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6 THE CHEMISTRY OF DIOXIRANE SYSTEMS.

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Professor of Chemistry

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Providence, R.I. 02912

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The recently-postulated ring peroxide intermediate dioxirane has been reacted with reducing agents (i.e., nucleophiles) in order to better understand its usefulness as an oxygen-transfer reagent and a decontaminant. With olefins (both water-soluble and water-insoluble), good yields of unusual epoxides have been obtained; in some instances, phase-transfer catalysis was found effective. With pyridine, a kinetic investigation brought out the various steps and processes that occur in the formation and subsequent reactions of the dioxirane ring. A number of exploratory investigations were carried out.		

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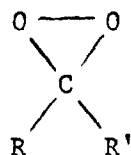
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STATEMENT OF THE PROBLEM

The purpose of this grant was to investigate the chemistry of the new, reactive peroxide dioxirane



which had been postulated in the ketone-catalyzed reactions of peroxomonosulfuric acid (Caro's acid). This reactive ring would show interesting properties, not the least of which would be high oxygen-transfer capability towards reducing agents that are only poorly nucleophilic.

BRIEF HISTORY

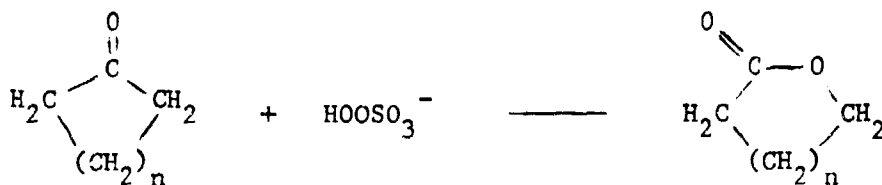
The postulation of the intermediacy of the dioxirane ring system by the principal investigator happened during a visit to an industrial laboratory where the ketone catalysis of peroxomonosulfate reactions was being studied. Such an intermediate is not forbidden by the bonding principles that govern chemical systems, but the combination of a weak oxygen-oxygen single bond with a small ring configuration dictated that it would be extremely reactive.

The first report on the possibility was a mention in the article dealing with ketone catalysis¹. An isotope study in conjunction with the industry gave results that strongly supported the postulation of dioxirane². It appears that many ketones will perform the catalytic function³.

RESULTS AT BROWN

Experiments on dioxirane were initiated at Brown University prior to the start of this grant; with the first substrate of interest being unusual olefins. Dr. K.M. Ibne-Rasa looked at the catalytic capabilities of some cyclic ketones, specifically cyclobutanone, cyclopentanone and cyclohexanone. It was found that some oxidizing power was lost as indicated by poor yields of epoxides. With cyclohexanone, about 15% of ketone was lost to side reaction (see below); with cyclopentanone, more than 50% was lost, whereas with cyclobutanone, no epoxide was formed.

This loss of oxidizing power was traced to a side-reaction, the Baeyer-Villiger oxidation of the ketone itself.



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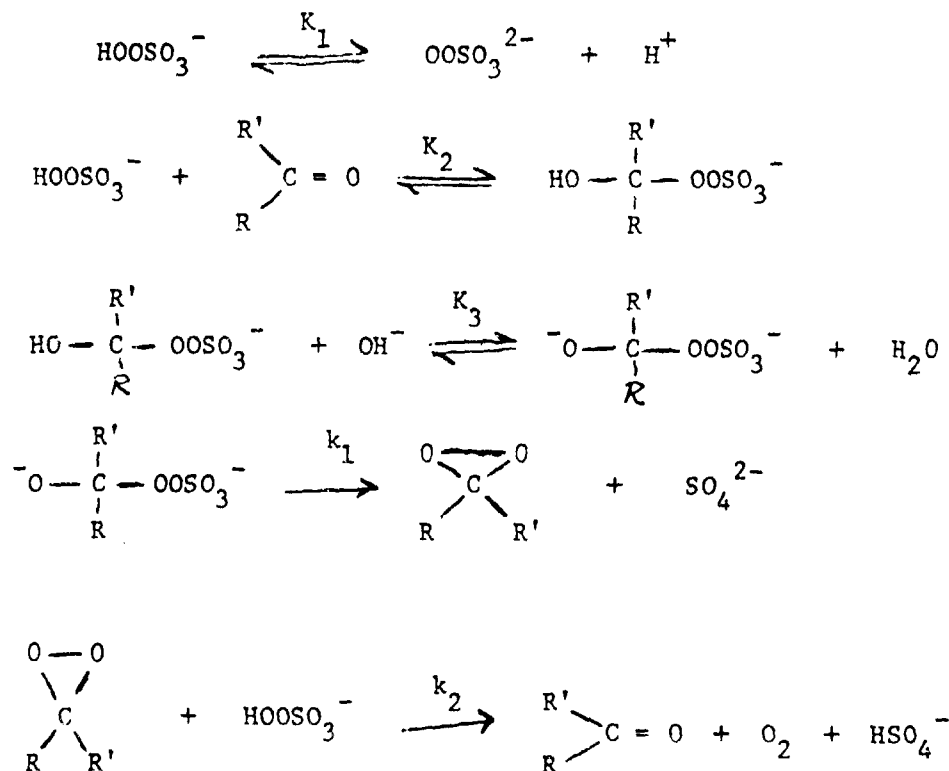
which clearly is more important as n decreases from 3 to 2 and then to 1. In the case of cyclohexanone, the product cyclic ester ϵ -caprolactone was isolated and shown not to be formed through a dioxirane intermediate by means of isotope experiments⁵. The Baeyer-Villiger mechanism will be mentioned below.

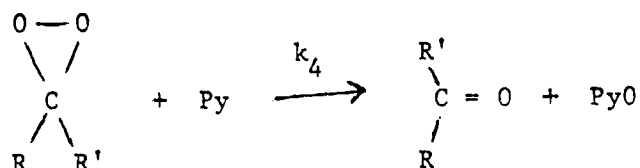
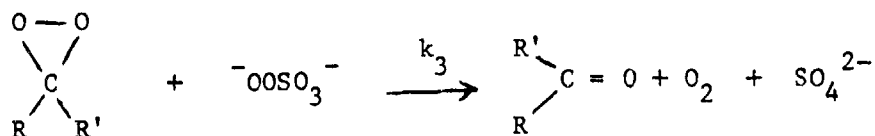
Dr. Ruth H. Pater made a careful study of oxidation of water-soluble olefins by the caroate and ketone system⁵. Since many of her results now have appeared in print^{6,7}, we can summarize them as follows: 1) olefins that are unreactive towards most peroxides can be epoxidized by the dioxirane intermediate, 2) some olefins that only give epoxides in very poor yield by normal procedures give up to quantitative amounts of the ring product when dioxirane is generated in situ from Caroate and ketone, and 3) the reagent can give both stereospecific and regio-specific epoxidations.

Our coworkers in Bari (Italy) have found that phase-transfer catalysis can be employed to epoxidize water-insoluble olefins in good yield⁷. It now seems possible to do a wide variety of epoxidations under mild conditions in good yields^{5,6,7}.

In order to broaden the type of substrate that could be oxidized by dioxirane, a study of poorly-nucleophilic organic nitrogen substrates was made. Some substrates react directly with Caro's acid, thus there is no need for ketone catalysis. Other substrates (such as azobenzene) are too unreactive even for dioxirane oxidation. Nevertheless, it was found that pyridine reacted at a very convenient rate and a mechanism study has been carried out and will soon appear in print⁸.

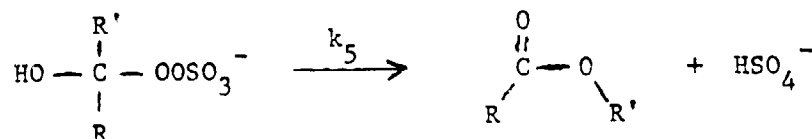
We can now present a general mechanism for dioxirane oxidation and decomposition. A number of individual steps have been uncovered; these steps are as follows:





The first three steps (K_1 , K_2 , K_3) are known to be rapid equilibria. The next step (k_1) is slow and in most instances rate-determining; it is in this step that the dioxirane intermediate is formed. There are two paths (k_2 and k_3) for oxygen production, that is to say, the net decomposition of Caro's acid. In k_4 where pyridine Py is representative substrate, oxidation by dioxirane is shown. Steps k_2 , k_3 and k_4 are rapid and competitive.

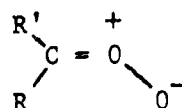
The step for the Baeyer-Villiger side reaction was shown to be



rather than a rearrangement following step k_1 .

PRESENT STATUS

It is of interest here to point out that our work has stimulated considerable interest. Professor Ruggero Curci of the University of Bari has been looking into the synthetic uses of the dioxirane system. Professor Waldemar Adam of the University of Puerto Rico and Wurzburg (Germany) is carrying out experiments to find out how the chemical behavior of dioxirane contrasts with that of its isomer the carbonyl oxide



which is another high energy intermediate. Attempts to isolate dioxiranes are now in progress in Professor Adam's laboratory. Although these attempts have not to date proven successful, the three-membered ring has been reported in transient intermediate spectroscopy. Finally, the possibility of chemiluminescence from a dioxirane rearrangement seems likely and is being looked for.

POTENTIAL DIOXIRANE USES

One use is immediately seen as a consequence of our work. The facile synthesis of unusual epoxides under mild conditions, both in aqueous and non-polar media, indicates that dioxirane has considerable potential for oxidation of poorly-reactive substrates. The principal investigator feels that oxidation of nitrogen substrates will be particularly important since present oxidation systems tend to "chew up" nitrogen substrates rather than giving clear oxidation.

Another use is in decontamination procedures. Oxidation of toxic substances can be very slow even by such peroxides as meta-chloroperoxybenzoic acid. The mixture of Caro's acid and ketone which forms the reactive dioxirane is made from two materials which can be stored conveniently.

The dioxirane system has some natural limitations. It is obvious that a reactive substrate such as thiacyclohexane can be conveniently oxidized without need of a ketone catalyst. Less apparent is the limit on poorly nucleophilic substrates; if a substrate is less reactive than Caro's acid, then oxygen production will obtain. We can therefore say that dioxirane will be most useful for substrates such as pyridine, cinnamic acid and certain acetylenes of low but not vanishing reactivity.

PERSONNEL

Ph.D.

During the course of this grant period, four chemists worked with the principal investigator. Dr. Ruth H. Pater (who started as a graduate student and stayed on as a Research Associate) and Dr. Khairat M. Ibne-Rasa studied olefin oxidations and the Baeyer-Villiger reaction. Dr. Gerrit Levey and Mr. Alex Chako carried out preliminary studies on several nucleophiles (chloride ion, nitrite ion, etc.) to find one that would be amenable to careful kinetic investigation. On the basis of this, Dr. Andrew R. Gallopo chose to carry out the experiments on pyridine which are now being published.

PUBLICATIONS

Four publications have stemmed from the investigations carried out under this grant. These are as follows:

- (1) R. H. Pater, "Chemistry of Dioxiranes", Ph.D. thesis, Brown University (1977).
- (2) J.O. Edwards, R.H. Pater, R. Curci and F. DiFuria, "On the Formation and Reactivity of Dioxirane Intermediates in the Reaction of Peroxoanions with Organic Substrates", Photochem. Photobiol., 30, 63 (1979).

(3) R. Curci, M. Fiorentino, L. Troisi, J.O. Edwards and R. H. Pater, "Epoxidation of Alkenes by Dioxirane Intermediates Generated in the Reaction of Potassium Caroate with Ketones", J. Org. Chem., 45, 4758 (1980).

(4) A. R. Gallopo and J.O. Edwards, "The Kinetics and Mechanism of the Oxidation of Pyridine by Caro's Acid Catalyzed by Ketones", J. Org. Chem., accepted for publication.

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- (1) R. E. Montgomery, J. Amer. Chem. Soc., 96, 7820 (1974).
- (2) J.O. Edwards and H. Smitherman, unpublished experiments.
- (3) R.E. Montgomery, U.S. Patent #3, 822, 114 (1974).
- (4) K.M. Ibne-Rasa and J.O. Edwards, unpublished experiments.
- (5) R.H. Pater, Ph.D. thesis, Brown University (1977).
- (6) J.O. Edwards, R.H. Pater, R. Curci, and F. DiFuria, Photochem. and Photobiol., 30, 63 (1979).
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- (8) A. R. Gallopo and J.O. Edwards, J. Org. Chem., accepted for publication.