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FINAL REPORT

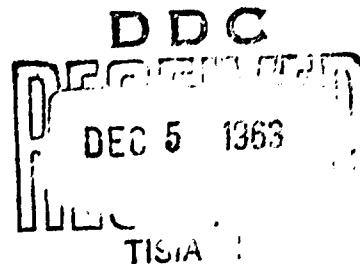
Title Page

- (a) University of Illinois
- (b) DA Project No. 59901004 AROD Project Number 2454-C
- (c) The Effect of Molecular Structure on the Cleavage of Oxygen-oxygen Bonds
- (d) DA-ARO(D)-31-124-G6
- (e) February, 1963
- (f) J. C. Martin, David Tuleen, Ernest Drew, Thomas Koenig, Thomas Fisher and John Schultz.
- (g) "Requests for additional copies by Agencies of the Department of Defense, their contractors, and other Government agencies should be directed to:

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- (h) Omit



Abstract

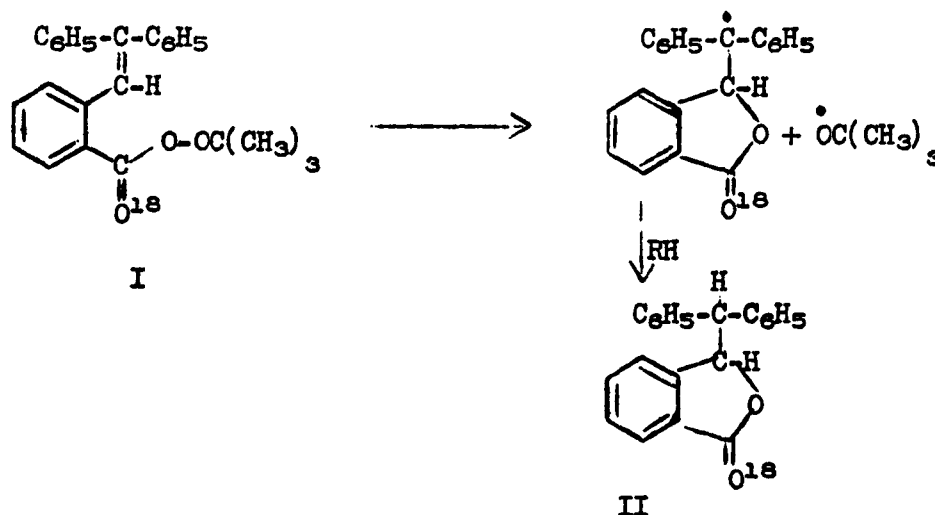
The importance of bridging to suitable neighboring groups in the transition states of reactions leading to free radicals has been demonstrated by kinetic studies on several systems. Accelerations of O-O bond cleavage by a factor of as much as 10^5 has been observed in favorable cases when sulfide sulfur is the neighboring group. Oxygen-18 traces techniques have been used to extend the concept to include the postulation of a bridged intermediate radical in one case.

Personnel Supported, On Grant DA-ARO(D)-31-124-G5

T. W. Koenig	May 1 - June 15, 1961	Ph.D.
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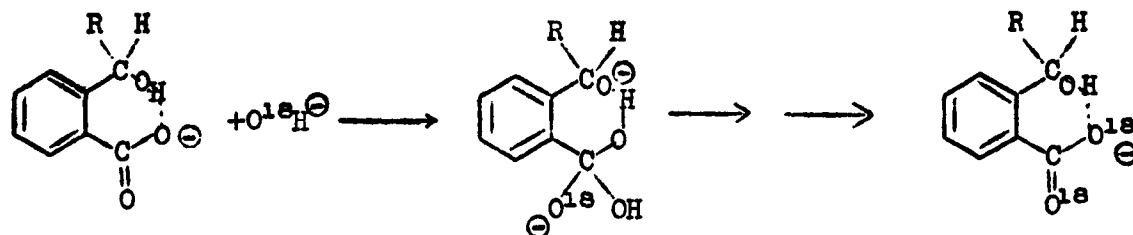
Final Report

Since our most recent Progress Report we have succeeded in establishing that Perester I decomposes with anchimeric acceleration (a factor of 67) by participation of the neighboring carbon-carbon double bond in the O-O bond cleavage. Perester I with oxygen-18 carbonyl label decomposes by a free rad-

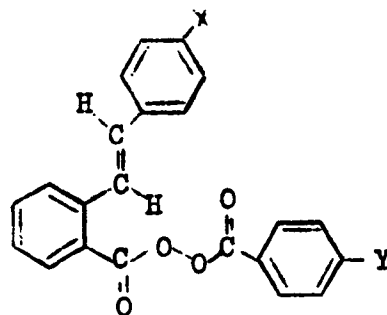


ical pathway to yield a lactone(II) in which at least 88% of the label remains in the carbonyl oxygen. This provides evidence against any mechanism involving intermediates in which the two carboxyl oxygens are indistinguishable and is most easily accommodated to the postulated mechanism shown, involving a bridged radical.

An interesting sidelight of this study evolved from observations made in the course of the analysis of the product lactone for position of labelling. It develops that the carboxylate ion from saponification of Lactone II exchanges oxygen with solvent water at a rate several orders of magnitude faster than do most carboxylate ions. Appropriate control experiments were run to show that the exchange occurs in the carboxylate ion, not the acid. A postulated mechanism involving neighboring hydroxyl group catalysis is in accord with the known facts. This finding is of interest from the viewpoint of the similarity

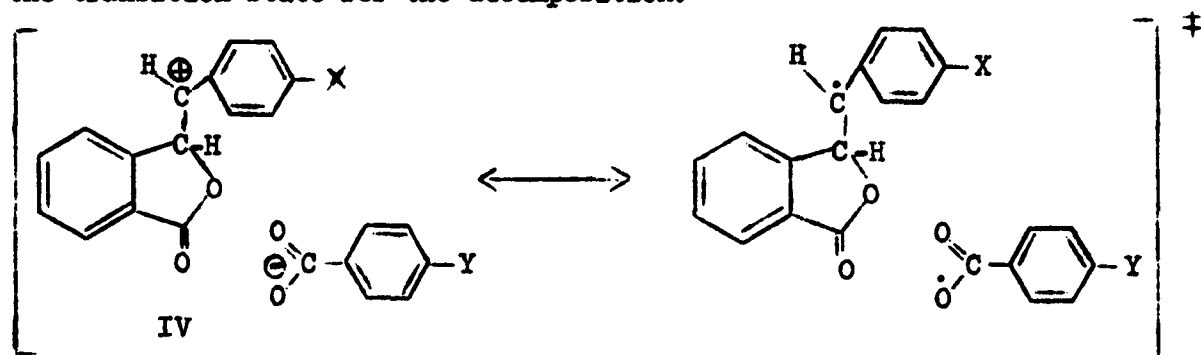


between this mechanism and postulated mechanisms of enzyme action. Its generality will be tested.

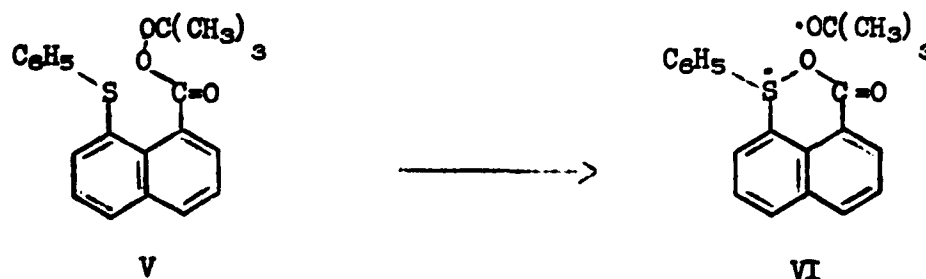


III

In the related series of diacylperoxides (III) rates of radical production vary with substituent Y in a manner correlated with a Hammett ρ value of +0.7. Both this value and a negative value of ρ for the variation of rate with substituent X suggest an important contribution of structure IV to the description of the transition state for the decomposition.



The formation of a six-ring bridged radical (VI) is indicated in the decomposition of Perester V.



The increase in rate of radical formation of a factor of 10^4 , relative to the unsubstituted t-butyl pernapthoate, is most readily explained within the context of our previous work (see reprints) in terms of neighboring sulfur participation in the transition state as in VI.

Four additional papers treating on the work supported by this grant will be submitted for publication shortly. Copies will be submitted to ARO(D) as a supplement to this report.