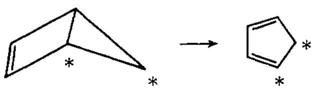
experimental error. For exclusive operation of the C(1)-C(2)/C(4)-C(5) and C(3)-C(4)/C(5)-C(1) processes, the predicted result would have been 40.4%.[11] Thus the thermal conversion of bicyclopentene to cyclopentadiene occurs through the C(1)-C(4) cleavage mechanism, and nonparticipation of the [$\sigma 2 + \sigma 2$] alternative is demonstrated.



The controversy over the reaction mode followed in the bicyclo[2.1.0]pent-2-ene to cyclopentadiene isomerization may thus be retired. The experimental distinction which proved so elusive in molecules labeled with substituents has been achieved through double labeling of carbons in bicyclopentene itself. The reality of hot-molecule effects at substantial pressures in the gas phase, and even in solution,[1,2] is confirmed, supporting the postulates of Brauman and coworkers[2] and of Flowers and Frey.[4]

One may anticipate that hot-molecule chemistry in solution will receive fresh attention; the conveniently simplifying generalization that collisional deactivation in solution always preempts thermal reactions of vibrational excited molecules can no longer be credited.

Acknowledgment. This work was supported by the National Science Foundation through Grant GP-40933X.

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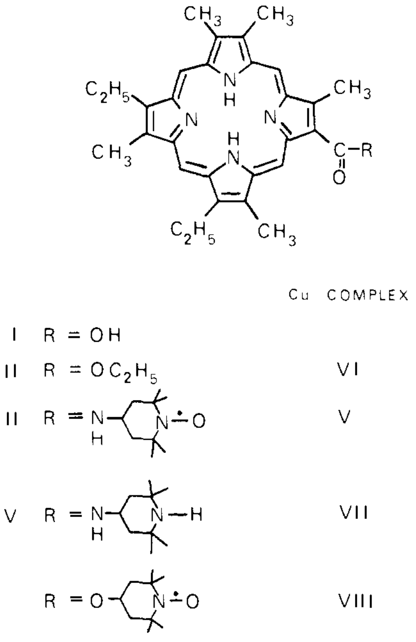
Received November 23, 1976

Metal-Nitroxyl Interactions. 4. Electron-Electron Exchange in Spin-Labeled Metalloporphyrins

Sir:

Most spin-label studies of hemoglobin have involved attachment of a nitroxyl radical to the β-93 sulfhydryl group or to reactive sites on the periphery of the porphyrin ring of the heme group. The first published suggestion that there could be observable interaction between a nitroxyl spin label and a paramagnetic transition metal in a spin-labeled molecule was made by Symons in the discussion of a paper by McConnell and Boeyens.[1] At that time no interaction had been detected.[1] Subsequently a large number of papers reported changes in the nitroxyl EPR spectrum upon changing the oxidation state and/or spin state of the iron in hemoglobin. Definite interaction between the heme iron and the nitroxyl spin label was established in a series of papers by Asakura and coworkers.[2] They observed that, when spin labels were attached to the propionic acid side chains of the heme group in hemoproteins, changes in the spin state of the iron caused changes in the amplitude of the nitroxyl EPR spectrum.[2a] Interpretation as dipolar interaction effects in accordance with Leigh's treatment[3] resulted in estimates of the distance between the iron and the nitroxyl in a variety of hemoproteins.[2]

In this paper we report observation of exchange interaction between copper and a nitroxyl radical in a spin-labeled copper porphyrin.



The porphyrin I, reported by Dolphin,[4] was condensed with 4-amino-2,2,6,6-tetramethylpiperidinooxy free radical via the acid chloride of I to yield III. The crude III was purified by chromatography on silica gel, eluting with $CHCl_3$ and keeping the second band. The product was analytically pure and homogeneous by TLC ($CHCl_3$/alumina and $CHCl_3$/silica gel). A similar reaction yielded the amine analogue IV. The copper complex (V) of III was made by refluxing III with copper(II) acetate in pyridine or *N,N*-dimethylformamide. Purification by repeated recrystallization from $CHCl_3$/hexane yielded analytically pure V. The copper complexes VI and VII of the porphyrins II and IV were prepared similarly. Details of the preparation and characterization of these compounds will be reported in a subsequent paper.

The EPR spectra of the spin-labeled and non-spin-labeled copper porphyrins are presented in Figure 1. The EPR spectra of the copper porphyrins VI and VII are essentially identical, indicating that the mere change from H to O on going from VII to V would not be expected to give observable changes in the Cu EPR spectrum in the absence of copper-nitroxyl interaction. The high-field copper hyperfine line in the spectra of VI and VII exhibits superhyperfine splitting from the porphyrin nitrogens (expected intensity ratio 1:4:10:16:19:16:10:4:1).[5] The EPR spectrum of the spin-labeled porphyrin III consisted of the well-known three-line pattern ($a_N \approx 15.9$ G), each line of which was further split by coupling to hydrogens in the piperidine moiety. The high-field multiplet was significantly

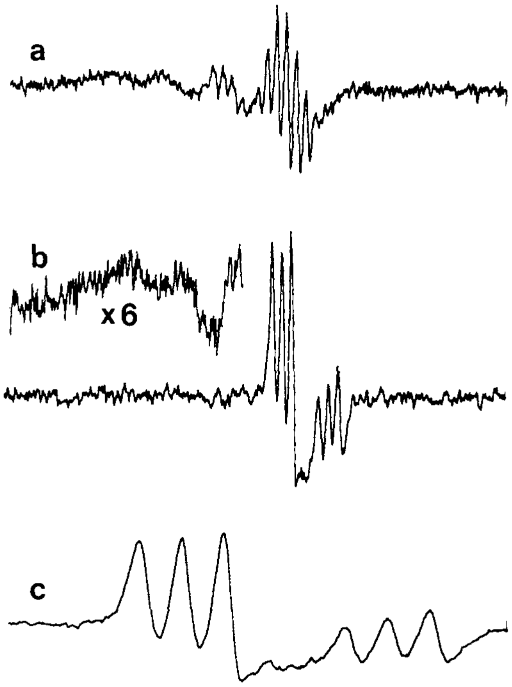


Figure 1. X-band EPR spectra of copper porphyrin complexes in $CHCl_3$ solution at ~21 °C: (a) copper porphyrin complex VI, 1000-G scan, (b) spin-labeled copper porphyrin complex, V, 1000-G scan, and (c) V, 200-G scan of nitroxyl region. All spectra were obtained at power levels well below saturation, using modulation amplitudes which did not cause observable broadening, on solutions sufficiently dilute that intermolecular exchange did not cause observable broadening.

broadened by incomplete motional averaging.[6] The EPR spectrum of the spin-labeled copper porphyrin V is substantially different from a superposition of the spectra of III and VII, exhibiting a doublet of triplets in the nitroxyl region and a greatly broadened copper spectrum. Integration of the spectrum relative to the spectra of III and VII indicates that the area is equivalent to two unpaired electrons. The splitting pattern in the nitroxyl region can be interpreted as an "AB"-type pattern (by analogy with NMR nomenclature[7]). The splitting between the two triplets is 77 G (0.0072 cm^{-1}). The g-value differences for copper porphyrin and nitroxyl correspond to a $\Delta g \approx 150$ G. Using the standard formulae for interpretation of AB spectra,[7] the intensities of the spectral components are predicted to be in the ratio of 3:1, as observed. J varied from 77 G in $CHCl_3$ to 92 G in CS_2, with no obvious correlation with commonly cited solvent characteristics.

Reduction of the nitroxyl by addition of phenylhydrazine[8] converts the spectrum of V to that of VII.

Preliminary results for related complexes indicate that the metal-nitroxyl interaction is very sensitive to the details of as yet unidentified molecular parameters. For example, replacement of the amide linkage in III by an ester linkage (VIII) yields a spectrum which does not have any features identifiable as "nitroxyl". Reduction of VIII with phenylhydrazine also returns the spectrum to that of the nonnitroxyl analogue.

Owing to the clearly defined splitting of the nitroxyl region of the spectrum in V, the magnitude of the exchange interaction can be obtained directly. The extent to which dipolar interactions affect the EPR spectrum cannot be proven without further studies, which are in progress. The relative contributions of exchange and dipolar effects may be dependent on electron spin relaxation time and molecular tumbling correlation times as well as details of metal-nitroxyl distance and nature of the intervening bonds.[9] Thus the observation of exchange in these spin-labeled copper porphyrin complexes does not prove that exchange contributes to the line shape of the nitroxyl in spin-labeled hemoproteins. Nevertheless, interpretation should proceed cautiously, considering quantitative data on both the metal and the nitroxyl EPR spectra.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the National Institutes of Health (GM21156) for partial support of this research.

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Received March 4, 1977

Photochemical Reaction Pathways of Ruthenium(III) Complexes. Ultraviolet Irradiation of Tris(*N,N*-dialkyldithiocarbamato)ruthenium(III)

Sir:

The photochemical behavior of metal complexes with sulfur-coordinating ligands has received little attention.[1-4] The electronic absorption spectra of complexes with the MS_6 core are very rich, consisting primarily of intense charge-transfer bands which extend well into the visible region of the spectrum.[5,6] Therefore, the photochemistry of these complexes is expected to be characteristic of reactions from charge transfer excited states. For example, electron transfer from ligand to metal (CTTM) resulting in oxidized ligand dissociation and metal reduction is commonly found.[7] The reactivity of charge-transfer excited states is currently receiving considerable attention due in part to recent interest in photocatalysis[8] and solar energy conversion[9] and because few systematic studies have been done on complexes other than the cobalt(III) amines.[7] We are in the process of studying the charge-transfer photochemistry of metal complexes with sulfur-containing ligands[4] and report here the results of experiments which demonstrate the rich photochemistry of tris(*N,N*-dialkyldithiocarbamato)ruthenium(III), $Ru(R_2dtc)_3$, complexes.

Irradiation at $\lambda = 265$ nm[10] of $Ru(R_2dtc)_3$[11] where R = methyl or ethyl in $CHCl_3$, CH_2Cl_2, or C_6H_5Cl solution at 30 °C yields only two ruthenium-containing products, **1a** and **1b**, according to eq **1**.