

# Radical Reactions of Peroxides and Disulfides<sup>1</sup>

WILLIAM A. PRYOR, Purdue University

Using the standard techniques of polymer chemistry, (1, 2, 3) the chain transfer constant has been determined in styrene solution at 60° for the following compounds: Propyl disulfide, isopropyl disulfide, *t*-butyl disulfide, propyl peroxide, isopropyl peroxide, and *t*-butyl peroxide. The rate constant for the unimolecular, homolytic scission of the three peroxides has also been measured. Table I gives the data. Comparable data for benzoyl peroxide and disulfide are also given.

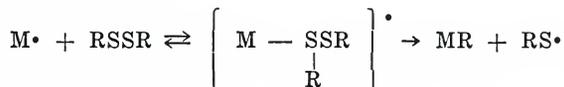
TABLE I  
Radical reactions of peroxides and disulfides compared

| R=              | ROOR                          |                     | RSSR                    |
|-----------------|-------------------------------|---------------------|-------------------------|
|                 | k <sub>d</sub> f              | C x 10 <sup>4</sup> | C x 10 <sup>4</sup> (2) |
| Propyl          | 2.7 x 10 <sup>-9</sup> (3, 5) | 8.4 (3, 5)          | 23.4                    |
| Isopropyl       | 2 x 10 <sup>-9</sup> (3, 6)   | 6. (3, 6)           | 6.60                    |
| <i>t</i> -Butyl | 1 x 10 <sup>-9</sup> (6)      | 8.6 (6)             | 1.42                    |
| Benzoyl         | 2.5 x 10 <sup>-6</sup> (3)    | 550. (3)            | 107.                    |

The unimolecular dissociation constants for all three aliphatic peroxides are similar. This reflects their similar bond energies and dissociation energies.

The chain transfer constants of the three aliphatic peroxides are also similar, and, therefore, the rate of reaction of the polystyryl radical with these three peroxides is very similar. This is unexpected in view of the known stability of *t*-butyl peroxide and the reputed explosiveness of primary and secondary peroxides. We have suggested (5) the following tentative explanation of this: The peroxides themselves are not explosives (7) at 25-60°. However, peroxides, like ethers, may be subject to peroxidation at their alpha-hydrogen atoms. Thus, isopropyl peroxide, like isopropyl ether, may be converted to an explosive by peroxidation. *t*-Butyl peroxide, then, could not form an explosive because it lacks alpha-hydrogens.

The transfer constant is very similar for each peroxide and its comparable disulfide. Since the O-O and S-S bond energies are very different (8), this suggests an addition-elimination mechanism for cleavage of the disulfides.

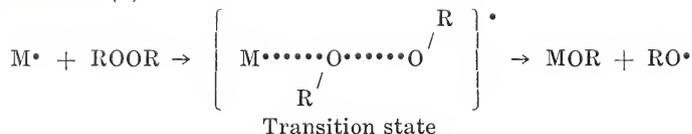


1. This research was financed in part by Grant RG 9020 from the National Institutes of Health and Grant AT(11-1) 1169 from the United States Atomic Energy Commission. The author expresses his gratitude for this support.

## Complex

The complex is similar to those proposed recently in other radical reactions (9).

Peroxides are more likely cleaved by a mechanism in which bond breaking accompanies bond making. This would be a radical displacement reaction (2).



## Literature Cited

1. WALLING, C. 1957. *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, pp. 67, 150-155, 159-161.
2. PRYOR, W. A. and T. L. PICKERING. 1962. *J. Am. Chem. Soc.* **84**: 2705
3. MAYO, F. R., R. A. GREGG and M. S. MATHESON. 1951. *J. Am. Chem. Soc.* **73**:1691
4. BEVINGTON, J. C. and T. D. LEWIS. 1960. *Polymer* **1**: 1.
5. PRYOR, W. A. and E. P. PULTINAS. 1963. *J. Am. Chem. Soc.* **85**: 133.
6. PRYOR, W. A. 1963. *J. Phys. Chem.* **67**: 519.
- 7a. HARRIS, E. J. 1939. *Proc. Roy. Soc. (London)* **173A**: 126.
- 7b. HARRIS, E. J. and A. C. EGERTON. 1938. *Proc. Roy. Soc. (London)* **168A**: 1.
8. PRYOR, W. A. 1962 *Mechanisms of Sulfur Reactions*, McGraw-Hill Book Co., New York.
9. THOMAS, J. R. and C. A. TOLMAN. 1962. *J. Am. Chem. Soc.* **84**: 2930