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 6.27×10^{-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.

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

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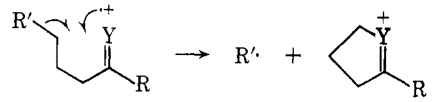
Unimolecular Gaseous Ion Reactions of Low Activation Energy. Five-Membered-Ring Formation[1]

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		Appearance potential[b]		
	Ion	m*[a]	Ion	m*	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).

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(1) Metastable Ion Characteristics. XI. Paper X: F. W. McLafferty and H. D. R. Schuddemage, *J. Amer. Chem. Soc.*, **91**, 1866 (1969).
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(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).

reaction[7] leading to the $(M - C_3H_6)\cdot^+$ ion. The lower frequency factor is consistent with the increased steric requirements of reaction 1.

Other examples are shown in Table II; in most cases, these are compounds whose normal spectra exhibit the characteristic rearrangement of a γ hydrogen through a six-membered-ring intermediate.[7] In the spectrum of hexanoic acid the metastable which would correspond to reaction 1 is even more abundant than the molecular ion. Competing metastable decompositions are also observed, some of which are analogous to those observed in other rearrangement reactions.[7,8] Cleavage of the β–γ bond is apparently enhanced by substituents on the β- and γ-carbon atoms. Anomalies such as the $(M - 29)^+$ metastable in 5-methyl-2-hexanone indicate that even more unexpected reactions are possible. The small abundance of metastables from reaction 1 in the spectrum of butylbenzene is inconsistent with the substantial abundance of $(M - C_3H_6)\cdot^+$ ions from rearrangement of γ-H and with the metastables exhibited by the alkenes of Table II. Several new reactions become competitive with reaction 1 in higher molecular weight compounds; for example, the loss of the α-methyl group yields abundant metastables in the spectra of higher 2-alkanones, consistent with the surprisingly abundant normal ions formed by this pathway at low ionizing voltages.[9]

Table II. Abundances[a] of Metastable Ions Corresponding to Those Expected in Ring Formation Reactions

Compound	Number of ring atoms 4	5	6
Hexanal	0.16	6.0[k,l]	0.04
2-Hexanone[b,c]	0.04	1.2	*d*
5-Methyl-2-hexanone[c,e]	0.06	0.02	
2-Octanone[c,f]	0.05	0.14	0.07
4-Methyl-2-heptanone[c,g]	0.27	0.36	0.05
6-Methyl-2-heptanone[h]	<0.02	5.6[l]	<0.02
5-Nonanone[c]	0.06	1.12	
Hexanoic acid	7.8	120[l]	0.48
Butyl formate	<0.15	25[i]	0.4
sec-Butyl acetate	2.4	0.3	
1-Chlorohexane	<0.07	24	0.09
1-Bromohexane	<0.05	31	<0.05
1-Thioheptane	<0.0002	0.0033	0.0005
1-Hexene	0.017	2.1	
4-Penten-1-ol[j]	<0.2	0.4	
n-Butylbenzene	0.083	0.024	

[a] $[m^*]/[M\cdot^+] \times 10^2$. Metastable abundances were determined by the Barber–Elliott defocusing method with a Hitachi RMU-7 mass spectrometer using the modification suggested by Major in which the electrostatic analyzer energy is lowered: F. W. McLafferty, J. Okamoto, H. Tsuyama, Y. Nakajima, T. Noda, and H. W. Major, *Org. Mass Spectrom.*, **2,** 751 (1969). [b] See Table I. We thank J. C. Tou and L. B. Westover, Dow Chemical Co., for a generous sample of this compound. [c] Based on the completely α-deuterated derivative. Not corrected for the partial H/D scrambling which is observed. [d] Values not measured for products due to loss of H. [e] $(M - 30)^+ = 1.6$; $(M - 31)^+ = 2.4$.[a,l] [f] $(M - \alpha\text{-Me})^+ = 1.0$.[a,c] [g] $(M - \alpha\text{-Me})^+ = 1.1$; $(M - 44)^+ = 1.2$; $(M - 45)^+ = 1.4$; $(M - 58)^+ = 0.21$.[a,l] [h] $(M - 29)^+ = 0.12$.[a] [i] High resolution shows that 95% of the $(M - 29)^+$ ion is due to the loss of ethyl at 13 eV. [j] $(M - 18)^+ = 6.3$.[a] [k] At 70 eV only 60% is loss of terminal ethyl: R. J. Liedtke and C. Djerassi, submitted for publication. We thank Professor Djerassi for communication of these results prior to publication. [l] See footnote 8a.

In normal mass spectra of *n*-alkyl chlorides and bromides[10] reaction 1 often accounts for the most abundant fragment ions, so that it is not surprising that the corresponding metastable ions are so important. In mass spectra of aliphatic thiols[11] this rearrangement is of only moderate importance (7% of base peak in 1-thioheptane), and is very substantially reduced in the corresponding metastable ions. Reaction 1 is of relatively little importance in both metastable and normal spectra of other common saturated functional groups such as alcohols, ethers, and amines.

Although further work is necessary to define the scope and limitations of this rearrangement, the data indicate that this, and other new metastable decompositions, will provide new structural information. In the normal mass spectra of the isomeric octanones simple cleavage at the carbonyl group and the γ-H rearrangement[7] indicate the substituents on the carbonyl group and on the α-C atoms, respectively; the β-CH_3 group of 4-methyl-2-heptanone is now indicated by the $(M - 29)^+$ metastable of reaction 1.

The ubiquitous existence of such reactions emphasizes that the energetically most-favored processes are often not those producing the most abundant fragment ions in ordinary mass spectra, and that metastable spectra offer a superior way of studying these processes.

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(8a) NOTE ADDED IN PROOF. Further study of labeled derivatives has defined additional low energy pathways that contribute to some of these peaks. Losses of the α,β-carbon atoms as C_nH_{2n+1} and C_nH_{2n} are generally favored by β or γ branching. Pentanoic acid-2,2-d_2 exhibits these reactions as well as reaction 1, indicating an additional source of the abundant metastable in hexanoic acid. Loss of α,β,γ carbon atoms as C_nH_{2n+1} is noted for some higher molecular weight compounds.

[9] W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer, Chem. Soc.*, 89, 6167 (1967).

[10] F. W. McLafferty, *Anal. Chem.*, **34,** 2 (1962).

[11] E. J. Levy and W. A. Stahl, *ibid.*, 33, 707 (1961).

F. W. McLafferty, D. J. McAdoo, J. S. Smith
Department of Chemistry, Cornell University
Ithaca, New York 14850

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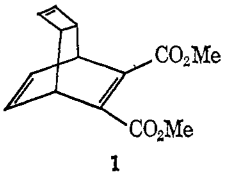
A Photochemical Precursor to Cyclobutadiene

Sir:

The Diels–Alder adducts of cyclooctatetraene with acetylene dicarboxylates are obvious potential sources of cyclobutadiene. However, the pyrolysis of 7,8-dicarbomethoxytricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (**1**)[1] has been reported to involve mainly rearrangement accompanied by a minor amount of fragmentation to 1,3-butadiene and dimethyl phthalate. In contrast, we have found that photolysis of **1** does lead to products which can be more convincingly ascribed to a cyclobutadiene intermediate.[2]



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