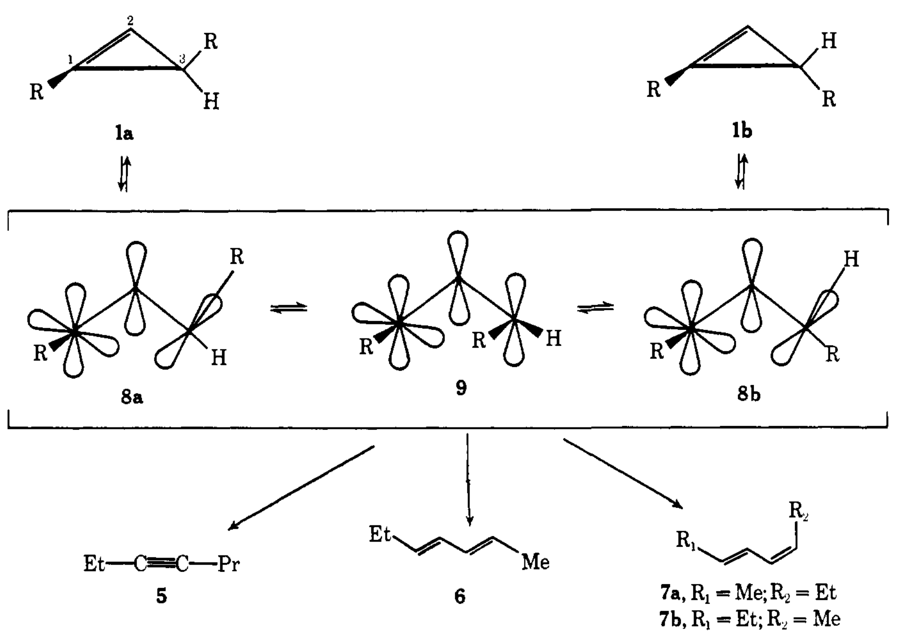
Scheme I

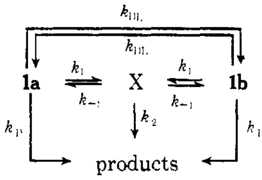


stituted "vinylcarbene."[9] Hydrogen shift in either **8** or **9** leads to acyclic products; further rotation and cyclization regenerate **1**.

Thermochemical analysis[10] predicts that the heat of formation of carbene **9** is +68 kcal/mol. That of **1** can be reliably estimated to be +42 kcal/mol,[11] and the racemization transition state is then $[\Delta H_f°]_1 + \Delta H^{\ddagger} =$ +73 kcal/mol. If one assumes that $\Delta H_f°$ for diradical **8** is +79 kcal/mol (one allylic resonance energy[12] higher than **9**), **8** is predicted to lie *higher* in energy than the racemization transition state. It therefore seems likely that configuration **8** is stabilized by some 1,3 bonding; *i.e.*, that rotation and ring closure are synchronous processes and perhaps the only true intermediate is **9**. A quantitative estimate of the overall favorability of recyclization can be obtained by kinetic analysis of the simplified Scheme II. The unimolecular rate constants k_{DL} and k_P can be extracted from k_α and k_i (Table I). Application of the steady-state assumption to the set of intermediates X shows that $[k_{DL}/k_P] = [k_{-1}/k_2]$. Our data give 8.8 as an average value for this ratio.

In summary we feel that the most reasonable intermediate for racemization of 1,3-diethylcyclopropene is a substituted vinylcarbene. Because the cyclization–hydrogen shift selectivity calculated for the set of intermediates X is only a factor of three different from that estimated[13a] for the trimethylene diradical (22), it seems unlikely that any barrier associated with ring closure has the onset of ring strain[14] as its source. Finally, the fact that vinyl diazo compounds have long been known[9] to yield cyclopropenes on thermal and photochemical decomposition suggests, in light of our observations, that such reactions proceed *via* intermediates very similar to those involved in the racemization of cyclopropene **1**.

Scheme II



Acknowledgments. We are grateful to the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society for financial support of this work and to Professor G. L. Closs for stimulating discussions.

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(9) See, for example, (a) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 99 (1963); (b) G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963); (c) H. Dürr, *Chem. Ber.*, **103**, 369 (1970); (d) T. Severin, H. Krämer, and P. Adhikary, *ibid.*, **104**, 972 (1971); (e) M. E. Hendrick, W. J. Baron, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 1554 (1971); (f) M. E. Hendrick, *ibid.*, **93**, 6337 (1971); (g) M. Franck-Neumann, *Tetrahedron Lett.*, 15 (1969); (h) G. Baum, R. Bernard, and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5307 (1967); (i) G. Büchi and J. D. White, *ibid.*, **86**, 2884 (1964); (j) G. Snatzke and H. Langen, *Chem. Ber.*, **102**, 1865 (1969); (k) L. Schrader, *ibid.*, **104**, 941 (1971); (l) G. L. Closs, L. R. Kaplan, and V. I. Bendall. *J. Amer. Chem. Soc.*, **89**, 3376 (1967); (m) 3,3-dimethylcyclopropene, on pyrolysis in olefin solution, gives a cyclopropane product which can be understood to have arisen by addition of 2-methylpropenylcarbene to the olefin; Professor G. L. Closs, private communication.

(10) The approach is that used by H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970), and references cited therein.

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Received February 4, 1972

Chlorophyll–Chlorophyll Interactions. Ring V Keto Carbonyl Donor Properties from Carbon-13 Nuclear Magnetic Resonance

Sir:

It has become increasingly evident that the state of chlorophyll in solution is largely determined by the co-

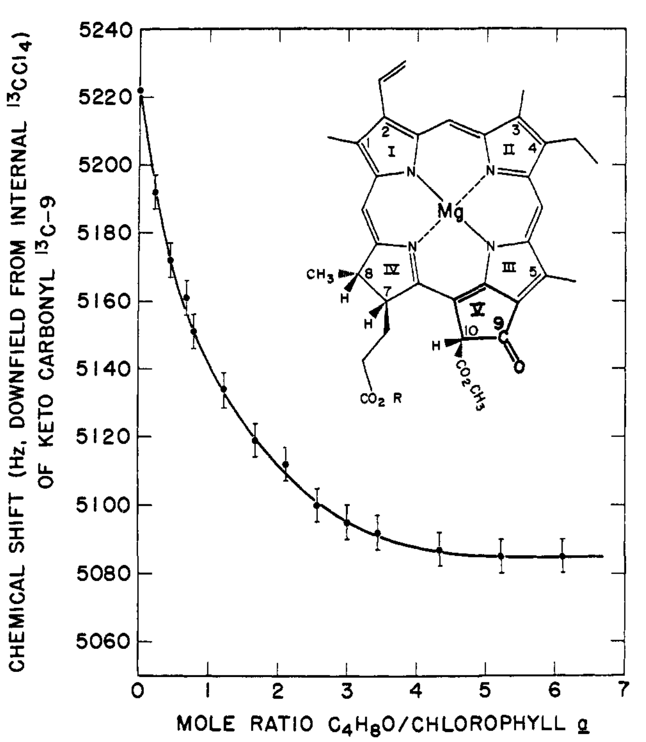

Figure 1. ^{13}C chemical shifts of keto carbonyl carbon-9 from titration of 0.22 *M* chlorophyll *a* (15% ^{13}C) in CCl$_4$ with tetrahydrofuran (THF, C$_4$H$_8$O). THF was introduced through a serum cap into the previously evacuated 5 mm sample tube from a microliter syringe. The ^{13}C-enriched chlorophyll was obtained by biosynthesis (R. A. Uphaus, E. Flaumenhaft, and J. J. Katz, *Biochim. Biophys. Acta*, **141**, 625 (1967); E. Flaumenhaft, R. A. Uphaus, and J. J. Katz, *ibid.*, **215**, 421 (1970)). Spectra were recorded at 55 MHz on a Varian HR-220 in C. W. mode.

ordination properties of its central magnesium atom. Absorption spectroscopy in the visible[1] and infrared,[2-7] proton magnetic resonance,[8-11] and molecular weight determinations by vapor phase osmometry[12] and ultracentrifugation[13] all support the view that the central Mg atom in chlorophyll always has a coordination number larger than 4, contrary to the way its structural formula is usually written (Figure 1), and that one or both of the Mg axial positions must always be occupied by an electron donor group.[14] In polar media (Lewis bases), solvent molecules act as electron donors and occupy the axial positions to form the monomeric chlorophyll species, Chl·L$_1$ and Chl·L$_2$. In the absence of extraneous nucleophiles, as in nonpolar solvents, the keto C=O function in ring V of one chlorophyll molecule acts as donor to the Mg atom of another to generate chlorophyll dimers and higher oligomers.[12] Pmr has proved to be a very serviceable tool in the investigation of the acceptor properties of Mg in chlorophyll because the large ring current associated with the dihydroporphyrin ring causes large upfield shifts in the protons of a ligand positioned above the plane of the ring by coordination to Mg.[10] Inferences on the donor properties of the keto C=O function from pmr have necessarily been indirect and have been based mostly on the ring current effect on the C-10 and other protons in the vicinity of the keto group of ring V. Because the chlorophyll oligomers formed by keto C=O---Mg interactions appear, on the basis of electronic transition spectra, to be very similar to if not identical with "antenna" chlorophyll in the plant,[1] a more direct assessment of the donor properties of the keto C=O function in chlorophyll is highly desirable. We show here that ^{13}C nmr is very well suited for this purpose.

We have followed the disaggregation of chlorophyll dimers by the base tetrahydrofuran (THF), which proceeds by the equilibrium $\mathrm{Chl_2} + 2\mathrm{THF} \rightleftarrows 2\mathrm{Chl\cdot THF}$, by observing chemical-shift changes of C-9 in the keto C=O group as a function of the Chl/THF ratio (Figure 1). Only the weighted average of the C-9 chemical shifts is observed as the equilibration rate between chlorophyll monomer and dimer is fast on the magnetic resonance time scale. In Chl$_2$, the C-9 resonance is observed at very low field as an ill-defined lump which sharpens and moves to higher field as successive increments of THF are added. The chemical-shift difference between C-9 in Chl$_2$, where the keto C=O is acting as donor to Mg, and the C-9 resonance in Chl·THF, where the keto C=O is free, is 2.42 ppm. This resonance in chlorophyll *a* monomer appears at the lowest field of any of the 55 carbon atoms of chlorophyll *a*. Its position, and the large shift that accompanies the disaggregation of chlorophyll dimer, make the assignment of this resonance to the C-9 keto carbon quite certain.

At first sight, it is surprising to observe an upfield shift in the keto ^{13}C=O resonance as disaggregation occurs. When two chlorophyll rings are juxtaposed in the dimer, those protons that are eclipsed by the ring of another chlorophyll experience an upfield shift, and move to lower field as the dimers are disaggregated. The ^{13}C nmr result can readily be rationalized by the assumption that the chemical shift of the C-9 keto C=O carbon in Chl$_2$ is the resultant of an upfield shift due to the ring current, and a downfield shift resulting from the keto C=O---Mg coordination interaction, with the latter effect the larger. This interpretation receives support from observations that the chemical shift of the keto C=O carbon in a 1 *M* solution of cyclopentanone (natural abundance) in benzene or CCl$_4$ is shifted to lower fields by no less than 8.71 (in benzene) and 8.02 ppm (in CCl$_4$) by the addition of an equivalent amount of magnesium hexafluoroacetylacetone (Mg-HFAA$_2$). The keto ^{13}C=O resonance of a 2 *M* solution of cyclohexanone (natural abundance) in benzene is shifted downfield 6.46 ppm by 0.5 equiv of MgHFAA$_2$. Strong hydrogen bonding agents such as trifluoroethanol likewise shift the carbonyl carbon resonance of

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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]

[15] This work was performed under the auspices of the U. S. Atomic Energy Commission.

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Received January 28, 1972

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).

I (n = 4-6)

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]

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) $\rightleftarrows$ 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

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

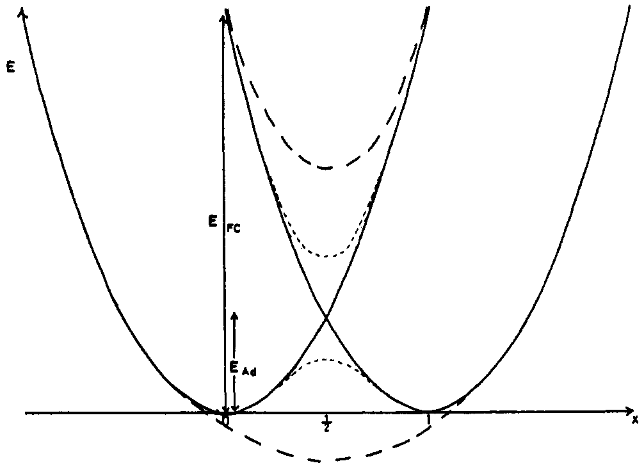

Figure 1. Reaction coordinates for valence interchange (X,Y) $\rightleftarrows$ (Y,X): (a) (——) energy surface for (X,Y), (Y,X) in the absence of resonance interaction between the sites; (b) (— — —) energy surface with $H_{res} > E_{Ad}$; (c) (- - - - - -) energy surface with $H_{res} < E_{Ad}$.

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 $\rightleftarrows$ 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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