

DEUTERIUM ISOTOPE EFFECTS IN THE DECOMPOSITIONS
OF ACETYL PEROXIDE AND TWO t-BUTYL PERESTERS

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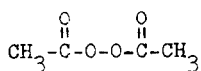
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While many quantitative studies (1) of the rates and products of the decomposition of acetyl peroxide have been reported, the detailed mechanism for this process remains a subject of controversy. Recently reported results (2) seem to indicate that acetoxyl radicals are produced in the reaction and that they add to olefinic substrates or are scavenged by diphenylpicrylhydrazyl (DPPH). At the opposite extreme the measurement of the oxygen-18 and carbon-13 heavy atom kinetic isotope effects on the reaction has led to the postulate that the process involves concerted cleavage of three bonds in a single rate determining transition state (3).

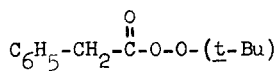
If the hybridization of a carbon radical species is assumed to be close to sp^2 then radical forming reactions should show a secondary deuterium kinetic isotope effects

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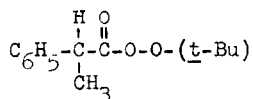
similar in magnitude to those found in solvolytic reactions (4). This effect has been observed recently for the β -scission of cumyloxy radicals (5). The concerted mechanism for the acyl peroxide cleavage is a β -scission. Thus it might be expected that the concerted character for the decomposition of acyl peroxides would be reflected by a change in observed rate constant with deuterium substitution at the α -position. In order to test this reasoning the rates of decomposition of acetyl peroxide (I) *t*-butyl phenylperacetate (III) and *t*-butyl α -phenylpropionate (V) and their deuterated analogs (II, IV, VI and VII) have been determined.



I

(II, 85% D₆)

III

(IV, 87% α -D₂)

V

(VI, 77% α -D)(VII, 70% β -D₃)

The acetyl peroxides were prepared by the method of Price and Morita (6). Acetic acid -d₃ was obtained by exchange of malonic acid (7). Phenylacetic acid- α -d₂ and α -phenylpropionic acid- α -d were obtained by exchange of the undeuterated compound in basic deuterium oxide. The peresters were obtained from the corresponding acid chlorides

by the method of Bartlett (8). α -Phenylpropionic acid- β - d_3 was synthesized starting with acetophenone which had been exchanged in basic deuterium oxide. The ketone was reduced with lithium aluminum hydride and the resulting alcohol converted to the chloride. The chloride was treated with cyanide and basic hydrolysis of the resulting nitrile gave the desired acid although some loss of deuterium did occur. Analysis for deuterium was accomplished using the proton magnetic resonance spectra of the compounds and an internal standard technique.

The rates of decomposition of the acetyl peroxides were measured through the disappearance of the infrared carbonyl absorption in isooctane with and without added styrene and by first order disappearance of galvinoxyl using its absorption at 575m μ (9). Rate constants for the peresters were obtained by the infrared method in chlorobenzene with added styrene. The rate plots were linear for three half lives and the rate constants were obtained by a least squares treatment* of the experimental data. The results of these measurements are summarized in Table I.

Concerted decomposition appears to be established for a series of t -butyl peresters in which the decarboxylated radicals are highly resonance stabilized (3). Both II and III are peresters of this type. As indicated in Table I there is an easily discernible decrease in the rate of

* We are indebted to C. Wilkins and C. E. Klopfenstein for making available to us their program for least squares treatment of kinetic data.

TABLE I
First Order Rate Constants for Decomposition of
Compounds I-VII

Compound	Solvent	Temp. °C	Conc.	$k \times 10^5 \text{sec}^{-1}$	k_H/k_D^d
I	isooctane	76.23+.05	0.04M	5.07+.46	
II	isooctane	76.23±.05	0.04M	4.97±.26	1.02
I	isooctane ^a	76.26+.05	0.04M	4.35+.12	
II	isooctane ^a	76.26±.05	0.04M	4.38±.10	0.99
I	isooctane ^b	78.80+.04	0.0004M	3.80+.03	
II	isooctane ^b	78.80±.04	0.0004M	3.86±.04	0.98
III	chlorobenzene ^a	76.04+.06	0.18M	7.03+.12	
IV	chlorobenzene ^a	76.04±.06	0.18M	5.37±.10	1.31
III	chlorobenzene ^a	76.03+.05	0.18M	7.04+.26	
IV	chlorobenzene ^a	76.03±.05	0.18M	5.51±.16	1.28
V	chlorobenzene ^c	60.65+.03	0.19M	13.7±0.3	
VI	chlorobenzene ^c	60.65±.03	0.19M	12.9±0.3	1.06
VII	chlorobenzene ^c	60.65±.03	0.19M	13.3±0.2	1.04
V	chlorobenzene ^a	60.67+.03	0.19M	14.2±0.3	
VI	chlorobenzene ^a	60.67±.03	0.19M	12.5±0.4	1.14

a) 0.5M added styrene b) By disappearance of Galvinoxyl
c) 0.1M styrene d) Uncorrected for deuterium content.

disappearance of II and III with deuterium substitution at the α -position. The values of k_H/k_D per deuterium atom are 1.17 and 1.14 for II and III respectively. These values agree with those observed for β -scission of the cumyloxy radical. There is also a small rate reduction for III on substitution of deuterium at the β position. This value is much smaller than that observed in most solvolytic reactions. A smaller effect is probably to be expected since there is

less demand for hyperconjugative stabilization of radicals than of cations.

It is possible to argue that induced decomposition of by abstraction of the α hydrogen (10) or deuterium contributes to the observed α -isotope effects for II and III. Styrene, which is an effective inhibitor for induced decompositions, was present in 0.5 M concentration in these kinetic runs. A reduction in the rate constants for the decompositions of II and III was observed with the addition of styrene. However, it seems unlikely that such an induced path would accidentally produce an apparent isotope effect for both II and III which is so close to the expected value. This would also leave the observed β -effect for III unexplained.

The rate of disappearance of acetyl peroxide is reduced by the presence of styrene and the rates observed by the galvinoxyl method are still smaller. This probably indicates some induced decomposition occurs which may be first order and thus not impart any curvature to the rate plots. Under none of the conditions of this study was there any indication of any significant change in the observed rates of decomposition of acetyl peroxide with deuterium substitution. Thus we must conclude from these data that there is little or no methyl radical character in the rate determining transition state for its decomposition. We are presently exploring other methods which may allow the measurement of the relative rates of diffusion and decarboxylation of acetoxy radicals.

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