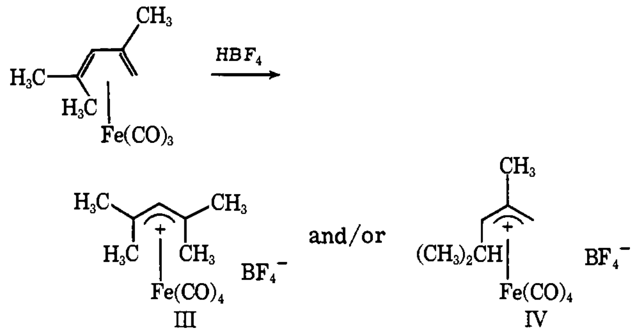

III

IV

stituent at C_2 if four additional ligands were bound to the iron atom.[12] Kaesz has further pointed out that some destabilization is expected in allyl complexes having anti substituents since these also would seriously interfere with an axial ligand in a pentacoordinate system.[1] As all of the cations listed in Table I possess one or both of these features, it seems that the steric limitations are not as stringent as earlier studies suggested.

From earlier work as well as our own observations of the changes which occur in the $\nu_{C\equiv O}$ region of the infrared spectrum during these reactions, it seems clear that protonation of the diene precedes carbon monoxide transfer. If it can be assumed that the geometry of a tricarbonyl cation is closely related to that of the corresponding diene complex, then the easiest way to convert the system to a trigonal bipyramid would seem to involve a path in which the entering carbon monoxide ligand assumes an axial position which is syn to C_2 of the allyl ligand. Systems which possess a substituent at this position should be slower to react than those which merely have an anti 1 substituent. In line with this the reaction which yields cation IV is somewhat slower than the ones which yield I and II but the slowest reaction yet examined is that of tricarbonyl-2,3-dimethyl-1,3-butadieneiron[13] in which cation V is obtained. A yield of only 5% is obtained after 3.5 hr.

We are now studying other dienes in hopes of establishing the steric limitations as well as the mechanism of the disproportionation reactions.

Acknowledgment. We thank the Research Corporation and the University of Louisville Arts and Sciences Research Committee for financial support of this work and American Standard for a Beckman IR-12 infrared spectrometer.

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[12] A. N. Nesmayanov, Yu. A. Ustynyuk, I. I. Kritskaya, and G. A. Schembelov, *J. Organometal. Chem.*, **14**, 395 (1968).

[13] We thank J. D. Smith for the preparation of this compound.

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Lattice Control of Free Radicals from the Photolysis of Crystalline Acetyl Benzoyl Peroxide[1]

Sir:

It is well known that homolysis of diacyl peroxides can open a Pandora's box of products especially under conditions where induced decomposition is important.[2] Thermolysis or photolysis of acetyl benzoyl peroxide (ABP) as a neat liquid at 60–80° gives a number of products resulting from induced decomposition which are absent after comparable homolysis in chlorobenzene solvent.[3] The first 11% of thermolysis of undiluted ABP is unusually rapid and gives 25% of the induced decomposition product, toluene, which is formed in only 2% yield in chlorobenzene solvent. Conversely, the geminate radical coupling product, methyl benzoate,[4] which accounts for 21% of the solution products, is formed in only 3% yield.

The crystal lattice of an azoalkane can exert a powerful influence over radicals generated by photolysis of the crystalline solid.[1a,5] An analogous influence appears in the photolysis of solid ABP.[6] When exposed to 2537-Å light[7] for 25 hr in an evacuated quartz tube at −69 to −72°, 200 mg of crystalline ABP (mp 36.5–37.5°) softened and coalesced appreciably. Iodometric titration,[8] gas evolution, and pmr analysis showed decomposition to be 15–17% complete. Pmr in CCl_4 showed methyl benzoate and toluene (in the ratio of 1.8:1) as the only detectable products. These products would be expected from cage coupling of methyl with benzoyloxy and phenyl radicals, respectively, since the lifetime of the radical pair in the solid could be sufficient to allow appreciable decarboxylation of the benzoyloxy radical.[4,9]

However, toluene might be formed in the solid by an induced pathway, as it is in the melt, and the possibility that methyl benzoate might also arise by an induced pathway in the solid was especially intriguing in light of the crystal structure of ABP.[10] The acetyl peroxy and benzoyl peroxy groups of ABP are each essentially planar with a synclinal torsional angle of 80° about the peroxide bond. The molecules pack about a screw axis in space group $P2_1/c$ as shown in Figure 1. Dashed lines in Figure 1 indicate intermolecular van der Waals contacts (3.45 Å) between methyl groups and the benzoyl oxygen atoms of molecules related by the screw axis.[11] A methyl radical could attack such a neighbor-

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(1) (a) Solvent Steric Effects. VII. For part VI see K. J. Skinner, R. J. Blaskiewicz, and J. M. McBride, *Israel J. Chem.*, in press. (b) We thank the National Science Foundation for support of this research under Grant No. GP-14607.

(2) See, for example, D. F. DeTar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967), and references therein.

(3) C. Walling and Z. Čekovič, *ibid.*, **89**, 6681 (1967); *cf.* M. M. Schwartz and J. E. Leffler, *ibid.*, **93**, 919 (1971).

(4) The observation of CIDNP in the products of decomposition of ABP in tetrachloroethylene solution demonstrates that *both* methyl benzoate and toluene can be formed by radical recombination in the solvent cage: A. I. Buchachenko, S. V. Rykov, A. V. Kessenikh, and G. S. Bylina, *Dokl. Akad. Nauk SSSR*, **190**, 839 (1970); *Dokl. Chem.*, **190**, 101 (1970).

(5) A. B. Jaffe, K. J. Skinner, and J. M. McBride, *J. Amer. Chem. Soc.*, in press.

(6) The effect of decomposition in the solid state has been studied with acetyl peroxide where photolysis in the solid was accompanied by a dramatic increase of ethane over methane as a product compared to photolysis in solution: O. J. Walker and G. L. E. Wild, *J. Chem. Soc.*, **139**, 1132 (1937).

(7) We thank Professors Harry H. Wasserman and Willis B. Hammond for making their photochemical equipment available to us.

(8) In ethanol, V. R. Kokatnur and M. Jelling, *J. Amer. Chem. Soc.*, **63**, 1432 (1941).

(9) One guess[2] at the rate constant for decarboxylation of this radical is 10^4 sec^{-1}, but the lifetime of the cage could be long enough for this to occur: A. V. Zubkov, A. T. Koritskii, and Ya. S. Lebedev, *Dokl. Akad. Nauk SSSR*, **180**, 1150 (1968); *Dokl. Phys. Chem.*, **180**, 437 (1968).

(10) E. T. Koh and J. M. McBride, to be published. At −30°, the temperature of the diffraction study, the crystals grown from pentane at 5° had monoclinic cell constants $a = 8.405$, $b = 7.522$, $c = 14.064$ Å, $\beta = 82.88°$.

(11) Each methyl group is also in van der Waals contact with the acetyl oxygen of the molecule beneath (3.44 Å), with the para carbon of the benzoyl group of a molecule related by a different screw axis (3.74 Å), and with several aromatic hydrogens.

ing oxygen and thereby induce homolysis of the peroxide bond in the molecule attacked forming methyl benzoate. The resulting acetoxy radical could then decarboxylate, and continue an induced chain spiraling along the screw axis.

Such an intermolecular mechanism was excluded by photolysis of 200 mg of approximately equimolar solid solutions of ABP-d_8[12,13] in unlabeled ABP prepared by removing ether from a fluid solution of the two. After photolysis to 13% conversion at −65 to −70° and titration of the remaining ABP, methyl benzoate and toluene were extracted into pentane and analyzed by vpc–mass spectrometry. The molecular ions of toluene from one run consisted of 50.6% d_0, 3.5% d_7, and 44.5% d_8 with 1.4% of d_3 and d_5 cross-products. Those of methyl benzoate from another run consisted of 50.7% d_0, 3.5% d_7, and 45.3% d_8 with no more than 0.5% of d_3 and d_5 cross-products. Thus, 97% of the toluene and greater than 99% of the methyl benzoate were formed intramolecularly showing that the crystalline matrix suppresses the induced chain mechanisms prevalent in the melt.

The lattice could exert a more subtle influence by favoring attack of the methyl radical on one of the two oxygens of the geminate benzoyloxy radical. Within a molecule in crystalline ABP the methyl carbon is slightly closer to the acyl oxygen of the benzoyloxy group (3.68 Å) than to the carbonyl oxygen (4.13 Å), but it is difficult to predict which benzoyloxy oxygen should be more accessible to the methyl radical formed by acetoxy radical decarboxylation in the crystalline matrix. It is also difficult to assess the likelihood of oxygen equilibration by rotation of the carboxy group or of the whole benzoyloxy radical about its major axis. ABP-$^{18}O_2$ with 97 atom % ^{18}O in the peroxidic positions[14] was prepared by autoxidation[12b] under $^{18}O_2$. An 84-mg sample of this solid was photolyzed to 8% conversion and the product methyl benzoate analyzed as above. The molecular ion showed 98.3% $^{16}O^{18}O$ and 1.7% $^{16}O^{16}O$.[15] The ratio[15] of unlabeled (m/e 105) to ^{18}O-labeled (m/e 107) benzoyl fragments is 1.65, demonstrating a preference for coupling of the methyl radical with the formerly peroxidic oxygen (acyl coupling) over its coupling with the previously carbonyl oxygen (carbonyl coupling). The mass spectrum of methyl benzoate from a photolysis to completion of 21 mg of ABP-$^{18}O_2$ in 0.5 ml of absolute ethanol (0°) showed an m/e 105/107 ratio[15] of 1.01 indicating random coupling in fluid solution. The solid-state preference for acyl coupling is not limited to the crystal photolysis, since complete photolysis of 20 mg of ABP-$^{18}O_2$ in 0.5 ml of ethanol as a glass at 77°K gave an acyl/carbonyl coupling ratio[15] of 2.62.

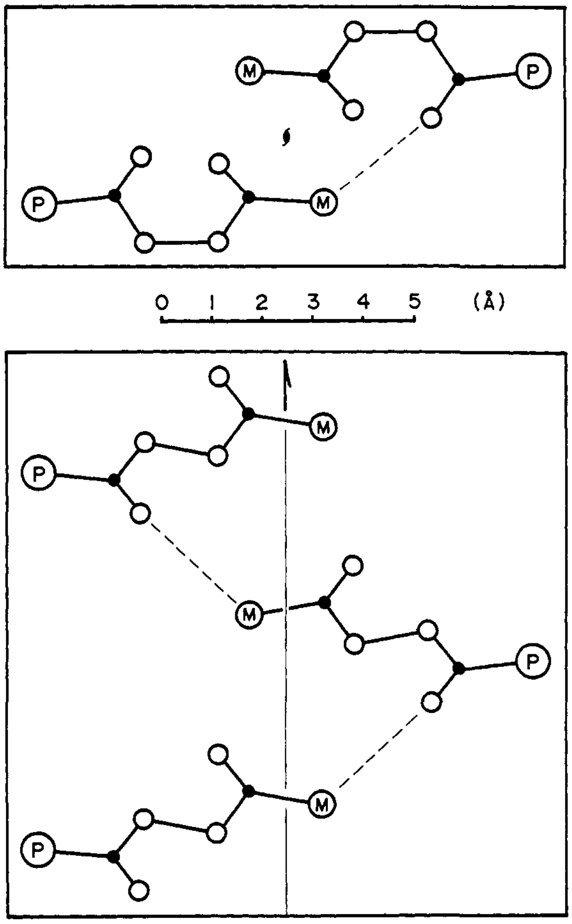

Figure 1. Top and side views of the crystal packing of ABP. Lower frame shows a family of molecules related by the indicated screw axis projected on (10$\bar{2}$) with [010] vertical. Upper frame shows molecules of the lower frame projected on (010) with (10$\bar{2}$) horizontal. Oxygens are denoted by open circles, carbonyl carbons by filled circles, methyl carbons by M, and C-1 of the phenyl rings by P. Dashed lines show the 3.45-Å contacts that might have led to induced methyl benzoate formation.

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(12) (a) Prepared by autoxidation[12b] of benzaldehyde-d_6[12c] in acetic acid-d_6;[12d] (b) C. Walling and E. A. McElhill, *J. Amer. Chem. Soc.*, **73**, 2927 (1951); (c) prepared by Ce(IV) oxidation of toluene-d_8, L. Syper, *Tetrahedron Lett.*, 4493 (1966); (d) A. Murray, III, and D. L. Williams, Ed., "Organic Synthesis with Isotopes," Part II, Interscience, New York, N. Y., 1958, p 1290.

(13) Mass spectral analysis of the methyl benzoate parent peaks showed 93% d_8–7% d_7, but the stronger benzoyl fragment showed 91%–9% d_4, implying that the methyl position was probably completely labeled. We thank Dr. Walter McMurray and Mr. Peter Arnesen for these measurements. The parent peaks of toluene gave 93% d_8–7% d_7.

(14) Mass spectral analysis of O_2 from permanganate oxidation of perchloric acid hydrolysate following treatment with sodium methylate; a modification of the procedure of J. C. Martin and S. A. Dombchik, *Advan. Chem. Ser.*, No. 75, 269 (1968). We thank Professor Martin for sending us a copy of the revised procedure.

(15) In light of the results in fluid ethanol below, we believe that the discrepancy between these numbers and those from peroxide oxygen analysis may be due to a small amount of scrambling during hydrolysis.[14] The 105/107 ratios reported below have been corrected for 1.7% $^{16}O^{16}O$ benzoate but not for any scrambling in the starting material before photolysis. Photolytic scrambling is negligible.

(16) (a) National Institutes of Health Predoctoral Fellow, 1968–1971; (b) Alfred P. Sloan Foundation Fellow.

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Nuclear Magnetic Resonance Studies of ^{13}CO Binding to Various Heme Globins

Sir:

Whether, and to what extent, the various subunits of hemoglobin interact differently with ligands (such as oxygen or carbon monoxide) remains one of the unanswered questions in the hemoglobin saga. These possible differences may manifest themselves in the kinetic or thermodynamic affinities for ligands or in the environments experienced by ligands when bound to various subunits.

We have studied the binding of ^{13}C enriched carbon