3614 J. Am. Chem. Soc. 1983, 105, 3614-3622

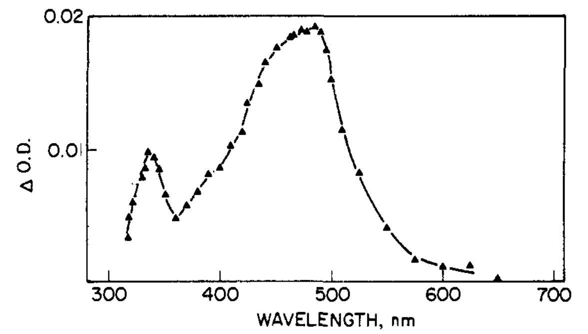

Figure 5. Transient spectrum showing the phenylcyclohexadienyl peak (330–340 nm), as well as the peak assigned to the complex between iodine atom and benzene (λ_{max} = 470 nm). Obtained by using iodobenzene (0.015 M) and benzene (1.8 M) in Freon 113.

of our study. Some exploratory experiments in the case of benzene led to a well-defined absorption band in the visible region (Figure 5), the formation of which seemed to be at least 100 times faster than the reactions of phenyl radicals; thus, while iodine atoms do generate absorptions, the time scale involved is sufficiently different from that in phenyl reactions that they do not interfere with the kinetic analysis. Further, in the UV region used for monitoring (usually 320–340 nm) the cyclohexadienyl bands are considerably stronger.

Similar signals were also observed for toluene and other alkylbenzenes. The signals were either much weaker or absent in the case of vinyl monomers.

Experimental Section

Materials. Benzoyl peroxide (Aldrich) was purified by reprecipitation by methanol from a chloroform solution. Iodobenzene (Eastman) was used as received. Freon 113 from various sources (Fluka, Aldrich, or Matheson) was purified by refluxing on calcium carbonate followed by fractional distillation. Diphenylmethanol was doubly sublimed. All other substrates were purified by distillation or recrystallization. In the case of vinyl monomers special care was taken to eliminate stabilizing additives.

Procedure. Static experiments were carried out with samples (usually 2 mL) contained in Suprasil cells made of square (7 × 7 mm^2) quartz tubing. They were deaerated by using oxygen-free nitrogen. Care was taken to use fresh samples for each measurement.

Flow experiments were carried out in a flow system where the reaction cell had been built of the same material (7 × 7 mm^2 Suprasil tubing) mentioned above. The solutions were prepared by adding the solutes to priorly deaerated solvent in a nearby container and bubbling with oxygen-free nitrogen for a few additional minutes. The container was connected to the reaction cell with Teflon tubing.

Laser Photolysis Facility. The apparatus used has been described in considerable detail in an earlier publication.[38] Since that report was published, a number of modifications have been introduced; the main one, and directly relevant to this work, is the addition of a Lumonics TE-860-2 excimer laser, which for the present study was operated with Xe–HCl–He mixtures and produced pulses at 308 nm (~4 ns, up to 80 mJ). These pulses were used for sample excitation at 90° with respect to the analyzing beam. Further details of the modifications to our instrument will be reported elsewhere.

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance.

Registry No. Phenyl radical, 2396-01-2; benzene, 71-43-2; chlorobenzene, 108-90-7; styrene, 100-42-5; β-methylstyrene, 637-50-3; methyl methacrylate, 80-62-6; cyclohexene, 110-83-8; toluene, 108-88-3; cumene, 98-82-8; *p*-xylene, 106-42-3; 2-propanol, 67-63-0; benzhydrol, 91-01-0; acetonitrile, 75-05-8; tetrahydrofuran, 109-99-9; carbon tetrachloride, 56-23-5; 2-bromobutane, 78-76-2; 1-bromopropane, 106-94-5; benzoyl peroxide, 94-36-0.

Supplementary Material Available: Tables (Tables II–XXXIX) giving detailed kinetic data (28 pages). Ordering information is given on any current masthead page.

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Reaction of Cumene with Ozone To Form Cumyl Hydrotrioxide and the Kinetics of Decomposition of Cumyl Hydrotrioxide

William A. Pryor,* Norio Ohto, and Daniel F. Church

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. *Received November 12, 1982*

Abstract: Cumene forms a charge-transfer complex with ozone in a number of solvents (e.g., with absorption at 360 nm in acetone). When this CT complex is photolyzed at −75 °C or warmed above −40 °C, reaction occurs to form both cumyl hydrotrioxide and ring-ozonated products (in a ratio of about 70/30). The decomposition of the hydrotrioxide, PhCMe$_2$OOOH, can be monitored by proton NMR in acetone-d_6 using either the CH$_3$ or the OOOH hydrogens; the decomposition is first order and gives activation parameters of E = 16.0 ± 0.1 kcal/mol and log A = 10.4 ± 0.1. These values agree with literature data on the decomposition of aroyl hydrotrioxide (from the reaction of ozone with aromatic aldehydes) and on the decomposition of trioxides of cyclic and acyclic acetals, but they are far from the values of E = 23 kcal/mol and log A = 16 calculated using thermokinetic methods. The low activation parameters undoubtedly result from a chain decomposition of the trioxide. Therefore, we also studied the decomposition in the presence of an inhibitor, 2,6-di-*tert*-butyl-4-methylphenol (BHT), to eliminate the chain decomposition. In the presence of BHT, the activation parameters become E = 23.9 ± 0.1 kcal/mol and log A = 16.4 ± 0.1, in agreement with theory. In addition, we can follow the disappearance of the phenolic hydrogen of BHT, and it disappears with the same rate constant as does cumyl hydrotrioxide, indicating that every decomposition of the hydrotrioxide leads to two scavengeable free radicals. In the presence of BHT, the hydrotrioxide decomposes to give cumyl alcohol as the only organic product; in the absence of BHT a small yield of acetophenone also is formed, perhaps as a result of the production of the cumyltrioxyl radical in a chain process and its exothermic loss of dioxygen and subsequent β-scission of the cumyloxyl radical. This is the first time that the hydrotrioxide of a hydrocarbon has been characterized by NMR and that Arrhenius parameters for decomposition of a hydrotrioxide have been obtained that agree with thermokinetic predictions.

The reaction of cumene with ozone is of interest from two perspectives. First, the mechanism for the reaction of hydrocarbons with ozone is under intense scrutiny,[1-3] and cumene, with its unique and reactive hydrogen, is an attractive substrate.

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Second, ozone reacts with olefins to produce small yields of radicals,[4-6] in addition to the normal Criegee products, and this radical production appears responsible for a large fraction of the biological damage that occurs when lung tissue and pulmonary unsaturated fatty acids are exposed to polluted air containing ozone.[7-11] We have suggested that the mechanism of radical production involves reaction of ozone at the allylic C–H bond, eventually leading to an allylic hydrotrioxide,[5] and cumene represents a more easily studied model for this process than does a typical olefin.

The reaction of ozone with C–H bonds has been studied extensively, primarily for compounds with adjacent oxygen atoms that could stabilize a positive charge or an electropositive radical center.[1] The ultimate products from such reactions suggest that a hydrotrioxide is an intermediate, but hydrotrioxides have been identified only from the reaction of aldehydes, acetals, and similar substrates,[12] and never for hydrocarbons.[1] The mechanism that has been accepted, eq 1, involves abstraction of a hydrogen atom

$$RH + O_3 \rightarrow [R\cdot \quad \cdot O_3H] \rightarrow ROOOH \qquad (1)$$

in a transition state with appreciable dipolar character.[1] Recently, however, Benson[2] has suggested that these reactions, which usually are studied at low temperatures, generally do not involve hydrogen atom transfer since reaction 1 is appreciably endothermic; he has suggested instead that the reaction involves a hydride abstraction, eq 2.

$$RH + O_3 \rightarrow [R^+ \ {}^-O_3H] \rightarrow ROOOH \qquad (2)$$

We here present evidence that supports an ionic mechanism. We have prepared the hydrotrioxide from cumene both by thermal reaction and by photolysis of the charge-transfer complex of cumene and ozone, and we have characterized a hydrocarbon hydrotrioxide by NMR for the first time. We also here report kinetics of the decomposition of the hydrotrioxide in both the presence and absence of an inhibitor.

Experimental Section

Materials. Cumene and *tert*-butylbenzene were washed with 80% sulfuric acid, neutralized with aqueous sodium hydroxide, washed with water, dried over calcium chloride, and distilled under reduced pressure. The cumyl alcohol, acetophenone, and cumene hydroperoxide used as NMR standards were commercially available and used without further purification. Spectrophotometric grade pentane was used for the dry ice slush bath in the low-temperature UV experiments. Acetone-d_6 was over 99% pure and used without further purification. Freon-11 was distilled over calcium hydride and treated with ozone before use.

Visible–UV Spectra. The visible–UV spectra of the cumene/ozone charge-transfer complex were recorded with a Varian Cary 219 spectrophotometer, using a quartz reaction cell with 1-cm path length and a special Dewar equipped with quartz windows. Dry ice/pentane was used as a cooling solution; the measured bath temperature was −75 °C. Solvent containing 3.58 M cumene was put into the cell, immersed in the cooling bath, and ozonated with an ozone/oxygen stream.

NMR. 200-MHz ^{1}H and 50-MHz ^{13}C NMR spectra were recorded with a Bruker WP-200 spectrometer equipped with a variable-temperature probe and Aspect computer. The temperature stability at the sample was ±0.1 K.

Product Studies. An aliquot of the reaction mixture in acetone-d_6 was transfered to an NMR sample tube by nitrogen pressure or by using a precooled pipet. The NMR tube was held in a liquid nitrogen bath during the transfer and then quickly transferred to the precooled NMR probe. The ^{1}H NMR spectra of the ozonation mixture and the standard samples were recorded at −73 °C. The NMR peaks of the products were confirmed by spiking the ozonation mixture with known samples at −73 °C.

The ozonation mixture also was treated with triphenylphosphine at −78 °C. A precooled acetone-d_6 solution of triphenylphosphine (0.1 M) was slowly added to the ozonation mixture at −78 °C and the resulting solution kept at this temperature for 30 min, and then the NMR spectrum of this sample recorded at −73 °C.

The ^{13}C NMR spectra of the ozonation mixture and of the standard products were also recorded at −73 °C in order to confirm the assignment of ^{1}H NMR spectra.

Cumyl alcohol and acetophenone also were determined by GC using a 10% Carbowax column, 10 ft × $^1/_8$ in., programmed from 80 to 220 °C at 10 °C/min. Cumene in acetone (2.39 M, 14.3 mmol) was ozonated with an ozone/oxygen stream for 2 h at −40 °C. After ozonation the solution was thoroughly flushed with nitrogen at −78 °C, and the ozonation mixture was warmed to room temperatures and allowed to decompose.

Thermal Preparation of Solutions of Cumyl Hydrotrioxide. Acetone-d_6 was used as the solvent for the thermal preparation of the hydrotrioxide since less polar solvents gave yields too low to detect by NMR. A 3.58 M acetone-d_6 solution of cumene containing a known amount of Me_4Si was ozonated with an ozone/oxygen stream in a reactor immersed in a −40 °C dry ice/benzyl chloride bath. Ozonation was conducted after the addition of Me_4Si, since it was difficult to mix Me_4Si into the sample completely at −78 °C after ozonation; however, ozonation of Me_4Si in acetone-d_6 at −40 to −78 °C showed no detectable products by NMR. The ozone stream contained about 0.1 mmol of ozone/min, but most of the ozone passes through the solution unchanged. Ozone was generated from a Welsbach Model T-23 ozonator. After ozonation, the reaction mixture was thoroughly flushed with nitrogen to remove excess ozone and oxygen.

Photochemical Preparation of Solutions of Cumyl Hydrotrioxide. A 3.58 M acetone-d_6 solution of cumene containing a known amount of Me_4Si was ozonated at −75 °C for 3–24 h with an ozone/oxygen stream while the solution was continuously irradiated with light. A rectangular quartz reaction cell, Dewar with windows, dry ice/pentane slush bath, and 200-W mercury lamp equipped with a Corning 7-37 filter were used. The ozone flow rate was ca. 0.1 mmol/min. After ozonation, the ozonation mixture was thoroughly flushed with nitrogen to remove excess ozone and oxygen.

Kinetic Studies. Aliquots of the ozonation mixture was transferred to a series of NMR sample tubes and stored at −198 °C until use. The sample tubes were transferred to the precooled NMR probe, and after thermal equilibrium was reached at each temperature, the decay of COOOH (where C is the cumyl group) was monitored by integrating the peak areas with time, using Me_4Si as an internal standard. The formation of cumyl alcohol and acetophenone were followed by integrating the methyl proton signals with time. In some runs, the decay of both the methyl proton signal and the OH signal of COOOH were monitored.

Runs were also done using BHT (2,6-di-*tert*-butyl-4-methylphenol) as inhibitor. Since BHT reacts very rapidly with ozone, a cold acetone-d_6 solution of BHT was added after ozonation and flushing the sample with nitrogen at −75 °C. The decay of BHT was monitored by integrating the hydroxyl proton with time.

Electron Spin Resonance. The ESR spectra were recorded with a IBM 100D ESR spectrometer and Aspect computer. Low-temperature experiments were done with an ER 4111VT low-temperature controller. The temperature stability at the sample was ±0.1 K. For convenience

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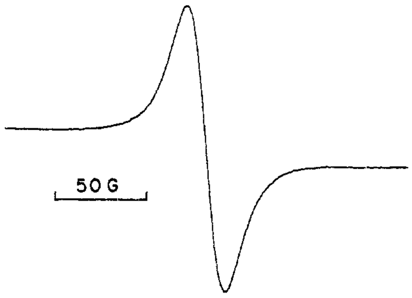

Figure 1. ESR spectrum of the peroxyl radical formed from the reaction of ozone with cumene at −40 °C in $CFCl_3$; the spectrum was recorded after the ozone stream was turned off and the sample cooled to −78 °C. The g value is 2.0151 ± 0.0001.

in generating ozone near the ESR spectrometer, ozone was adsorbed onto silica gel at −78 °C and then desorbed in a stream of either oxygen or nitrogen and bubbled through the ESR tube in the ESR cavity by using a very fine glass capillary so a very tiny stream of bubbles resulted. Surprisingly, the spectrum obtained with ozone/nitrogen was not very much less intense than that with ozone/oxygen. (Oxygen was present in both experiments, however, since the solvent was not deaired and the ozone/silica gel was not deoxygenated by a prolonged flushing with nitrogen.) Either $CFCl_3$ or pentane was used as solvent in the ESR experiments; the concentration of peroxy radicals was higher in $CFCl_3$ than in pentane. The g value of the radical was determined using DPPH as a standard. (DPPH powder was diluted with NaBr and the mixture sealed in a capillary that could be placed in an ESR tube.) Spectra were accumulated by using 2000 0.5-s scans.

Results

ESR Study of the Reaction of Ozone with Cumene at Low Temperatures. The ozonation of cumene was conducted by bubbling ozone into an ESR tube containing a 3.58 M solution of cumene in either pentane or $CFCl_3$ in the ESR cavity. When the ozonation was conducted at −78 °C, the reaction mixture turned green but no ESR signal was observed. ESR signals could be observed by using two protocols. The ozone/oxygen or ozone/nitrogen stream could be very slowly bubbled through a glass capillary into an ESR tube containing cumene in pentane or Freon-11, and ESR signals were observed providing the temperature in the cavity was −40 °C or higher. (Temperatures up to 0 °C were studied.) Alternatively, the sample could be exposed to ozone at −78 °C, the sample rapidly warmed to −40 °C and recooled to −78 °C, and the ESR spectrum recorded. In this second protocol, the ozonation could be repeated several times at low temperatures, and each time the signal was observed when the sample was warmed to −40 °C and recooled. The spectrum in this second protocol was less noisy than in the first; Figure 1 shows this spectrum. The signal observed is a single line with g = 2.0151 ± 0.0001 in both pentane and $CFCl_3$. Blank runs with the solvent alone showed no ESR absorbance.

The same experiment was done with Tetralin in place of cumene. An ESR signal was observed as long as bubbling of ozone was continued at −45 °C, but no signal could be observed below −45 °C. The signal has a g value of 2.0141 ± 0.0001 and consists of two lines with hyperfine splitting of 6.2 G, consistent with the splitting expected for the secondary peroxyl radical from Tetralin.[13] The tetralyl peroxy radical at −45 °C and the cumyl peroxyl radical at −40 °C were observed to decay when the ozone bubbling was stopped; the tetralyl peroxyl radical decayed more rapidly, as would be expected for a secondary peroxyl radical.

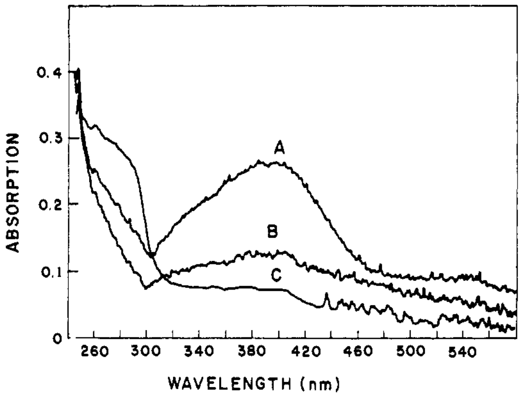

Figure 2. UV-visible spectra of cumene/ozone mixtures in pentane at −75 °C: (A) 3.58 M cumene after a brief exposure to a flow of ozone/oxygen; (B) the same solution after flushing out the ozone with nitrogen; (C) the control spectrum of a saturated solution of ozone in pentane (about 10^{-3} M) without cumene.

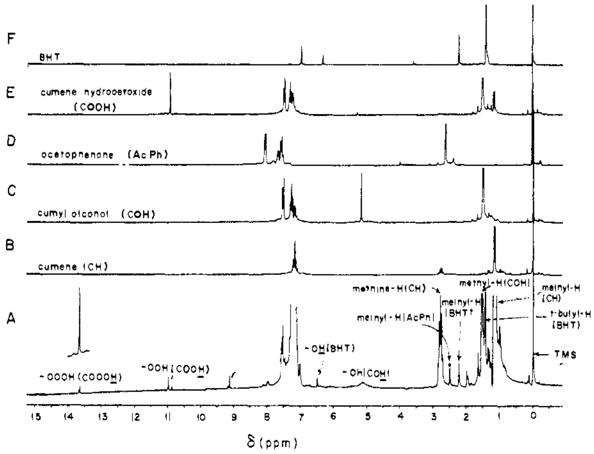

Figure 3. 200-MHz ^1H NMR spectra recorded in acetone-d_6 at −73 °C: (A) 3.58 M cumene solution photolyzed and ozonated at −75 °C for 15 h; (B) 3.58 M cumene without ozonation; (C) 3.57 M cumyl alcohol; (D) 2.85 M acetophenone; (E) 3.49 M cumyl hydroperoxide; (F) BHT.

Charge-Transfer (CT) Spectra of Ozone–Aromatic Compounds. Visible–UV spectra were recorded during ozonation at −75 °C using a quartz Dewar equipped with windows. Figure 2 shows the absorption spectra in pentane with and without cumene (3.58 M) and ozone. The ozone/cumene CT absorption is seen as a broad peak centered at about 390 nm; this is close to the absorption maximum of the CT complex of ethylbenzene and ozone in isopentane glass at −195 °C as reported by Bailey et al.[14b] Bailey et al. reported that the CT complexes of toluene and ethylbenzene are stable in a isopentane glass at −195 °C but disappear above −150 °C. Our detection of the complex in fluid solution at higher temperatures appears to result from the fact that we used concentrated cumene solutions whereas Bailey et al. used dilute (0.1 M) concentrations in the glass. The equilibrium constant for charge-transfer complex formation can be calculated to be about 40 at −150 °C and about 1 at −75 °C;[1m] using these values, the concentration of the CT complex is calculated to be about 10^{-3} M both in the low-temperature, dilute conditions used by Bailey et al. and in the higher temperature, more concentrated solutions used here.

Solutions of cumene (3.6 M) and ozone in acetone give a CT absorption maximum at about 350 nm that can be seen as a shoulder on the strong acetone solvent peak that goes off scale between 320 and 340 nm. Solutions of cumene and ozone in $CFCl_3$ give a CT maximum at about 360 nm.

NMR Studies: Identification of Hydrotrioxide. Although the hydrotrioxide of a hydrocarbon has not previously been characterized, hydrotrioxides have been detected by ^1H NMR in the

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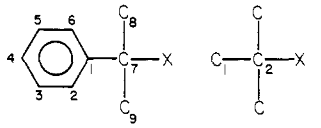
Table I. Proton NMR Chemical Shifts of Cumyl Compounds

compd[a]	temp, °C	solvent	chem shift, ppm β-CH_3	chem shift, ppm -$(O)_nH$
CH	−73	acetone-d_6	1.15, 1.19 (d)	
COH	−73	acetone-d_6	1.50 (s)	5.18 (s)
COOH	−73	acetone-d_6	1.52 (s)	10.95 (s)
COOOH	−73	acetone-d_6	1.64 (s)	13.67 (s)
COOC[b]	37	CCl_4	1.53 (s)	
COOOC[c]	−50	$CFCl_3$	1.67 (s)	

[a] C is $PhCMe_2$–. [b] Swern, D.; Clements, A. H.; Luong, T. *Anal. Chem.* 1969, *41*, 412. [c] Bartlett, P. D.; Lahav, M. *Isr. J. Chem.* 1972, *10*, 101.

Table II. ^{13}C NMR for Cumyl and *tert*-Butyl Derivatives[a,b]



X	C-1	C-2,6	C-3,5	C-4	C-7	C-8,9
			Cumyl–X			
H	148.8	126.8	128.8	126.3	34.6	24.3
	(149.3)	(126.4)	(128.4)	(125.8)	(34.2)	(24.1)
OH	150.7	125.1	128.4	126.6	72.1	32.3
	(148.8)	(124.5)	(127.9)	(126.3)	(72.5)	(31.6)
OOH	145.5	125.9	128.3	127.2	84.0	26.6
OOOH	134.5				104.3	

C-1	C-2	C-1	C-2
tert-Butyl-OH		*tert*-Butyl-OOH	
(31.3)	(68.8)	(25.9)	(80.9)

[a] Solvent acetone-d_6; Values in parts per million from the internal standard, Me_4Si. [b] Literature references in parentheses are from the Sadler Standard ^{13}C NMR Spectra, Sadler Research Laboratories, 1980.

low-temperature ozonation of aldehydes,[12] ethers,[12] and acetals.[15] Therefore, we examined the ozonation of cumene by ^1H and ^{13}C NMR at low temperatures to identify intermediates. We have previously[3] published the spectra of ozonized cumene and its comparison with the stable products cumyl alcohol, acetophenone, and cumyl hydroperoxide. Figure 3 shows another preparation of cumyl hydrotrioxide, this time in the presence of an inhibitor of free-radical chain reactions, BHT. The spectra also are shown of cumene, cumyl alcohol, acetophenone, cumyl hydroperoxide, and BHT. Signals due to the stable products cumyl alcohol, acetophenone, and cumene hydrotrioxide were confirmed by spiking the ozonation mixture with the products at low temperature. Two singlet peaks, whose relative intensity is about 1:6, at 13.7 and 1.64 ppm, disappear at the same rate on warming the ozonized cumene from −73 to −20 °C. These signals are compared with those of other cumyl compounds in Table I. The chemical shift at 1.64 ppm is very close to that of the β-methyl protons of other oxygenated cumene derivatives, especially that of dicumyl trioxide. The peak at 13.67 ppm can reasonably be assigned to the trioxide hydrogen in COOOH (where C is $PhCMe_2$) by comparison with COH and COOH.

The ozonation of cumene also was examined by ^{13}C NMR. Table II compares our assignments for the stable products with literature values and also shows the assignment of absorbances at 134.5 and 104.3 ppm to ring carbon 1 and the benzyl carbon, respectively, in COOOH. Also shown for comparison are the absorbances for *tert*-butyl alcohol and hydroperoxide. Figure 4 shows these ^{13}C NMR spectra.

The hydrotrioxide also was identified by its reaction with triphenylphosphine at −73 °C. When the ozonized cumene solution in acetone was treated with a slight excess of Ph_3P, the peaks at 1.64 and 13.8 ppm assigned to the hydrotrioxide disappeared.

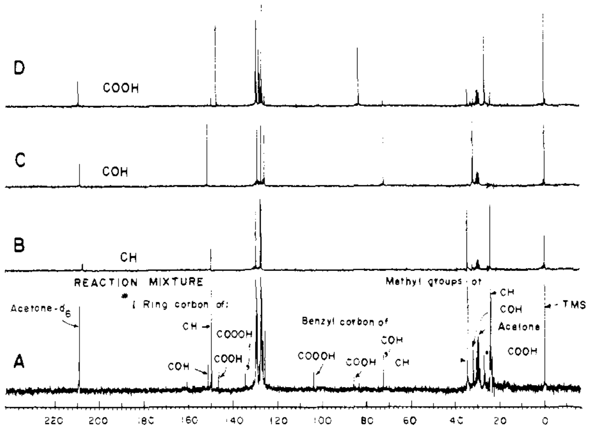


Figure 4. ^{13}C NMR spectra of the cumene/ozone reaction mixture and of cumene, cumyl alcohol, and cumyl hydroperoxide.

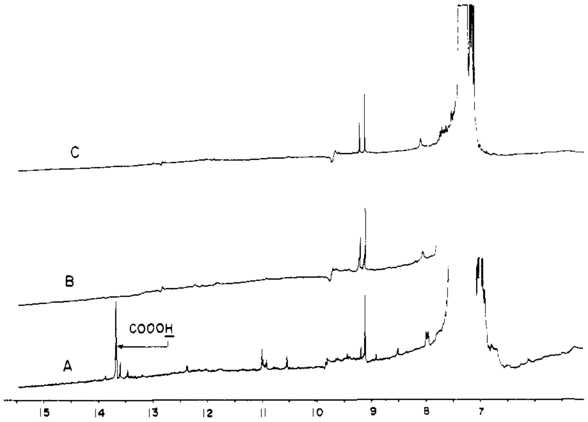
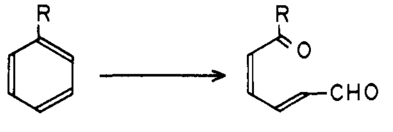


Figure 5. ^1H NMR spectra of the ozone/cumene and ozone/*tert*-butylbenzene reaction mixtures in acetone-d_6: (A) ozone/cumene reaction mixture at −73 °C; (B) is the ozone/*tert*-butylbenzene reaction mixture at −73 °C; (C) ozone/*tert*-butylbenzene reaction mixture warmed to room temperature.

Ring Ozonation. *tert*-Butylbenzene also undergoes ozonation at −40 °C under our conditions. The products were not identified, but Figure 5 compares the NMR of COOOH with that of the ozonation products of *tert*-butylbenzene. Note that ozonation of *tert*-butylbenzene produces no compounds absorbing at 13.8 ppm, the region assigned to the trioxide hydrogen. However, there are two peaks at 9.0–9.2 ppm. We have used the largest of these peaks to quantify the amount of ring ozonation that occurs in cumene in competition with side-chain ozonation (see Figure 5). We have assumed that this large peak represents a single proton, because that gives data that agree roughly with our GC analysis of the amount of cumene that undergoes side-chain vs. ring ozonation. These peaks might be the aldehydic protons of compounds like those shown in eq 3. If cumene undergoes ring ozonation to give



(3)

aldehydes, and since aldehydes are known to react with ozone to give acyl hydrotrioxides, the compound we have identified as COOOH actually might be an acyl hydrotrioxide. Figure 5 disproves this possibility by showing that the spectrum of the ozonation mixture from *tert*-butylbenzene does not change on warming to room temperature, indicating the absence of labile compounds in the mixture produced by ring ozonation.

We have quantified the partition between side-chain and ring ozonation for cumene both by GC and by NMR. Ozonation at −40 °C for 2 h followed by warming to room temperature under nitrogen and GC analysis gave 0.67 mmol of acetophenone and 1.23 mmol of cumyl alcohol; 2.64 mmol of cumene was found to

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(15) Kovac, F.; Plesnicar, B. *J. Am. Chem. Soc.* **1979**, *101*, 2677.

Table III. Product Distribution after Ozonation of 3.58 M Solutions of Cumene in Acetone-d_6 during the Preparation of Cumyl Hydrotrioxide[a]

temp, °C	time, h	products, M				
		COOOH	COOH	AcPh	COH	ring product[b]
		Photochemical Preparation				
−75	4	0.03	tr[c]	0.01	0.18	0.05
−75	13	0.20	tr	0.09	0.24	0.14
−75	15	0.22	tr	0.07	0.26	0.17
−75	24	0.42	tr	0.11	0.36	0.29
		Thermal Preparation				
−40	4	0.05	0.11	0.05	0.21	0.07
−40	3	0.07	0.14	0.07	0.22	0.11
−40	3	0.04	0.07	0.05	0.21	0.08
−40[d]	3					0.07

[a] C is $PhCMe_2$–. [b] The peak at 9.0-9.1 ppm was assumed to be a product of ring attack and the yield was calculated under the assumption that the signal was due to one proton. [c] Trace. [d] Obtained from ozonation of 3.23 M *tert*-butylbenzene in acetone-d_6 for 3 h at −40 °C. Several unidentified peaks were formed as well as a sharp singlet at 9.1 ppm, which was used to estimate ring ozonation in the same way as was done for cumene.

be consumed. The cumyl alcohol and acetophenone account for 72% of the cumene reacted. Thus, 28% of the cumene is unaccounted for and might be assumed to have given ring-ozonation products. Ring ozonation was monitored by NMR as follows. Ozonation of both *tert*-butylbenzene and cumene gives peaks at 9.0–9.2 ppm. If these peaks are used to quantify the amount of ring ozonation of cumene (and assuming they represent a single proton), then both the thermal preparative method at −40 °C and the photochemical method at −75 °C give 18–25% ring ozonation.

Preparation of Solutions of Cumyl Hydrotrioxide. Solutions of cumene hydrotrioxide were prepared by two methods. Since the conversion of CT complex to COOOH is very slow at −78 °C, COOOH solutions were prepared by continuously ozonating cumene at about −40 °C in the dark or by continuously photolyzing ozone/cumene reaction solutions during ozonation at −75 °C. The yields of the products were calculated from the ^1H NMR spectra by integrating the peaks vs. Me_4Si, as shown in Table III. Experimental errors in calculating concentrations of products are estimated as about ±10%.

The thermal preparation at −40 °C for 3 h gave ca. 0.04–0.07 M solutions (ca. 1–2% yield based on cumene) of the trioxide contaminated with ca. 0.2 M cumyl alcohol, 0.1 M cumene hydroperoxide, 0.07 M acetophenone, and 0.1 M ring-ozonated products. The low-temperature photolytic method gave more concentrated solutions of the hydrotrioxide, 0.2–0.4 M, contaminated with 0.2–0.4 M cumyl alcohol, ca. 0.1 M acetophenone, 0.1–0.3 M ring-ozonated products, and only traces of cumene hydroperoxide.

Products from the Decomposition of COOOH. During decomposition of COOOH, the formation of products was followed by integrating each peak with time by using Me_4Si as an internal standard (Table IV). In the absence of an inhibitor, COOOH decomposes to give cumyl alcohol and acetophenone as the main products. Cumyl hydroperoxide is not formed during decomposition; the solutions were deaired by bubbling with nitrogen before the decomposition was studied, so autooxidation of cumene could not occur. The yields of acetophenone are higher than expected from the β-scission of cumyloxyl radicals during decomposition; a rationalization of this is discussed below. In the presence of 2,6-di-*tert*-butyl-4-methylphenol, BHT, the decomposition of COOOH gives no detectable acetophenone.

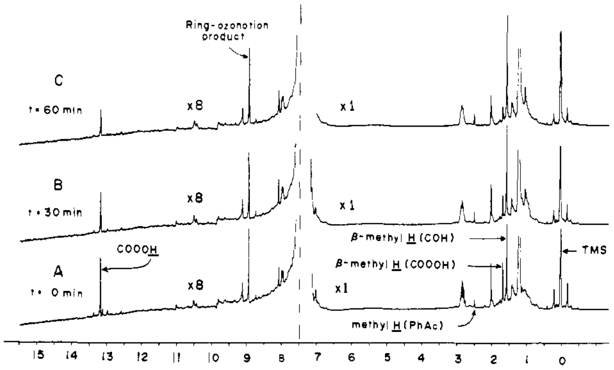

Figure 6. Changes in the ^1H NMR spectrum of COOOH in acetone-d_6 at −20 °C over time intervals of 0, 30, and 60 min. The left-hand portion of the spectra were taken at a sensitivity 8-fold greater than the right.

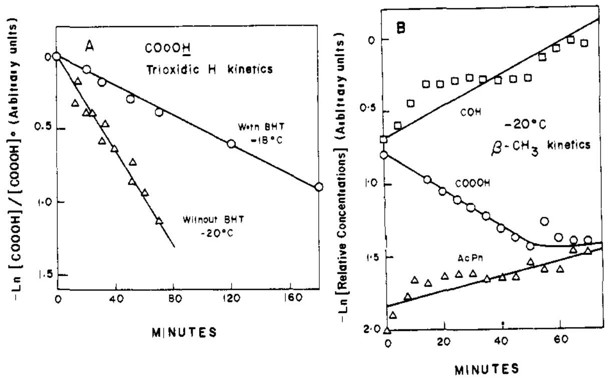

Figure 7. Kinetic plots of COOOH solutions in acetone-d_6: (A) disappearance of the hydrotrioxide hydrogen in the presence and absence of BHT; (B) disappearance of the protons in the methyl groups of COOOH (corrected by a statistical factor of $^1/_6$) and the appearance of the methyl protons of acetophenone ($\times^1/_3$) and cumyl alcohol ($\times^1/_6$). All spectra are integrated vs. Me_4Si, so concentrations are expressed in relative, arbitrary units.

Kinetics Studies. The decomposition of cumyl hydrotrioxide was studied by following the decay of the hydrotrioxide by ^1H NMR at several temperatures. Hydrotrioxide concentration was monitored by integrating the peak area at 13.8 ppm with time, using Me_4Si as an internal standard. In some runs, decay of the hydrotrioxide was also monitored by integrating the β-methyl proton peak area with time.

Figure 6 shows changes in a typical spectrum of a COOOH solution with time, and Figure 7 shows kinetic plots. Rate constants were calculated from eq 4, where k_d is the rate constant

$$-d[COOOH]/dt = -d[BHT]/dt = k_d[COOOH] \quad (4)$$

Table IV. Appearance of Products and Disappearance of COOOH in Acetone-d_6[a]

additive, M	dec temp, °C	[COOOH]$_0$, M	−Δ[COOOH], M	Δ[AcPH], M	Δ[COH], M
none	−33	0.42	0.16	0.02	0.13
none	−23	0.20	0.14	0.02	0.13
none	−20	0.22	0.14	0.03	0.14
BHT[b] (0.27)	−15	0.16	0.05	0	0.05
BHT (0.27)	−13	0.14	0.07	0	0.06

[a] During the ozonation of cumene to prepare the hydrotrioxide, some cumene is used. Therefore, the concentration of cumene in the samples of hydrotrioxide is reduced to between 2.4 and 2.9 M. Since the products from the decomposition of COOOH are present at time zero (they are produced during the preparation of the hydrotrioxide), the values given in this table are the differences between concentrations at *t* = 0 and the completion of the kinetic run. [b] 2,6-Di-*tert*-butyl-4-methylphenol.

Table V. Rate Constants for the Decomposition of Cumyl Hydrotrioxide (COOOH) in Acetone-d_6

			10^4k, s		
additive, M	temp, °C	$[COOOH]_0$, M	COOOH^b	β-$CH_3{}^c$	BHT^d
none	−33.0	0.42^a	$0.70\ (0.10)^e$	0.84 (0.20)	
none	−23.0	0.07	2.28 (0.50)		
none	−23.0	0.20^a	2.59 (0.32)	2.30 (0.07)	
none	−20.0	0.04	3.09 (0.08)		
none	−20.0	0.32^a	2.93 (0.23)	2.21 (0.05)	
none	−17.0	0.08	5.35 (0.67)		
none	−15.0	0.04	5.89 (0.10)		
none	−12.0	0.03	12.1 (0.40)		
BHT (0.076)	−18.0	0.07^a	0.83 (0.02)	0.59 (0.03)	0.62 (0.02)
BHT (0.076)	−15.0	0.07^a	2.49 (0.15)	2.03 (0.37)	2.52 (0.08)
BHT (0.090)	−13.0	0.04^a	2.99 (0.20)		2.40 (0.05)
BHT (0.28)	−13.0	0.14^a	2.76 (0.30)	2.38 (0.27)	3.17 (0.18)
BHT (0.076)	−8.0	0.08^a	4.23 (0.12)		3.86 (0.08)
BHT (0.090)	−3.0	0.04^a	16.5 (0.11)	12.4 (0.22)	19.6 (0.08)

[a] Photochemical preparation (see text). [b] Disappearance of the trioxide proton of COOOH. [c] Disappearance of the β-methyl proton of COOOH. [d] Disappearance of the OH proton of BHT. [e] Number in parentheses is standard deviation in 10^4k.

Table VI. Arrhenius Parameters for the Decomposition of Cumyl Hydrotrioxide in the Presence and Absence of BHT[a]

	no BHT		with BHT	
	log *A*	*E*	log *A*	*E*
all data	$9.3\ (0.1)^b$	14.8 (0.1)	$18.5\ (0.1)^c$	26.3 (0.2)
trioxide hydrogen only	10.4 (0.1)	16.0 (0.1)	16.4 (0.1)	23.9 (0.1)

[a] Numbers in parentheses are the standard deviations of the least-squares Arrhenius plot. [b] Includes both methyl group and trioxidic hydrogen data for following the disappearance of COOOH. [c] Includes both methyl group and trioxidic hydrogen data for the disappearance of COOOH as well as data for the disappearance of the BHT phenolic hydrogen.

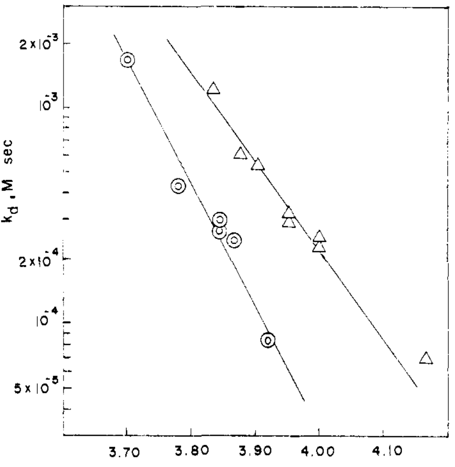

Figure 8. Arrhenius plots of the rate constants for the decomposition of cumene hydroperoxide in deoxygenated acetone-d_6: (◎) with added BHT; (△) without added BHT.

for homolysis of cumyl hydrotrioxide. Although Figure 6 shows data obtained from following the changes in the methyl groups of COOOH, acetophenone, and cumyl alcohol, none of these data is as precise as are the data obtained by monitoring the trioxidic hydrogen of COOOH, since all of the methyl protons occur in a group such that base-line resolution is not obtained. Nevertheless the data indicate within reasonable precision that the methyl group and the trioxidic hydrogen of COOOH disappear with the same rate constant, as shown in Table V. This eliminates the assignment of the unstable species as an acyl hydrotrioxide or a peracid that might result from ozonation of the ring to produce an aldehyde that then reacts with further ozone. Also, although the methyl proton data are not of sufficient precision to obtain kinetics, stoichiometric relationships can be obtained. (In some cases it was necessary to use only the linear portion of the kinetic plots; see Figure 7.) The stoichiometric data, shown in Table IV, indicate that in the absence of BHT about a 17% yield of acetophenone is obtained and the yields of acetophenone and cumyl alcohol equal the starting concentration of COOOH. (Note that some of the products are present at time zero of the kinetics runs, since they are produced during the ozonation of cumene, and so changes in concentrations of the species are monitored.) In the presence of BHT, acetophenone is not formed, and the yield of cumyl alcohol is approximately equal to the starting concentration of the trioxide.

In runs with BHT as an inhibitor, it also was possible to follow the phenolic hydrogen of the inhibitor. Both COOOH and BHT disappear in a process that follows first-order kinetics. Table V shows that COOOH and BHT both disappear with the same rate constant, implying that each hydrotrioxide molecule decomposes exclusively to form two free radicals that are then quantitatively scavenged by one BHT molecule.

Table V shows least-squares values of rate constants calculated from data of this type. In runs where rate constants were obtained from the integration of more than one type of hydrogen, the average standard deviation for duplicate or triplicate determinations of the same rate constant is ±14%.

Figure 8 shows the Arrhenius plot of our data in both the presence and absence of BHT. The Arrhenius parameters are shown in Table VI. The most reliable data are those in which only the hydrotrioxide hydrogen was used to monitor kinetics, for the reasons discussed above.

Discussion

Charge-Transfer (CT) Complex of Ozone with Cumene. Ozone forms CT complexes with many types of organic molecules;[14] Mazur and his group have suggested, in fact, that ozone complexes even with saturated hydrocarbons.[14c] This is not surprising; oxygen, which is less electronegative and less polarizable than ozone, forms CT complexes with virtually every type of organic molecule, including alkanes.[16a] Olefins, however, react with ozone so rapidly by the Criegee mechanism that it is difficult or im-

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(16) (a) For references see: Pryor, W. A.; Patsiga, R. A. *Spectrosc. Lett.* **1969**, *2*, 61, 353. (b) A referee has suggested that a complex between ozone and acetone could be the actual oxidant. We did not study the reaction in detail in solvents other than acetone and therefore have no data that explicitly eliminate this possibility. However, it appears unlikely, since we obtain small yields of COOOH in pentane by the photochemical method. (c) Note that the decomposition to give cumylperoxyl radicals directly from COOOH is not expected. Thermokinetic calculations show that eq I is 9 kcal/mol more favorable than is eq II. Thus, cumyl hydroperoxide would not be expected to be formed from COOOH by a route consisting of eq II and III.

$$\text{COOOH} \rightarrow \text{CO}\cdot + \text{HOO}\cdot \qquad \text{(I)}$$

$$\text{COOOH} \rightarrow \text{COO}\cdot + \text{HO}\cdot \qquad \text{(II)}$$

$$\text{COO}\cdot + \text{CH} \rightarrow \text{COOH} + \text{C}\cdot \qquad \text{(III)}$$

Table VII. Calculated Rate Constants for the Hydrogen Atom Abstraction from RH by Ozone[a-c]

RH	ΔH	log k^b		
		−78 °C	−35 °C	37 °C
isobutane	29	−25	−19	−12
propene	18	−12	−8	−4
1,4-pentadiene	15	−9	−5	−2
cumene	13	−6	−4	−1

[a] BDE from ref 20. [b] Enthalpy in kcal/mol and k in $M^{-1}\ s^{-1}$. [c] Assuming the BDE of ·OOO–H is 69 kcal/mol and log A for eq 1 is 8.5.

possible to detect their CT complexes prior to their reaction.[14b]

Bailey et al.[14b] appear to be the first to have studied the CT complexes of alkyl aromatics in detail. They prepared complexes in Freon or isopentane glasses at −195 °C and showed that the maximum wavelength of the complexes is directly proportional to the ionization potential of the aromatic compound. More recently, Shereshovets et al.[1m] reported a Hammett correlation for the equilibrium constant for complex formation with $\rho = -1.74$ and enthalpy of formation of −1.4 to −2.6 kcal/mol and entropies of −9.9 to −11.8 cal/(mol K).

We have observed green complexes of ozone with cumene at −78 °C, using 1:1 solutions of cumene in pentane, Freon-11, or acetone. Complexation is reversible; blowing out the ozone with nitrogen causes the absorption to disappear (Figure 1). The absorption maxima for the CT complexes in pentane, Freon-11, and acetone are at 382, 380, and 360 nm, respectively. Bailey et al.[14b] found the maximum for toluene and ethylbenzene in a pentane glass to be at 382 nm.

Preparation of Cumyl Hydrotrioxide. Hydrotrioxides have been proposed as intermediates in the ozonation of alkanes and other saturated compounds, but they have not previously been detected by spectral methods.[1] Hydrotrioxides have previously been detected by NMR from the reaction of ozone with aldehydes, ethers, and both acyclic and cyclic acetals.[12,15]

We were able to prepare COOOH by allowing ozone to bubble through cumene in acetone at −40 °C, but the 0.04–0.07 M solutions of hydrotrioxide prepared by this thermal method are contaminated with about 0.2 M cumyl alcohol and 0.1 M acetophenone, the decomposition products of the trioxide, and also with 0.1 M cumyl hydroperoxide, the product of the autoxidation of cumene. (Note that ozone would be expected to initiate the autoxidation of cumene, even at temperatures as low as −40 °C.[1-5]) Solutions of COOOH that are both more concentrated in the hydrotrioxide and less contaminated with impurities could be prepared by photolyzing a solution of cumene and ozone in acetone in the region of 360 nm, the absorption of the cumene/ozone charge-transfer band in acetone, while bubbling ozone through the solution at −73 °C. The reaction of ozone with cumene to give the hydrotrioxide depends very much on the polarity of the solvent; we did not detect hydrotrioxide hydrogen absorption in either Freon-11 or dichloromethane as solvents using our thermal preparative method, but we did detect a small yield of COOOH in pentane using the photochemical preparative method.[16b] In addition, cumene was found to react much faster than ethylbenzene or toluene, in agreement with the literature.

The fact that photolysis of the CT complex of cumene and ozone gives the same hydrotrioxide as is obtained by thermal reaction strongly suggests that the CT complex is on the reaction coordinate for reaction of cumene with ozone, and therefore that polar structures are involved in the reaction.[17] The dependence of the yield of hydrotrioxide on the polarity of the solvent also indicates a polar character for the reaction.

These results support the suggestion of Nangia and Benson[2] that the ozone/alkane reaction involves polar intermediates. Their argument is as follows. The ·OOO–H bond dissociation energy (BDE) is 69 kcal/mol. Using this value and assuming a preexponential A factor for the bimolecular reaction of ozone with an alkane of $10^{8.5}\ M^{-1}\ s^{-1}$, the rate constants for reaction 1 can be calculated to be those shown in Table VII. The rate constant for abstraction of the tertiary hydrogen from isobutane is $10^{-25}\ s^{-1}$ at −78 °C, far too slow to explain the production of ROOOH at that temperature. Even allylic and benzylic hydrogens react too slowly by hydrogen atom abstraction for this to be the dominant process at −78 °C. However, both olefins and dienes undergo hydrogen abstraction at an appreciate rate at body temperatures, so H atom abstraction by ozone may contribute to radical production in the lung when mammals breathe ozone-containing polluted air.[8-11]

Table VIII. Calculated Ratios of the Rate Constants for β-Scission and Hydrogen Abstraction by the Cumyloxyl Radical

system	temp, °C	k_β/k_H	
		apparent values in our systems	measd from CO· reactions[a]
photosensitized reaction of CH + O_3	−75	1.2	0.004
reaction of CH + O_3	−40	0.9	0.03
decomposition of COOOH	−20	0.6	0.07
decomposition of COOOH but in presence of BHT	−13	0	

[a] Reference 18a.

Since the hydrogen-atom abstraction reaction is eliminated at reduced temperatures, Benson suggested an ionic mechanism. The process he proposed is hydride ion abstraction, as shown in eq 2. The heat of reaction for this process for isobutane is the difference in the BDE of the C–H bond broken and the H–OOO· bond that is formed (1.0 eV), the ionization potential of the *tert*-butyl radical (6.9 eV) less the electron affinity of the HOOO· radical (1.8 eV), less the electrostatic interaction term (5.4 eV) and the solvation energy of the ion pair (0.5 eV in hexane and 1.0 eV in acetone). Thus, hydride abstraction from isobutane by ozone is endothermic by 4 kcal/mol in hexane and exothermic by 7 kcal/mol in acetone. The analogous reactions of cumene are calculated to be 10 kcal/mol more exothermic than that of isobutane, due to cumene's weaker C–H bond.

Benson did not consider CT complexes as intermediates in these reactions, but our data suggest that CT complexes are on the reaction coordinate. For this reason, we have modified Benson's mechanism, as shown in eq 5–7. The CT complex cannot undergo

$$\mathrm{CH} + \mathrm{O_3} \rightleftharpoons \underset{\text{CT complex}}{[\mathrm{CH,\ O_3}]} \tag{5}$$

$$[\mathrm{CH,\ O_3}] \xrightarrow{\text{hydride shift}} [\mathrm{C^+\ {}^-OOOH}] \tag{6a}$$

$$[\mathrm{CH,\ O_3}] \xrightarrow[\text{transfer}]{\text{electron}} [\mathrm{CH^{+}\cdot\ O_3^{-}\cdot}] \xrightarrow{\text{H}\cdot\text{ shift}} [\mathrm{C^+\ {}^-OOOH}] \tag{6b}$$

$$[\mathrm{C^+\ {}^-OOOH}] \rightarrow \mathrm{COOOH} \tag{7}$$

a shift of a hydrogen atom at low temperatures, since this leads to the same pair of radicals [R··OOOH] that would be formed in an endothermic process by direct H atom abstraction. However, either a hydride ion shift, eq 6a, or an electron transfer followed by an H atom shift, eq 6b, leads to the ion pair written by Benson as the first intermediate. Ion pair collapse, eq 7, produces the hydrotrioxide, which of course can then cleave homolytically to form radicals.[17b]

Production of Acetophenone. The ratios of acetophenone to cumyl alcohol in our experiments are larger than predicted from literature values of the rate constants for β-scission and hydrogen atom abstraction by the cumyloxyl radical.[18] Table VIII shows

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[17] (a) Colter, A. K.; Dack, M. R. J. In "Molecular Complexes"; Foster, R., Ed.; Crane Russak: New York, 1974; Vol. 2, Chapter 1. (b) The ionization potential of cumene and the electron affinity of ozone suggest an electron transfer, eq 6b, is feasible. See ref 2 and Koppenol; Koppenol, W. H. *FEBS Lett.* **1982**, *140*, 169.

the apparent values of k_β/k_H that are calculated from our observed yields of acetophenone and cumyl alcohol (eq 8 and 9). Walling

$$\mathrm{CO\cdot} \xrightarrow{k_\beta} \mathrm{PhCOCH_3 + CH_3\cdot} \tag{8}$$

$$\mathrm{CO\cdot + CH} \xrightarrow{k_H} \mathrm{COH + C\cdot} \tag{9}$$

and Padwa[18a] measured the ratio of rate constants, k_β/k_H, for β-scission and H abstraction by the cumyloxyl radical at 0–70 °C in carbon tetrachloride with 1.5 M cyclohexane as the hydrogen donor. They found a large solvent effect for this reaction, and our solvent and temperatures (and consequently viscosities) are very different from theirs. However, if we use their data and extrapolate to our temperatures, we obtain the predicted values of k_β/k_H shown in Table VIII. The system we have studied that is nearest to the temperature range studied by Walling and Padwa is the third system listed, the uninhibited decomposition of COOOH at -20 °C. For this system, our value of k_β/k_H is about 9-fold larger than the literature value. Our solvent is 1:1 acetone/cumene (with some cumyl alcohol as impurity). Thus, our solvent is considerably more polar than is that used by Walling and Padwa, and polar solvents favor β-scission. For example, Sakurai and Hosomi find that k_β/k_H for the *tert*-butoxyl radical increases from 0.5 in Freon-113 to 0.8 in chlorobenzene and 1.9 in acetonitrile.[18e] Furthermore, the solvent effects are known to be greater for the reactions of the cumyloxyl radical than for those of *tert*-butoxyl radical.[18d] Thus, the solvent difference in our system and that of Walling and Padwa appears to be the explanation of the 9-fold difference in our apparent value and their measured value of k_β/k_H. However, the 1000-fold difference we observe at -75 °C in the first system listed appears to be far beyond any errors from temperature extrapolation or from differences in solvent polarity. In this case, we suggest that there may be photoactivation to produce a hot cumyloxyl radical. Another possibility is that a chain reaction can lead to a hot radical, as shown in eq 10 and 11; eq 11 can be calculated to be 17 kcal/mol exothermic if the dioxygen is produced in its ground state.

$$\mathrm{COOOH} \xrightarrow[\text{the system}]{\text{any radical in}} \mathrm{COOO\cdot} \tag{10}$$

$$\mathrm{COOO\cdot \rightarrow CO\cdot^* + O_2} \tag{11}$$

In the absence of BHT, cumyl hydroperoxide is produced during the synthesis of the hydrotrioxide. This probably results from hydrogen abstraction from cumene by any oxy radicals in the system, eq 12, followed by eq 13 and 14.[16c] (Note that O_3/O_2

$$\mathrm{CO\cdot + CH \rightarrow COH + C\cdot} \tag{12}$$

$$\mathrm{C\cdot + O_2 \rightarrow COO\cdot} \tag{13}$$

$$\mathrm{COO\cdot + CH \rightarrow COOH + C\cdot} \tag{14}$$

was used and oxygen is present during ozonations, but the samples were deaired before kinetic study of the hydrotrioxide decomposition.)

Observation of the ESR Signal of the Cumylperoxyl Radical. Either ozonation of cumene at -78 °C followed by warming to -40 °C and rapid cooling back to -78 °C or simply ozonizing at -40 °C gave solutions in which the ESR of the cumylperoxyl radical could be detected. It seems likely that eq 12–14 also explain this observation. The g value of the radical we observe is 2.0150, in agreement with the literature value for cumylperoxyl.[13a] The cumyloxyl radical, which occurs in eq 12, is much more difficult to observe than is the cumylperoxyl radical.[13] When the experiment is repeated with Tetralin as the substrate, the tetralylperoxyl radical is observed, with its characteristic hyperfine splitting.[13] The tetralylperoxyl radical is observed to decay faster than does the tertiary peroxyl radical from cumene, as would be expected.[13c] Perhaps this faster decay is the explanation for our failure[4] to be able to detect radicals by direct ESR during the ozonation of methyl linoleate; the peroxyl radical from this substract should undergo rapid termination reactions. Our present results do, however, leave open the possibility that some temperature and concentration regime may exist under which the peroxyl radical from the polyunsaturated fatty acid might be observable.

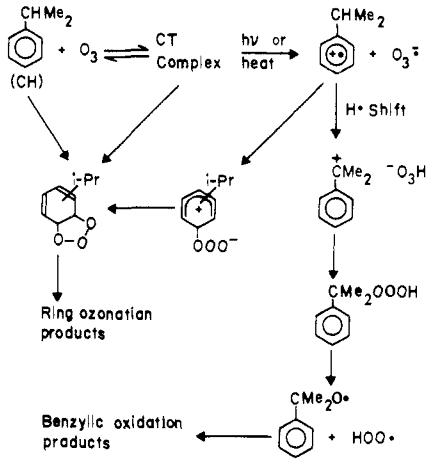

Figure 9. Hypothesis suggesting a mechanism with common intermediates in the ring and side-chain ozonation of cumene.

Mechanism for Decomposition of the Hydrotrioxide. The fact that BHT and the hydrotrioxide decompose with the same rate constant indicates that a quantitative yield of radicals is obtained from the decomposition of the trioxide. Previous hydrotrioxides that have been studied have been found to give less than a 50% yield of radicals,[12,15] perhaps since they are all compounds in which the H of the hydrotrioxide is hydrogen bonded to an oxygen atom, leading to a molecular decomposition pathway favoring the production of singlet oxygen.[1,12]

Our data allow us to formulate the decomposition as follows.[16c] In the *presence* of BHT the homolysis of COOOH, eq 15, is

$$\mathrm{COOOH \rightarrow CO\cdot + \cdot OOH} \tag{15}$$

$$\mathrm{CO\cdot/HOO\cdot + BHT \rightarrow COH + ArO\cdot} \tag{16}$$

$$\mathrm{CO\cdot/HOO\cdot + ArO\cdot} \rightarrow \text{nonradical products} \tag{17}$$

followed by eq 16 and 17, since both BHT and the trioxide disappear at the same rate and the stoichiometric factor for BHT must therefore be 2. A stoichiometric factor of 2 would be expected for BHT in this system.[19] Note that for this system we obtain $E = 23.9 \pm 1.0$ and $\log A = 16.4 \pm 0.1$; thus, for the first time, we obtain Arrhenius parameters for the decomposition of a hydrotrioxide that are in agreement with thermochemical predictions and support the structural assignment.[18f,20]

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[21] (a) Nakagawa, T. W.; Andrews, L.; Keefer, R. *J. Am. Chem. Soc.* **1960**, *82*, 269. Alkyl aromatics are oxidized by ozone; comparison of rate constants for benzene (0.028) and cumene (0.35) at 25 °C suggests ring ozonation is 8% of the ozone/cumene reaction in carbon tetrachloride. (b) Shereshovets, V. V.; Komisarov, V. D.; Denison, E. T. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1979**, 1132. These authors find ozone initiates the autoxidation of cumene at 25–65 °C and report 40%/60% ring vs. side-chain ozonation at 25 °C.

In the *absence* of BHT, a chain reaction occurs, eq 18–20,

$$\mathrm{CO\cdot + COOOH \rightarrow COH + COOO\cdot} \qquad (18)$$

$$\mathrm{HOO\cdot + COOOH \rightarrow H_2O_2 + COOO\cdot} \qquad (19)$$

$$\mathrm{COOO\cdot \rightarrow CO\cdot + O_2} \qquad (20)$$

leading to cumyl alcohol and acetophenone; additional expected products, as shown, are hydrogen peroxide[15] and oxygen (probably singlet[12,15]). Acetophenone is produced from β-scission of cumyloxyl radicals, eq 21.

$$\mathrm{CO\cdot \rightarrow PhCOCH_3 + CH_3\cdot} \qquad (21)$$

Ring vs. Side-Chain Ozonation. We obtain a partition between ring and side-chain ozonation of about 30/70 at temperatures from −78 to −40 °C. Literature data are not in complete accord on this ratio for cumene, but it is clear that side-chain ozonation is faster for this substrate than is attack on this ring.[14b,22]

It is tempting to propose that the CT complex is an intermediate in both ring and side-chain ozonation and that partition occurs following complexation, as shown in Figure 9. Bailey has previously suggested complexation prior to reaction for aromatic compounds.[14b,22]

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Registry No. COOOH, 82951-48-2; BHT, 128-37-0; COO·, 7175-54-4; CH, 98-82-8; COH, 536-60-7; COOH, 80-15-9; H, 12385-13-6; isobutane, 75-28-5; propene, 115-07-1; 1,4-pentadiene, 591-93-5.

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Uncatalyzed and General Acid Catalyzed Decomposition of Alkyl Xanthates and Monothiocarbonates in Aqueous Solutions

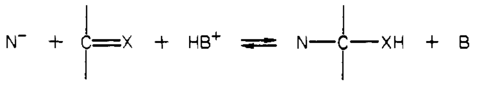
Robert J. Millican, Maria Angelopoulos, Anita Bose, Bram Riegel, Darlyne Robinson, and Carol K. Wagner*

Contribution from the Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903. *Received August 9, 1982. Revised Manuscript Received January 20, 1983*

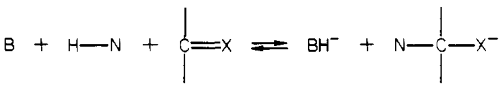
Abstract: The decomposition of potassium alkyl xanthates and alkyl monothiocarbonates follows the rate law $k_{\mathrm{obsd}} = k_{\mathrm{H_3O^+}}[\mathrm{H_3O^+}] + k_{\mathrm{HA}}[\mathrm{HA}] + k_{\mathrm{H_2O}}$ in aqueous buffer solutions. The Brønsted coefficient β_{lg} for the $k_{\mathrm{H_2O}}$ term is −1.1 for the monothiocarbonates and −1.3 for the xanthates. These results complement the value of −1.1 observed for the alkyl monocarbonates and have been interpreted as late transition states in the decomposition direction. The reactions are also subject to general acid catalysis with α values of 0.9 ± 0.2 and 0.8 ± 0.1 for ethyl and methoxyethyl xanthates; α values for the monothiocarbonates are 0.58 ± 0.05 and 0.57 ± 0.01 for the methyl and methoxyethyl compounds, respectively. Solvent kinetic isotope effects ($k_{\mathrm{D_3O^+}}/k_{\mathrm{H_3O^+}}$) for ethyl and methoxyethyl xanthates are 2.53 and 2.12, respectively; for ethyl, methyl, and methoxyethyl monothiocarbonate they are 1.95, 1.94, and 1.91, respectively. The high Brønsted value for ethyl xanthate and the resultant uncertainty in its numerical value coupled with the high inverse solvent isotope effect place this reaction on the borderline between a specific acid catalyzed mechanism and a concerted mechanism. The latter is favored because the value for $k_{\mathrm{H_3O^+}}$ is larger than that predicted for the protonation of the alcohol oxygen of the xanthates and monothiocarbonates; further, the formation of such protonated species is estimated to be sufficiently unfavorable as to require a breakdown step faster than a molecular vibration to account for the observed rates. Acetic acid does not catalyze the $k_{\mathrm{H_3O^+}}$ term for ethyl xanthate at very low pH; the small amount of catalysis at higher pH must therefore be true general acid catalysis and not a solvent effect. Brønsted β_{lg} values for the acid-catalyzed decompositions of the xanthates and monothiocarbonates are small. These results have been interpreted in terms of concerted general acid catalysis where little change in charge occurs on the leaving group oxygen in going from the starting material to the transition state.

Introduction

The behavior of the Brønsted coefficients for reactions in aqueous solution involving the addition–elimination reactions of nucleophiles with carbonyl groups has been used to differentiate between mechanisms for general acid catalysis designated as type e and type n.[1,2] The mechanisms are illustrated in eq 1 and 2.

type e  (1)

$$\mathrm{N^-} + \overset{|}{\underset{|}{\mathrm{C}}}{=}\mathrm{X} + \mathrm{HB^+} \rightleftharpoons \mathrm{N}{-}\overset{|}{\underset{|}{\mathrm{C}}}{-}\mathrm{XH} + \mathrm{B} \qquad (1)$$

type n  (2)

$$\mathrm{B} + \mathrm{H}{-}\mathrm{N} + \overset{|}{\underset{|}{\mathrm{C}}}{=}\mathrm{X} \rightleftharpoons \mathrm{BH^-} + \mathrm{N}{-}\overset{|}{\underset{|}{\mathrm{C}}}{-}\mathrm{X^-} \qquad (2)$$

Type e reactions are characterized by a decrease in α when the $\mathrm{p}K_\mathrm{a}$ of the nucleophile is increased,[3] whereas type n reactions show an increase in α (measured for the reverse of eq 2) with increasing basicity of the nucleophile in a number of related systems.[4-12] The

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