

initial absorbance change following photolysis of (L)-FeTPP-Im allowed the quantum yield to be calculated. The results are given in Table I. The quantum yield of the photolysis of hemochromes is of the same order of magnitude as the yield for photodissociation of oxyhemoglobin.¹⁶

Hemochromes were previously reported to be photoinert.^{8,17} We believe that the failure to observe any photodissociation was due to the insufficient time resolution of conventional flash photolysis techniques. At the ligand concentrations required for total complex formation, the recombination reaction is completed within a few microseconds.

The rate constants for the recombination of nonhindered ligands with (L)-FeTPP complexes is found to vary in the reverse order of their pK_a values (Table I). The recombination rates of the additional ligands are higher when imidazole occupies the fifth coordination site as in FeTPP-Im complexes. This "trans effect" is particularly marked in the case of piperidine, which presents the largest pK_a difference with respect to imidazole. On the contrary, the rate constants for the recombination of α -substituted ligands do not show a clear dependence on the pK_a and steric hindrance is probably the limiting factor responsible for their lower reactivity.

More extensive studies of these reactions with other ferrous porphyrins are in progress, principally in order to determine the various parameters involved in the recombination kinetics of the axial bases.

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Electron Paramagnetic Resonance Spectra of Carbalkoxycarbenes. Geometric Isomerism in Ground-State Triplets

Sir:

We have observed the electron paramagnetic resonance spectra of the ground-state triplets carbomethoxy- and carbethoxycarbene (**2**, R = CH₃, C₂H₅) upon direct or photosensitized decomposition of the corresponding diazo esters (**1**) in frozen solutions or in vacuum-deposited, rigid matrices. These spectra indicate the presence of two similar but non-identical triplets, to which we assign the two rotameric structures, **2-c** and **2-r**. The carbalkoxycarbenes are the third class of methylenes to exhibit geometric isomerism, a phenomenon

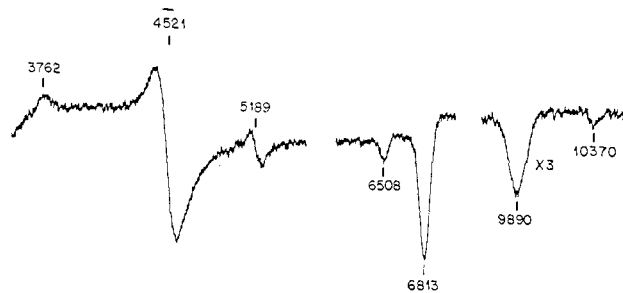
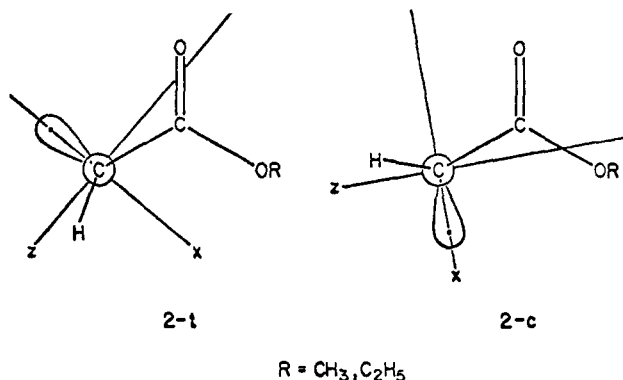


Figure 1. EPR spectrum of the isomeric carbomethoxycarbenes generated by benzophenone photosensitized irradiation of methyl diazoacetate in methylcyclohexane at 10 K. Fields are given in gauss: $h\nu/g\beta = 3305.1$ G. The low-field z line of the trans isomers is not observed. Its expected position (~ 3250 G) falls in the region of the spectrum which is obscured by an intense signal due to radicals produced during photolysis.

previously observed for the naphthylmethylenes¹ and for a series of vinylmethylenes.²

Beginning with the pioneering studies of Doering and co-workers,³ carbalkoxycarbenes have been among the most thoroughly investigated divalent-carbon intermediates.⁴ The overwhelming majority of the reported reactions are compatible with a singlet intermediate; in contrast, evidence for the involvement of the corresponding triplet states is scarce.⁵ Since no direct observation of either singlet or triplet state has been reported, the ground states cannot be identified unambiguously. The triplet state has been postulated as the ground state on the basis of extended Hückel calculations and of the nonstereospecific addition of **2** to *cis*-octene.^{5c} However, neither result is unequivocal since even sophisticated calculations substantially overestimate the relative energies of singlet carbenes⁶ and since the thermal population of a higher lying state cannot, in principle, be ruled out.⁷ The EPR data presented here provide unequivocal experimental evidence that the carbalkoxycarbenes have triplet ground states.

The EPR spectra of carbomethoxy- and carbethoxycarbene were observed upon direct irradiation or photosensitized decomposition of methyl or ethyl diazoacetate using either frozen solutions (methylcyclohexane, methyltetrahydrofuran, Nujol) or vacuum-deposited matrices (sulfur hexafluoride, acetophenone). Under comparable conditions the signal intensities of samples containing benzophenone or acetophenone were an order of magnitude higher than those of samples without a photosensitizer. The spectrum shown in Figure 1 is typical for both carbomethoxy- and carbethoxycarbene. The zero-field splittings are $D_t = 0.617$ and $E_t = 0.053$ cm⁻¹ and $D_c = 0.663$ and $E_c = 0.030$ cm⁻¹ for the two rotamers of carbomethoxycarbene and $D_t = 0.616$ and $E_t = 0.053$ cm⁻¹ and $D_c = 0.661$ and $E_c = 0.031$ cm⁻¹ for the two rotamers of carbethoxycarbene. The differences between methyl and ethyl derivatives are not significantly larger than the differences observed for any of the species in different matrices, $\Delta D \leq 0.002$ and $\Delta E \leq 0.001$ cm⁻¹. Variations of this magnitude are typical of the



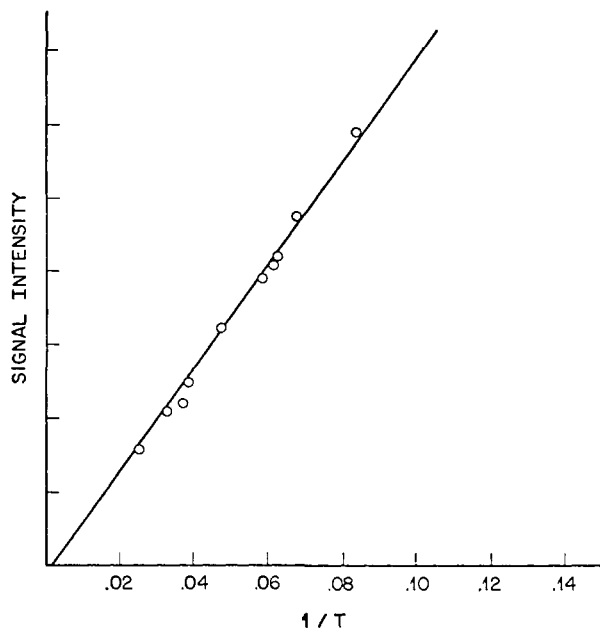


Figure 2. Signal intensity of the x line of *trans*-carbomethoxycarbene vs. $1/T$. Experimental results are shown as circles; the line represents the best linear least-squares fit of the data.

changes documented for triplets in different environments.⁸

The assignment of the zero-field parameters to the two rotamers is based on an analysis of the unpaired spin density distribution in these species.^{1,2} The zero-field parameter D is determined by the distance, r , between the two unpaired electrons and by the component of r along the z axis of the molecule.⁹

$$D \propto \langle (r^2 - 3z^2)/r^5 \rangle \approx \langle 1/r^3 \rangle$$

For the carbalkoxycarbenes D may be approximated as the sum of three terms due to point spins at the divalent carbon (C_1) and at the carbon (C_2) and oxygen atoms of the carbonyl moiety. By far the most important contribution to D is due to the spin density at the divalent carbon atom; this contribution should be the same for both isomers and is responsible for the order of magnitude of their D values. The average D value of the carbalkoxycarbenes (0.640) is lower than that of methylene (0.75; localized π electron)¹⁰ but considerably higher than that of diphenylmethylene (0.405; delocalized π electron)¹¹ indicating a π spin density, ρ , ~ 0.85 , for the divalent carbon atom. This value is in good agreement with the π spin densities of the carboxymethyl¹² and alkanonyl radicals¹³ as indicated by their hyperfine coupling constants.

The second contribution to D , due to the spin density at the carboxyl carbon (C_2), should be similar for both isomers because the position of C_2 relative to the z axis is similar. This contribution can be expected to be small because the spin density at C_2 should be low; the analogy to alkanonyl radicals suggests $\rho_2 \approx -0.05$ since the alkanonyl oxygen has been assigned the value, $\rho_3 \approx 0.2$, on the basis of an ^{17}O hyperfine coupling constant.¹³

The third contribution to D has its origin in the π spin density on the carbonyl oxygen. This contribution provides the key to the assignment of the zero-field parameters to the two rotamers. A large negative contribution is expected for the *trans* isomer; r_{CO} is approximately parallel to z ; therefore, $z \approx r$ and $\langle (r^2 - 3z^2)/r^3 \rangle \approx -2z^2/r^3$. In contrast, the analogous contribution to the *cis* isomer is small since $r^2 - 3z^2 \approx 0$. Based on this consideration, the *trans* isomer is assigned the lower value of D and the *cis* isomer is identified as that with the higher D value.

The observation of geometric isomerism excludes a linear arrangement of the substituents at the divalent carbon atom and, thus, is direct evidence for a bent structure.^{1,2} The approximate angle can be derived from the ratios E/D .¹¹ For the rotamers of the carbalkoxycarbenes these ratios are of the same magnitude as those of the vinylmethylenes and of most aromatic methylenes indicating angles near 140° .

The electron spin multiplicity of the ground state of a carbene may be determined from the temperature dependence of the intensity of its EPR signals. A ground-state triplet will follow the Curie law; i.e., the EPR intensity will vary linearly with $1/T$. In contrast, the $1/T$ plot of a thermally populated triplet will deviate from linearity.¹⁴ For the carbalkoxycarbenes the x and y lines of the spectra assigned to the *trans* isomers are sufficiently strong to allow a meaningful study of their temperature dependence. These signals show the linear relation (Figure 2) expected for a ground-state triplet or for a triplet state that lies a maximum of 10 cal above the singlet state.¹⁵ The observed changes are reversible in the temperature range of 10–40 K. At higher temperatures, the signals vanish irreversibly, presumably by reaction of the triplet with the matrix or by conversion of the triplet state to a more reactive state capable of undergoing intra- or intermolecular reactions. An interconversion of the geometric isomers is not observed under these conditions; apparently, the energy of activation for the reaction is lower than that for isomerization.

In conclusion, we note that the results reported here do not answer all questions concerning the chemistry of carbalkoxycarbenes; in fact, they pose several new ones. Nonetheless, we regard the observation of geometric isomerism for these species and the assignment of a triplet ground state to at least one of the isomers as a significant contribution toward the understanding of carbalkoxycarbene chemistry.

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