**Table I.** Nmr Spectra in Methylene Chloride

| Compound | Temp, °C | δ values, ppm Aryl | S-Methyl | Alkoxy |
|---|---|---|---|---|
| $\overset{\mathrm{OCH_3}}{\underset{+}{\mathrm{C_6H_5SCH_3}}}\ \mathrm{BF_4^-}$ | 37 | 7.85 (m) | 3.43 | 3.86 |
| $\overset{\mathrm{O\text{-}\mathit{t}\text{-}C_4H_9}}{\underset{+}{\mathrm{C_6H_5SCH_3}}}\ \mathrm{BF_4^-}$ | −46 | 8.05 (2 H, m)<br>7.75 (3 H, m) | 3.42 | 1.54 |
| $\overset{\mathrm{O\text{-}\mathit{t}\text{-}C_4H_9}}{\underset{\mathrm{Cl}}{\mathrm{C_6H_5SCH_3}}}$ | −46 | 8.25 (2 H, m)<br>7.70 (3 H, m) | 3.78 | 1.49 |

stable tetracovalent sulfur species. Owsley and Helmkamp[7] have recently discussed evidence for a similar intermediate (9-chloro-9-methyl-9-thiabicyclo[6.1.0]-nonane) formed by the nucleophilic addition of chloride ion to an episulfonium species.

[7] D. C. Owsley and G. K. Helmkamp, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. ORGN 121.

[8] (a) Alfred P. Sloan Research Fellow, 1965–1968; (b) Fellow of the Economic Development Administration, Commonwealth of Puerto Rico.

**Carl R. Johnson,**[8a] **Juan J. Rigau**[8b]
*Department of Chemistry, Wayne State University*
*Detroit, Michigan 48202*

*Received March 28, 1969*

---

## The Cage Recombination of Benzoyloxy Radicals: An Important Pathway in the Decomposition of Benzoyl Peroxide

*Sir:*

A recent report[1] that the decomposition of benzoyl peroxide is not accompanied by scrambling of carbonyl-$^{18}$O label in recovered peroxide is surprising in view of the evidence[2–4] for important amounts of such scrambling in the closely related reactions of acetyl peroxide. We wish to report experiments which show that scrambling of label by a radical-cage process does indeed occur for benzoyl peroxide.

Benzoyl-$^{18}$O peroxide containing 1.36 atom % label in the carbonyl was prepared by the method of Denney,[5] and its decomposition was studied at 80° in 0.01 *M* solutions in isooctane and mineral oil. The demonstrated[3] greater sensitivity of isotopic label determination by observation of the increase in peroxy oxygen label, rather than disappearance of carbonyl label, led us to use this technique. The acid hydrolysis of benzoyl peroxide to hydrogen peroxide was found to proceed too slowly to allow adoption of the published method *in toto*. We therefore devised a procedure in which *t*-butyl alcohol solutions of the solid residues left after removal of the solvent under reduced pressure (or after extraction with acetone, followed by removal of the acetone under reduced pressure, in the mineral oil experiments) were treated with aqueous solutions of barium hydroxide. The analysis of the resulting oxygen for $^{18}$O content was accomplished with a Consolidated-Nier isotope ratio mass spectrometer. That indeed we were isolating oxygen from the peroxy oxygens was demonstrated by the observation that the oxygen derived from carbonyl-labeled peroxide before any thermolysis contained no label and that the use of water-$^{18}$O as solvent for the generation of $O_2$ from the peroxide gave no introduction of label into the $O_2$.

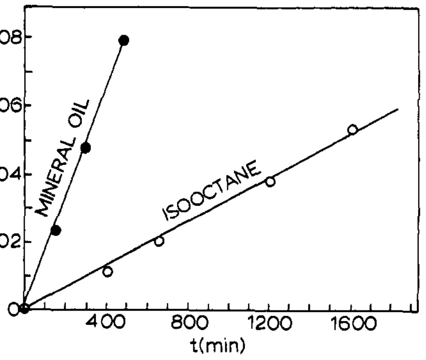
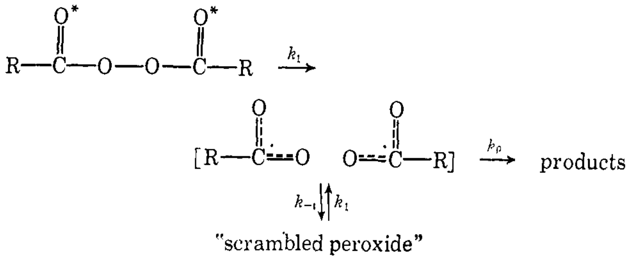


Figure 1. Scrambling of carbonyl-$^{18}$O label in recovered benzoyl peroxide, measured by appearance of peroxide label in isooctane (closed circles) and mineral oil (open circles) at 80°.

Figure 1 shows first-order rate plots for the scrambling of carbonyl label during decomposition in isooctane and mineral oil. The fraction of peroxide with specific carbonyl label is designated *A* (calculated from the excess of label in the carbonyl oxygen over that in the peroxide oxygen). At infinite time, equal labeling is expected in the oxygens and the fraction specifically labeled is zero. The kinetic scheme used for the analysis of the data is shown in Scheme I. The rate constants $k_s$ for scrambling of the carbonyl label and $k_d$ for disappearance of peroxide are given by $k_s = k_1k_{-1}/(k_{-1} + k_p)$ and $k_d = k_1k_p/(k_{-1} + k_p)$. Thus, $k_d/k_s = k_p/k_{-1}$, and the fraction of the benzoyloxy radicals recombining to form "scrambled" peroxide can easily be calculated. The rates for the over-all decomposition of the peroxide were followed by iodometric titration[6] of solutions with 0.2 *M* styrene added to inhibit induced decomposition of the peroxide giving $k_d = 2.70 \times 10^{-5}$ sec$^{-1}$ in isooctane and $2.89 \times 10^{-5}$ sec$^{-1}$ in mineral oil. (The determination of $k_d$ in mineral oil is not very reliable. It is difficult to make sure that all induced decomposition is eliminated in so viscous a solvent. We therefore attach little significance to the indication that $k_d$ is larger in mineral oil than in isooctane.)

**Scheme I**



---

[1] M. Kobayashi, H. Minato, and Y. Ogi, *Bull. Chem. Soc. Jap.*, **41**, 2822 (1969).

[2] J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, **88**, 3650 (1966); J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967).

[3] J. C. Martin and S. A. Dombchik, "Oxidation of Organic Compounds," Vol. I, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 269.

[4] S. A. Dombchik, Ph.D. Thesis, University of Illinois, 1969.

[5] D. B. Denney and D. Z. Denney, *J. Amer. Chem. Soc.*, **79**, 4806 (1957).

[6] V. R. Kokatnur and M. Jelling, *ibid.*, **63**, 1432 (1941).

**Table I.** Specificity of Labeling in Benzoyl Peroxide Recovered from Partial Decomposition at 80°

| Solvent | Time, min | Fraction of carbonyl specifically labeled |
|---|---|---|
| Isooctane | 0 | 1.000 |
| | 400 | 0.979 |
| | 660 | 0.959 |
| | 850 | 0.938 |
| | 1200 | 0.919 |
| | 1600 | 0.884 |
| Mineral oil[a] | 0 | 1.000 |
| | 150 | 0.951 |
| | 300 | 0.897 |
| | 485 | 0.834 |

[a] American White Oil No. 31, Heavy, viscosity 10.7 cP at 80°.

The data in Table I provide $k_s = 1.30 \times 10^{-6}$ sec$^{-1}$ in isooctane and $6.27 \times 10^{-6}$ sec$^{-1}$ in mineral oil. These data indicate that 4.3% of the benzoyloxy radicals recombine, with scrambling, in isooctane, while 17.8% recombine in the more viscous mineral oil (more than 17.8% if our value for $k_d$ in mineral oil is in fact, too large).

The smaller importance of cage return, as evidenced by scrambling of label, for benzoyl peroxide is surprising. The processes leading to products ($k_p$) include, for acetyl peroxide, diffusion from the solvent cage and decarboxylation of the acetoxy radical. The decarboxylation of benzoyloxy radical is too slow[7] to compete with cage recombination, and diffusion of the larger radical should be slower. Since diffusion is the process responsible for the variation of $k_s$[3,4] and $k_d$[8,9] with solvent viscosity, it is not surprising to find benzoyl peroxide, for which diffusion is the sole component in $k_p$, more responsive to solvent viscosity than is acetyl peroxide which has a component in $k_p$ for the decarboxylation reaction. (The former shows a 4.8-fold increase in $k_s$ on going from isooctane to mineral oil while the latter shows[3,4] only a 1.6-fold increase for the same change.) The smaller amount of cage return seen for benzoyl peroxide in our tracer studies may result from (a) an appreciable fraction of cage return without scrambling of label in the benzoyloxy radical, (b) an activation barrier for the recombination of benzoyloxy radicals higher than the near zero[4] barrier for acetoxy radical pair recombination, or (c) an unfavorable $\Delta S^{\ddagger}$ for the recombination. These possibilities are presently the object of further experimentation.

**Acknowledgment.** This research was supported by a grant from the National Science Foundation.

---

(7) D. F. DeTar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967).
(8) T. Koenig, *ibid.*, **91**, 2558 (1969).
(9) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967).

**J. C. Martin, J. H. Hargis**
*Department of Chemistry, University of Illinois*
*Urbana, Illinois 61801*

*Received July 11, 1969*

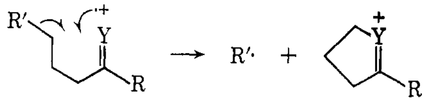
## Unimolecular Gaseous Ion Reactions of Low Activation Energy. Five-Membered-Ring Formation[1]

*Sir:*

Until recently, metastable transitions in mass spectra have been used mainly to identify reaction pathways. This use was based on the assumption that unimolecular ion reactions in the ion source and in the metastable drift region are qualitatively similar. However, recent studies indicate that the ratio of products from rearrangement reactions to those from simple cleavages is often two to three orders of magnitude higher for metastable than for ion-source decompositions.[2,3]

Although it was postulated that this increase should be characteristic of low frequency factor reactions, the only ones examined were rearrangement reactions known from studies of normal spectra. We have now studied the metastable transitions of a wide variety of compounds and find that often the most abundant ions arise from reaction pathways that have been unrecognized in normal spectra. Many of these reactions would not have been predicted by the use of previous conclusions concerning structural factors which lead to reactions of low activation energy.

As an example, the formation of an abundant metastable in the spectra of many compounds is consistent with a rearrangement leading to a five-membered ring product (reaction 1). For $CH_3CH_2CH_2CD_2COCD_3$



(1)

this reaction would lead to the loss of $CH_3$;[4] the corresponding metastable is not only the most abundant from the molecular ion, but is much greater than that of $(M - CD_3)^+$ (Table I). The nonbonding orbital of the oxygen atom should be the main locus of ionization at threshold energies;[5] thus, the low appearance potential of $(M - CH_3)^+$ is evidence that this orbital is involved in reaction 1. Despite the low activation energy for this reaction, it yields a very low abundance of product ions in the 75-eV mass spectrum. This is consistent with a very low frequency factor for the reaction,[3,6] even lower than that for the rearrangement

**Table I.** Ions and Metastables (m*) from $CD_3COCD_2CH_2CH_2CH_3$

| Ion | Relative abundance Ion | Relative abundance m*[a] | Appearance potential[b] Ion | Appearance potential[b] m* | Appearance potential[b] Lit.[c] |
|---|---|---|---|---|---|
| $M\cdot^+$ | 31 | | (9.37[c]) | | 9.37 |
| $(M - CH_3)^+$ | 3.4 | 1.20 | 9.5 | 9.5 | (9.66) |
| $(M - CDH_2)^+$ | 1.0 | 0.40 | | | |
| $(M - CD_2H)^+$ | 1.0 | 0.12 | | | |
| $(M - CD_3)^+$ | 8.9 | 0.021 | 10.2 | | (9.66) |
| $(M - C_2H_5)^+$ | 11.1 | 0.042 | 10.9 | 9.5 | 10.03 |
| $(M - C_3H_6)\cdot^+$ | 100 | 0.011 | 10.4 | 10.4 | 10.00 |
| $C_2D_3O^+$ | 100 | <0.001 | 12.2 | 12.2 | 10.8 |

[a] Abundance relative to that of the molecular ion × $10^2$. [b] Nominal values, ±0.2 eV, determined by the 50-eV normalization method: F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951). [c] $C_6H_{12}O$, E. Murad and M. G. Inghram, *ibid.*, **40**, 3263 (1964).

---

(1) Metastable Ion Characteristics. XI. Paper X: F. W. McLafferty and H. D. R. Schuddemage, *J. Amer. Chem. Soc.*, **91**, 1866 (1969).
(2) F. W. McLafferty and R. B. Fairweather, *ibid.*, **90**, 5915 (1968).
(3) F. W. McLafferty in "Topics in Organic Mass Spectrometry," A. L. Burlingame, Ed., Wiley-Interscience, New York, N. Y., 1969.
(4) Since the submission of this paper similar data have been published on the loss of methyl from this compound: A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 3582 (1969).
(5) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 129.
(6) W. A. Chupka, *J. Chem. Phys.*, **30**, 191 (1959).