Found: V, 12.0; P, 14.9; Na, 12.1; H, 2.6. Esr of a solution of the solid gave the 22-line spectrum described above. The esr of a glycerol–water solution at −170° showed a complicated spectrum in the vicinity of $g = 2$, and a single strong feature at approximately 1650 G. The latter, which most likely corresponds to a $\Delta m_S = 2$ transition, and some preliminary magnetic susceptibility studies ($\mu_{\text{eff}} = 3.6$ BM) suggest that the trimer contains three unpaired electrons.

Since the solution esr spectrum at room temperature shows an uncomplicated 22-line pattern, the three unpaired electrons must be relatively strongly coupled so that the exchange term in the spin Hamiltonian

$$\sum_{i \neq j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

is large compared with the hyperfine terms. This situation is analogous to that observed for the vanadyl *dl*-tartrate dimer where the V–V distance is 4.08 Å. In the vanadyl *d*-tartrate dimer, the V–V distance is larger, 4.35 Å, and the exchange coupling is smaller, resulting in a much more complex spectrum.[1]

Since the three vanadium nuclei are magnetically equivalent and apparently in rather close proximity, a cyclic structure is suggested with each pyrophosphate acting as a bidentate ligand with each of two vanadyl ions. Further work on this and related systems is in progress.

Acknowledgment. Valuable discussions with Professor J. O. Edwards are gratefully acknowledged. This work was supported by the National Science Foundation through Grants No. GP-7811 and GP-8536.

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α-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N*-*tert*-butylnitrone. A Novel Probe for Radical Detection and Identification

Sir:

The detection and identification of short-lived free radicals by electron spin resonance trapping techniques has recently received wide attention.[1–5] Janzen and coworkers[3–5] showed that nitrones (*e.g.*, phenyl-*tert*-butylnitrone) function as convenient probes for studying, in solution, the mechanisms of reactions which involve short-lived radical intermediates. Nitrones react with short-lived radicals to produce stable nitroxide radicals ("spin adducts").[6] The magnitude of the β-hydrogen and nitrogen hyperfine couplings (hfc) of the spin adduct define the structure of the trapped radical.

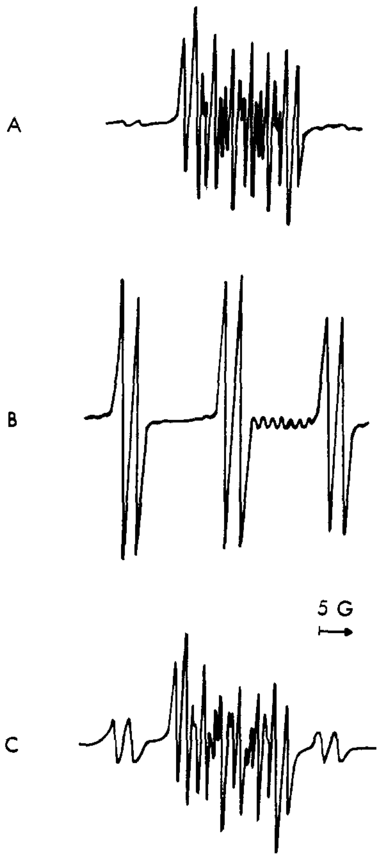

Figure 1. (A) The esr spectrum of II obtained by reaction of benzoyloxy radical from thermal decomposition of benzoyl peroxide in benzene at 70° with nitrone I. (B) The esr spectrum of the phenyl spin adduct of nitrone I obtained from phenyl radicals generated from the thermal decomposition of PAT at 70°. (C) The esr spectrum obtained from the thermal decomposition of benzoyl peroxide in benzene at 70° in the presence of nitrone I.

We report that α-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-*tert*-butylnitrone[7] (I) serves as a novel probe for differentiation between oxy radicals and carbon radicals.[9] Some preliminary results with known radical sources are presented in Table I. The concentrations of the radical sources and the nitrone were *ca.* 0.01 and 0.1 *M* in benzene, respectively, except where otherwise noted. The samples were purged with dry nitrogen for several minutes prior to thermolysis or photolysis. The stable radicals produced were detected and identified by esr analysis of the reaction mixtures at room temperature.[10] The color changes, in initially colorless solutions, upon reaction of the nitrone and the short-lived species, gave a qualitative indication of the reaction course. Solutions in which only phenoxyl radicals

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(6) The term "spin adduct" designates the addition product of the reaction of the short-lived radical and the nitrone.[3–5]

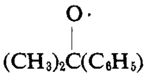
(7) I was prepared in 92% yield by reaction of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (Aldrich Chemical Co., Inc.) with *N*-*tert*-butylhydroxylamine[8] in ethanol. The compound is a white, crystalline solid: mp 200° dec; ir (CHCl$_3$) 3640 cm^{-1} (s, OH); nmr (CDCl$_3$) 1.45 (s, 18 H), 1.58 (s, 9 H), 5.60 (s, 1 H), 7.40 (s, 1 H), and 8.17 ppm (s, 2 H). *Anal.* Calcd for C$_{19}$H$_{31}$NO$_2$: C, 74.71; H, 10.23; N, 4.58. Found: C, 74.57; H, 10.23; N, 4.55.

(8) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957).

(9) The terms "oxy radical" and "carbon radical" refer to radicals in which the odd electron is primarily localized on an oxygen atom and on a carbon atom, respectively.

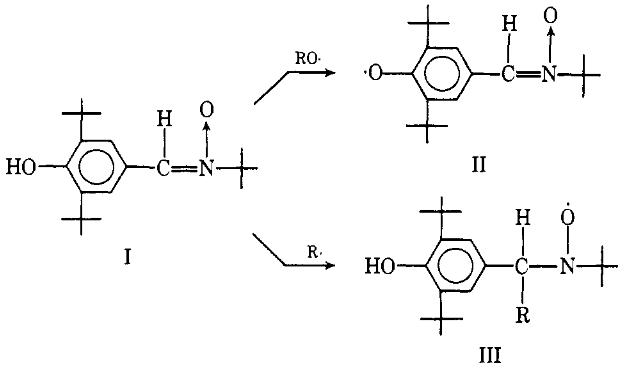
(10) The esr spectra were recorded in standard esr sample tubes with the Varian Associates V-4500-10 EPR spectrometer by using 100-kHz modulation at a frequency of about 9300 MHz.

Table I. Trapping of Short-Lived Radicals With Nitrone I

Radical source and conditions	Radical	Product	Hyperfine coupling constants, G		
			A_N	A_β^H	A_m^H
Phenylazotriphenylmethane (PAT) 28–80°, benzene	$C_6H_5\cdot$	Nitroxide	14.6	2.3	
Azobisisobutyronitrile (AIBN) 28–80°, benzene	$(CH_3)_2\dot{C}CN$	Nitroxide	13.4	3.7	
Benzophenone,[a] 3660 Å light in benzene[b]	$(C_6H_5)_2$—$\dot{C}O$	Phenoxyl	5.05	2.60	1.70, 1.50
Benzophenone,[a] 3660 Å light in isopropyl alcohol[b]	$(CH_3)_2\dot{C}OH$	Nitroxide	15.5	4.2	
Dicumyl peroxide 90°, benzene	 $(CH_3)_2\overset{O\cdot}{\overset{\vert}{C}}(C_6H_5)$	Phenoxyl	5.05	2.60	1.70, 1.50
Benzoyl peroxide 60–80°, benzene[c]	$C_6H_5COO\cdot$	Phenoxyl[d]	5.05	2.60	1.70, 1.50
	$C_6H_5\cdot$	Nitroxide	14.6	2.3	
Acetyl peroxide 60–80°, benzene	$CH_3COO\cdot$	Phenoxyl	5.05	2.60	1.70, 1.50
	$CH_3\cdot$	Nitroxide	15.0	3.6	

[a] Benzophenone concentration was 0.1 *M*. [b] Medium-pressure mercury-arc (GE H 100 PSP 44-4) with Corning filter kit No. 7-83 was used. [c] Nitrone concentration was 0.05 *M*. [d] Phenoxyl radical/nitroxide ratio was *ca.* 3/1.

were formed became blue upon reaction, whereas the solutions containing nitroxyl radicals became yellow-orange. The short-lived oxy radicals abstracted the phenolic hydrogen of the nitrone (Table I) to produce the stable phenoxyl radical II, whereas the short-lived carbon radicals preferentially added to the α carbon of the nitrone I to yield a stable nitroxide III. These results show that reaction with the nitrone I will distinguish between a short-lived oxy radical and a short-lived carbon radical.



The 18-line phenoxyl radical spectrum (Figure 1A) is attributable to hfc of the electron to the nitrogen and to the HC=N proton, with secondary, inequivalent splittings by the two aromatic protons (A_N = 5.05 G, A_{CH} = 2.60 G, A_m^H = 1.50 and 1.70 G).[11] These splittings are consistent with values obtained for similar phenoxyl radicals.[12,13] The spectra of the nitroxides (Figure 1B) were consistent with hfc of the β-hydrogen with nitrogen.[3–5]

The results obtained on the photolysis of benzophenone in benzene and in isopropyl alcohol (Table I) warrant further discussion. II was the only radical detected in benzene. This result is reasonable, since hydrogen abstraction from suitable donors by the triplet state of benzophenone is a well-known phenomenon.[14] The absence of the nitroxide radical shows that the initially formed benzophenone ketyl does not undergo addition to I.[15] Unlike the benzophenone ketyl, the 2-hydroxypropyl radical, formed during photolysis of benzophenone in isopropyl alcohol, added to I. Although the nitroxide radical III, where R is $(CH_3)_2\dot{C}OH$, was the major product, a small amount (<1%) of the radical II was observed.[16]

The results obtained on the thermal decomposition of benzoyl peroxide and acetyl peroxide are of particular interest. For benzoyl peroxide, both hydrogen abstraction and addition occurred under the conditions used (Table I and Figure 1C). Hydrogen abstraction occurred *via* direct abstraction of the phenolic hydrogen by the benzoyloxy radical. Addition occurred *via* decarboxylation of the benzoyloxy radical and subsequent spin trapping of the resulting phenyl radicals. The relative amounts of the phenoxyl and nitroxide radicals were dependent on the initial concentration of the nitrone I. That is, at a nitrone concentration of 0.15 *M*, the initially formed benzoyloxy radical quantitatively abstracted hydrogen from the nitrone to produce the phenoxyl radical II (Figure 1A). However, when the concentration of I was reduced to 0.015 *M*, significant decarboxylation of the benzoyloxy radical occurred, with spin trapping of the resulting phenyl radical (Figure 1C). Earlier studies[17–22] suggest that acetoxy radicals produced from the thermal decomposition of acetyl peroxide in solution undergo cage decomposition

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(11) The inequivalency obtained for the two aromatic protons is a result of steric interaction of a ring proton with the oxygen atom of the nitrone group.

(12) R. W. Kreilick, *J. Amer. Chem. Soc.*, **88**, 5284 (1966).

(13) Samples of the pure phenoxyl radical II were obtained in high yield by oxidation of I with PbO_2 in ethyl ether. The radical was a blue, crystalline solid, mp (from benzene) dec above 175°, absorption spectrum $\lambda_{max}^{benzene}$ 375 (ϵ 6.7 × 10^4), 728 nm (ϵ 3.7 × 10^3).

(14) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 143.

(15) No evidence was observed for the addition of the benzophenone triplet to I. If addition occurred, a nonparamagnetic product resulting from a 1,3 cycloaddition would be anticipated. Further investigations are necessary to test this hypothesis.

(16) From these results and from the known rate constant for hydrogen abstraction from isopropyl alcohol by the triplet state of benzophenone (k_r = 2.0 × 10^6 l. mol^{-1} sec^{-1}), one can place an upper limit of *ca.* 1 × 10^6 l. mol^{-1} sec^{-1} on the rate constant for abstraction of hydrogen from I by the benzophenone triplet.

(17) M. Levy and M. Szwarc, *J. Amer. Chem. Soc.*, **76**, 5981 (1954).

(18) L. Herk and M. Szwarc, *ibid.*, **82**, 3558 (1960).

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at a rate ($k = 1.6 \times 10^9$ sec^{-1} at 60°)[22] comparable with that of diffusion from the solvent cage. Our preliminary results support the existence of a noncage acyloxy or acetoxy radical.[5,23–27] Directly analogous to our findings, Janzen[5] showed that an acetoxy radical has a sufficient lifetime to undergo spin trapping *via* addition to α-phenyl-*N*-*tert*-butylnitrone. Our results indicate that the acetoxy radical survives long enough to abstract the phenolic hydrogen from I.

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(25) D. B. Denney, R. L. Ellsworth, and D. Z. Denney, *ibid.*, **86**, 1116 (1964).

(26) R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *ibid.*, **87**, 3928 (1965).

(27) A direct reaction between I and the diacyl peroxides leading to II and acyloxy radicals may account for the observed results; however, others[28,29] have demonstrated that induced decompositions of peroxides by phenols occur *via* an ionic, nonradical-producing mechanism.

(28) C. Walling and R. B. Hodgdon, Jr., *J. Amer. Chem. Soc.*, **80**, 228 (1958).

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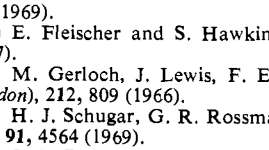
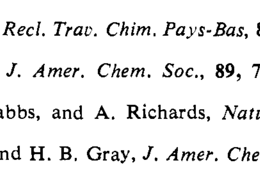
Preparation, Electronic Properties, and Structure of a Binuclear Iron(III) Complex Containing a Four-Membered Iron–Oxygen Ring

Sir:

Recently there has been a considerable amount of interest in oxygen-bridged complexes of iron(III) because of the spin exchange that is possible in such systems. Structures have been reported for complexes which have a triangular arrangement of three metal ions around a central oxide ion,[1] a linear M–O–M arrangement,[2] and a four-membered iron–oxygen ring;[3] evidence for a four-membered iron–oxygen ring in a hydroxide complex has also been presented.[4] Recent studies[5–7] of complexes of the type CuL (where H_2L represents imines I and II) have prompted the authors to investigate similar complexes of other metal ions. The



Ia, $n = 2$
b, $n = 3$



IIa, $n = 2$
b, $n = 3$

preparation of the iron(III) complex of IIa, FeLCl, was reported recently.[8]

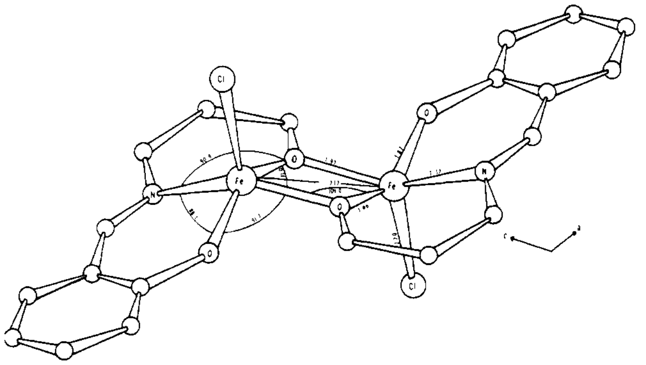


Figure 1. Perspective drawing of the dimer with all atoms except carbons labeled. Bond distances and bond angles about iron are shown; estimated standard deviations are about 0.04 Å for bond lengths and about 1° for bond angles.

Herein, the preparation, structure, and properties of the iron(III) complex of IIb are described. This complex was prepared by mixing iron(III) chloride and the Schiff's base in methanol; the compound was recrystallized from tetrahydrofuran. The crystals are monoclinic [$a = 9.85\ (2)$,[9] $b = 14.86\ (2)$, $c = 9.39\ (2)$ Å, and $\beta = 124.25\ (10)°$] of space group $P2_1/c$ (conditions for nonextinction: $0k0$, $k = 2n$; $h0l$, $l = 2n$) with two dimers per unit cell (density obsd, using carbon tetrachloride, 1.59 (2); calcd, 1.57).

Three-dimensional X-ray data were collected with a precession camera using Mo Kα radiation. A total of 418 unique, nonzero reflections from the hkl (k = 0–3) and hkl (l = 0–2) levels were obtained. Coordinates of the iron and chlorine atoms were obtained from successive calculations of the structure factors and electron density. With isotropic temperature factors (the largest temperature factor after refinement was 10.8) and with all reflections weighted at unity, the structure refined to a conventional R value of 0.12. Initially, only very small crystals were available for data collection; larger crystals have now been obtained and a more complete set of data will be collected for final refinement. However, the main features of the structure are apparent from the present refinement.

The dimer, which occupies a site of inversion symmetry, is shown in Figure 1. As in the copper complex of Ib,[5] the four-membered M–O ring is planar, the coordination of the bridging oxygen is planar (C_9 is only 0.08 Å out of the plane of the four-membered ring), and a delocalized π system is possible. The coordination of the iron can be described as square pyramidal—the three oxygens and the nitrogen form a planar base and the iron is 0.55 Å above this base.

The Mössbauer spectrum of this complex was measured at room and liquid nitrogen temperatures. The spectrum at each temperature, as the result of quadrupole splitting, consisted of two distinct lines. Table I presents the Mössbauer spectral parameters. The values for the quadrupole splitting, ΔE_Q, and the isomer shift, δ, are consistent with the formulation of the complex as one containing Fe(III) in the $S = {}^5/_2$ spin state and are similar to the Mössbauer parameters reported[10]

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