and Taube[1] we can then show that the extent of valence delocalization in compound I lies well below this limit.

For a class II system regarded formally as $A^{X+}\ B^{Y+}$ the ground state may be written

$$\Psi_G = [\Psi(A^{X+}B^{Y+}) + \alpha\Psi(A^{Y+}B^{X+})]/\sqrt{1 - \alpha^2} \quad (4)$$

and the excited state

$$\Psi_{MV} = [\Psi(A^{Y+}B^{X+}) - \alpha'\Psi(A^{X+}B^{Y+})]/\sqrt{1 - \alpha^2} \quad (5)$$

The dipole length transition moment governing the spectral intensity of the transition $\Psi_G \rightarrow \Psi_{MV}$ is

$$\mu = {}^1/_2(\alpha + \alpha')R_{AB} \quad (6)$$

R_{AB} is the distance separating the two centers A and B, and α and α' are given by first-order perturbation theory as

$$\alpha = \beta/(E_{MV} - E_G) \quad (7a)$$

$$\alpha' = \beta'/(E_{MV} - E_G) \quad (7b)$$

where $(E_{MV} - E_G)$ is approximately equal to the energy of the mixed-valence absorption band, while β and β' are resonance energies in the ground and excited states, respectively. Since $\Psi(A^{X+}B^{Y+})$ and $\Psi(A^{Y+}B^{X+})$ are effectively orthogonal when A and B are well separated, they may interact only *via* mutually nonorthogonal A → (ligand)*, (ligand) → B charge-transfer states. This situation is quite analogous to that occurring in the theory of superexchange.[7] Since the metal–ligand charge-transfer states are closer in energy to Ψ_{MV} than to Ψ_G, perturbation theory yields the result $\beta' > \beta$, $\alpha' > \alpha$. The experimentally observed quantity $(\alpha + \alpha')/2$ is then greater than α, which in turn equals β/E_{FC} (eq 7a). However, for trapping of valence, $\beta < E_{FC}/4$, so that

$$\alpha < 1/4 \quad (8)$$

In a class III system $\alpha^2 = 0.5$ so that any experimentally determined value of α^2 between 0.07 and 0.5 would invalidate the valence-trapping criterion suggested above.

From the data of Taube and Creutz[1] the transition dipole μ of the mixed-valence band in I may be estimated at roughly 1.07 eÅ, yielding a value of about 0.15 for $^1/_2(\alpha + \alpha')$. Thus $\alpha^2 \leqslant 0.025$, which satisfies the criterion for trapping (8). From the same data a resonance integral for valence interaction at the point $x = 0$ in the energy surface of Figure 1 may be estimated as $\beta \leqslant 975$ cm^{-1} (0.12 eV). Resonance interaction H_{res} at the point $x = {}^1/_2$ will be of similar magnitude, and the energy of adiabatic charge-transfer E_{Ad} is 1625 cm^{-1}.

We can also show that our estimate of the resonance integral β is realistic by another simple theoretical approach. If the states $\Psi[Ru_A{}^{2+}Ru_B{}^{3+}]$ and $\Psi[Ru_A{}^{3+}Ru_B{}^{3+}]$ are considered to be orthogonal, interacting only by a second-order mechanism involving nonorthogonal ligand $\pi \rightarrow Ru^{3+}$ and $Ru^{2+} \rightarrow$ ligand π^* charge-transfer states,[8] the resonance integral β is given by perturbation theory as

$$\beta = \sum_i \frac{\langle\Psi_0|H|\Psi_{CTi}\rangle\langle\Psi_{CTi}|H|\Psi_{CT}\rangle}{E_{CTi} - E_0}$$

where $\Psi_0 = \Psi[Ru_A{}^{2+}Ru_B{}^{3+}]$, $\Psi_{CT} = [Ru_A{}^{3+}Ru_B{}^{2+}]$, and Ψ_{CTi} are all other ligand $\pi \rightarrow Ru^{3+}$, $Ru^{2+} \rightarrow$ ligand π^* charge-transfer states; β' is given by a similar expression having denominator $(E_{CTi} - E_{CT})$. The integrals defining β may be estimated semiempirically from the energies and intensities of observed metal(II) → ligand π^* and ligand $\pi \rightarrow$ metal(III) charge-transfer bands. We have employed the method used by Sanders and Day[9] in the assignment of the charge-transfer spectra of iron complexes with conjugated ligands. The value of β calculated by this method is 1040 cm^{-1}. This estimate involves the assumption that the unpaired electron density in the Ru(III) d^5 system is distributed almost equally over the d_{xy}, d_{xz}, d_{yz} orbitals, which seems reasonable in view of the high spin–orbit coupling constant for Ru(III) (1000 cm^{-1} [10]) and the similar ligand field strengths of ammonia and pyrazine.[10] Such a distribution of spin-unpaired electron density gives a good agreement between calculated and observed intensities for the ligand $\pi \rightarrow$ Ru(III) charge-transfer absorption at 28.5 kK in the (III,III) complex when $\beta_{Ru(III)N}$ is set equal to $\beta_{Ru(II)N}$. Using our calculated values of β and β' we estimate the transition dipole of the mixed-valence absorption band as 1.4 eÅ. The observed value is 1.07 eÅ.

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(7) P. W. Anderson, *Phys. Rev.*, **79**, 350 (1950).

(8) B. Mayoh and P. Day, to be published.

(9) N. Sanders and P. Day, *J. Chem. Soc. A*, 1191 (1970); 2303 (1969); 1530, 1536 (1967).

(10) B. N. Figgis, "An Introduction to Ligand Fields," Wiley, New York, N. Y., 1966.

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Thermal Decomposition of Tetramethyl-1,2-dioxetane. Selective and Efficient Chemelectronic Generation of Triplet Acetone[1]

Sir:

The mechanism of production and the nature of electronically excited state(s) involved in chemelectronic reactions (*i.e.*, reactions in which at least one elementary step involves the conversion of chemical energy into electronic excitation energy) are of great interest to kineticists,[2] biochemists,[3] and photochemists.[4]

The involvement of an oxygen molecule, or its equivalent (*e.g.*, a peroxide), in bioluminescent systems[5] and the probable involvement of singlet oxygen[6] in many reactions which are chemiluminescent, has led to the postulate of 1,2-dioxetanes as reaction intermedi-

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(1) Molecular Photochemistry. LII. Paper LI: N. J. Turro, *et al.*, *J. Amer. Chem. Soc.*, **94**, 1392 (1972). The authors thank the Air Force Office of Scientific Research (Grant AFOSR-70-1848) and the National Science Foundation (Grant No. GP-26602x) for their generous support of this work.

(2) R. F. Vassilev, *Progr. React. Kinet.*, **4**, 305 (1967); *Russ. Chem. Rev.*, **39**, 529 (1970).

(3) F. H. Johnson and Y. Haneda, "Bioluminescence in Progress," Princeton University Press, Princeton, N. J., 1966.

(4) E. H. White, J. Wiecko, and D. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969); H. E. Zimmerman, D. Dopp, and P. S. Huyffer, *ibid.*, **88**, 5352 (1966).

(5) T. Gato, *Pure Appl. Chem.*, **17**, 421 (1968).

(6) F. McCapra and R. A. Hahn, *J. Chem. Soc. D*, 442 (1969).