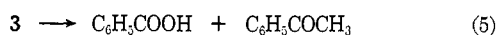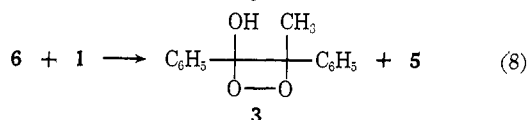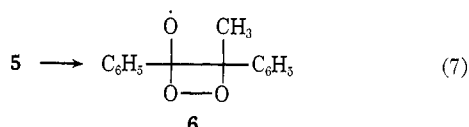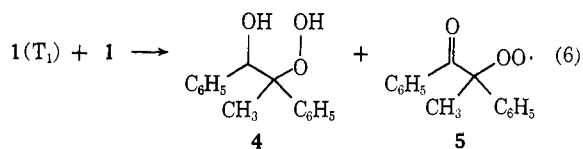Figure 1. Quantum yields as a function of initial concentration in the photolysis of 1,2-diphenyl-2-hydroperoxy-1-propanone in degassed carbon tetrachloride.

Figure 2. Stern–Volmer plot for the piperylene quenching of 1,2-diphenyl-2-hydroperoxy-1-propanone in degassed carbon tetrachloride, where $^0\Phi/\Phi$ = (% reaction without piperylene)/(% reaction with piperylene) and the slope = $k_q\tau$ = 3.90 M^{-1}.

Quantum yields for **1**, determined relative to a benzophenone–benzhydrol actinometer,[11] were found to be concentration dependent. The Φ values ranged from about 0.47 at 0.0250 M **1** to 1.44 at 0.480 M **1**. Kinetically higher order processes in Scheme II are

Scheme II

$$1(T_1) + 1 \longrightarrow 4 + 5 \quad (6)$$

$$5 \longrightarrow 6 \quad (7)$$

$$6 + 1 \longrightarrow 3 + 5 \quad (8)$$

$$3 \longrightarrow C_6H_5COOH + C_6H_5COCH_3 \quad (5)$$

$$6 + 4 \longrightarrow 3 + 1 \quad (9)$$
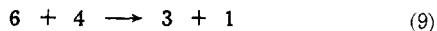
proposed to explain this result *in addition* to the unimolecular processes in Scheme I. Some steps in Scheme II are analogous to those proposed earlier by Walling and Gibian for the benzophenone sensitized decomposition of *tert*-butyl hydroperoxide.[12] A steady-state treatment on the combined Schemes I and II reveals that a reciprocal plot (Figure 1) is most informative. The data follow the curved line, while the straight line corresponds to the hypothetical result if Scheme II is solely operative but without the chain propagation step (eq 8). The actual data clearly deviate from this latter prediction, and, at concentrations of 0.05 M or less of **1**, the slope is zero which is indicative that only Scheme I is functional. Here, the limiting quantum yield is 0.47. Deviation from the hypothetical straight line at higher

concentrations of **1** is then indicative of the importance of chain propagation (eq 8).

Quenching studies with piperylene were carried out at 0.050 M **1**, where only the unimolecular processes (Scheme I) are important and the results are shown in Figure 2. From the slope and a calculated[13] diffusion controlled rate coefficient (k_q) of 7.55 × 10^9 M^{-1} sec^{-1}, the lifetime of **1** (T_1) is then 5.2 × 10^{-10} sec. With the usual assumption that $k_r \gg k_d$ (Scheme I),[1] k_r = 1.9 × 10^9 sec^{-1}, a value which is two orders of magnitude greater than that reported for α,α-dimethylbutyrophenone.[7] This rate acceleration is in qualitative agreement with hydrogen atom abstraction by *tert*-butoxy radicals[1] from an OO–H vs. a C–H bond.[2a] Other aspects of the type-II reaction with α-hydroperoxy ketones are currently under investigation.

(13) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 95.

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(11) (a) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962); (b) T. R. Evans in "Technique of Organic Chemistry," Vol. 14, P. A. Leermakers and A. Weissberger, Ed., Interscience, New York, N. Y., 1969, p 331.
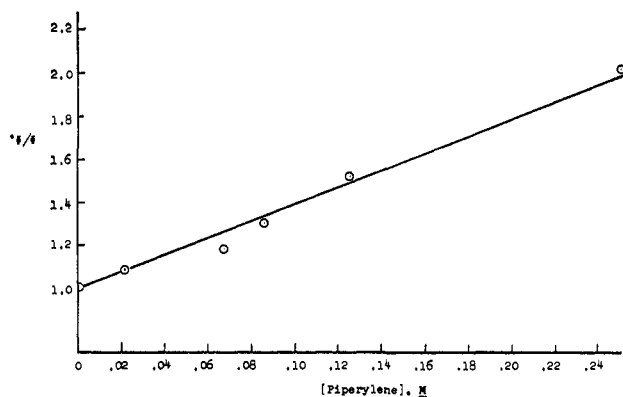(12) C. Walling and M. G. Gibian, *J. Amer. Chem. Soc.*, **87**, 3413 (1965).

Electron Paramagnetic Resonance of Mononuclear Cobalt Oxygen Carriers Labeled with Oxygen-17

Sir:

The structure of oxygen carriers, both natural and synthetic, and in particular the nature of the metal–oxygen bond has been a subject of controversy ever since Pauling and Coryell[1] proposed that the M–O–O unit was linear in oxyhemoglobin. Subsequently Pauling[2] proposed a bent structure and Griffith[3] a π-bonded structure with equivalent oxygens equidistant from the metal atom. It is conceivable that for a given complex the energy difference between the two forms is small, and environmental factors may influence which of the forms is more stable. The crystal structure of a mononuclear

(1) L. Pauling and C. D. Coryell, *Proc. Nat. Acad. Sci. U. S.*, **22**, 210 (1936).
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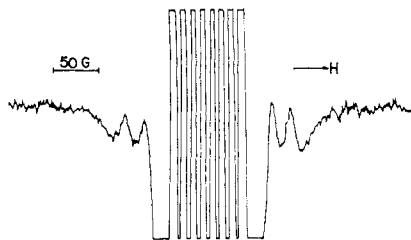(3) J. S. Griffith, *Proc. Roy. Soc., Ser. A*, **235**, 23 (1956).

Figure 1. Second derivative X-band esr spectrum of Co(bzacen)-pyO$_2$, containing 33 atom % ^{17}O, in CH$_2$Cl$_2$ solution at *ca.* − 30°.

Figure 2. Experimental and computer simulated second derivative X-band esr spectrum of Co(bzacen)pyO$_2$, containing 95 atom % ^{17}O, in CH$_2$Cl$_2$ solution at *ca.* − 30°.

oxygen carrier Co(bzacen)pyO$_2$ has been determined[4] and the M–O–O bond found to be bent, with an angle of 126 ± 2°. We now wish to report esr measurements on the complex in solution.

Co(bzacen)pyO$_2$ was synthesized with 33 atom % ^{17}O and 95 atom % ^{17}O using O$_2$ gas enriched in ^{17}O (Yeda, Rehovoth, Israel). The second derivative esr spectra in CH$_2$Cl$_2$ are shown in Figures 1 and 2. The spectra are insensitive to the addition of a considerable excess of pyridine. The experimental temperatures were chosen to give maximum resolution. At higher temperatures spin–rotational line broadening obscures the hyperfine structure, as does modulation of the *g* and hyperfine tensors at lower temperatures. The ratio of unlabeled and singly and doubly ^{17}O labeled molecules in the complex enriched to 33 atom % of ^{17}O is 4/9: 4/9:1/9, respectively. The intensities of the satellites from the two ^{17}O nuclei in the doubly labeled molecules are much less than those from the singly labeled molecules, and therefore only the latter contribute to the observed spectra under our experimental conditions. The outermost ^{17}O satellites therefore have a separation of $7a_{Co} + 5a_{O_1}$, where a_{O_1} is the unique or larger value of a_O, depending on whether the ^{17}O nuclei are equivalent or not. The value of $|a_{Co}|$ was found, from the spectrum of the isotopically normal complex, to be 12.8 G. The total spread of the spectrum, 198 G, leads to a value of $|21.7|$ for a_O, or a_{O_1}.

The complex synthesized from 95 atom % ^{17}O is a superposition of hundreds of lines due to the unlabeled and singly and doubly labeled molecules which are present in the ratios of 0.001:0.018:0.810. The spectrum was therefore simulated on the computer for a wide range of values of a_{O_1} and a_{O_2}. A satisfactory simulation requires the taking into account of the m_I dependent line widths of the esr lines due to modulation of the *g* and hyperfine tensors by tumbling. To calculate the relative line widths, it is necessary to know the *g* tensor and the anisotropic ^{17}O and ^{59}Co hyperfine tensors. The ^{59}Co tensor can be taken, on the basis of much previous work, as being effectively isotropic.[5] The ^{17}O tensors can be confidently estimated from the assumed values of a_{O_1} and a_{O_2}, by using the equation $a_O = 41\rho_O$ to estimate the spin densities[6] and taking the anisotropic ^{17}O splitting for an electron in a 2p orbital, $2\beta(^{17}$O), to be -103 G.[7] This procedure has been shown to be consistent with the known data for the

peroxyl group.[8] The *g*-tensor was estimated from that for the peroxyl group,[8] but the results are comparatively insensitive to the exact values taken. The esr spectrum of the 95% ^{17}O enriched complex was simulated for a very wide range of values of a_{O_1}, a_{O_2}, and τ_c, the rotational correlation time for molecular tumbling. The best fit to the experimental spectrum, shown in Figure 2, was obtained for $|a_{O_1}| = |a_{O_2}| = 21.6$ G, $\tau_c = 10^{-12}$ sec, and natural line width (m_I (independent)) = 16 G. *It should be noted that the range over which the values of $|a_O|$ could be allowed to stray from 21.6 g without causing marked differences between the observed and simulated spectrum was no more than ±0.5 G.* For unsymmetrically bonded peroxy groups the values of $|a_O|$ for the unequivalent oxygens fall in the range 16–18 G and 22–24 G.[8,9]

The present esr results are consistent with a complex containing magnetically equivalent oxygen atoms.

It is possible that this equivalence reflects a π-bonded symmetrical structure or that the observed equivalence in solution is the result of a rapid flipping of the O–O group between two bent positions. A dynamic equilibrium would result in line width effects of a kind which we found unnecessary to take into account to give excellent computer simulations of the experimental spectra.

Further work is in progress on this and other synthetic and natural oxygen complexes containing porphyrin ligands in solution. Preliminary results indicate that in all cases so far studied the oxygens are magnetically equivalent.

(8) (a) E. Melamud and B. L. Silver, *J. Magn. Resonance*, in press; (b) E. Melamud, S. Schlick, and B. L. Silver, *ibid.*, in press.
(9) K. Adamic, K. U. Ingold, and J. R. Morton, *J. Amer. Chem. Soc.*, **92**, 922 (1970).

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(4) G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972).
(5) (a) A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 55 (1970); (b) B. M. Hoffmann, D. L. Diemente, and F. Basolo, *ibid.*, **92**, 61 (1970).
(6) E. Melamud and B. L. Silver, *J. Phys. Chem.*, **77**, 1896 (1973).
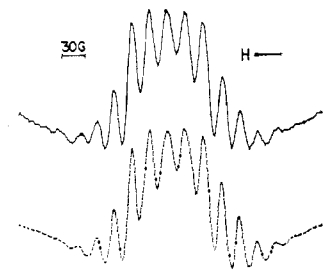(7) J. R. Morton, J. R. Rowlands, and D. H. Whiffen, *Nat. Phys. Lab.*, (*U.K.*) *Circ.*, No. BPR 1.3 (1970).

Triboluminescence of Coumarin. Fluorescence and Dynamic Spectral Features Excited by Mechanical Stress

Sir:

The excited state origins of triboluminescence (TL), the emission of light caused by the mechanical deforma-