

THE REACTION OF 3,3-DIMETHYL-1,2-DIOXETANE

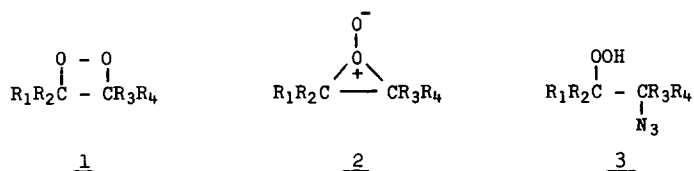
WITH SODIUM AZIDE<sup>1</sup>

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Previously we had demonstrated the presence of 3,3-dimethyl-1,2-dioxetane (1a, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = R<sub>4</sub> = H) as an intermediate in the basic decomposition of chloro-*t*-butyl hydroperoxide (CBHP)<sup>2</sup> and reported the reactions of a few nucleophiles with 1a.<sup>2c</sup> This study is extended to include the more nucleophilic azide ion, which is of particular interest, since an intermediate produced in the reaction of olefins with photochemically generated singlet oxygen is reported to be trapped by azide ion.<sup>3</sup> It was suggested<sup>3,4</sup> that the intermediate was either a 1,2-dioxetane (1) or a perepoxide (2) and that reaction with azide ion gave a β-azido hydroperoxide (3).



Additional evidence has been presented for the generation of 1,2-dioxetanes from the reaction of singlet oxygen with olefins.<sup>5</sup> Our results with 1a indicate that azide ion attacks the 1,2-dioxetane to give acetone and nitrogen, but that the β-azido hydroperoxide (3a, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = R<sub>4</sub> = H) is either not produced or if formed, it is a transient intermediate.

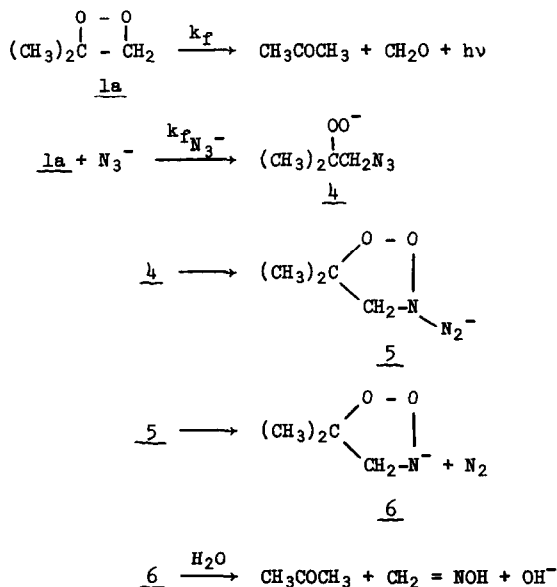
During the decomposition of CBHP (initial concentration, 0.0139 M) with base (0.200 M sodium

hydroxide) in 60% aqueous methanol at 30.0°, the iodometric titer decreased at approximately the same rate in the absence ( $1.36 \times 10^{-3} \text{ sec}^{-1}$ ,  $\mu = 1.58 \text{ M}$ ) or the presence of 1.00 M sodium azide ( $1.2 \times 10^{-3} \text{ sec}^{-1}$ ,  $\mu = 1.2 \text{ M}$ ). Similarly, the rate coefficient for decay of light emission, which was shown to equal the iodometric rate coefficient,<sup>2b</sup> was approximately equal in the absence ( $2.19 \times 10^{-3} \text{ sec}^{-1}$ ,  $\mu = 1.58 \text{ M}$ ) or presence ( $1.99 \times 10^{-3} \text{ sec}^{-1}$ ,  $\mu = 1.58 \text{ M}$ ) of 0.182 M sodium azide at 30° with an initial CBHP concentration of  $1.00 \times 10^{-2} \text{ M}$  and a base concentration of 1.58 M. Product studies, with reactant concentrations the same as in the former reaction, indicate a 67% yield of acetone (by glc) and 35% yield (by vacuum line, mass spectral analysis) of nitrogen based on the hydroperoxide. Control experiments with *t*-butyl hydroperoxide, base and azide ion give no reaction. This indicates that the potential intermediate  $\beta$ -azido hydroperoxide (3a) does not build up in concentration under the basic reaction conditions. Furthermore, significant concentrations of 3a are not formed in the absence of strong base. When an isolated sample of 1a<sup>2c</sup> (0.2 M) is treated with sodium azide (0.5 M) in aqueous solution, an immediate evolution of nitrogen results and acetone is the only observable product in the nmr spectrum after nitrogen evolution is complete. A potassium iodide-starch test at this time indicates the absence of peroxides.

By a previously reported kinetic analysis,<sup>2b,c</sup> it is found that azide ion does increase the rate disappearance of the 1,2-dioxetane 1a. The rate coefficient ( $k_{f_{\text{obs}}}$ ) for disappearance of 1a in the absence of sodium azide is  $9.00 \times 10^{-3} \text{ sec}^{-1}$  at 30° in 60% aqueous methanol ( $[\text{CBHP}]_0 = 1.00 \times 10^{-2} \text{ M}$ ,  $[\text{Base}] = 1.58 \text{ M}$ ), while in the presence of 0.182 M sodium azide  $k_{f_{\text{obs}}}$  increases to  $23.6 \times 10^{-3} \text{ sec}^{-1}$ . It was shown<sup>2c</sup> that  $k_{f_{\text{obs}}} = k_f + k_{f_B}[\text{OH}^-] + k_{f_d}[\text{X}]$ ; where  $k_f$ ,  $k_{f_B}$  and  $k_{f_d}$  are the unimolecular, base catalyzed and added reactant rate coefficients for the decomposition of 1a. In this instance,  $k_{f_d} \equiv k_{f_{\text{N}_3^-}}$  and it is calculated to be  $80.3 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$ .

Mechanisms can be written where azide ion attacks either oxygen or carbon of 1a to eventually give acetone and nitrogen. The claim that  $\beta$ -azido hydroperoxides are isolable,<sup>3</sup> would suggest that attack by azide ion on 1a occurs at oxygen, since attack at carbon would give 3a. However, analysis of the above kinetic data with the aid of the Edwards Equation<sup>6</sup> suggests that attack at carbon is most likely and that 3a is a transient intermediate. It was demonstrated previously<sup>2c</sup> that attack by bromide ion on 1a occurred at oxygen, where  $k_{f_d} \equiv k_{f_{\text{Br}^-}} = 18.7 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$  at 30° in 60% aqueous methanol ( $[\text{CBHP}]_0 = 1.00 \times 10^{-2} \text{ M}$ ,  $[\text{Base}] = 1.58 \text{ M}$ ,  $[\text{Br}^-] = 1.00 \text{ M}$ ). If azide ion also attacks 1a at oxygen, one calculates<sup>7</sup> the ratio  $k_{f_{\text{N}_3^-}}/k_{f_{\text{Br}^-}}$  to be  $3.4 \times 10^{-5}$ .

Instead, the observed ratio is 4.29 ( $= 80.2 \times 10^{-3} / 18.7 \times 10^{-3}$ ), which differs significantly in magnitude as well as being reversed in order compared to the calculated value and suggests displacement at carbon. A reasonable mechanism for the decomposition of 1a in the presence of azide ion, which explains the products and is initiated by attack at carbon is given below.



#### References

1. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society.
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3. W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, 91, 7771 (1969).
4. See also: A. G. Schultz and R. H. Schlessinger, *Tetrahedron Lett.*, 2731 (1970).
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7.  $\text{Log} k_{\text{N}_3^-} / k_{\text{Br}^-} = \alpha(E_{\text{N}_3^-} - E_{\text{Br}^-}) + \beta(\text{H}_{\text{N}_3^-} - \text{H}_{\text{Br}^-})$ , with  $\alpha = 6.31$ ,  $\beta = -.394$ ,  $E_{\text{N}_3^-} = 1.58$ ,  $E_{\text{Br}^-} = 1.51$ ,  $\text{H}_{\text{N}_3^-} = 6.46$  and  $\text{H}_{\text{Br}^-} = -6.00$ .<sup>6,8</sup>
8. The values of  $\alpha$  and  $\beta$  correspond to the reaction of nucleophiles with hydrogen peroxide ("Rate Law I").<sup>9</sup>
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