

THE PERACID OXIDATION OF SINGLET OXYGEN ACCEPTORS

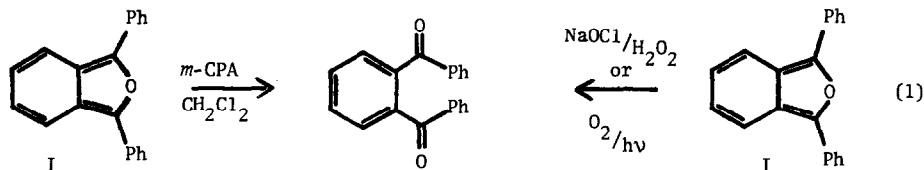
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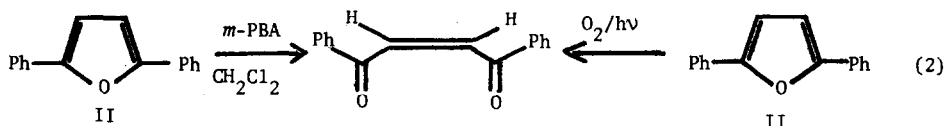
Although peroxyacids have received considerable attention as epoxidizing agents, the possibility that they yield singlet oxygen upon bimolecular decomposition¹ has not been thoroughly investigated. This is surprising in view of the intensive research directed toward the intriguing implications of singlet oxygen chemistry in monooxygenase-catalyzed oxidation reactions.² The finding that peroxyacids have the ability to mimic the hydroxylation reactions catalyzed by monooxygenases³ has prompted us to study the peroxyacid oxidation of singlet oxygen acceptors. We report here on the *m*-chloroperoxybenzoic acid (*m*-CPA) oxidation of the singlet oxygen acceptors, 1,3-diphenylisobenzofuran (I) and 2,5-diphenylfuran (II). In a typical experiment the *m*-CPA (0.002 mole in 30 ml CH₂Cl₂) was added dropwise to a solution of the furan (0.002 mole in 30 ml CH₂Cl₂) and the resulting mixture was refluxed in the dark (2 hr. for I, 4 hr. for II). After work-up, I yielded only *o*-dibenzoylbenzene in 90% recovered yield. (Rx. 1).



The product was identical in every respect (mp, mmp, ir, tlc) with authentic *o*-dibenzoylbenzene produced by the photooxidation and the sodium hypochlorite-hydrogen peroxide oxidation of I. The product from II was *cis*-dibenzoylethylene recovered in 85% yield (Rx. 2). This product could also

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be obtained by the reaction of photochemically generated singlet oxygen with II. In each of our



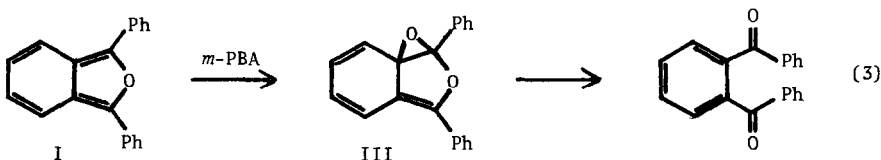
reactions the product from *m*-CPA breakdown was shown to be *m*-chlorobenzoic acid.

Peroxyacids decompose in aqueous solutions to produce molecular oxygen and the parent acid in a second order kinetic pathway.⁴ The suggestion that the oxygen produced was in the singlet state led to an attempt to trap it with 9-methyl-10-phenylanthracene, resulting in a 21% yield of 9-methyl-10-phenyl-anthracene *endo* peroxide.¹

Since both singlet oxygen and peroxyacids yield the same products with commonly used reactants I and II, it is important to further investigate the mode of peroxyacid oxidation. One must consider two possible mechanisms: (1) singlet oxygen produced by bimolecular decomposition of the peroxyacid and (2), epoxidation by oxygen atom transfer, followed by rearrangement.

When *m*-CPA was refluxed in CH_2Cl_2 with 9,10-diphenylanthracene, a known singlet oxygen acceptor, no stable endoperoxide could be isolated, in fact, no products could be detected by tlc. The singlet oxygen quenchers β -carotene and DABCO⁵ had no inhibitory effect on the yields of *o*-dibenzoylbenzene and *cis*-dibenzoylethylene produced by *m*-CPA oxidation of the acceptors I and II. Because of the bimolecular nature of peroxyacid decomposition a kinetic study could be used to further eliminate the involvement of singlet oxygen, since an epoxidation mechanism should be first order in each component, diene acceptor and peroxyacid. The rate of the reaction was determined by following the disappearance of *m*-CPA acid according to the procedure of Banerjee and Budke.⁶ Figure 1 shows the rate of disappearance of the peroxyacid in the presence and absence of singlet oxygen acceptor. A plot of $\log C$ vs time yields a straight line and the calculated pseudo first order rate constant is 3.5×10^{-5} mole/l-min.. In further studies not described here the disappearance of I or II with excess *m*-CPA was also shown to obey pseudo first order rate kinetics.

In view of the above results one can rule out the involvement of free singlet oxygen and



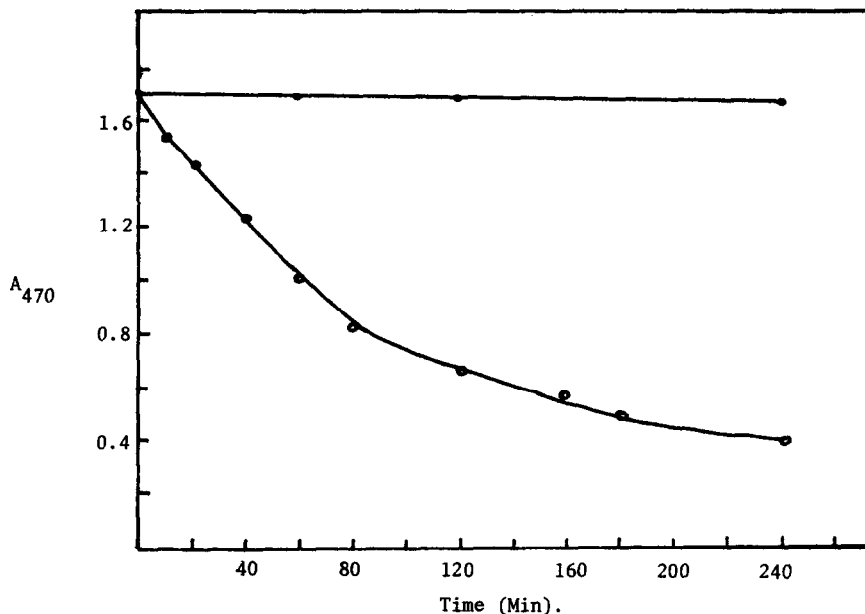


Figure 1. Effect of 2,5-Diphenylfuran on the rate of decomposition of *m*-CPA at 6.0°C.

- *m*-CPA (0.016 M) in CH₂Cl₂
- *m*-CPA (0.016 M) in CH₂Cl₂ plus 2,5-DPF (0.16 M).

instead consider oxygen atom transfer (Rx. 3). This mechanism is consistent with observed second order kinetics and with the normal results of peroxyacid oxidation. A careful analysis of the reaction mixture failed to show the presence of products derived from *m*-chlorobenzoic acid cleavage of intermediate III, but this intermediate would be expected to undergo rapid rearrangement to *o*-dibenzoylbenzene. This rearrangement to the diketone is analogous to that occurring during the peroxyacid oxidation of diphenylacetylene,^{7,8} and substituted cyclopropenes.⁹

Our results demonstrate the care one must use when attempting to gather evidence for or against the involvement of singlet oxygen in various chemical and physical processes. Chemical trapping experiments with furan derivatives to prove the existence of singlet oxygen are not justified unless they are used in conjunction with other experiments, i.e., competitive quenching,⁵ rate differences in deuterated solvents¹⁰ and azide trapping of dioxetane intermediates.¹¹ Finally, we can conclude that the ability of peroxyacids to be acceptable models of monooxygenases depends upon oxygen atom transfer (oxenoid mechanism)¹² rather than oxygen molecule transfer (singlet oxygen).

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