MULTICENTER CLEAVAGE OF ACETYL PEROXIDE[*]

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Initial formation of two acetoxyl radicals has long been consider-
ed the exclusive path for thermal dissociation of acetyl peroxide.[1a,b,c]
Often used as a model for related systems, this hypothesis rests on
suprisingly fragile evidence. Only two of the many reports[2,3,4a,5a,6a,7a]
of successful acetoxyl trapping, under conditions where induced
decomposition was believed absent, have survived subsequent discover-
ies[4b,5b,6b,7b] and even these[2,3] need not implicate more than a
small fraction of reactant molecules.

The problems of quantitive scavenging are indeed formidable and so
we have measured, instead, the intermolecular carbon and oxygen kinetic
isotope effects. Abundances of C^{13} and O^{18} in CO_2, isolated and puri-

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fied after partial reaction, were compared with those identically obtain-

ed from complete decompositions and provide the experimental values list-

ed in Table 1. The technique is insensitive to isotopic discrimination in

any step following the rate-controlling one, identified with O-O cleavage

by virtue of previous oxygen labeling experiments.[7a]

TABLE 1

Corrected[a] Isotopic Ratios and Isotope Effects Isooctane,

0.096 $\underline{M}$, 44.8°

f^b	$10^5 \times C^{13}/C^{12}$	$10^5 \times O^{18}O^{16}/O_2^{16}$	k_{12}/k_{13}	k_{16}/k_{18}
0.020	1073	404	1.023	1.026
0.039	1072	407	1.024	1.017
0.039	1069	402	1.027	1.031
0.039[c]	1075	408	1.021	1.016
0.059	1076		1.020	
0.99	1097±1[d]	414±1[d]		
		mean:	1.023±0.003	1.023±0.007

[a]As in ref. 8.   [b]Calculated from data reported in ref. 9.   [c]Contain-
ed 0.60 $\underline{M}$ α-methyl styrene. [d]Mean and standard deviation of four
runs at 65°, 75°, and 85°.

Should no other covalent bonds be altered in the transition state,

application of the $\overline{Y}$ technique[8,10] leads to a predicted oxygen isotope

effect of 1.027, in good agreement with experiment, and a carbon isotope

effect of 1.004 which clearly is not.

Exact calculation of ratios of (almost) complete partition functions[11,12] permits greater rigor and more versatile models. Essential ground state input parameters (force constants, bond distances and angles) are taken from related molecules. Those for the transition state are adjusted, within the limits of any one mechanism, until experimental values are duplicated. Table 2 illustrates the futility of such attempts for one-center cleavage. A and B represent outer limits of a reasonable a priori description of such a transition state. C demonstrates the cost of reproducing the carbon isotope effect: an unrealistic model and disagreement with the oxygen value.

TABLE 2

Predicted Isotope Effects for One-Center Transition States

	Stretching Force Constants (mdyn/Å)			k_{12}/k_{13}	k_{16}/k_{18}		
	O-O	C-O	C=O		C-O	C=O	Average
Ground State	4.0	5.4	10.5				
Transition State A	0	5.4	10.5	1.003	1.051	1.004	1.027
B	0	7.95	7.95	1.002	1.037	1.016	1.026
C	0	5.4	5.4	1.022	1.051	1.031	1.041

Similar evaluation of concerted, three-center cleavage first requires an operational definition: a smaller increase in potential energy results from simultaneous extension of O-O and C-C bonds than would be required by equal, but successive, extensions. More concisely, two identical and

negative off-diagonal elements are introduced into an (otherwise diagonal) $\underline{F}$ matrix. If these now be chosen by:
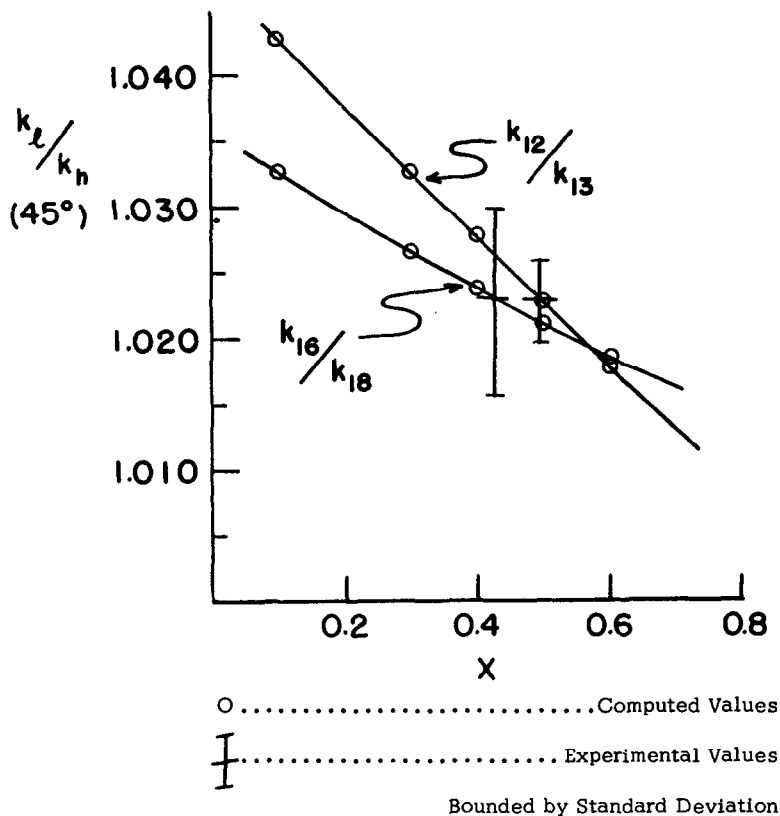
$$F_{ij} = -\left(\frac{F_{ii}F_{jj}}{2}\right)^{\frac{1}{2}}$$

where F_{ii} and F_{jj} are C-C and O-O stretching force constants, one vibrational mode becomes unrestrained and a transition state is formed[13], irrespective of the magnitudes of any diagonal elements[14]. Fig. 1 shows the agreement between experimental and computed results for $X = 0.50 \pm 0.07$ where X is the single parameter by which all ground state force constants, incorporating O-O or C-C bonds, are to be multiplied in the transition state.

The possibility of still smaller X, whose effect is diminished by concurrent one- and/or two-center[15] cleavage, cannot be excluded. Our yield of CO_2 (83±2%) does suggest its formation by multiple paths but we consider radical-induced decomposition, known to be present under these conditions,[16] a more reasonable choice for the minor route. If so, the experimental isotope effects underestimate the true magnitudes of the unimolecular ones and our conclusion is strengthened: C-C cleavage must accompany O-O cleavage of acetyl peroxide to a predominant, if not exclusive, extent.

FIG.1

Three-Center Transition States

k_l / k_h (45°)

k_{12} / k_{13}

k_{16} / k_{18}

X

O ....Computed Values

⊥..........................Experimental Values

Bounded by Standard Deviation

[1] (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, New York, 1957, p. 491; (b) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, New York, New York, 1959, p. 717; (c) M. Szwarc, "Decomposition Involving a Simultaneous Fission of Two or More Bonds" in J. O. Edwards, "Peroxide Reaction Mechanism," Interscience Publishers, New York, 1962, p. 153.

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16 (1958); (b) M. J. Stern and M. Wolfsberg, J. Chem. Phys., 39, 2776 (1963).

[11] To avoid irrelevant conformation considerations, hindered rotation about C-O and C-C bonds was ignored and so only 32 (ground state) frequencies were computed. This neglect introduces no detectable isotope effects.

[12] The computer program, already described, [10b] was provided by M. Wolfsberg whose kind generosity is gratefully acknowledged.

[13] Cf. H. S. Johnson, W. A. Bonner, and D. J. Wilson, J. Chem. Phys., 26, 1002 (1957).

[14] In practice, ground state values are assumed for force constants not incorporating bonds to be broken and the F_{ij} are multiplied by 1.1. The latter procedure permits calculation of ν_{1L} / ν_{2L}, required for external checks, and introduces curvature at the top of the barrier, but has no practical effect on computed ratios.

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