Tetrahedron Letters No. 18, pp. 1201-1204, 1963. Pergamon Press Ltd.
Printed in Great Britain.

REACTIONS OF RADICALS. A COMPARISON OF PEROXIDES AND DISULFIDES [1a]

William A. Pryor [1b]

Department of Chemistry, Purdue University, Lafayette, Indiana

(Received 15 May 1963)

We here report the rates of the unimolecular and the induced decomposition of aliphatic peroxides, [2,3] and a comparison of these data with our previously published data [4] on the analogous disulfides. In contrast with disulfides, which radicals attack mainly at the sulfur atom, [2b,5] the aliphatic peroxides appear to be largely attacked at hydrogen.

$$M\cdot + RSSR \longrightarrow M{-}SR + RS\cdot$$

$$M\cdot + ROOR \longrightarrow M{-}H + ROOR({-}H)\cdot$$

Peroxides undergo a unimolecular decomposition in styrene at 60°, as well as the bimolecular induced deocmposition. [3,4] All the peroxides studied (propyl, butyl, isopropyl and *t*-butyl peroxide) were found to have very similar rate constants for unimolecular dissociation ($k_d f$ = 1×10^{-8} sec.$^{-1}$), reflecting their similar O-O bond strengths (34-37 kcal). [6] The disulfides do not undergo a unimolecular decomposition

---

[1] (a) Supported in part by Contract AT(11-1)1169 from the Atomic Energy Commission and Public Health Service Research Grant RG-9020 from the National Institutes of Health. Grateful acknowledgement is made to the donors of these funds. (b) Address after September 1963: Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana.

[2] (a) C. Walling, "*Free Radicals in Solution*," John Wiley and Sons, N.Y., 1957; pp. 150-161; (b) W. A. Pryor, "*Mechanisms of Sulfur Reactions*," McGraw-Hill Book Co., N.Y., 1962, pp. 42-57.

[3] W. A. Pryor and E. P. Pultinas, *J. Am. Chem. Soc.*, 85, 133 (1963).

[4] W. A. Pryor and T. L. Pickering, *ibid.*, 84, 2705 (1962).

[5] W. A. Pryor and P. K. Platt, *ibid.*, in press.

[6] T. L. Cottrell, "*Strengths of Chemicals Bonds*," Academic Press, Inc., N.Y., 1958, pp. 213,279.

at 60°, as expected from their larger bond energy (70-72 kcal).[2b]

Table I compares the transfer constants for these peroxides with data for the disulfides,[4] and in parentheses gives the main site of attack on the compound by the polystyryl radical.

Table I

Transfer Constants in Styrene at 60°

R	$C \times 10^4$	
	ROOR	RSSR
Benzoyl	550(O)[a]	107. (S)
Propyl	9(H?)	23. (S)
Isopropyl	4(H)	6.6(S+H)
t-Butyl	10(H)	1.4(H+S)

(a) Ref. 9

When R is benzoyl, the peroxide is attacked faster than the disulfide. Benzoyl peroxide is attacked at the O-O bond by radicals,[2b] and benzoyl disulfide is probably attacked at sulfur. This pair, therefore, might be considered "normal"; i.e., the O-O bond is cleaved faster than the S-S bond because it is weaker.

Isopropyl peroxide can be concluded to be attacked on hydrogen by the following argument. The same value of $\underline{k_d f}$ is obtained for this peroxide[7] (as well as for *t*-butyl peroxide[8]) by either the classical method[9] or by the new Bevington[10] tracer technique. This implies that that the alkoxy radical RO· adds to styrene faster than it fragments to lose its C-14 label. However, the transfer constant of isopropyl peroxide measured by the tracer technique is only 1/6 the value measured by the classical method. (In the case of *t*-butyl peroxide, both techniques

---

[7] W. A. Pryor and T. L. Pickering, to be published.

[8] Ref. 2b; W. A. Pryor, *J. Phys. Chem.*, **67**, 519 (1963).

[9] F. R. Mayo, R. A. Gregg and M. S. Matheson, *J. Am. Chem. Soc.*, **73**, 1691 (1951).

[10] J. C. Bevington and T. D. Lewis, *Polymer*, **1**, 1 (1950).

give approximately the same value of the transfer constant.) This implies that an unstable radical is formed in the transfer reaction which decomposes to lose its C-14 label faster than it adds to styrene, and it is reasonable to identify this radical as $C_3H_7O\text{-}OC_3H_6{:}$. These data imply that the radical resulting from hydrogen abstraction from isopropyl peroxide decomposes rapidly whereas that from t-butyl peroxide is stable enough to add styrene before fragmentation. Isopropyl peroxide gives $(CH_3)_2\dot{C}\text{-}OOC_3H_7$, and β-scission of the 0-0 bond can occur; t-butyl peroxide gives $\cdot CH_2\text{-}(CH_3)_2C\text{-}OO\text{-}C_4H_9$ and the radical center is insulated from the 0-0 bond.

Propyl peroxide might be postulated to transfer largely by H-abstraction since it reacts twice as fast as isopropyl peroxide and has two α-hydrogens. t-Butyl peroxide is known to be attacked at hydrogen by chlorine atoms and methyl radicals, and the polystyryl radical also probably attacks hydrogen.

The rate of hydrogen abstraction from all of the aliphatic peroxides is similar; the reaction is exothermic, the transition state is not far along the reaction coordinate, and the structure of the peroxide is not critical in determining rates. It is surprising, however, that t-butyl peroxide, which as no α-hydrogens, reacts faster than isopropyl peroxide. A possible explanation is that t-butyl peroxide is strained and that this causes a steric acceleration. (The actual heat of formation of t-butyl peroxide is -84.6 kcal., whereas a hypothetical strainless model would have -87.0 kcal; therefore, roughly 2 kcal. of strain is present.) t-Butyl sulfide, which is also strained, has an unusually large transfer constant.[4]

Bond energies [12] rationalize different mechanisms for reaction of peroxides and disulfides with polystyryl radicals. Eqs. 1-6 give the calculated heats of reaction for a simplified model. The most exothermic process for peroxides is H-abstraction with synchronous β-scission to form the strong C=O bond (reaction 2). Sulfur does not form a strong C=S bond, and disulfides are predicted to react by attack on the sulfur atom (reaction 6).

			Approx. ΔH
$\phi CH_2^{\cdot} + CH_3OOCH_3$	1	$\phi CH_3 + CH_3OOCH_2\cdot$	0
	2	$\phi CH_3 + CH_2{=}O + CH_3O\cdot$	-108
	3	$\phi CH_2OCH_3 + CH_3O\cdot$	-93
$\phi CH_2^{\cdot} + CH_3SSCH_3$	4	$\phi CH_3 + CH_3SSCH_2\cdot$	0
	5	$\phi CH_3 + CH_2{=}S + CH_3S\cdot$	0
	6	$\phi CH_2SCH_3 + CH_3S\cdot$	-10

Comments on the relative stability of the aliphatic peroxides [13] should not be understood as implying an unusual stability of _t_-butyl peroxide toward homolytic reactions. We have not been able to detonate any aliphatic peroxide in the liquid state, but we have had an accidental explosion of isopropyl peroxide in the gas phase (during an elemental analysis) at about 200° in an oxygen stream. Apparently the explosion of the aliphatic peroxides is either a molecular reaction [14a] or is a radical reaction of different mechanism [14b] from that which operates at 60°. We conclude that at moderate temperatures in the liquid phase all of the pure aliphatic peroxides are of similar stability toward homolytic reactions.

---

[12] Ref. 6; P. Gray and A. Williams, Chem. Revs., 59, 239 (1959); T. F. Palmer and F. P. Lossing, J. Am. Chem. Soc., 84, 4661 (1962).

[13] For example, Frost and Pearson, "Kinetics and Mechanism," John Wiley and Sons, N.Y., 2nd Ed., 1961, p. 365.

[14] (a) E. J. Harris, Proc. Roy. Soc. (London), 173A, 126 (1939); E. J. Harris and A. C. Egerton, ibid., 168A, 1 (1938); (b) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book., N.Y., 1960, p. 488.