

U33, U36, and U47) are all exposed, and their imino hydrogens should exchange with water rapidly. One might argue that crystalline tRNA^{Met} changes conformation in solution to shield U33, the "swivel base". It is unlikely, however, that the barrier to conformational interchange would be high enough to explain the persistence of the peak at 54 °C.

The number of imino resonances between 11 and 15 ppm for *E. coli* tRNA^{Met} can be estimated from Figure 2d. The highly resolved spectrum has 22 distinct peaks in the low-field region, and only the peak at 12.35 ppm clearly represents more than one hydrogen. Warming the sample to 45 °C produces substantial changes in the spectrum, as shown in Figure 2c. The peaks at 12.55 and 13.10 ppm disappear, and a peak in the envelope at 12.35 ppm moves upfield to combine with the peak at 12.30 ppm, producing new two-proton peaks at 12.30 and 12.35 ppm. It follows that the envelope at 12.35 ppm in Figure 2a contains peaks for three protons. The peaks at 11.95 and 12.10 ppm shift, and a new, broad signal appears at 12.05 ppm. Assignment of this peak to an imino proton in *E. coli* tRNA^{Met} is, however, tenuous. There is no distinct two-proton envelope in the region near 12.0 ppm in Figure 2d. Although less than integral values for some peaks in tRNAs are expected,⁴ the small peaks at 13.55, 13.75, and 14.25 ppm raise the possibility of a minor contaminant in the sample. Nevertheless, it is evident that signals for only 24-25 imino protons are clearly seen for *E. coli* tRNA^{Met} at 35 °C. Since 21 imino hydrogens participate in presumably more stable secondary interactions, only 3 or perhaps 4 peaks for tertiary hydrogen bonds are visible. Our results with ¹⁵N-labeled material indicate that uridine imino hydrogens in s⁴U8-A14, rT54-A58, and G18-Ψ55-P58 (or U60) account for three of these tertiary signals.

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Registry No. Uridine, 58-96-8; guanosine, 118-00-3; pseudouridine, 1445-07-4.

Reaction of Cumene with Ozone. Formation of a Charge-Transfer Complex, Its Thermal and Photochemical Conversion to Cumyl Hydrotrioxide, and the Mechanism of Decomposition of the Hydrotrioxide

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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,^{1,2} and cumene, with its unique and reactive hydrogen, is an attractive substrate. Second, ozone reacts with olefins to produce small yields of radicals,³⁻⁵ 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 in vivo or polyunsaturated fatty acids in vitro are exposed to polluted air containing ozone.⁶⁻¹⁰ We have suggested that the mechanism of

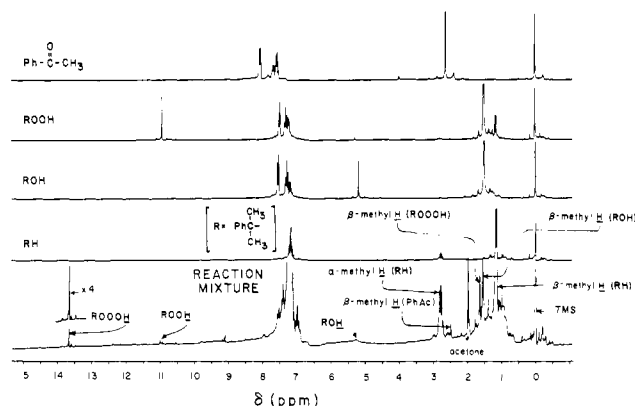
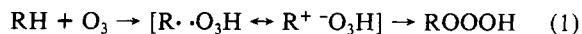


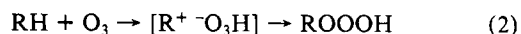
Figure 1. 200-MHz ¹H NMR spectra of the cumene-ozone reaction mixture, cumene, cumyl alcohol, cumyl hydroperoxide, and acetophenone in acetone-*d*₆ at -73 °C. Abbreviations: ROOOH = cumyl hydrotrioxide, RH = cumene, ROH = cumyl alcohol, ROOH = cumyl hydroperoxide, AP = acetophenone, TMS = tetramethylsilane.

radical production involves the formation of an allylic hydrotrioxide,⁴ 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.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, and not for hydrocarbons.¹ The mechanism that has been accepted, eq 1, involves abstraction of a hydrogen atom in



a transition state with appreciable dipolar character.^{1,11} Recently, however, Benson² has suggested the mechanism involves hydride abstraction, eq 2.



We here report the production of cumyl hydrotrioxide both by a thermal process and by photolysis of the charge-transfer (CT) complex of cumene and ozone. We also describe a kinetic study of the decomposition of the hydrotrioxide.

We find that ozonation of cumene in acetone at -78 °C produces a CT complex with absorption at 360 nm.¹² Formation of the CT complex is reversible: blowing out the ozone with nitrogen causes the absorbance to disappear.

Cumyl hydrotrioxide could be prepared by bubbling ozone (0.1 mmol/min) in oxygen through 3.58 M cumene in 4 mL of acetone-*d*₆ at -40 °C for 3 h in the dark or by irradiating the solution with light of 340-390 nm while ozonating for 15 h at -75 °C. The thermal preparation gave ca. 0.07 M solutions (ca. 2% yield) of ROOOH (where R is PhCMe₂), contaminated with 0.22 M cumyl alcohol, 0.14 M cumyl hydroperoxide, and 0.07 M ace-

(7) Pryor, W. A.; Dooley, M. M.; Church, D. F. In "Advances in Modern Toxicology"; Mustafa, M. G., Mehlman, M. A., Eds.; Ann Arbor Press, Ann Arbor, MI, 1982.

(8) Menzel, D. B. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press, New York, 1976; Vol. II, Chapter 6.

(9) Pryor, W. A. In "Environmental Health Chemistry"; McKinney, J. D., Ed.; Ann Arbor Press, Ann Arbor, MI, 1980; pp 445-467.

(10) Pryor, W. A. In "Molecular Basis of Environmental Toxicity"; Bhatnagar, R. S., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; pp 3-36.

(11) (a) Hamilton, G. A.; Ribner, B. S.; Hellman, T. M. *Adv. Chem. Ser.* **1968**, 77, 15. (b) Hellman, T. M.; Hamilton, G. A. *J. Am. Chem. Soc.* **1974**, 96, 1530.

(12) (a) Charge-transfer complexes also were observed in Freon-11, CFC1₃ (380 nm) and pentane (382 nm). The absorption in pentane solvent agrees with that reported^{12b} for toluene and ethylbenzene in a pentane glass at -195 °C. (b) Bailey, P. S.; Ward, J. W.; Carter, T. P.; Nich, E.; Fischer, C. M.; Khashab, A. Y. *J. Am. Chem. Soc.* **1974**, 96, 6136. (c) Varkony, T. H.; Pass, S.; Mazur, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 709. (d) Charge-transfer complexes of O₂ and hydrocarbons are well-known; for references see: Pryor, W. A.; Patsiga, R. A. *Spectrosc. Lett.* **1969**, 2, 61, 353. (e) Full details of our experiments will be published: Pryor, W. A.; Ohto, N.; Church, D. F., to be submitted for publication.

(1) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1982; Vol. II, Chapter 9.

(2) Nangia, G. A.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, 102, 3105.

(3) Pryor, W. A.; Prier, D. G.; Church, D. F. *Environ. Res.* **1981**, 24, 42.

(4) Pryor, W. A.; Prier, D. G.; Church, D. F., submitted for publication in *J. Am. Chem. Soc.*

(5) Pryor, W. A.; Govindan, C. K.; Church, D. F.; *J. Am. Chem. Soc.*, in press.

(6) Pryor, W. A.; Govindan, C. K. *J. Am. Chem. Soc.* **1981**, 103, 7681.

Table I. Rate Constants for the Decomposition of Cumyl Hydrotrioxide in Acetone- d_6 at Low Temperatures

additive (M)	temp, °C ^a	10 ⁴ <i>k</i> (s ⁻¹) determined by following the disappearance of:		
		OOOH	-CH ₃	-OH of BHT
none	-33.0	0.70	0.84	
none	-23.0	2.28		
		2.59 ^c	2.30 ^c	
none	-20.0	3.09		
		2.93 ^c	2.21 ^c	
none	-17.0	5.35		
none	-15.0	5.89		
none	-12.0	12.1		
BHT (0.076) ^b	-18.0	0.83	0.59	0.62
BHT (0.076)	-15.0	2.49	2.03	2.52
BHT (0.090)	-13.0	2.99		2.40
BHT (0.277)	-13.0	2.76 ^c	2.38 ^c	3.17 ^c
BHT (0.076)	-8.0	4.23		3.86
BHT (0.090)	-3.0	16.5		19.6

^a Temperature control estimated to be ± 0.1 °C. ^b 2,6-Di-*tert*-butyl-4-methylphenol. ^c Trioxide prepared by the photochemical method; see text.

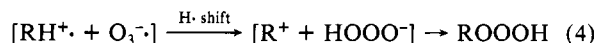
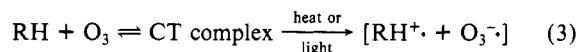
tophenone. The low-temperature photolytic method gave more concentrated solutions of the trioxide, ca. 0.22 M, contaminated with 0.26 M ROH, 0.07 M acetophenone, and virtually no ROOH.^{12c} In both the thermal and the photolytic methods, about 25% ring ozonation also occurs.^{12a,13}

Kinetics. The proton NMR spectra of the trioxide and its decomposition products are shown in Figure 1. Kinetic studies were performed by measuring the change in area of the proton signals due to the OOOH (13.8 ppm), the CH₃ groups in the trioxide (1.67 ppm), and in some runs, the OH of the inhibitor, 2,6-*tert*-butyl-4-methylphenol (BHT) (6.49 ppm). The disappearance of the OOOH and CH₃ hydrogens of the trioxide both follow a first-order dependence; Table I gives the rate constants from least-squares analysis. The trioxide decomposes to give cumyl alcohol as the only organic product in the presence of BHT. In the absence of BHT, some acetophenone also is formed.¹⁸

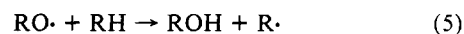
The Arrhenius parameters for the uninhibited decomposition of the trioxide give $E = 16.0 \pm 0.1$ kcal/mol and $\log A = 10.4 \pm 0.1$. These values compare well with literature values for the decomposition of aroyl hydrotrioxides from aldehydes^{14a} and trioxides from acetals.^{14b} However, both for our data and the literature data, the parameters are far from the values of $E = 23$ kcal/mol and $\log A = 16$ expected^{2,4,15} for the decomposition of a trioxide. We hypothesize that these low values result from a chain decomposition.¹⁶ Therefore, we studied the decomposition of ROOOH in the presence of BHT. Using data from the inhibited runs (Table I), we obtain $E = 23.9 \pm 0.1$ and $\log A = 16.4 \pm 0.1$; thus, for the first time, we obtain Arrhenius parameters for the decomposition of a trioxide that are in agreement with thermochemical predictions and that support the structural assignment.¹⁷

Mechanisms for the Reaction of Ozone with Hydrocarbons. Since photolysis of the CT complex leads to the hydrotrioxide, it appears reasonable to postulate¹⁹ that the CT complex and,

therefore, polar species are on the reaction coordinate leading from cumene to the trioxide. This appears to be strong support for a polar mechanism² rather than for hydrogen atom abstraction. Furthermore, since the CT complex of aliphatic hydrocarbons with ozone also has been reported,^{12c} it appears reasonable to suggest the general reaction pathway for any hydrogen donor, RH, shown in eq 3 and 4.

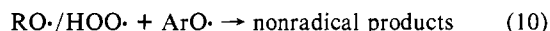
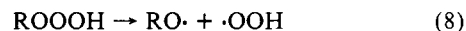


In the absence of BHT, cumyl hydroperoxide is produced during the synthesis of the hydrotrioxide. This probably results from hydrogen abstraction from cumene by any oxy radicals in the system, eq 5, followed by eq 6 and 7.²⁰ (Note that oxygen is present during ozonations, but the samples were deaerated before the kinetics of the hydrotrioxide decomposition were studied.)

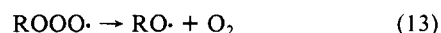
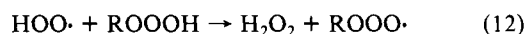


Mechanism for Decomposition of the Hydrotrioxide. The fact that BHT and the trioxide decompose with the same rate constant indicates that a quantitative yield of radicals is obtained from the decomposition of the trioxide.²⁰ Previous hydrotrioxides that have been studied decompose either to give radicals or by a nonradical path giving ¹O₂.^{1,14}

Our data allow us to formulate the decomposition of ROOOH as follows. Homolysis, eq 8, in the presence of BHT is followed



by eq 9 and 10.²¹ In the absence of BHT, a chain decomposition must occur, eq 11–13, leading to cumyl alcohol; additional ex-



pected products, as shown, are hydrogen peroxide¹⁵ and oxygen (probably singlet^{14,15}). Acetophenone is produced from β scission of cumyloxyl radicals, eq 14.^{12c}



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Registry No. Cumene, 98-82-8; cumyl hydrotrioxide, 82951-48-2; BHT, 128-37-0.

(13) (a) Nagawa, T. W.; Andrews, L.; Keefer, R. *J. Am. Chem. Soc.* **1960**, *82*, 269. (b) Shereshovets, V. V.; Komisarov, V. D.; Denison, E. T. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **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.

(14) (a) Stary, F. E.; Emge, D. E.; Murray, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 1880. (b) Kovac, F.; Plesnicar, B. *Ibid.* **1979**, *101*, 2677.

(15) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(16) The decomposition of di-*tert*-butyl trioxide, where no induced decomposition should occur, gives $E = 23$ and $\log A = 17$. See: Bartlett, P. D.; Gunther, P. *J. Am. Chem. Soc.* **1966**, *88*, 3288.

(17) The parameters cited are for the more precise HOOO NMR data only. If both the CH₃ and the BHT–OH data are included, the parameters are $E = 26.3 \pm 1.2$ kcal/mol, $\log A = 18.5 \pm 0.1$.

(18) (a) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593. (b) Pryor, W. A.; Kurz, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 7953.

(19) Colter, A. K.; Dack, M. R. J. In "Molecular Complexes"; Foster, R., Ed.; Crane Russak: New York, 1974; Vol. 2, Chapter 1.

(20) (a) When cumene is ozonated at –78 °C, quickly warmed to –40 °C, and cooled back to –78 °C, an ESR signal is observed that can be assigned^{20b} to the cumylperoxy radical ($g = 2.0150 \pm 0.0001$).^{12c} (b) Thomas, J. R. *J. Am. Chem. Soc.* **1966**, *88*, 2064. Adamic, K.; Ingold, K. U.; Morton, J. R. *Ibid.* **1970**, *92*, 922.

(21) The stoichiometric factor of 2 for BHT agrees with prior research. See: Burton, G. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 6472. Pryor, W. A.; Lightsey, J. W.; Church, D. F. *Ibid.*, in press.