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## Radical Production from the Interaction of Closed-Shell Molecules. 9. Reaction of Ozone with *tert*-Butyl Hydroperoxide<sup>1a</sup>

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**Abstract:** Ozone reacts rapidly at -60 to 24 °C with *tert*-butyl hydroperoxide (TBH) in various halogenated solvents to produce *tert*-butyl alcohol (70%), acetone (2-10%), and di-*tert*-butyl peroxide (1-9%). A reaction scheme involving both peroxy and alkoxy radicals in radical chain reactions is proposed to account for the products. Evidence for the involvement of the *tert*-butoxy radical in this system was obtained by determining relative rates of hydrogen abstraction from added cyclohexane (to form *tert*-butyl alcohol) vs.  $\beta$ -cleavage (to form acetone). Kinetic studies were carried out for both TBH and *tert*-butyl hydroperoxide-*d*<sub>1</sub> by two methods: (1) by monitoring the disappearance of dissolved ozone by UV in the presence of excess hydroperoxide; and (2) by measuring peroxide decomposition in an ozone air-flow system. A mechanism is suggested consisting of eq 1-5 (see Scheme I). In addition, the data require a reaction between peroxy radicals and ozone to yield alkoxy radicals and O<sub>2</sub>, eq 6. A primary kinetic isotope effect,  $k_H/k_D = 2.8 \pm 0.3$ , is observed for the radical-producing reaction between ozone and hydroperoxide at -4 °C. The overall Arrhenius parameters are  $E_a \approx 7 \text{ kcal/mol}$  and  $\log A \approx 7 \text{ s}^{-1}$ . We believe that the initial reaction of ozone with hydroperoxide is best formulated as a molecule-assisted homolysis (MAH) reaction. Electron transfer and dipolar insertion mechanisms are eliminated by our data. A series of compounds was studied, and TBH was found to possess a reactivity toward ozone intermediate between that of typical alkanes and alkenes.

### Introduction

Reactions in which closed-shell molecules interact to produce free radicals are of considerable theoretical and practical interest.<sup>2-4</sup> In this context, we became fascinated by the reactions of ozone with various organic materials that can lead to radical production even at very low temperatures in the dark. Ozone reacts with olefins to produce radicals under certain conditions<sup>5</sup> and with saturated compounds in processes that often are formulated as involving radicals.<sup>6-8</sup>

We decided to examine the reaction of ozone with hydroperoxides, since the brief communication by Barnard, McSweeney, and Smith<sup>9</sup> suggested that ozone reacts with *tert*-butyl hydroperoxide (TBH) by a molecule-assisted homolysis (MAH) process. Earlier, Bray and Taube<sup>10</sup> had reported a study of the ozone-H<sub>2</sub>O<sub>2</sub> reaction and also had proposed a mechanism involving an assisted homolysis. And recently, Bartlett and co-workers<sup>11,12</sup> have used the reaction of ozone with hydroperoxides at temperatures below -50 °C to prepare solutions of trioxides, which they propose are formed by combination of alkoxy and peroxy radicals.

In addition, we are studying the autoxidation of polyunsaturated fatty acids by ozone-air mixtures (at parts per million levels) in an investigation of the mechanisms of ozone-induced lung damage.<sup>13</sup> Fatty acid hydroperoxides are produced in this process; thus, the ozone-lipid hydroperoxide re-

action is a possible source of radicals under these autoxidation conditions.

### Experimental Section

***tert*-Butyl Hydroperoxide.** Lubrizol (90%) material was fractionally distilled at 20 mm pressure. The main fraction, shown to be 98.6% pure by iodometry, was collected at 40 °C following a forecut containing azeotroped water. *tert*-Butyl hydroperoxide-*d*<sub>1</sub> was prepared<sup>14</sup> by treating TBH (40 g) in CDCl<sub>3</sub> (30 mL) with D<sub>2</sub>O (5 × 50 mL). Direct fractional distillation gave a middle cut (15 g) with an active oxygen titer of 98.8% (iodometry). Quantitative IR analysis (O-H stretch, 3530; O-D stretch, 2610 cm<sup>-1</sup>) indicated about 10% O-H impurity, while quantitative NMR indicated only a trace of O-H proton at 9.1 ppm (ratio of 0.03:9 for methyl proton, indicating 3% proton impurity).

**Other Materials.** Chloroform (AR grade) was washed with sulfuric acid and then water, dried on CaCl<sub>2</sub>, and distilled to rid of alcohol stabilizer. Isopropyl alcohol, used as solvent for iodometry, was dried on magnesium sulfate, refluxed with magnesium and iodine, then fractionally distilled.<sup>15</sup> The remaining solvents were found to be greater than 99.98% pure by gas chromatography (GC) and were used directly; if ozone solutions were to be made up in them, they were first pretreated with ozone.<sup>16,17</sup>

**Ozonolysis Reactions.** Ozonolyses were carried out using a Welsbach T-23 ozonator and appropriate gas-washing apparatus. A high-porosity sintered glass frit was used in reactions carried out at -4 or -24 °C, but a plain tube without a frit was employed to intro-

Table I. Products from *tert*-Butyl Hydroperoxide (TBH) Plus Ozone Reactions<sup>a</sup>

[TBH], M	temp, °C	solvent	products <sup>b</sup>					ozone consumed <sup>c</sup>
			<i>t</i> -Bu <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COCH <sub>3</sub>	<i>t</i> -BuOH	TBH		
0.20	-4	CCl <sub>4</sub>	9	8	66	10	43	
0.20 <sup>d</sup>	-4	CCl <sub>4</sub>	8	7	68	16	40	
0.40	-4	CCl <sub>4</sub>	9	7	66	11	36	
1.00	-4	CCl <sub>4</sub>	8	8	66	13	34	
0.20	-24	CCl <sub>4</sub>	8	7	67	14	<sup>e</sup>	
<sup>f</sup>	-25	CCl <sub>4</sub>	8	10	68	0 <sup>g</sup>		
0.20	-4	CCl <sub>4</sub> <sup>h</sup>	3	<sup>i</sup>	29	14 <sup>j</sup>		
0.40	-4	CHCl <sub>3</sub>	2	5	74 <sup>k</sup>	20	31	
0.20	-28	CHCl <sub>3</sub>	2	7	77 <sup>k</sup>	18	45	
0.20 <sup>l</sup>	-28	CHCl <sub>3</sub>	1	8	65 <sup>k</sup>	29	83	
0.20	-60	CHCl <sub>3</sub>	3	5 <sup>m</sup>	69 <sup>k</sup>	28	67 <sup>o</sup>	
0.20 <sup>l</sup>	-60	CHCl <sub>3</sub>	1	11	55 <sup>k</sup>	35	133 <sup>o</sup>	
0.40	-60 <sup>n</sup>	CHCl <sub>3</sub>	3	4	68 <sup>k</sup>	20	53 <sup>o</sup>	
0.20	-4	CFCl <sub>3</sub>	7	4 <sup>m</sup>	78	8	42	
0.20 <sup>l</sup>	-4	CFCl <sub>3</sub>	6	6	83	5	63	
0.20	-25	CFCl <sub>3</sub>	5	2 <sup>m</sup>	67	17	40	
0.20 <sup>l</sup>	-25	CFCl <sub>3</sub>	6	7	59	25	91	

<sup>a</sup> Ozone was introduced at a flow rate of  $0.10 \pm 0.01$  mmol/min until peroxide decomposition slowed markedly and most of the ozone passed through unreacted; generally 0.25–0.50 mol of ozone per mol of starting TBH was absorbed. <sup>b</sup> mmol/100 mmol of TBH; average of two or more runs in good agreement. <sup>c</sup> mmol/100 mmol of TBH consumed, determined at 50% reaction. <sup>d</sup> Ozone introduced at 0.20 mmol/min. <sup>e</sup> Not determined, erratic ozone flow. <sup>f</sup> Reference 9; exact TBH and ozone parameters not given. <sup>g</sup> *tert*-Butyl chloride (4%) and water (26%) also found. <sup>h</sup> Also contained cyclohexane (0.20 M). <sup>i</sup> Not determined. <sup>j</sup> Cyclohexanone (11%), cyclohexanol (2%), and unidentified peroxidic material also present. <sup>k</sup> Varying amounts were present as *tert*-butyl chloride; other minor products also found. <sup>l</sup> TBH-*d*<sub>1</sub>. <sup>m</sup> Less than 1% observed upon analysis at 50–60% hydroperoxide decomposition. <sup>n</sup>  $\pm 10$  °C. <sup>o</sup> Subject to some error owing to enhanced ozone solubility at this temperature.

duce ozone–oxygen into the reaction vessel at  $-60$  °C. The voltage and oxygen flow rate were adjusted so as to allow  $0.10 \pm 0.01$  mmol/min of ozone to be produced. The amount of ozone delivered was calibrated by bubbling for a timed period into a neutral aqueous potassium iodide trap, acidifying with dilute hydrochloric acid, and titrating with standard sodium thiosulfate. This calibration was performed immediately preceding and following each reaction with little variance (<10%) noted. Reactions were performed by bubbling such an ozone–oxygen mixture into the precooled reaction mixture (immersed in an ice–salt, dry ice–CCl<sub>4</sub>, or dry ice–xylene bath) for the length of time required to introduce the desired amount of ozone. Following a short nitrogen flush, the reaction mixture was analyzed for products by GC, IR, and NMR, and unreacted hydroperoxide by iodometry.<sup>18</sup> Under these analytical conditions (NaI in 10%/90% acetic acid–isopropyl alcohol)<sup>18</sup> di-*tert*-butyl peroxide was not titrated. Unreacted ozone flowing through the system was captured in a potassium iodide trap and titrated. The same flow system method was used to introduce ozone–oxygen into TBH solutions in acetonitrile containing varying amounts of cyclohexane (0.05–0.20 M). Despite apparent side reactions of ozone with this solvent, the ratio of *tert*-butyl alcohol to acetone in the product mixture could be determined.

**Kinetic Analyses. A. Measurement of Hydroperoxide Decomposition.** Analyses were done in the following manner. Ozone was allowed to impinge into the solution for set time intervals and then was temporarily replaced by a nitrogen flow while 0.5-mL aliquots were removed for iodometric titration<sup>18</sup> and GC (and frequently IR) analysis. The potassium iodide trap in series behind the reaction vessel was changed at each interruption so that the amount of ozone passing through could be determined. Controls confirmed that no further hydroperoxide decomposition or product formation occurred in the reaction vessel during the sampling periods except for runs at  $-60$  °C (see below). In all cases plots of hydroperoxide concentration vs. time were linear to at least 50% reaction (correlation coefficient >0.98). The initial rates reported are the average ( $\pm 10\%$ ) of two or more reactions.

For the reactions involving addition of potential trapping agents (2,6-di-*tert*-butyl-*p*-cresol (BHT) or 2-methyl-2-pentene), the amount of ozone required to cause about 40–50% hydroperoxide decomposition was introduced at  $-60$  °C. An aliquot was removed, allowed to warm up (vigorous oxygen evolution), and analyzed. To the remainder was added a precooled solution of either BHT or 2-methyl-2-pentene in CHCl<sub>3</sub>. After warming (no oxygen evolution noted with BHT), these reaction mixtures were analyzed.

**Measurement of Ozone Decay.** Ozone solutions, prepared by dissolving ozone in pretreated carbon tetrachloride or fluorotrichloromethane<sup>15,17</sup> and diluting to the desired volume, were used within 6 h for kinetic experiments. Aliquots of the initial solution were analyzed iodometrically and spectroscopically to determine ozone concentration. Extinction coefficients (in  $M^{-1} cm^{-1}$ ) determined for ozone in CCl<sub>4</sub> are 2420 at 267 nm, 2280 at 270 nm (lit.<sup>19</sup> 2539), and 1490 at 280 nm (lit.<sup>19</sup> 1670), while in CFCl<sub>3</sub> at  $-4$  °C they are 1830 at 267 nm, 1685 at 270 nm, and 1025 at 280 nm. Ozone decay was monitored by recording the absorbance at any of these three wavelengths.

A 3.5-mL cuvette was filled with the appropriate ozone solution ( $1-4 \times 10^{-4}$  M), then placed in a thermostated cell compartment of a Gilford Model 222 spectrophotometer for about 10 min, and its initial absorbance measured relative to a reference cell containing  $10^{-3}$  M TBH in the same solvent. To initiate reaction, the sample cuvette cap was removed and the desired amount (10–30  $\mu$ L of 0.2–0.5 M solutions of TBH or TBH-*d*<sub>1</sub>) was injected from an SMI “micro-pettor” with a glass capillary delivery tube. The resulting initial peroxide concentration was  $8-34 \times 10^{-4}$  M. The glass tube was used to stir the solution for about 5 s, the cap replaced, and the resulting absorbance change vs. time recorded until no further absorbance decrease was noted (0–0.03 absorbance units, designated as  $A_{\infty}$ ). Initial stirring or shaking of the sample cuvette after addition of hydroperoxide was essential for a smooth kinetic curve. The amount of hydroperoxide actually delivered by the “micro-pettor” used in this fashion was calibrated and an appropriate correction factor, particularly for the 10- $\mu$ L runs, applied to the initial peroxide concentration. Absorbance scans for reactants and potential products in CCl<sub>4</sub> indicated little interference with the ozone absorbance (e.g., at 267 nm the extinction coefficients, in  $M^{-1} cm^{-1}$ , were TBH, 7.3; acetone, 6.7; and *tert*-butyl alcohol, negligible.)

Plots of  $\ln(A - A_{\infty})$  vs. time are reasonably linear over 3 half-lives, where  $A$  is the absorbance at 267–280 nm, despite a rather complex rate law (see Results). Least-squares treatment of  $t = k' \ln(A - A_{\infty}) + B$  was used to determine pseudo-first-order rate constants,  $k'$ , over 3 half-lives ( $\pm 5\%$  standard deviation from the mean). Alternatively, the pseudo-first-order rate was determined from  $k' = 0.693/t_{1/2}$  where  $t_{1/2}$  was the mean ( $\pm 5\%$ ) of the times for the first 3 half-lives. For TBH–ozone reactions in CFCl<sub>3</sub>, where the rate law is known, initial rates were plotted against the appropriate concentration terms in order to determine the second-order rate constant,  $k_1$  (see Results).

Reactions of other substrates with ozone solutions in CCl<sub>4</sub> were carried out with only slight modifications. A Beckman Model 24 recording spectrophotometer was used, the cell compartment was at

**Table II.** Initial Rates of TBH Decomposition with Ozone Using a Flow System for Ozone Introduction

[TBH], M	temp, °C	solvent	% O <sub>3</sub> <sup>a</sup> used	10 <sup>3</sup> initial rate, <sup>b</sup> M min <sup>-1</sup>	TBH dec per O <sub>3</sub> absorbed <sup>c</sup>
0.20	-4	CCl <sub>4</sub>	94	9.4	2.3
0.20 <sup>d</sup>	-4	CCl <sub>4</sub>	90	19.1 <sup>c</sup>	2.5
0.40	-4	CCl <sub>4</sub>	96	9.6	2.8
1.00	-4	CCl <sub>4</sub>	98	12.8	2.9
0.40	-4	CHCl <sub>3</sub>	95	14.6	3.2
0.20	-28	CHCl <sub>3</sub>	84	8.9	2.2
0.20 <sup>e</sup>	-28	CHCl <sub>3</sub>	75	4.7	1.2
0.40	-60	CHCl <sub>3</sub>	80	8.9 <sup>f</sup>	1.9
0.20	-60	CHCl <sub>3</sub>	81	6.8 <sup>f</sup>	1.5
0.20 <sup>e</sup>	-60	CHCl <sub>3</sub>	62	2.2 <sup>f</sup>	0.7
0.20	-4	CFCl <sub>3</sub>	96	11.8	2.4
0.20 <sup>e</sup>	-4	CFCl <sub>3</sub>	88	6.9	1.6
0.20	-25	CFCl <sub>3</sub>	91	9.2	2.5
0.20 <sup>e</sup>	-25	CFCl <sub>3</sub>	87	5.6	1.1

<sup>a</sup> Percent of ozone delivered that is consumed. <sup>b</sup> Corrected to ozone delivery rate of 0.10 mmol/min; actual delivery rate varied  $\pm 10\%$ ; average of two or more runs in good agreement. <sup>c</sup> Calculated from mmol TBH reacted/mmol O<sub>3</sub> absorbed at 50% decomposition. <sup>d</sup> Used ozone delivery rate of 0.20 mmol/min; rate at that delivery. <sup>e</sup> Using TBH-1. <sup>f</sup> Rates may be up to 50% too high owing to further peroxide decomposition during sampling (see Experimental Section).

ambient temperature (24 °C), the sample cuvette was shaken after addition of neat substrate (10  $\mu$ L), and the ozone decay was followed for up to 3 half-lives. Initial ozone concentrations were in the range  $1-2 \times 10^{-4}$  M, and the organic substrate was initially 0.025–0.035 M. Cyclohexene was added as a 0.2 M solution in CCl<sub>4</sub> (10  $\mu$ L) to give an initial concentration of  $1.14 \times 10^{-3}$  M; the reaction was complete in less than 5 s and a lower limit second-order rate constant was estimated.

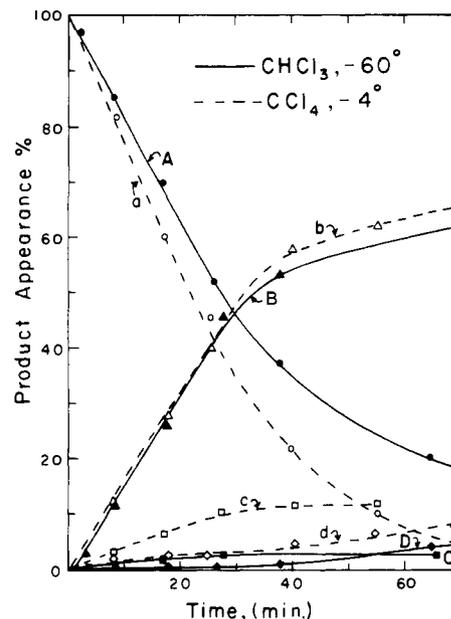
**Analytical Methods.** Gas chromatographic analyses were performed on a 6 ft  $\times$  1/4 in. glass-10% Carbowax 20M on Chromosorb W (AW-DMCS) column at 35 °C, using either *tert*-butyl chloride or ethanol as an internal standard. Correction factors obtained from analysis of known concentrations of products and internal standard were used to correct area ratios. The stability of *tert*-butyl hydroperoxide under these conditions was checked from time to time, and small corrections (0–6%) were applied for products formed on the GC. The same column at higher temperatures was used to analyze for pentenols, hexachloroethane, and other potential higher boilers in the various systems.

Infrared analyses on reaction mixture aliquots were carried out in a matched set of 0.1-cm cells on a Perkin-Elmer Model 621 infrared spectrophotometer. The following characteristic bands were chosen to monitor the various species: *tert*-butyl alcohol, 915 cm<sup>-1</sup>; di-*tert*-butyl peroxide, 875 cm<sup>-1</sup>; acetone, 1715 cm<sup>-1</sup>; and TBH, 3550 cm<sup>-1</sup>. Beer's law plots of absorbance vs. concentration of each product in CCl<sub>4</sub> and CHCl<sub>3</sub> were constructed from standard solutions, and used to determine products quantitatively. Good agreement ( $\pm 10\%$  of value reported) was observed between GC and IR analyses.

Direct NMR analyses on reaction mixtures were used to confirm the presence of acetone (2.1 ppm) and *tert*-butyl chloride (1.60 ppm) in various cases.

## Results

The reaction of TBH with an ozone–oxygen flow system in various halogenated solvents was studied under a variety of conditions (see Table I). In carbon tetrachloride, the products varied little with conditions and are in good agreement with those reported earlier at -25 °C.<sup>9</sup> Trace amounts of *tert*-butyl chloride were found in some instances, and water was observed as an insoluble phase at the end of the reactions. Incorporation of hydrocarbons (e.g., 0.20 M cyclohexane) led to more complex product mixtures with lesser amounts of *tert*-butyl alcohol, di-*tert*-butyl peroxide, and acetone accompanied by oxidation products of the hydrocarbon (cyclohexanone, cyclohexanol,



**Figure 1.** Product appearance in the TBH–ozone reaction vs. time. Products from TBH (0.4 M) in CHCl<sub>3</sub> at -60 °C are indicated by the solid lines A–D and closed symbols. Products from TBH (0.4 M) in CCl<sub>4</sub> at -4 °C are indicated by the dashed lines a–d and open symbols. A(a) = TBH (disappearance); B(b) = *tert*-butyl alcohol; C(c) = di-*tert*-butyl peroxide; D(d) = acetone.

and a compound tentatively identified as a mixed peroxide containing the cyclohexyl fragment, Table I).

In chloroform, less di-*tert*-butyl peroxide and acetone were found compared with CCl<sub>4</sub> solvent, but the yields of *tert*-butyl alcohol were similar. However, some of the alcohol was converted to *tert*-butyl chloride under reaction conditions and subsequent aging, presumably by HCl; HCl could be detected in freshly ozonized solutions in CHCl<sub>3</sub>. In CFCl<sub>3</sub> only 2–4% acetone was found as well as slightly less di-*tert*-butyl peroxide. This solvent appeared to give the cleanest reaction; no other organic byproducts were detected.

Product studies for runs involving TBH-*d*<sub>1</sub> with ozone in CHCl<sub>3</sub> and CFCl<sub>3</sub> showed more acetone and less di-*tert*-butyl peroxide than for TBH under the same conditions (Table I). Good material balance for the *tert*-butyl group was found in all cases except when cyclohexane was present. The last column (Table I) shows the quantity of ozone required to consume the amount of hydroperoxide indicated.

The appearance of products and disappearance of hydroperoxide were followed as a function of time for a number of reactions in each of the three solvents listed in Table I. Figure 1 shows typical plots for TBH–ozone in CCl<sub>4</sub> at -4 °C and in CHCl<sub>3</sub> at -60 °C. In all cases, *tert*-butyl alcohol and di-*tert*-butyl peroxide are formed as TBH disappears, but the appearance of acetone lags until late in the reaction (after 60% peroxide decomposition). Note that less than 1% acetone is produced at 60% peroxide decomposition in -4 and -24 °C in CFCl<sub>3</sub> (Table I) and at -60 °C in CHCl<sub>3</sub> (Figure 1); this is important in the kinetic analysis given below.

**Kinetic Studies.** This same method of analyzing for the disappearance of TBH by iodometry was used to follow the reaction of TBH or TBH-*d*<sub>1</sub> with ozone under various conditions (Table II). The initial rate of peroxide decomposition is primarily dependent on the rate of ozone introduction, which is consumed at better than 90% efficiency for most reactions with TBH. The initial rate is only slightly affected by the nature of the solvent, the temperature, and the hydroperoxide concentration. Generally the faster decomposition rates are attended by larger ratios of hydroperoxide consumed per ozone

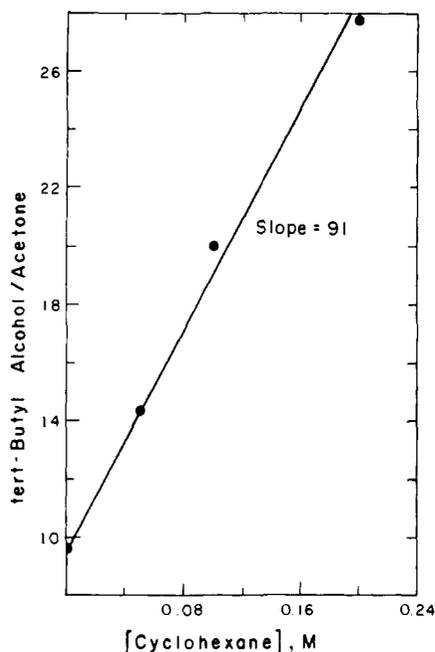


Figure 2. *tert*-Butyl alcohol acetone product ratios from TBH-ozone reactions in  $\text{CH}_3\text{CN}$  with added cyclohexane,  $0^\circ\text{C}$ . The slope equals  $k_q/k_\beta$  (see eq 5 and 7); the literature value<sup>21</sup> in this solvent is 82.

absorbed at 50% decomposition (Tables I and II). This ratio generally ranges from 2 to 3 except at  $-60^\circ\text{C}$ .

Also shown in Table II are the rates of TBH- $d_1$  decomposition with ozone in various solvents and temperatures. In all cases the rate of decomposition of the deuterated compound was slower than that of the corresponding hydrogen analogue (by factors ranging from 1.6 to 3.1), a smaller fraction of the ozone was absorbed, and the ratio of peroxide decomposed to ozone absorbed was closer to one.

A second method of kinetic analysis was used that involves following the ozone decay by monitoring the UV absorbance of  $10^{-3}$ – $10^{-4}$  M solutions of ozone in  $\text{CFCl}_3$  or  $\text{CCl}_4$  upon addition of excess hydroperoxide. Initial rates, which were followed to about 25–40% reaction, are shown for a variety of peroxide (TBH and TBH- $d_1$ ) and ozone concentrations at various temperatures in  $\text{CFCl}_3$  in Table III.

**Kinetic Analysis.** The products can be rationalized by steps 1–5 (Scheme I). However, this simple scheme predicts that the yield of di-*tert*-butyl peroxide should equal the amount of ozone consumed (since eq 3a terminates two radicals and eq 1a forms two). However, the data in Table I show a much lower relative yield of di-*tert*-butyl peroxide; therefore, eq 6 has been added to the kinetic scheme (see Discussion).

The involvement of radicals in the ozone-TBH reaction is indicated by the production of acetone (eq 5) and di-*tert*-butyl peroxide (eq 3a), by the occurrence of autoxidation upon addition of hydrocarbons to ozone-TBH<sup>9</sup> (eq 7), and by the trapping of di-*tert*-butyl trioxide at low temperatures<sup>11</sup> (eq 8). Nevertheless, we have measured the competition between  $\beta$ -scission to give acetone (eq 5) and hydrogen abstraction from cyclohexane (QH in eq 7) in acetonitrile solvent at  $0^\circ\text{C}$ . Figure 2 shows a plot of the product ratio vs. cyclohexane concentration,<sup>20,21</sup> the slope of which equals  $k_q/k_\beta$ . Our data yield 91 for this ratio, in reasonable agreement with the literature value of 82 at  $4^\circ\text{C}$ .<sup>21</sup> Thus, *tert*-butoxy radicals are the precursor of both acetone and *tert*-butyl alcohol.

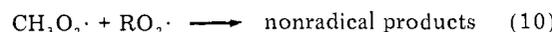
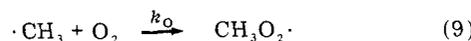
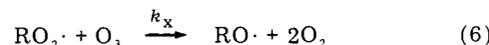
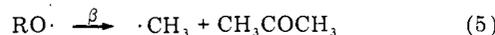
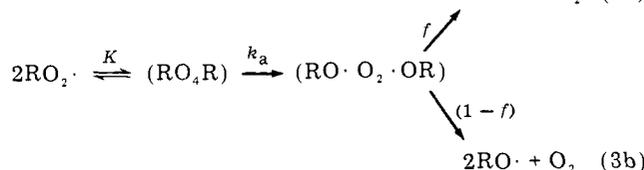
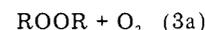
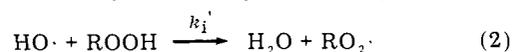
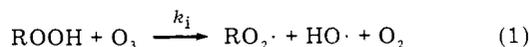
Early in the reaction when the TBH concentration is still relatively high, eq 4 is faster than eq 5, and the acetone yields are very low. (In  $\text{CFCl}_3$  at  $-4^\circ\text{C}$ , the acetone yield is less than 1% at 50% reaction; see Table I.) Under these conditions eq 5 can be neglected and a steady-state analysis of eq 1–4 and

Table III. Initial Rates of Ozone Decay in TBH (TBH- $d_1$ )-Ozone Reaction

conditions	$10^4[\text{TBH}]$ av <sup>a</sup>	$10^4[\text{O}_3]$ av <sup>a</sup>	$10^7$ rate (av), M s <sup>-1b</sup>
TBH in $\text{CFCl}_3$ ( $-4^\circ\text{C}$ )	11.3	3.7	40.3
	14.8	1.5	15.3
	32.5	2.3	56.8
	25.9	1.7	32.2 <sup>c</sup>
	15.1	0.9	9.5 <sup>c</sup>
TBH- $d_1$ in $\text{CFCl}_3$ ( $-4^\circ\text{C}$ )	34.1	1.0	22.3
	13.1	4.0	23.7
	14.8	3.1	20.1
	15.1	2.3	16.9
	13.3	1.1	6.0
	15.4	1.3	9.5
	34.6	2.4	30.5
TBH in $\text{CFCl}_3$ ( $-23^\circ\text{C}$ )	27.3	1.4	12.9
	41.0	1.4	18.9
	13.3	4.1	19.3
	11.6	3.3	11.3 <sup>d</sup>
TBH- $d_1$ in $\text{CFCl}_3$ ( $-23^\circ\text{C}$ )	13.1	4.4	10.6
	13.5	1.9	4.7 <sup>c</sup>
TBH in $\text{CFCl}_3$ ( $20^\circ\text{C}$ )	5.2	0.5	5.0 <sup>c</sup>
	8.7	3.5	84.0 <sup>c</sup>
TBH- $d_1$ in $\text{CFCl}_3$ ( $20^\circ\text{C}$ )	10.4	2.8	50.0 <sup>d</sup>
	10.7	1.6	21.0 <sup>d</sup>

<sup>a</sup> Average concentrations during portion of reaction studied. <sup>b</sup> Followed to 25–40% reaction, average of two or more runs in good agreement ( $\pm 10\%$  standard deviation). <sup>c</sup> Up to 20% standard deviation. <sup>d</sup> Single run.

Scheme I<sup>a</sup>



<sup>a</sup>R = *tert*-butyl.

6 gives the rate laws for initial ozone (eq 11) and hydroperoxide (eq 12) decomposition. Equation 11 can be rearranged to give eq 13.

$$\text{rate}[-\text{O}_3] = k_i[\text{TBH}][\text{O}_3] + k_x(k_i/k_1)^{1/2}[\text{TBH}]^{1/2}[\text{O}_3]^{3/2} \quad (11)$$

$$\text{rate}[-\text{TBH}] = (2k_i/f)[\text{TBH}][\text{O}_3] + k_x(k_i/k_1)^{1/2}[\text{TBH}]^{1/2}[\text{O}_3]^{3/2} \quad (12)$$

$$\frac{\text{rate}[-\text{O}_3]}{[\text{O}_3]^{3/2}[\text{TBH}]^{1/2}} = k_i \frac{[\text{TBH}]^{1/2}}{[\text{O}_3]^{1/2}} + k_x(k_i/k_1)^{1/2} \quad (13)$$

**Table IV.** Approximate Second-Order Rate Constants for the Reaction of TBH and TBH-*d*<sub>1</sub> with Ozone

solvent	temp, °C	$k_H, M^{-1} s^{-1a}$	$k_D, M^{-1} s^{-1a}$
CCl <sub>4</sub>	24	36.9 <sup>b</sup>	33.7 <sup>c</sup>
CCl <sub>4</sub>	-23	3.9 <sup>d</sup>	3.0 <sup>e</sup>
CFCl <sub>3</sub>	20	31.0 <sup>f</sup>	20.7 <sup>g</sup>
CFCl <sub>3</sub>	-4	9.3 <sup>h</sup>	5.8 <sup>i</sup>
CFCl <sub>3</sub>	-23	4.2 <sup>j</sup>	2.3 <sup>k</sup>

<sup>a</sup> Determined from  $k = k'/[TBH]_{av}$  for 3 half-lives where  $k'$  = pseudo-first-order rate constant for ozone decay and  $[TBH]_{av}$  = average hydroperoxide concentration over 3 half-life period. These data are not useful for the calculation of accurate isotope effects; see ref 28. <sup>b</sup>  $n = 16$ , SD = 6.3; includes ten runs in which  $k'$  was determined from  $t_{1/2}$  to  $t_{1/4}$  only. <sup>c</sup>  $n = 10$ , SD = 8.6;  $k'$  was determined from  $t_{1/2}$  to  $t_{1/4}$  only. <sup>d</sup>  $n = 6$ , SD = 0.2. <sup>e</sup>  $n = 7$ , SD = 0.6. <sup>f</sup>  $n = 4$ , SD = 9.5. <sup>g</sup>  $n = 2$ , SD = 3.1. <sup>h</sup>  $n = 4$ , SD = 0.9. <sup>i</sup>  $n = 4$ , SD = 0.5. <sup>j</sup>  $n = 3$ , SD = 0.04. <sup>k</sup>  $n = 4$ , SD = 0.07.

The rate constants  $k_i$  and  $k_x$  apply to eq 1 and 6, respectively, and  $k_t$  is for eq 3 and is defined according to the notation suggested by Howard.<sup>22-24</sup> Thus, a plot of  $\text{rate}/[O_3]^{3/2} [TBH]^{1/2}$  vs.  $[TBH]^{1/2}/[O_3]^{1/2}$  has a slope equal to  $k_i$ , the rate constant for the initial ozone-TBH reaction. Plots for reaction of both TBH and TBH-*d*<sub>1</sub> in CFCl<sub>3</sub> at -4 °C are shown in Figure 3 and give  $k_i$  values of 5.4 and 1.9 M<sup>-1</sup> s<sup>-1</sup>, respectively. Thus,  $k_H/k_D$  is 2.8 for eq 1.<sup>25</sup>

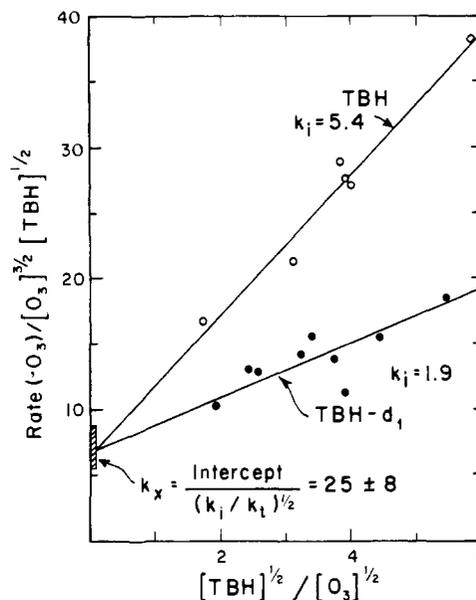
Figure 3 also leads to a value of  $k_x$  for eq 6. (The value of  $2k_t$  is 74 M<sup>-1</sup> s<sup>-1</sup> at -4 °C.<sup>22-24,26</sup>) However, as expected for slope-intercept plots of this type, the value of  $k_x$  is not determined with high precision.<sup>27</sup> Figure 3 shows that  $k_x$  is about 25 ± 8 M<sup>-1</sup> s<sup>-1</sup> for both TBH and TBH-*d*<sub>1</sub>.

This full analysis was done only at -4 °C. However, kinetic studies of the reaction of CFCl<sub>3</sub> at -24 and 20 °C were done using the method of Cvetanovic et al.<sup>16,19</sup> In this method, the reaction is treated as a simple second-order reaction that can be plotted as a reaction that is pseudounimolecular in ozone. Ozone absorption data plot reasonably well as a first-order reaction for over 3 half-lives. Rate constants for this pseudo-unimolecular reaction,  $k'$ , were determined from semi-logarithmic plots and converted to second-order rate constants,  $k_i = k'/[TBH]_{av}$ . These values are given in Table IV for reactions in CCl<sub>4</sub> and CFCl<sub>3</sub> at several temperatures. Values determined in this way are systematically somewhat high (see Discussion) but they give reasonable approximations of  $k_i$ .<sup>28</sup> Arrhenius plots of all the values of  $k_i$  give the energy of activation as 7 kcal/mol and the preexponential as 10<sup>7</sup> s<sup>-1</sup>.

We also measured the rate of reaction of several other compounds with ozone by the Cvetanovic method<sup>16,19</sup> to place TBH on a relative reactivity scale with other organic compounds. These data are shown in Table V, and in some cases, the agreement with Cvetanovic is only approximate. However, the data suffice to show that hydroperoxides rank intermediate in reactivity between alkanes and alkenes.

**Low-Temperature Trapping Studies.** Ozonolyses at -60 °C were carried out in CHCl<sub>3</sub>; products and ultimate yields were found to be similar to those of the higher temperature runs (see Table I). In these -60 °C runs, oxygen was evolved from an unstable species, probably di-*tert*-butyl trioxide, as the ozonized solutions were warmed. Bartlett and Lahav observed that butylated hydroxytoluene (BHT) effectively scavenges both the *tert*-butylperoxy and *tert*-butoxy radicals formed from di-*tert*-butyl trioxide upon warming.<sup>11</sup> When BHT was added to an aliquot of our ozonized TBH solution at -60 °C, the peroxide titer was higher, and no oxygen was given off when the solutions were warmed.

To determine whether singlet oxygen was being evolved from the unstable intermediate upon warming, as observed for

**Figure 3.** Plots of the rate law (eq 13) for the reaction of TBH and TBH-*d*<sub>1</sub> with ozone in CFCl<sub>3</sub> at -4 °C. The slopes give values of  $k_i$  for eq 1 for *t*-C<sub>4</sub>H<sub>9</sub>OOH (TBH) and *t*-C<sub>4</sub>H<sub>9</sub>OOD (TBH-*d*<sub>1</sub>). The intercept gives approximate values of  $k_x(k_i/k_t)^{1/2}$ .**Table V.** Second-Order Rate Constants for Substrate-Ozone Reactions in CCl<sub>4</sub>

substrate	$k, M^{-1} s^{-1a}$	$k, M^{-1} s^{-1b}$	$k_{rel}^c$
2,3-dimethylbutane	0.200		1
cyclohexane	0.011	0.031 <sup>d</sup>	0.05
<i>tert</i> -butyl alcohol	0.050	0.005 <sup>e</sup>	0.25
cyclopentanol	1.35		6.75
benzene	0.028	0.070 <sup>f</sup>	0.14
<i>tert</i> -butyl hydroperoxide		37 <sup>g</sup>	185
1-pentene	80 000 <sup>h</sup>		4 × 10 <sup>5</sup>
cyclohexane		>300 <sup>i</sup>	

<sup>a</sup> Reference 16, 25 °C. <sup>b</sup> This work, 24 °C. <sup>c</sup> See ref 16. <sup>d</sup>  $n = 3$ , SD = 0.013. <sup>e</sup>  $n = 2$ , SD < 0.001. <sup>f</sup>  $n = 4$ , SD = 0.010. <sup>g</sup>  $n = 16$ , SD = 6.3; approximate value determined by assuming simple second-order kinetics, 24 °C; the rate constant at -23 °C is 3.9 ± 0.2 M<sup>-1</sup> s<sup>-1</sup> ( $n = 6$ ). <sup>h</sup> Reference 19, 25 °C. <sup>i</sup> Maximum rate measurable by us.

certain hydrotrioxides,<sup>8a</sup> 2-methyl-2-pentene was incorporated into a partially ozonized solution at -60 °C. The product mixtures was allowed to warm up, then reduced with NaBH<sub>4</sub> and analyzed for pentenols.<sup>29,30</sup> None were found.

## Discussion

**Mechanism.** Scheme 1 lists most of the potential reactions for the ozone-TBH system. The initial reaction, eq 1, produces peroxy and hydroxy radicals. The HO· radicals rapidly react with hydroperoxide (eq 2)<sup>22</sup> to generate a second peroxy radical, so the net effect is that 2 mol of peroxy radical is generated per mol of ozone absorbed. Reversible combination of such radicals to form a tetroxide (eq 3) has been documented in previous hydroperoxide studies with ozone<sup>12</sup> and oxy radicals,<sup>31</sup> as has the subsequent partitioning of cage radicals to the termination product, di-*tert*-butyl peroxide (eq 3a), and to *tert*-butoxy radicals (eq 3b).<sup>22,31</sup>

Once formed, *tert*-butoxy radicals have a variety of paths available. Their reaction with hydroperoxide to regenerate peroxy radicals (eq 4) has a large rate constant<sup>18</sup> (4 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> at 30 °C) and should be the predominant reaction in inert solvents above -30 °C, especially early in the reaction. Hy-

drogen abstraction from other species with labile hydrogens (eq 7) does not occur in the solvents  $\text{CFCl}_3$  and  $\text{CCl}_4$ , but may occur in  $\text{CHCl}_3$ , since traces of  $\text{HCl}$  are observed. And, of course, eq 7 is an important reaction in the runs in which cyclohexane is deliberately added (see Figure 2).

Another path for peroxy radical reaction, reversible trioxide formation (eq 8), is slow above  $-30^\circ$ ,<sup>11</sup> and thus does not occur in most of our runs. The  $\beta$ -cleavage process leading to acetone (eq 5) occurs in  $\text{CCl}_4$  and in the later stages of reactions in both  $\text{CHCl}_3$  and  $\text{CFCl}_3$  as the TBH is depleted and eq 4 becomes slower. However acetone formation is negligible during the first half of all reactions performed in  $\text{CFCl}_3$  and the lower temperature reactions in  $\text{CHCl}_3$  (Table I and Figure 1). Larger amounts of acetone are formed from  $\text{TBH-d}_1$  in all of the solvents we studied (Table I). This is consistent with a competition between hydrogen abstraction (eq 4) and  $\beta$ -cleavage (eq 5) being biased toward  $\beta$ -scission in  $\text{TBH-d}_1$  with its stronger O-D bond.

The  $\beta$ -cleavage step, eq 5, produces a methyl radical that rapidly reacts with  $\text{O}_2$  (eq 9), and the resultant  $\text{CH}_3\text{OO}\cdot$  radicals undergo fast termination reactions with other peroxy radicals (eq 10). Thus,  $\beta$ -cleavage is, in essence, a termination process.<sup>18</sup> The unimolecular rate constant for  $\beta$ -cleavage varies from  $97\text{ s}^{-1}$  at  $-4^\circ\text{C}$  to  $331\text{ s}^{-1}$  at  $30^\circ\text{C}$ .<sup>32</sup> Thus, at  $30^\circ\text{C}$  and with TBH concentrations as low as  $10^{-3}\text{ M}$ , the ratio of hydrogen abstraction (eq 4) to  $\beta$ -cleavage (eq 5) should be about 12. At  $-4^\circ\text{C}$ , where most of our kinetics were performed, this ratio is still larger because of the lower activation energy for H abstraction relative to  $\beta$ -cleavage.

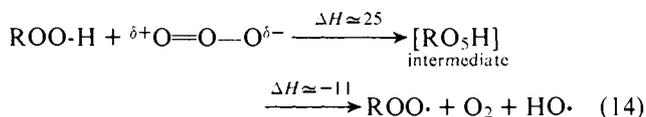
Thus, in  $\text{CFCl}_3$ , eq 5, 7, 8, 9, and 10 can be neglected and eq 3a is the sole termination reaction.<sup>24</sup> A chain reaction consisting of eq 3b and 4 as propagation steps should occur with a chain length dependent on the rates of diffusion (eq 3b) vs. recombination (eq 3a) of the caged alkoxy radicals. Ratios ranging from 5 to 13 have been reported for this competition in solvents such as benzene,<sup>26</sup> chlorobenzene,<sup>31</sup> and carbon tetrachloride<sup>33</sup> at temperatures of 22–57  $^\circ\text{C}$ . Activation energy differences of 3.5<sup>18</sup> and 5.3<sup>26</sup> have been reported for diffusion vs. combination; using an average value, the approximate ratios of the rates of diffusion (3b) to combination (3a) can be calculated to be 2.4 at  $-4^\circ\text{C}$  and 1 at  $-25^\circ\text{C}$ . From these values, the predicted yields of di-*tert*-butyl peroxide should be about 15 and 25%, respectively, at these two temperatures. However, the actual yield of the dialkyl peroxide, particularly in  $\text{CFCl}_3$  where the analysis is the simplest, is considerably less (Table I). Furthermore, a kinetic scheme that includes only eq 1–4 predicts that the amount of ozone consumed should equal the amount of di-*tert*-butyl peroxide formed (i.e., 15 and 25%), since each ozone molecule produces two radicals and each peroxide formation step terminates two. This is clearly not the case: approximately 0.4 mol of ozone is consumed per mol of TBH destroyed in  $\text{CFCl}_3$  solvent (Table I). These data can be explained most easily by assuming that peroxy radicals react with ozone (eq 6),<sup>9</sup> since this step provides an alternate path to eq 3 for the conversion of peroxy to alkoxy radicals.<sup>34,35</sup>

Thus, two competing chain processes occur, both producing *tert*-butyl alcohol as the product. The first involves eq 3b and 4 and the second involves eq 6 and 4. The chain involving eq 3b and 4 (assuming  $f = 0.3\text{--}0.5$ )<sup>18,26</sup> predicts that 0.15–0.25 ozone molecules are used per hydroperoxide consumed, whereas the chain involving eq 4 and 6 predicts the consumption of one ozone molecule per hydroperoxide decomposed at long chain lengths. Based on our observed ratios of di-*tert*-butyl peroxide and ozone utilization in  $\text{CFCl}_3$  (Table I), the former chain appears to account for nearly  $2/3$  and the latter chain about  $1/3$  of the TBH decomposition in  $\text{CFCl}_3$ .

**Nature of the Initiation Step.** Several mechanisms can be envisioned for eq 1. The first, and perhaps the one most likely from the standpoint of the cycloaddition literature, is a con-

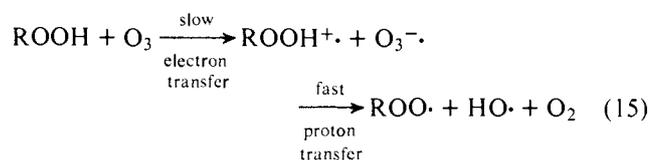
certed dipolar insertion. In this mechanism, *tert*-butyl hydroperoxide,  $\text{RO}_2\text{H}$ , is produced as a transient intermediate that subsequently undergoes homolysis. Using Benson's group additivity terms,<sup>36</sup> however, the heats of the two steps in mechanism I can be calculated to be the values shown in eq 14. The low value of the activation energy, about 7 kcal/mol, convincingly excludes the possibility of the highly endothermic pentaoxy compound as an intermediate, and the insertion mechanism can be eliminated.

mechanism I: concerted insertion



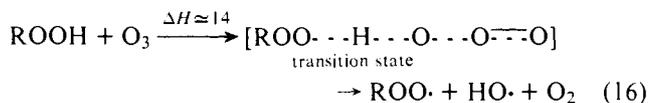
The second mechanism that might be considered is an electron transfer (eq 15). This mechanism is excluded by the isotope effect,  $k_{\text{H}}/k_{\text{D}} = 2.8$ . It is also inherently improbable since the difference in the electron affinity of ozone<sup>37</sup> and ionization potential of TBH<sup>38</sup> is over 8 eV.

mechanism II: electron transfer



The mechanism we favor is a molecule-assisted homolysis (MAH) step<sup>2,4b,c</sup> that can be formulated as in eq 16. (Since the decomposition of  $\text{HO}_3\cdot$  is exothermic, eq 17 is more endothermic than eq 16 and can be excluded.) The heat of reaction 16 is calculated to be 15 kcal/mol. Thus the activation energy for the first term on the right-hand side of eq 16 is 14 kcal/mol; the activation energy for the second term on the right side of eq 11, the term representing the chain mechanism, is given by  $5 + 14/2 - 7.5/2 = 8$  kcal/mol. Thus, the MAH mechanism predicts an observed  $E_a$  between 8 and 14 kcal/mol, depending on the kinetic chain lengths, in satisfactory agreement with the observed value of 7 kcal/mol. (All these values are probably  $\pm 2$  kcal/mol.)

mechanism III: molecule-assisted homolysis



A comparison of the rate constants for the reaction of ozone with TBH and with other substrates (Table V) shows TBH to be intermediate in reactivity between alkenes and alkanes.<sup>16,18</sup> On an approximate scale with cyclohexane as the reference, the relative reactivities towards ozone are alkene,  $10^6$ ; hydroperoxide,  $10^3$ ; alcohol,  $10^2$ ; alkane,  $10^1$ . Thus, though its reaction with ozone is 1000 times slower than that of alkenes, TBH is still quite reactive relative to other saturated organic molecules.

## Conclusion

Assisted homolysis reactions have been identified in a number of systems and have been the subject of a number of recent reports and reviews.<sup>2–4</sup> In several examples, a hydrogen atom is postulated to be transferred, usually to an olefin as the acceptor molecule,<sup>4b,c</sup> but in few cases is the evidence completely compelling. However, the reaction of ozone with *tert*-

butyl hydroperoxide does appear to involve an assisted homolysis reaction in which a hydrogen atom is transferred in the radical-producing step.

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- (23) Our notation for the termination rate constant copies that of Howard<sup>22,24</sup> where  $2k_t = 2k_a/K$ , and  $K = (\text{RO}_2)^2/(\text{RO}_4\text{R})$ .
- (24) J. A. Howard in "Free Radicals", Vol. II, J. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1975, Chapter 12.
- (25) (a) Approximate isotope effects can also be determined for the hydroperoxide decomposition rates given in Table II in the following manner. Substitution of the appropriate rate constants and concentrations into eq 12 indicates that the second term is considerably smaller than the first; therefore, the ratios of the initial rates of peroxide decomposition followed in the ozone flow system give a rough measure of the isotope effects. In  $\text{CFCl}_3$ , this procedure gives approximate  $k_H/k_D$  values of 1.7 at both  $-25$  and  $-4$  °C. The ratios of decomposition rates for TBH and TBH- $d_1$  in  $\text{CHCl}_3$  at  $-60$  and  $-28$  °C, for which the rate law (eq 12) does not strictly hold, were 3.1 and 1.9, respectively. However, at these higher initial peroxide concentrations (Table II), intermolecular hydrogen bonding may occur. It is known that radicals react more slowly with hydrogen-bonded hydroperoxides,<sup>14</sup> phenols [J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044 (1964); D. Grilles and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 630 (1974)], and alcohols [K. D. Adams, H. Mockel, and A. Heuglein, *J. Phys. Chem.*, **77**, 1218 (1973)] compared to the monomeric species. One would expect similar behavior toward ozone. (b) Hydroperoxides also exhibit isotope effects in their reactions with oxy radicals, eq 4. For example,  $k_H/k_D = 5$  for the cumyloxy radical-cumene hydroperoxide interaction.<sup>33</sup> However, since eq 4 does not appear in the rate laws (eq 11 and 12) it does not contribute to the isotope effect we determined.
- (26) J. R. Thomas, *J. Am. Chem. Soc.*, **87**, 3935 (1965). The value of  $2k_t$  was reported to be  $1.4 \times 10^{10} e^{-10200/RT}$ .
- (27) As expected from a plot of this type, the  $k_x$  values determined from the intercept fluctuate more ( $\pm 25\%$ ) than do the  $k_t$  values from the slopes ( $\pm 10\%$ ). A more precise way of determining  $k_x$  involves plotting  $\text{rate}/[\text{O}_3][\text{TBH}]$  vs.  $[\text{O}_3]^{1/2}/[\text{TBH}]^{1/2}$ , where the slope gives  $k_x$  and  $k_t$  is given by  $[\text{intercept} (k_t/k_x)^{1/2}]$ . Although the least-squares analyses of these plots were not as satisfactory as Figure 3, the values of  $k_x$  were 20 and  $16 \text{ M}^{-1} \text{ s}^{-1}$  for TBH and TBH- $d_1$ , respectively as compared with average values of  $25 \text{ M}^{-1} \text{ s}^{-1}$  from Figure 3. Thus, a better estimate of  $k_x$  may be  $18 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$ . The  $k_t$  values determined from the intercept of this alternate plot are  $5.2 \text{ M}^{-1} \text{ s}^{-1}$  for TBH and  $2.7 \text{ M}^{-1} \text{ s}^{-1}$  for TBH- $d_1$ . These values are less precise than the slope-derived values shown in Figure 3.
- (28) Substitution of the rate constants from Figure 2 and the actual concentrations of ozone and TBH in  $\text{CFCl}_3$  at  $-4$  °C from Table III into eq 11 yields total calculated rates in good agreement (within 10%) with the measured rates (Table III). Thus, the relative contributions of the first and second terms of eq 11 can be determined; the first contributes 50–77%, depending on the TBH/ozone ratios. Since product studies and peroxide decomposition rates (Tables I and II) show very similar behavior for TBH-ozone reactions in both  $\text{CFCl}_3$  and  $\text{CCl}_4$  at different temperatures, it is felt that the rate constants measured by a simple treatment that neglects the second term in eq 11 are systematically high by about 60%. (Compare the values of  $9.4 \text{ M}^{-1} \text{ s}^{-1}$  in Table V for TBH- $\text{O}_3$  at  $-4$  °C to the correct value of 5.4 in Figure 2.) Thus their use of the determination of Arrhenius parameters should be a reasonable approximation. However, since the balance between the first and second terms in eq 11 changes for TBH- $d_1$ , the data in Table V do not yield reliable isotope effects.
- (29) C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Lett.*, 4111 (1965).
- (30) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968), and references cited therein.
- (31) (a) A. Factor, C. A. Russell, and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3692 (1965); (b) R. Hiatt and T. G. Traylor, *ibid.*, **87**, 3766 (1965).
- (32) K. U. Ingold in "Free Radicals", Vol. I, J. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1975, Chapter 2, lists a value of  $k_\beta = 3.4 \times 10^{12} e^{-13900/RT}$ .
- (33) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **47**, 3797 (1969).
- (34) Equation 6 is written as yielding  $\text{RO}\cdot + 2\text{O}_2$  directly for simplicity. Our data do not allow us to determine whether or not  $\text{RO}_2\cdot$  is an intermediate, but the reaction  $\text{RO}_2\cdot \rightarrow \text{RO}\cdot + 2\text{O}_2$  is exothermic by more than about 50 kcal/mol if  $\text{O}_2$  is formed in its ground state.
- (35) Gas-phase data [see J. N. Pitts, *Angew. Chem.*, **14**, 1 (1974), and references cited therein] indicate that hydroxyl radicals react with ozone somewhat more readily ( $k = 10^9 e^{-1900/RT}$ ) than do hydroperoxy radicals ( $k = 10^8 e^{-2800/RT}$ ). These reactions undoubtedly proceed by a different mechanism than do the *tert*-butoxy and *tert*-butylperoxy reactions. However, these data suggest that *tert*-butoxy reacts with ozone with a rate constant only slightly greater than does *tert*-butylperoxy. Thus, given a much lower steady-state concentration of alkoxy vs. peroxy radicals in our system, the reaction,  $\text{RO}\cdot + \text{O}_3 \rightarrow \text{RO}_2\cdot + \text{O}_2$ , would not effectively compete with eq 10, and we ignore it.
- (36) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley-Interscience, New York, N.Y., 1976, p 156 ff.
- (37) J. Berkowitz, W. A. Chupka, and D. Gutman, *J. Chem. Phys.*, **55**, 2733 (1971).
- (38) C. Batich and W. Adam, *Tetrahedron Lett.*, 1467 (1974).