inconsistent with the complex also possessing an ionic ground state in solution.[14]

The measurements reported here are being extended and refined, and it is anticipated that they will be expanded to include other complexes having particular relevance to the question of ionic ground states.

(14) It should be noted in this regard, however, that ref 10 presents rather strong evidence for the complex being nonionic in solution.

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Received May 21, 1966

The Cage Recombination of Acetoxy Radicals to Yield Acetyl Peroxide

Sir:

The reactions within the solvent cage of radical pairs formed in the thermal decomposition of acetyl peroxide have been generally[1-3] credited with the formation of the observed methyl acetate and ethane. We wish to report evidence for an even more important cage reaction, the recombination of acetoxy radicals to yield acetyl peroxide.

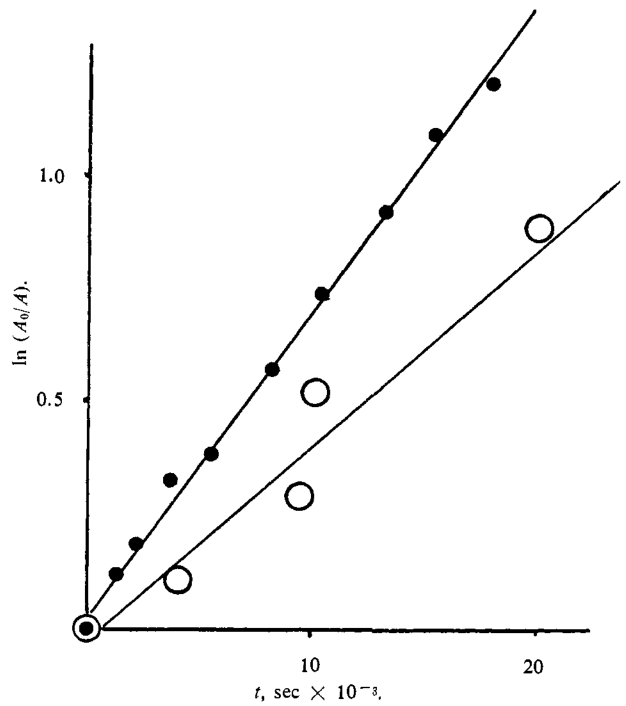

Figure 1. First-order rate plots for the disappearance of total acetyl peroxide (small circles, data obtained by infrared spectroscopy) and for scrambling of carbonyl label in recovered acetyl peroxide (large circles).

Acetyl peroxide initially labeled with oxygen-18 (0.6–1.5% excess), specifically in the carbonyl oxygen,[4] was recovered after partial decomposition at 80° in isooctane. Samples recovered after varying lengths of time were subjected to parallel treatment with samples of starting peroxide. A series of low-temperature recrystallizations from isooctane gave samples showing no infrared absorption in the 1700–1800 cm^{-1} region except that found in pure acetyl peroxide. These samples were identically treated with anhydrous methanolic sodium methoxide. The resulting methyl acetate was isolated by gas chromatography and assayed[5,6] for oxygen-18 by mass spectrometry. The starting peroxide gave methyl acetate from this treatment which invariably contained a level of label (calculated assuming one oxygen labeled per molecule) identical with that in the acetic anhydride from which it was made by treatment with unlabeled barium peroxide. The labeling of the methyl acetate therefore reflects the level of label in the carbonyl oxygen of the acetyl peroxide. Samples recovered after increasingly lengthy periods of heating gave methyl acetate containing steadily decreasing amounts of oxygen-18, without any decrease of total label in the peroxide. These data (Table I) show a kinetically first-order decrease in the fraction of recovered peroxide which is specifically labeled. The plot of Figure 1 (large circles) gives a rate constant for scrambling of label ($k = 4.4 \times 10^{-5}$ sec^{-1}, 80°) which can be compared with that for the over-all disappearance of acetyl peroxide, followed by infrared spectroscopy at 1800 cm^{-1}, in the same solvent ($k = 7.2 \times 10^{-5}$ sec^{-1}, 80°). The comparison suggests that *ca.* 38% of all radical pairs formed in the decomposition of acetyl peroxide recombined to give acetyl peroxide with scrambling of label.[7]

Table I. Specificity of Labeling in Acetyl Peroxide Recovered from Partial Decomposition at 80° in Isooctane

Time, sec	Carbonyl label, % excess	Fraction not scrambled
0	0.618	1.000
4080	0.574	0.896
8700	(0.541)[a]	0.749
9900	0.492	0.590
19800	0.439	0.410

[a] Normalized value calculated from a run showing 0.984% excess carbonyl-^{18}O from acetyl peroxide initially containing 1.124% excess.

The failure to observe exchange between labeled acetic acid and unlabeled acetyl peroxide combines with the observation of the first-order form of the rate

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(1) For a review see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 491 ff, or M. Szwarc in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 153 ff.

(2) L. Herk, M. Feld, and M. Szwarc, *J. Am. Chem. Soc.*, 83, 2998 (1961).

(3) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, 66, 1591 (1962).

(4) J. C. Martin and E. H. Drew, *J. Am. Chem. Soc.*, 83, 1232 (1961).

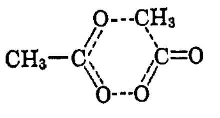
(5) W. von E. Doering and E. Dorfman, *ibid.*, 75, 5595 (1953); D. B. Denney and M. A. Greenbaum, *ibid.*, 79, 979 (1957).

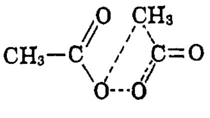
(6) We wish to thank Mr. J. Nemeth for carrying out the oxygen-18 analyses. These were run in parallel with quantitative direct oxygen analyses, using the same pyrolysis train. Failure to perform this control experiment led to an earlier report,[4] now recognized to be in error, of a specific attack by cyclohexene on acetyl peroxide. Spurious results in the isotopic assay of cyclohexanol (which will be discussed in a later publication) suggested incomplete scrambling of label in the formation of cyclohexyl acetate from acetyl peroxide and cyclohexene. In reality the scrambling of label in the ester is complete (J. C. Martin, E. H. Drew, and J. W. Taylor, to be published). For a discussion of this reaction see H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, 85, 3613 (1963).

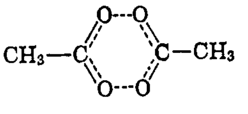
(7) An earlier attempt[2] to use tracer techniques to detect this process used infrared spectroscopy to assay for carbonyl label in peroxide with *ca.* 0.6% enrichment and failed to detect scrambling in material recovered after 55% reaction. Presumably the technique of this paper provides a more sensitive assay method.

law for scrambling of label to rule out mechanisms involving intermolecular exchange with traces of acetic acid formed in the reaction.

The intramolecular nature[1,2] of the reaction leading to ethane and methyl acetate was confirmed in this work by failure to observe more than 0.1% of trideuterio cross-product in the ethane and methyl acetate formed in the decomposition of an equimolar mixture of ordinary diacetyl peroxide and diacetyl-d_6 peroxide. Methyl acetate (containing the equivalent of 0.627% excess oxygen-18 in one oxygen), formed directly in the decomposition of the peroxide (0.630% label in the carbonyl oxygen), showed complete scrambling of label. This was determined by lithium aluminum hydride reduction to give methanol (0.314% excess, 50.0% of the total label) and ethanol (0.312% excess, 49.8% of the label) with equivalent label, thus ruling out the operation of cyclic mechanisms A or B for the intramolecular route leading to this product. The analogous mechanism, C, for scrambling of label in recovered peroxide cannot definitely be ruled out until the results of double labeling experiments are in hand.

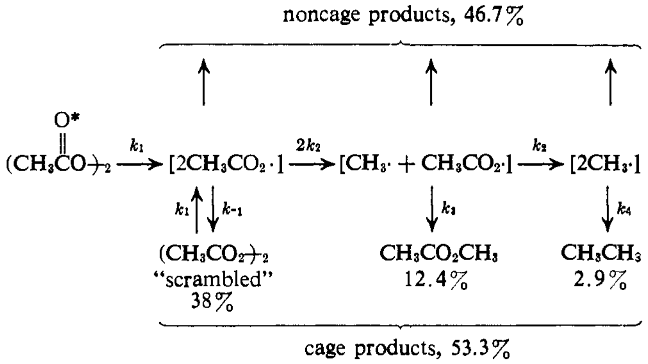

A


B


C

It should be noted that the cage return of acetoxy radicals to give acetyl peroxide to the extent here indicated provides a competition between decarboxylation ($2k_2$, expected to show a ^{13}C kinetic isotope effect) and recombination (k_{-1}, showing only a secondary kinetic isotope effect). This provides an alternative basis for explaining the over-all kinetic isotope effect reported[8] for carboxy carbon-13 in the decomposition of the peroxide. It is clear that in the limiting case with $k_{-1} >> 2k_2$ the apparent kinetic isotope effect will approach that for the decarboxylation of acetoxy radical. Our observations suggest that k_{-1} is at least comparable with $2k_2$. It is therefore possible to approach the task of explaining the observed[8] kinetic isotope effect without postulating multiple bond cleavage, leading directly to methyl radicals from acetyl peroxide,[8] as an important pathway in the decomposition scheme.[9]

Diacyl peroxides which on decarboxylation lead to *sec*-alkyl radicals have been shown[10] to decompose *via* the carboxy inversion route. The methyl ester of the mixed carbonic–acetic anhydride has been shown,[11] however, to be too stable to serve as an intermediate in the decomposition of acetyl peroxide.



All of the data now available seem to be consistent with the simple O–O bond cleavage of acetyl peroxide, followed by cage reactions of the two initially formed acetoxy radicals which are competitive with decarboxylation and diffusion from the cage.

The cage recombination of acetoxy radicals may also explain the monotonic decrease in over-all rate of decomposition observed[3] for acetyl peroxide with increasing solvent viscosity and account for its faster decomposition in the gas phase. Rate comparisons from the work of Herk, Feld, and Szwarc[2] suggest $k_{\text{gas}}/k_{\text{isooctane}} = 1.55$ at 80°, compared with a ratio of 1.61 calculated from our data, equating cage return to scrambling of label, and assuming the cage effect to be the only solvent effect on rate. While the close agreement must be considered fortuitous, this result makes it seem unlikely that a large amount of cage return occurs without scrambling of label.

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(8) M. J. Goldstein, *Tetrahedron Letters*, 1601 (1964), reports k_{12}/k_{13} = 1.023 (45°) as reflected in the isotopic composition of the initially evolved carbon dioxide.

(9) T. W. Koenig and W. D. Brewer, *ibid.*, 2773 (1965), arrive at the same conclusion on the basis that they observe essentially no secondary kinetic isotope effect in the decomposition of diacetyl-d_6 peroxide. Rationalization of this result in terms of our findings must await further work. We note a small ^{13}C kinetic isotope effect (1.005–1.010) reflected in the isotopic composition of methane generated from decomposition of acetyl peroxide in isooctane, 80°.

(10) F. D. Greene, H. A. Stein, C. C. Chu, and M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964).

(11) F. D. Greene, private communication.

(12) Rohm and Haas Company Fellow, 1962–1963; National Institutes of Health Predoctoral Fellow, 1963–1964.

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Received May 16, 1966

Deuterium Isotope Effect in Amine-Catalyzed Aromatic Nucleophilic Substitution. The Reaction of 4-Chloro-3-nitrobenzotrifluoride with Piperidine and N-Deuteriopiperidine in Benzene

Sir:

In reactions of halonitrobenzenes with amines the over-all second-order rate coefficient k_T generally increases with the initial amine concentration, and this kinetic order, higher than one with respect to the nucleophile, is consistent with the base-catalyzed mechanism (I), studied by Ross,[1] Bunnett,[2-4] and others.[5-10]

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(1) S. D. Ross, *Progr. Phys. Org. Chem.* 1, 31 (1963).

(2) J. F. Bunnett and J. J. Randall, *J. Am. Chem. Soc.*, **80**, 6020 (1958).

(3) J. F. Bunnett and R. H. Garst, *ibid.*, **87**, 3875 (1965).

(4) J. F. Bunnett and R. H. Garst, *ibid.*, **87**, 3879 (1965).

(5) N. E. Sbarbati, T. H. Suarez and J. A. Brieux, *Chem. Ind.* (London), 1754 (1964).

(6) O. L. Brady and F. R. Cropper, *J. Chem. Soc.*, 507 (1950).

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(8) H. Suhr, *Ber. Bunsenges Physik. Chem.*, 67, 893 (1963).

(9) H. Zollinger and C. Bernasconi, *Tetrahedron Letters*, 1083 (1965).

(10) F. Pietra, *ibid.*, 2405 (1965).