

ON THE MECHANISM OF THE REACTION OF OZONE WITH *tert*-BUTYL HYDROPEROXIDE:  
1,3-DIPOLAR INSERTION, ELECTRON-TRANSFER, OR MOLECULE-ASSISTED HOMOLYSIS,<sup>1,2</sup>

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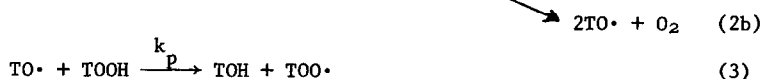
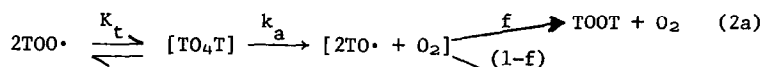
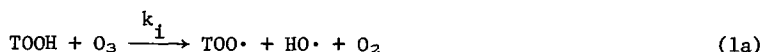
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The mechanism of the reaction of 1,3-dipolar compounds such as ozone is a matter of considerable current interest and controversy.<sup>3</sup> For the cycloaddition of such substances with unsaturated compounds, arguments have been advanced for a concerted mechanism<sup>3a</sup> and also for one that involves diradical intermediates.<sup>3b</sup> We here report evidence on the mechanism of one reaction of a related type, the reaction of ozone with *tert*-butyl hydroperoxide, a reaction that formally involves the insertion of ozone into an O-H bond. The formal insertion of ozone into C-H bonds is known, and both concerted and radical mechanisms have been proposed.<sup>4</sup>

The reaction of ozone with organic hydroperoxides is known ultimately to produce free radicals.<sup>5</sup> We have examined the reaction of ozone with *tert*-butyl hydroperoxide (TOOH) at -60 to 20°C in several solvents. When the reaction is nearly complete, the products (by glpc) consist of 78% *tert*-butyl alcohol (TOH); 6% di-*tert*-butyl peroxide (TOOT); 4% acetone, and 8% recovered TOOH. At 50% reaction, 42 mmoles of ozone are consumed per 100 mmoles of TOOH used.<sup>2</sup> We have studied the kinetics of the reaction in CFCl<sub>3</sub> at -4°C, using pre-prepared solutions of ozone, mixing in the TOOH at time zero, and following the disappearance of the UV band of ozone at 267 nm ( $\epsilon = 2420$ ) with time. (Ozone is generally about  $4 \times 10^{-4}$  M and is the limiting reagent.)

The products can be rationalized<sup>2,5</sup> by steps 1-4. However, this simple scheme predicts



that the yield of TOOT should equal the amount of  $O_3$  used (since eq 2a terminates two radicals and eq 1a forms two). Since our products show a much lower relative yield of TOOT, eq 5 also must be added to the kinetic scheme.



Acetone clearly arises from  $\beta$ -scission of *tert*-butoxy radicals (eq 4), demonstrating the radical nature of the reaction. Nevertheless, we have measured the competition between  $\beta$ -scission to give acetone (eq 4) and hydrogen abstraction from an added hydrogen donor QH (eq 6).



We have used cyclohexane as the hydrogen donor in acetonitrile solvent at  $0^\circ C$ . Figure 1 shows a plot of the product ratio versus cyclohexane concentration, the slope of which equals  $k_H/k_\beta$ . As can be seen, our data yield 91 for this ratio, in good agreement with the literature value of 82.<sup>6</sup> Thus, *tert*-butoxy radicals are involved in the production of both acetone and *tert*-butyl alcohol.

When the TOOH concentration is relatively high, eq 3 is faster than eq 4, and the acetone yields are very low. Thus, in  $CFCl_3$  at  $-4^\circ C$ , the acetone yield is <1% at 50% reaction. Under these conditions, eq 4 can be neglected, and a steady state analysis of eqs 1, 2, 3, and 5 gives eq 7. Equation 7 can be rearranged and plotted (using initial rates and

$$\text{Rate}(-O_3) = k_i [TOOH][O_3] + k_x \left( \frac{k_i}{k_t} \right)^{0.5} [TOOH]^{0.5} [O_3]^{1.5} \quad (7)$$

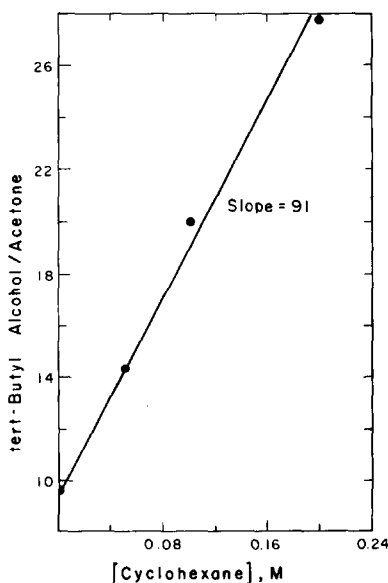


Figure 1. A plot of relative yields of TOH/acetone versus the concentration of  $C_6H_{12}$  as hydrogen donor. The slope equals  $k_H/k_\beta$ .

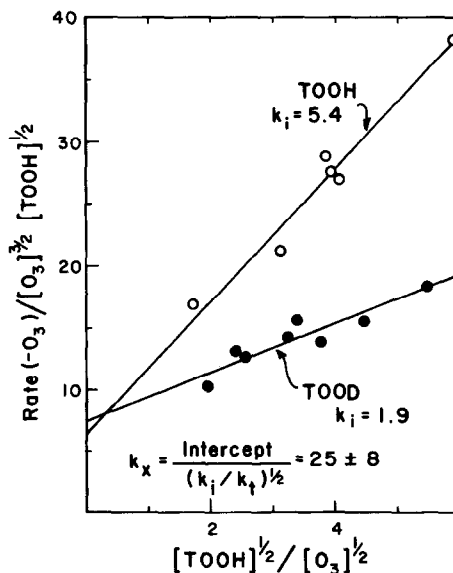


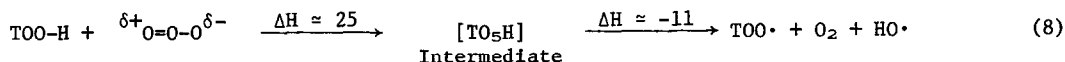
Figure 2. A plot of eq 7. The slope equals  $k_i$ , and values of this rate constant for both TOOH and the deuterated analogue, TOOD, are shown.

initial or average concentrations) as  $\text{Rate}/[\text{O}_3]^{1.5}[\text{TOOH}]^{0.5}$  versus  $[\text{TOOH}]^{0.5}/[\text{O}_3]^{0.5}$ ; the slope of this plot equals  $k_1$ . (See Figure 2.) For TOOH, this plot yields  $k_1 = 5.4 \text{ sec}^{-1} \text{ M}^{-1}$ ; for *tert*-butyl hydroperoxide- $d_1$  (TOOD),  $k_1$  is obtained as  $1.9 \text{ sec}^{-1} \text{ M}^{-1}$ . Thus,  $k_H/k_D = 2.8$  for step 1a. The intercept of these plots is equal to  $k_x(k_1/k_t)^{0.5}$ , from which approximate values of  $k_x$  can be obtained. (The value of  $2k_t = 74 \text{ sec}^{-1} \text{ M}^{-1}$  at  $-4^\circ$ .<sup>7</sup>) This treatment gives  $k_x \approx 25 \pm 8$  for both TOOH and TOOH, as shown in Figure 2.

This full analysis was done only at  $-4^\circ$ . However, approximate second order rate constants were obtained at  $20^\circ$  and  $-23^\circ\text{C}$  by assuming eqs 1-3 describe the system and plotting  $\ln(\text{O}_3)$  versus time. These plots are quite precise. (A similar technique has been used by Cvetanovic.<sup>8</sup>) Using rates obtained in this way,  $E_a = 7 \text{ kcal/mole}$ .

Several mechanisms can be envisioned for eq 1a. The first, and perhaps the one that might be regarded as most likely from the cycloaddition literature, is a concerted dipolar insertion.

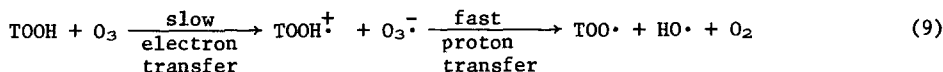
MECHANISM I: CONCERTED INSERTION.



In this mechanism, *tert*-butyl hydroperoxide,  $\text{TO}_5\text{H}$ , is produced as a transient intermediate that subsequently undergoes homolysis.<sup>9a</sup> Using Benson's group additivity terms,<sup>9b</sup> however, the heats of the two steps in Mechanism I can be calculated to be the values shown in eq 8. Thus, the low value of the activation energy convincingly excludes the possibility of the endothermic penta-oxy compound being involved as an intermediate, and the insertion mechanism can be eliminated.

The second mechanism that might be envisioned is an electron transfer. This mechanism is

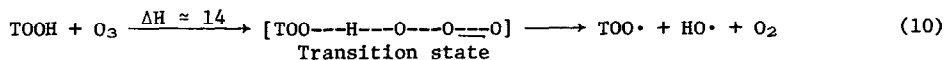
MECHANISM II: ELECTRON-TRANSFER.



excluded by the isotope effect,  $k_H/k_D = 2.8$ . It also is inherently improbable since the difference in the electron affinity of ozone and ionization potential of TOOH is over 8 eV.<sup>10</sup>

The mechanism we favor is a molecule-assisted homolysis (MAH) step<sup>11</sup> that can be formulated

MECHANISM III: MOLECULE-ASSISTED HOMOLYSIS.



as in eq 10. (Since the decomposition of  $\text{HO}_3\cdot$  is exothermic, eq 11 is more endothermic than 10 and can be excluded.) The heat of reaction 10 is 14 kcal/mole.<sup>12</sup> Thus, the  $E_a$  of the first, non-chain term in eq 7 would be expected to be approximately 14 kcal/mole, whereas that of the second chain term would be:  $5 + 14/2 - 6/2 = 9 \text{ kcal/mole}$ . Thus, this mechanism predicts an observed  $E_a$  between 9 and 14 kcal/mole, depending on the kinetic chain lengths, in reasonable agreement with the observed value of 7 kcal/mole. (All these values are probably  $\pm 2 \text{ kcal/mole}$ .)

MAH reactions have been identified in a number of systems and have been the subject of a number of recent reports and reviews.<sup>11</sup> In several examples, a hydrogen atom is postulated to be transferred, usually to an olefin as the acceptor molecule,<sup>11d</sup> but in few cases is the evidence completely compelling.<sup>11e-h</sup> However, the reaction of O<sub>3</sub> with TOOH does appear to involve an MAH reaction in which a hydrogen atom is transferred in the radical-producing step.<sup>12</sup>

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12. S. W. Benson (private communication) has suggested a fourth mechanism in which O<sub>3</sub> → O<sub>2</sub> + O is the initiation step, and a chain sequence with eq 5 as the key step. His treatment gives a rate law with a chain term that is 3/2-order in ozone (our data plot as first order, since chain lengths are short) and activation energies for the initiation (non-chain) step of 25 kcal/mole and 15 kcal/mole for the chain term. Although a reaction with E<sub>a</sub> = 25 kcal/mole could contribute to radical production at 20 or -4°C, it is unlikely that the unassisted homolysis of ozone can explain the formation of radicals at -24 or -60°C. The half lives for homolysis of O<sub>3</sub> at -60, -24, -4 and 20°C are: 10<sup>11</sup>, 10<sup>8</sup>, 10<sup>6</sup>, and 10<sup>4</sup> sec, respectively.