U33, U36, and U47) are all exposed, and their imino hydrogens should exchange with water rapidly. One might argue that crystalline $\text{tRNA}_\text{f}^\text{Met}$ 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* $\text{tRNA}_\text{f}^\text{Met}$ 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* $\text{tRNA}_\text{f}^\text{Met}$ 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* $\text{tRNA}_\text{f}^\text{Met}$ 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 ^{15}N-labeled material indicate that uridine imino hydrogens in s^{4}U8-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 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.

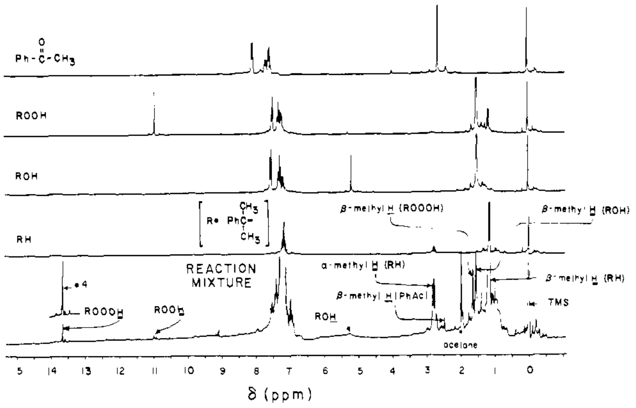

Figure 1. 200-MHz ^{1}H NMR spectra of the cumene–ozone reaction mixture, cumene, cumyl alcohol, cumyl hydroperoxide, and acetophenone in acetone-d_6 at −73 °C. Abbreviations: ROOOH = cumyl hydrotrioxide, RH = cumene, ROH = cumyl alcohol, ROOH = cumyl hydroperoxide, AP = acetophenone, TMS = tetramethylsilane.

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

$$\mathrm{RH} + \mathrm{O_3} \rightarrow [\mathrm{R\cdot\ \cdot O_3H} \leftrightarrow \mathrm{R^+\ {}^-O_3H}] \rightarrow \mathrm{ROOOH} \qquad (1)$$

a transition state with appreciable dipolar character.[1,11] Recently, however, Benson[2] has suggested the mechanism involves hydride abstraction, eq 2.

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

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 PhCMe$_2$), contaminated with 0.22 M cumyl alcohol, 0.14 M cumyl hydroperoxide, and 0.07 M ace-

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

		10^4k (s^{-1}) determined by following the disappearance of:		
additive (M)	temp, °C[a]	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.[12e] In both the thermal and the photolytic methods, about 25% ring ozonation also occurs.[12e,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 CH_3 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 CH_3 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 postulate[19] 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 mechanism[2] 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.

$$RH + O_3 \rightleftharpoons \text{CT complex} \xrightarrow[\text{light}]{\text{heat or}} [RH^{+}\cdot + O_3^{-}\cdot] \qquad (3)$$

$$[RH^{+}\cdot + O_3^{-}\cdot] \xrightarrow{\text{H}\cdot\text{ shift}} [R^{+} + HOOO^{-}] \rightarrow ROOOH \qquad (4)$$

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.)

$$RO\cdot + RH \rightarrow ROH + R\cdot \qquad (5)$$

$$R\cdot + O_2 \rightarrow ROO\cdot \qquad (6)$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot \qquad (7)$$

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 $^1O_2$.[1,14]

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

$$ROOOH \rightarrow RO\cdot + \cdot OOH \qquad (8)$$

$$RO\cdot/HOO\cdot + BHT \rightarrow ROH + ArO\cdot \qquad (9)$$

$$RO\cdot/HOO\cdot + ArO\cdot \rightarrow \text{nonradical products} \qquad (10)$$

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-

$$RO\cdot + ROOOH \rightarrow ROH + ROOO\cdot \qquad (11)$$

$$HOO\cdot + ROOOH \rightarrow H_2O_2 + ROOO\cdot \qquad (12)$$

$$ROOO\cdot \rightarrow RO\cdot + O_2 \qquad (13)$$

pected products, as shown, are hydrogen peroxide[15] and oxygen (probably singlet[14,15]). Acetophenone is produced from β scission of cumyloxyl radicals, eq 14.[12e]

$$PhC(CH_3)_2O\cdot \rightarrow PhCOCH_3 + CH_3\cdot \qquad (14)$$

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

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