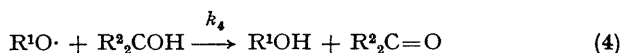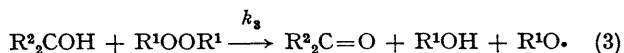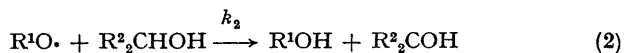# Isotope Effects in the Reaction of α-Hydroxy-alkyl Radicals with t-Butyl Peroxide

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Summary A primary isotope effect observed in the decomposition rate of t-butyl peroxide in $[O\text{-}^2H_1]$butan-2-ol indicates transfer of the oxygen-bonded hydrogen occurs in the induced decomposition of the peroxide by the alcohol-derived α-hydroxy-alkyl radical.

THE enhanced rates of decomposition of alkyl[1] and acyl[2] peroxides and peresters[3] in secondary alcohols can be attributed to participation of the peroxide in a chain reaction that includes interaction of an alcohol-derived α-hydroxy-alkyl radical with the peroxide linkage. The derived steady-state rate law for the decomposition of the

$$R^1OOR^1 \xrightarrow{k_1} 2\ R^1O\cdot \tag{1}$$

$$R^1O\cdot + R^2_2CHOH \xrightarrow{k_2} R^1OH + R^2_2COH \tag{2}$$

$$R^2_2COH + R^1OOR^1 \xrightarrow{k_3} R^2_2C{=}O + R^1OH + R^1O\cdot \tag{3}$$

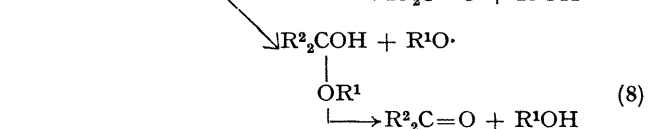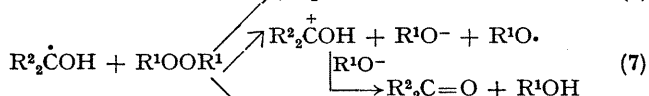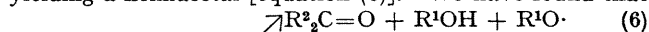$$R^1O\cdot + R^2_2COH \xrightarrow{k_4} R^1OH + R^2_2C{=}O \tag{4}$$

peroxide undergoing an induced decomposition is that shown in equation (5), provided the cross-termination process [equation (4)] is operative. Reactions that are

first-order in peroxide are observed in the decompositions

$$\frac{-d[R^1OOR^1]}{dt} = \left[\frac{3}{4}k_1 \pm \frac{1}{2}k_1\left(\frac{1}{4} + 2\frac{k_2k_3}{k_1k_4}[R^2_2CHOH]\right)^{1/2}\right][R^1OOR^1] \tag{5}$$

of t-butyl peroxide ($R^1 = Bu^t$) in secondary alcohols for at least two half-lifes of the peroxide at 125°. Alcohol to peroxide ratios of 5:1 were used and the decomposition rate of the peroxide determined by g.l.c.[1]

The mechanism of the reduction of t-butyl peroxide by the α-hydroxy-alkyl radical [reaction (3)] may be either a hydrogen-atom transfer reaction [equation (6)], an electron-transfer process, [equation (7)], or a direct displacement yielding a hemiacetal [equation (8)]. We have found that

$$\begin{array}{l} \quad\quad\quad\nearrow R^2_2C{=}O + R^1OH + R^1O\cdot \quad\quad (6) \\[4pt] \quad\quad\quad\nearrow \overset{+}{R^2_2COH} + R^1O^- + R^1O\cdot \\ R^2_2\overset{\cdot}{C}OH + R^1OOR^1 \Big/ \quad\quad\; \big|R^1O^- \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\; \big|{\longrightarrow} R^2_2C{=}O + R^1OH \quad (7) \\[4pt] \quad\quad\quad\searrow R^2_2COH + R^1O\cdot \\ \quad\quad\quad\quad\quad\quad\;\; | \\ \quad\quad\quad\quad\quad\quad\; OR^1 \quad\quad\quad\quad\quad\quad\quad\quad (8) \\ \quad\quad\quad\quad\quad\quad\; {\longrightarrow} R^2_2C{=}O + R^1OH \end{array}$$

decomposition rates of t-butyl peroxide in $[O\text{-}^2H_1]$butan-2-ol

are markedly slower than those in the non-deuteriated alcohol. The rate data in the Table were determined at

Decomposition of t-butyl peroxide at 125°

Alcohol	$10^4 k'$ (sec.$^{-1}$)	$10^{-5} t_{1/2}$ (sec.)
$CH_3 \cdot CHOH \cdot C_2H_5$	0·458 (0·009)[a]	0·141
	0·452 (0·009)	0·143
	0·454 (0·014)	0·143
$CH_3 \cdot CHOD \cdot C_2H_5$	0·287 (0·003)	0·226
	0·280 (0·002)	0·231
	0·289 (0·005)	0·223

[a] Standard deviation.

125° using a 5:1 ratio of alcohol to peroxide. The rates were followed through about one half-life of the peroxide up to which point a maximum of only 20% exchange of deuterium of the $[O\text{-}^2H_1]$butan-2-ol could have occurred with the t-butyl alcohol formed in the reaction. The pseudo-first-order rate constants (k') include all of the terms in the brackets of the rate law [equation (5)]. The magnitude of k'_H/k'_D (1·59) indicates a primary isotope effect caused by either a retardation of the rates of reactions (1), (2), or (3),

or an increase in the rate of the termination reaction (4) in $[O\text{-}^2H_1]$butan-2-ol relative to butan-2-ol. Rupture of the oxygen–hydrogen bond would be required for a primary isotope effect and such reactions occur only in (3) and (4). Since a sizeable inverse isotope effect is necessary to explain the decrease in rate in terms of reaction (4), the observed effect is most likely the result of retardation of reaction (3). Of the suggested mechanisms for reaction (3), the observed effect is most plausibly explained in terms of the hydrogen atom transfer reaction (6), the only reaction of the three which would give a primary effect. In both the electron-transfer reaction (7) and the displacement reaction (8), secondary isotope effects should be expected, since rupture of the oxygen–hydrogen bond occurs after the rate-determining reaction of the α-hydroxy-alkyl radical with the peroxide.

No differences were observed in the rates of the induced decompositions of either acetyl peroxide or t-butyl per-acetate in butan-2-ol and $[O\text{-}^2H_1]$butan-2-ol. In these cases, the α-hydroxy-alkyl radical probably reacts with the peroxide linkage in either an electron-transfer reaction or a direct displacement.

[1] E. S. Huyser and C. J. Bredeweg, *J. Amer. Chem. Soc.*, 1964, **86**, 2401.
[2] M. S. Kharasch, H. N. Friedlander, and W. H. Urry, *J. Org. Chem.*, 1949, **14**, 91.
[3] C. Walling and J. C. Azar, *J. Org. Chem.*, 1968, **33**, 3888.