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ROLE OF AZIDE IN SINGLET OXYGEN REACTIONS: REACTION OF AZIDE WITH SINGLET OXYGEN.

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In previous publications we noted that the normal products from the photooxidation of various olefins can be intercepted by nucleophilic species such as methanol and azide ion.[1,2] Although we interpreted the azide effect in terms of interception of a peroxirane intermediate, we could not rule out the possibility of an azide reaction with singlet oxygen or with the triplet state of the sensitizer used in the photooxidation. Recently, we constructed a pulsed ruby laser photolysis apparatus and used this to measure the lifetime of singlet molecular oxygen in various solutions.[3] We have now used this apparatus to reexamine in more detail the role which azide ion plays in singlet oxygen reactions.[4] The essential observations are as follows.

The rate constants for the reaction of azide ion with the triplet states of the sensitizers methylene blue and pyrene are $5 \times 10^5 M^{-1} sec^{-1}$ and $< 5 \times 10^2 M^{-1} sec^{-1}$ respectively, whereas the rate constant for energy transfer to ground state oxygen is $3 \times 10^9 M^{-1} sec^{-1}$.[5] Hence, under our typical reaction conditions (0.3 M N_3^- and $5 \times 10^{-3} M$ oxygen) quenching of triplet state sensitizer by molecular oxygen very efficiently competes with azide quenching of triplets. This confirms our earlier suggestion that azide ion does not interfere with energy transfer to ground state oxygen when either pyrene or methylene blue is used as the sensitizer.[2] This need not always be true, and we suspect that other dyes (Rose Bengal for example) may be more susceptible to reaction with azide ion.

The other major assumption we were not previously able to test was that azide does not react with singlet oxygen. We have now used the laser photolysis apparatus to determine the lifetime of singlet oxygen in solution and have measured the effect of azide on the lifetime of singlet oxygen and

and these results are presented in Fig. 1.

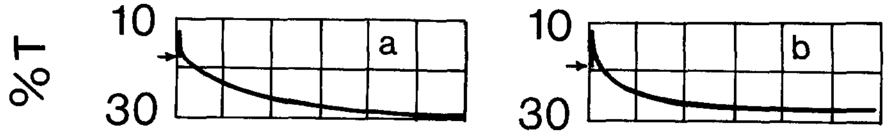

Fig. 1. (a) Bleaching at 410 nm of 2×10^{-5}M 1,3-diphenylisobenzofuran (1 cm cell)

(b) Bleaching at 410 nm of 2×10^{-5}M 1,3-diphenylisobenzofuran with 5×10^{-4}M NaN_3 (1 cm cell). [1 div. = 5 μsec, solvent methanol]

With low concentration of acceptor (1,3-diphenylisobenzofuran) the lifetime of singlet oxygen is calculated to be about 5 μsec in methanol. Addition of 5×10^{-4}M sodium azide produces a significant decrease in the lifetime of singlet oxygen and from the experiment shown in Fig. 1b we compute that the rate constant for the quenching of singlet oxygen by azide ion is $2.2 \times 10^{8}M^{-1}sec^{-1}$. Since azide is usually present in a 5-10 fold excess over the acceptor in our photooxidation reactions, and since the rate constants for reaction of acceptors with singlet oxygen are usually less than $4 \times 10^{7}M^{-1}sec^{-1}$, the value for tetramethylethylene (TME),[3] we expect singlet oxygen reactions to be strongly quenched by azide. We have used the absolute rate constants for reaction of the various acceptors with singlet oxygen to compute the effect which azide ion should have had on the rate of photooxidation of the various acceptors and these values are shown in Table I along with observed results.

Although reductions by factors of 150 up to 70,000 were expected on the basis of azide ion quenching of singlet oxygen, the observed oxidation rates are retarded only by factors of 5-10 by azide. This indicates that some fraction of the quenching acts produce a new species which can react with the acceptors and form the observed azide hydroperoxides. Thus, our initial assumption that azide ion does not react with singlet oxygen is shown to be invalid and this eliminates one piece of evidence for peroxirane intermediates in the reaction of singlet oxygen with olefins.[1,2] The interception of the normal oxidation products by other nucleophiles, such as methanol,[1] water and hydroxide ion, and the effects of pH and solvent on the oxidation reactions still remain in our view as best interpreted in terms of peroxirane intermediates.[6-8] Such a view is also supported by the close correlation between the rates of photooxidation and peracid oxidation of olefins noted some time ago by Kopecky and Reich.[8]

In a recent publication Foote[9] has reached similar conclusions regarding the behavior of azide ion in photooxygenation reactions, but these studies involved the use of sensitizers which may undergo photochemical reaction with azide ion.

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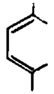
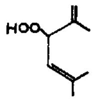
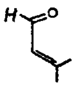
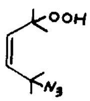
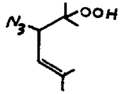
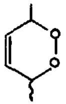
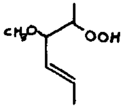
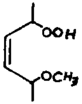
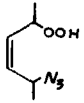
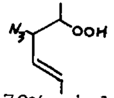
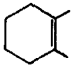
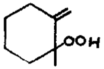
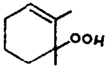
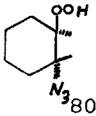
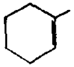
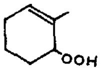
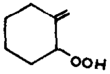
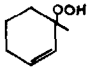
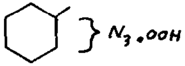
References

1. W. Fenical, D. R. Kearns and P. Radlick, J. Amer. Chem. Soc., 91, 7771 (1969).
2. D. R. Kearns, W. Fenical and P. Radlick, Ann. N.Y. Acad. Sci., 171, 34 (1970).
3. P. B. Merkel and D. R. Kearns, Chem. Phys. Letters (to be published).
4. A preliminary account of this work was presented at the A.C.S. Meeting in Washington, D.C., Sept., 1971, Div. of Petr. Res. Abstracts, p. A9.
5. R. Nilsson, P. B. Merkel and D. R. Kearns (submitted for publication).
6. W. Fenical, D. R. Kearns and P. Radlick, J. Amer. Chem. Soc., 91, 3396 (1969)
7. N. Hasty, D. R. Kearns and P. Radlick (unpublished results).
8. K. R. Kopecky and H. H. Reich, Can. J. Chem., 43, 2265 (1965).
9. C. S. Foote, T. T. Fujimoto and Y. C. Chang, Tetrahedron Letters, this issue, and private communication (1970).

TABLE I

ACCEPTOR	NORMAL PRODUCTS^a	AZIDE INCORPORATION PRODUCTS	SENSITIZER	$[N_3]$, (M)	OBSERVED RATE REDUCTION^b	PREDICTED RATE REDUCTION^b
	 	  53% yield	MB Pyrene	0.31 0.33	7.0 60	3,000
	  	  70% yield	MB Pyrene	0.31 0.33	0.5 1.7	9,000
		UNKNOWN	MB	0.31	7.0	1,500
	 	 80% yield	MB Pyrene	0.23 0.15	7.7 25	1,500
	  	 10% yield	MB	0.5	4.5	70,000

a. Photolysis in methanol with Methylene Blue as sensitizer.

b. Rate reduction is the ratio of the rate of photooxidation with no azide present to the rate in the presence of sodium azide.