# Rate Constants for Oxidation of Cumene

**Dale G. Hendry**

*Contribution from the Department of Physical Organic Chemistry, Stanford Research Institute, Menlo Park, California 94025.* *Received November 16, 1966*

**Abstract:** Lifetime measurements for chain-carrying species have been determined for the oxidations of cumene without and with *t*-butyl hydroperoxide. The apparent chain-termination constants for these systems at 35° are $1.0 \times 10^4$ and $7.0 \times 10^2$ l. mole$^{-1}$ sec$^{-1}$, respectively. The propagation rate constants in these systems are 0.20 and 0.10 l. mole$^{-1}$ sec$^{-1}$, respectively. These numbers are the rate constants for attack on cumene by an $\alpha$-cumylperoxy radical and by a *t*-butylperoxy radical. The Arrhenius parameters for the interaction of two cumylperoxy radicals are $A = 10^{9.8\pm1.0}$ l. mole$^{-1}$ sec$^{-1}$ and $E = 7.0 \pm 1.5$ kcal/mole. Participation of methylperoxy radicals in termination for a cumene oxidation depends on both cumene and radical concentrations. Under our conditions participation by methylperoxy radicals accounts for only 10–24% of the termination and does not significantly affect the measurements of cumylperoxy interaction. Literature values are discussed in light of our values.

The elementary reactions involved in the autoxidation of cumene have received considerable attention, but the efforts to evaluate the rate constants for the various steps have led to inconsistent and incomplete results. Thus our objective in studying the oxidation of cumene has been to evaluate the rate constants for propagation, termination, and interaction of peroxy radicals and to estimate the importance of the methylperoxy radical on the over-all termination.

Investigators have used a number of techniques to analyze the rate constants of the cumene oxidation: Melville and Richards[1] by following oxygen consumption in intermittent light, Howard and Robb[2] by following heat evolution of the photochemical aftereffect, Vichutinskii[3] by following the chemiluminescence of the photochemical aftereffect, and Thomas[4] by measuring the radical concentration using esr techniques. The values for the termination constants range from 1.7 to $9.0 \times 10^4$ l. mole$^{-1}$ sec$^{-1}$ at 35° with a diffusion activation energy of 0–2.5 kcal/mole. Thus the apparent frequency factor is $10^5$–$10^6$ l. mole$^{-1}$ sec$^{-1}$, which is unusually small for a radical–radical interaction. The reported propagation constant at this temperature varies from 0.25 to 0.48 l. mole$^{-1}$ sec$^{-1}$ with a frequency factor of about $3 \times 10^4$ l. mole$^{-1}$ sec$^{-1}$. This frequency factor also appears small compared to other radical reactions. Thus these data appear suspect, and the system deserves further investigation.

Further evidence for error in the above investigations comes from the studies of Blanchard[5] and Traylor[6] which indicated that the interactions of cumylperoxy radical need not always terminate. Traylor has shown that at least under some conditions termination actually results from reaction of methylperoxy and cumylperoxy radicals. Thus if such complications are significant, the above rate constants, which are based upon the usual simple kinetic sequence, will be in error.

Our approach has been to study the oxidation at the lowest possible rate of initiation, where the complications of methyl termination should be a minimum, then to estimate the contribution of methyl peroxy radicals on termination. In order to satisfactorily follow rates of oxygen consumption at small rates of initiation, we first found it necessary to design an apparatus for this purpose.

## Apparatus

All reactions were carried out in a cylindrical Pyrex vessel of 30-ml volume encased in a cylindrical Pyrex jacket through which water was circulated at the desired temperature. Solutions were added through a side port and stirred by a Teflon-coated bar rotated by an Alnico horseshoe magnet (1.5-mm pole separation) joined to the shaft of a Heller variable-speed motor. Consumption of oxygen was monitored by a Dynisco PT14-05 strain gage–pressure transducer; output of the transducer was recorded on a Model SR Sargent recorder. The resolution of this system was a pressure ±0.002 torr. In order to minimize temperature variation, the transducer was mounted in the constant temperature bath, and the temperature of the bath was regulated to ±0.005° with a proportional heating regulator (Sargent Thermonitor Model S). This temperature variation corresponds to a pressure of 0.005 torr; however, the actual pressure variation in the system was less, because of the lag time in the heat change of the reaction vessel. The 0.3% full-scale volume change of the transducer was sufficiently small to be disregarded.

A Model 109 PEK Labs 100-w, high-pressure mercury lamp with a Model 401 power supply was the source of ultraviolet light. The light was focused to a point with two quartz lenses and then to a parallel beam with a third lens. Before the light reached the reaction vessel, it was filtered through a Dow Corning No. 7-51 filter to remove all light except in the region of 3500 A. The rotating sector, which was used to interrupt the light beam at the focal point, gave a light to dark ratio of 1:2 and was driven by a 22-speed Troemner instrument drive (0.0015–30 rpm). The apparatus was constructed so that the light would enter the reaction vessel through the top and pass through liquid at a minimum thickness, about 2.5 mm for 4.0 ml of solution. Since the rate of oxygen consumption was directly proportional to solution volume, the rate was uniform throughout the liquid.

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(1) H. W. Melville and S. Richards, *J. Chem. Soc.*, 944 (1954). These data have been recalculated by V. F. Tsepalov, V. Ya. Shlyapintokh, and C. Pei-huang, *Zh. Fiz. Khim.*, **38**, 351 (1964); *Russ. J. Phys. Chem.*, **38**, 184 (1964).

(2) J. A. Howard and J. C. Robb, *Trans. Faraday Soc.*, **59**, 1590 (1963).

(3) A. A. Vichutinskii, *Dokl. Akad. Nauk SSSR*, **157**, 150 (1964); *Trans. Acad. Sci. USSR*, **157**, 663 (1964).

(4) J. R. Thomas, *J. Am. Chem. Soc.*, **87**, 3698 (1965); **85**, 591 (1963).

(5) H. S. Blanchard, *ibid.*, **81**, 4548 (1959).

(6) T. G. Traylor and C. A. Russell, *ibid.*, **87**, 3698 (1965).

## Theory of Lifetime Measurements

The steady-state rate of oxygen consumption ($R_{ss}$) for oxidation reactions involving log chain lengths at constant rates of initiation ($R_i$) is expressed by eq 1. The derivation asumes that the total radical concentration is constant ($R_i = 2k_t[RO_2\cdot]^2$) and that the rate-determining step for oxygen consumption $R_{O_2}$ is the reaction of peroxy radicals with hydrocarbon ($R_{O_2} = k_0[R\cdot][O_2] = k_p[RO_2\cdot][RH]$).

$$-d[O_2]/dt \equiv R_{ss} = k_p[RH](R_i/2k_t)^{1/2} \quad (1)$$

In intermittent light (as in the rotating sector method) eq 2 gives the average rate of oxygen consumption ($R_{av}$).[7]

$$\bar{R} = \frac{1}{(q+1)(\tau_2-\tau_1)} \ln\left[\frac{\cosh \tau_2}{\cosh \tau_1}\frac{R_2 \sinh q\gamma(\tau_2-\tau_1)}{\gamma} + \cosh q\gamma(\tau_2-\tau_1)\right] \quad (2)$$

where $q$ is the ratio of dark to light periods in the intermittent light cycle, $\gamma = (R_i^T/R_i^L)^{1/2}$, $\tau_2$ and $\tau_1$ are durations of illumination in multiples of lifetime required to obtain the maximum rate ($R_2$) and minimum rate of the cycle, respectively, and thus $\tau_2 - \tau_1$ is the duration in units of lifetime over which the reaction is illuminated in the intermittent cycle. This equation has been evaluated by Kwart,[7] who reports the average rate of reaction as a function of $\tau_2 - \tau_1$ for various values of $q$ and $\gamma$. The time interval of the intermittent cycle, $t_2 - t_1$, for each point equals some $\tau_2 - \tau_1$ or multiple of lifetimes from the theoretical curve with the corresponding average rate of reaction. Thus the lifetime ($\lambda$) equals the ratio of $(t_2 - t_1)/(\tau_2 - \tau_1)$. The relation of $\lambda$ to other parameters is

$$\lambda = [RO_2\cdot]/2k_t[RO_2\cdot]^2 = {}^1/_2k_t[RO_2\cdot] = 1/(2k_tR_i)^{1/2} \quad (3)$$

Another method for evaluating $k_p/k_t$, referred to as the photochemical pre- and aftereffect method,[8] can be used if the absorption of oxygen can be monitored as the reaction makes the transition between the steady-state dark and light reactions. First, in the variation where the photoinitiation is stopped and the rate of reaction slowly decays to the thermal dark rate, eq 4 is applied. The

$$I_d = \int_0^\infty (R_{ss} - R_T)dt = (k_p/2k_t)[RH] \times \ln[(R_T + R_L)/2R_T] \quad (4)$$

decay intercept $I_d$ is obtained from the recorder display of oxygen pressure *vs.* time by extrapolating the thermal reaction back to the time at which the photoinitiation was stopped (where time and oxygen consumption are defined as zero). In the variation where the photoinitiation is started and the rate of reaction slowly increases to the steady light rate, eq 5 is applied. The growth in-

$$I_g = \int_0^\infty (R_L - R_{ss})dt = (k_p/2k_t)[RH] \times \ln[2R_L/(R_L + R_T)] \quad (5)$$

tercept $I_g$ is obtained from the recorder display of oxygen pressure *vs.* time by extrapolating the steady-state reaction back to the time at which the photoinitiation was stopped (where time and oxygen consumption are defined as zero). Thus both eq 4 and 5 give $k_p/k_t$, and with $k_p/k_t^{1/2}$ from the steady-state measurement (eq 1), $k_p$ and $k_t$ can be separated. These pre- and aftereffect variations give the same values for $k_p/k_t$ as the sector method if $\Delta O_2$ can be accurately measured. When this method is applicable, it is more rapid than the sector method. In general this method is limited by the sensitivity of the oxygen measurement, and accurate measurement of $k_p/k_t$ appears possible only when $k_p/k_t \geq 10^{-6}$. However, if there is a large difference between thermal and light rates, the method becomes more sensitive. Bateman and Gee[8] have been able to apply it to a number of systems where $k_p/k_t < 10^{-6}$, although with limited accuracy.

The oxygen in solution depends on a dynamic equilibrium, governed by both its rate of consumption and its rate of diffusion into the liquid. Therefore the measured values of $I_d$ and $I_g$ are both in error by an amount which corresponds to the difference in concentrations of oxygen at the steady-state rates for light and dark reactions. When this error is significant, subtracting eq 5 from 4 cancels this error and gives an expression for $k_p/k_t$ free from the complication, although obviously with increased experimental error. Earlier workers found that the values for $k_p/k_t$ as determined by eq 4 and 5 differed because of this change of oxygen concentration with rate, but we obtained essentially the same value with either equation. Thus our design of apparatus has eliminated the problems of diffusion of oxygen into the solution. In general, we have found the photochemical pre- and aftereffect method is more reproducible and rapid than the sector method.

## Results

Oxidations of cumene have been studied by the rotating sector procedure using di-*t*-butyl peroxide as photoinitiator. Table I summarizes these data. For each point the log ($\tau_2 - \tau_1$) has been determined from the average rate (in per cent of maximum rate) *vs.* log ($\tau_2 - \tau_1$) curves published by Kwart.[7] The lifetime is determined from $(t_2 - t_1)/(\tau_2 - \tau_1)$ for each point, and then all lifetimes are averaged. The precision for the cumene data is excellent at 35° but only satisfactory at 45°.

Table II summarizes the data for cumene obtained by the photochemical pre- and aftereffect method using 1,1-azobis(1-cyanocyclohexane) (ABC) as photoinitiator. Values of $k_p/k_t$ were reproducible to ±10%. Included in the table are values of $k_p/k_t^{1/2}$ evaluated from steady-state rates using 2,2′-azobis(2-methylpropionitrile) (ABN) as thermal initiator; this value was reproducible to ±3%. Because of the uncertainty of the effect of temperature of $ek_d$ (the product of the efficiency factor and decomposition rate constant) for ABN, the product which is used for calculating $k_p/k_t^{1/2}$ has been evaluated at different temperatures, and the data are included in Table II. The presence of *t*-butyl hydroperoxide in the cumene oxidation increases the value of $k_p/k_t$ and $k_p/k_t^{1/2}$ significantly; in fact, the lifetime was so long that evaluation by the sector method was impractical. Analysis of the data for pure cumene in the typical Arrhenius plots (Figure 1) gave the activation energies and frequency factors shown in Table III. Figure 1 summarizes all the available data for propagation and ter-

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[7] H. Kwart, *J. Phys. Chem.*, 64, 1250 (1960); M. S. Matheson, E. S. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, 71, 497 (1949).

[8] L. Bateman and G. Gee, *Trans. Faraday Soc.*, 47, 155 (1951).

Table I. Autoxidations of Cumene at 35–45° by the Rotating Sector Method[a]

| Log $(t_2 - t_1)$ | $\bar{R}/R_{ss}$ | Log $(\tau_2 - \tau_1)$ | Log λ |
|---|---|---|---|
| | | Cumene at 35° [b] | |
| 0.653 − 1 | 57.1 | ... | ... |
| 1.875 | 57.1 | ... | ... |
| 2.080 | 55.9 | 0.05 | 2.03 |
| 2.285 | 51.4 | 0.38 | 1.90 |
| 2.489 | 50.2 | 0.48 | 2.01 |
| 2.896 | 44.9 | 1.00 | 1.89 |
| | | | Av log λ = 1.96 ± 0.05[c] |
| | | Cumene at 45° [d] | |
| 1.381 | 64.0 | ... | ... |
| 1.789 | 62.4 | 0.80 − 1 | 1.99 |
| 1.928 | 62.4 | 0.80 − 1 | 2.13 |
| 2.199 | 56.6 | 0.80 | 1.40 |
| 2.199 | 56.0 | 0.95 | 1.25 |
| | | | Av log λ = 1.9 ± 0.3 (first three values)[e] |

[a] All units in l., moles, and sec; $(t_2 - t_1)$ is the length of light period of the intermittent cycle in seconds; $\bar{R}$ is the average rate of reaction for each $(t_2 - t_1)$; $R_{ss}$ is the steady-state rate in full light; $(\tau_2 - \tau_1)$ is the number of lifetimes evaluated from the theoretical curve corresponding to the same $\bar{R}/R_{ss}$ experimentally observed; λ is the lifetime in seconds obtained from $(t_2 - t_1)/(\tau_2 - \tau_1)$. [b] [$t$-$Bu_2O_2$] = 0.01 $M$; $\gamma = 0.155$; $R_i^L + R_i^T = 0.420 \times 10^{-8}$; $k_p/k_t^{1/2} = 2.01 \times 10^{-3}$. [c] $\lambda = 98.2 \pm 4.0$ sec; $k_t = 1.2 \pm 0.2 \times 10^4$; $k_p = 0.23 \pm 0.05$. [d] [$t$-$Bu_2O_2$ = 0.01 $M$; $\gamma = 0.330$; $R_i^L + R_i^T = 0.177 \times 10^{-8}$; $k_p/k_t^{1/2} = 2.86 \times 10^{-3}$. [e] $\lambda = 90 \pm 50$ sec; $k_t = 3.5 \pm 2.0 \times 10^4$; $k_p = 0.54 \pm 0.20$.

Table II. Photochemical Pre- and Aftereffect Studies in Oxidizing Cumene[a]

| Temp, °C | $ek_d \times 10^6$ [b] | $k_p/k_t^{1/2} \times 10^3$ [c] | $k_p/k_t \times 10^5$ [d] | $k_p$ | $k_t \times 10^{-4}$ |
|---|---|---|---|---|---|
| 25.0 | ... | 1.36[e] | 1.46 | 0.129 | 0.87 |
| 35.0 | 0.141 | 2.01 | 2.02 | 0.199 | 0.99 |
| 45.0 | 0.628 | 2.86 | 2.27[e] | 0.36 | 1.59 |
| 55.0 | 2.82 | 4.10 | 2.84 | 0.59 | 2.07 |
| 65.0 | 12.3 | 5.77 | 3.32 | 1.00 | 3.05 |
| 35.0[f] | ... | 3.77 | 14.1 | 0.10 | 0.070 |

[a] Reactions were carried out without added solvents, with ABC as photoinitiator; constants in l., moles, and sec. [b] Averages of three or four values measured by inhibition periods with di-*t*-butyl-*p*-cresol in thermal decompositions of ABN [G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955); D. G. Hendry and G. A. Russell, *ibid.*, **86**, 2368 (1964)]. [c] Evaluated from ABN-catalyzed steady-state oxidation. $R_i \times 10^8 = ek_d[\text{ABN}] \times 10^8$ = 2.46 (35°), 8.87 (45°), 5.06 (55°), 10.6 (65°). [d] Evaluated from eq 1 and observed $R_{ss}$. $R_i \times 10^8$ = 3.73 (25°), 0.858 (35°), 2.56 (55°), 3.45 (65°). [e] Value obtained by extrapolating or interpolating data for other temperatures. [f] Cumene concentration 5.72 $M$, *t*-butyl hydroperoxide 1.95 $M$ (no solvent). $k_p/k_t^{1/2}$ was evaluated using $3.6 \times 10^{-3}$ $M$ di-*t*-butyl peroxalate as thermal initiator with efficiency of 0.95 [D. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960); R. Hiatt and T. G. Traylor, *ibid.*, **87**, 3766 (1965)]. Hydroperoxide served as photoinitiator for $k_p/k_t$ measurements.

Table III. Arrhenius Parameters for Various Rate Constants in the Oxidation of Cumene

| Constants[a] | Log $A$ | $E$, kcal |
|---|---|---|
| $ek_d$ (for ABN) | 16.11 ± 0.35 | 30.96 ± 0.60 |
| $k_p/k_t^{1/2}$ | 2.37 ± 0.19 | 7.15 ± 0.27 |
| $k_p/k_t$ | −1.77 ± 0.33 | 4.17 ± 0.46 |
| $k_p$ | 6.51 ± 0.71 | 10.13 ± 1.00 |
| $k_t$ | 8.28 ± 1.04 | 5.96 ± 1.46 |

[a] Units are l., moles, and sec.

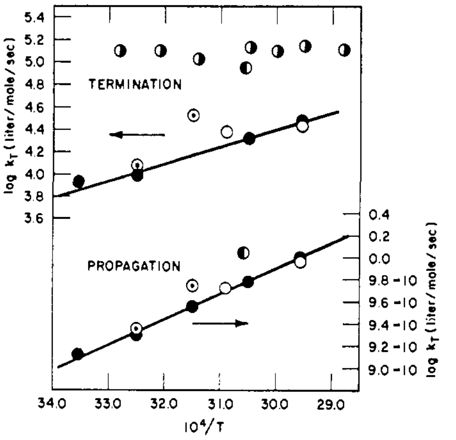

Figure 1. Arrhenius plot of propagation and termination rate constants in autoxidizing cumene: ●, photo aftereffect method (this work); ⊙, rotating sector (this work); ○, rotating sector (ref 1); ◑, radical concentration measurement (ref 4); ◐, thermocouple (ref 2).

mination, including the literature values obtained from esr measurements of peroxy radical concentrations[4] and those obtained by the pre- and aftereffect method by following heat evolution.[2] Both of these methods may have complicating factors. The photochemical pre- and aftereffect data have been used for determining the Arrhenius parameter because of their consistency and the temperature range over which they were obtained.

## Discussion

**Chain Length.** The sensitivity of apparatus has made it possible to measure rates of oxygen consumption as low as $10^{-7}$ $M$ sec$^{-1}$ over a several-minute period with ±5% precision. In the case of cumene this rate corresponds to a rate of initiation of $10^{-10}$ $M$ sec$^{-1}$; previous workers have operated at rates of initiation of $10^{-6}$ to $10^{-7}$. This difference in rate of initiation has allowed us to work at chain lengths 10–100 times longer than heretofore possible. Longer chain lengths reduce the possible interference from reactions involving either initiator radicals or alkoxy radicals produced by nonterminating interactions.

**Termination.** Termination rate constants for cumene in Figure 1 evaluated by the rotating sector method and by the pre- and aftereffect method agree within experimental error although the uncertainty is larger for the sector method. Values obtained from radical concentration measurements[4] and by the thermocouple technique[2] are two to ten times larger. In Table III, the value of log $A_t$ obtained by the pre- and aftereffect method falls in the range of the better values of $A_t$ for other hydrocarbons. The data obtained by the rotating sector method are not precise enough to allow accurate evaluation of log $A_t$. However, $k_t$ cannot be associated with one single step, and the following section discusses the meaning of $k_t$ values.

**Interaction of Cumylperoxy ($CuO_2\cdot$) Radicals.** Both the oxidation of cumene (CuH) at low chain lengths[5,9] and the radical-induced decomposition of cumene hydroperoxide[6] point to a reaction of two peroxy radicals to give two free alkoxy radicals and also chain termination. Both reactions probably proceed through forma-

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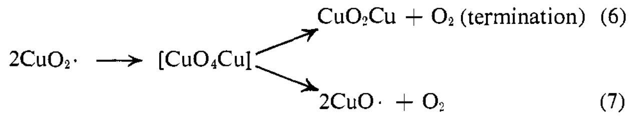
(9) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963).



$$2CuO_2\cdot \longrightarrow [CuO_4Cu] \begin{cases} \nearrow CuO_2Cu + O_2 \text{ (termination)} & (6) \\ \searrow 2CuO\cdot + O_2 & (7) \end{cases}$$

tion of two alkoxy radicals in the solvent cage, followed either by coupling or by diffusion, as suggested for the reaction of two $t$-BuO$_2\cdot$.[4,6,10–13] The ratio of $k_7/k_6$ appears to be of the order of 7–10, although solvent, the amount of hydroperoxide, and temperature affect the ratio.[4,6,11,12]

The over-all rate constant for the reaction of two cumylperoxy radicals is then the sum of those for reactions 6 and 7. If the measured termination constant is $k_6$ and, as the data of Factor, *et al.*, suggest,[12] $k_7/k_6$ does not change significantly with temperature ($E \cong 1$ kcal), then the log of the frequency factor is 9.8 ± 1.0 for the interaction of two cumylperoxy radicals to give two alkoxy radicals and $E_a$ is 7.0 ± 1.5 kcal/mole. This value for the frequency factor compares satisfactorily with values for other radical–radical interactions in solution.[14] Thomas[4] has reported a temperature dependence of $k_7/k_6$ which would make the log frequency factor for cumylperoxy radical $A = 11 \pm 1$. However, his data are suspect, since the initiator (ABN) generates peroxy radicals which could interfere. In addition, Bartlett and Gunther have presented further evidence for a small activation energy for this ratio.[15] Thus while sequence 7 may be exothermic,[16] it has an over-all activation energy of about 7 kcal/mole. Since the formation of the $R_2O_4$ intermediate also appears to be exothermic relative to $2RO_2\cdot$[16] and since further decomposition to $2RO\cdot + O_2$ requires activation energy, $R_2O_4$ must be considered as having a finite lifetime contrary to other suggestions.[12] The actual activation energy to convert $R_2O_4$ to $2RO\cdot + O_2$ is 7 kcal/mole plus the exothermicity of the formation of $R_2O_4$.

**Role of Methylperoxy Radicals in Chain Termination.** Blanchard[5] has observed both cumyl alcohol and acetophenone in cumene oxidation at low chain lengths (2–15); the following reactions occur.

$$CuO\cdot \longrightarrow PhCOMe + Me\cdot \qquad (8)$$

$$Me\cdot + O_2 \longrightarrow MeO_2\cdot \qquad (9)$$

$$CuO\cdot + CuH \longrightarrow CuOH + Cu\cdot \qquad (10)$$

The methylperoxy radical formed by reactions 8 and 9 then undergo the reactions[6,9]

$$MeO_2\cdot + CuH \longrightarrow MeO_2H + Cu\cdot \qquad (11)$$

$$MeO_2\cdot + CuO_2\cdot \longrightarrow CuOH + CH_2O + O_2 \text{ (termination)} \qquad (12)$$

By the use of labeled oxygen, Bartlett and Traylor[9] have determined the quantity $(R_6 + R_7 + R_{12})/(R_6 + R_{12})$ from the number of molecules of oxygen formed in reactions 6, 7, and 12 per termination by reactions 6 and 12. This value increased from 1.67 to 2.62 as the kinetic chain length increased from 1.47 to 7.73. Since $R_7/R_6 = k_7/k_6 = 10$ at 60° (from the induced decomposition of cumene hydroperoxide[12] corrected for viscosity and temperature),[6] the fraction of all terminations by methylperoxy radicals decreased from 0.93 to 0.84 as the chain length increased from 1.47 to 7.73. Thus the complications due to participation of methylperoxy radicals in termination decrease as the chain length increases. Since our experiments were carried out under conditions where chain lengths were 70–150 instead of 1–8, we need to estimate to what degree methylperoxy radicals participate in termination under our conditions. The following discussion shows how we estimate that contribution is no more than 24% of the chain terminations at our low rates of initiation.

Assuming that reaction 6–12 completely characterize the system, the importance of $MeO_2\cdot$ termination (reaction 12) can be determined by starting with the steady-state expressions for cumyloxy, methylperoxy, and total radical concentrations.

$$2k_7[CuO_2\cdot]^2 = k_8[CuO\cdot] + k_{10}[CuO\cdot][CuH] \qquad (13)$$

$$k_8[CuO\cdot] = k_{11}[MeO_2\cdot][CuH] + k_{12}[MeO_2\cdot][CuO_2\cdot] \qquad (14)$$

$$R_i = 2k_6[CuO_2\cdot]^2 + 2k_{12}[MeO_2\cdot][CuO_2\cdot] = 2k_t[CuO_2\cdot]^2 \qquad (15)$$

where $k_t$ is the experimental termination constant. From these relationships eq 16 relates $k_t$ to the actual reactions.[17]

$$k_t = 2k_7F + k_6 \qquad (16)$$

where

$$F = \frac{k_8}{(k_8 + k_{10}[CuH])} \frac{k_{12}[CuO_2\cdot]}{(k_{12}[CuO_2\cdot] + k_{11}[CuH])}$$

The two factors in $F$ are, respectively, the fraction of cumyl radicals which cleave to methyl radicals and the fraction of methylperoxy radicals which terminate by reaction 12.

The first factor in $F$ is evaluated from the relative rates of cleavage and hydrogen abstraction from cumene for cumyloxy radicals.

$$(\text{rate}_8)/(\text{rate}_{10}) = \Delta[PhCOMe]/\Delta[CuOH] = k_8/k_{10}[CuH] \qquad (17)$$

At 60° Blanchard[5] found the ratio of acetophenone to cumyl alcohol[18] to be about 1.5 in 0.85 $M$ cumene. Here $k_8/k_{10} = 1.5 \times 0.85 = 1.3$. In pure cumene, where $[CuH] = 6.9\ M$, the ratio of acetophenone to cumyl alcohol should be $1.3/6.9 = 0.19$,[19,20] and 16% of

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[10] D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, International Oxidation Symposium, San Francisco, Calif., 1967; *J. Phys. Chem.*, in press.

[11] R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem. Soc.*, **87**, 3692 (1965).

[12] A. Factor, C. A. Russell, and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3692 (1965).

[13] R. Hiatt and T. G. Traylor, *ibid.*, 87, 3766 (1965).

[14] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 607.

[15] P. D. Bartlett and P. Gunther, *J. Am. Chem. Soc.*, **88**, 3288 (1966).

[16] S. W. Benson, *ibid.*, **86**, 3922 (1964).

[17] A private communication from T. G. Traylor indicated a factor of 2 was inadvertently left out of a similar expression in ref 6.

[18] While Blanchard did not accurately measure the cumyl alcohol formed, he was able to estimate it from the material balance and qualitatively checked the value by glpc analysis.

[19] H. C. Bailey and G. W. Godin, *Trans. Faraday Soc.*, **52**, 68 (1956); M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **16**, 105 (1951).

[20] This value for the ratio of acetophenone and cumyl alcohol is in excellent agreement with that determined from ref 19, where the cumoxy radicals were formed by thermal decomposition of dicumyl peroxide. The difference discussed in ref 5 was apparently the result of failure to correct for the concentration of cumene. This agreement indicates that "free" cumoxy radicals are generated in reaction 7, and mechanisms wherein acetophenone is the initial product are not necessary to explain the data. The decomposition of cumoxy in the initial solvent cage is improbable, since the lifetime of cumoxy cage is of the order of $10^{-11}$ sec (ref 14, p 496), while the half-life of cumoxy is $10^{-8}$ sec.

the cumoxy radicals should produce methylperoxy radicals in pure cumene at this temperature. At the lower temperatures applying in most of our work, more alcohol should be formed. Since $E_8 - E_{10} = 7.3$ kcal/mole,[19] we estimate that only about 5% of the cumyloxy radicals should produce methylperoxy radicals at 25°.

The second factor in $F$, the fraction of methylperoxy radicals which terminate, is estimated from the relative importance of reactions 11 and 12. Since there is no

$$(\text{rate}_{12})/(\text{rate}_{11}) = k_{12}[\text{CuO}_2\cdot]/k_{11}[\text{CuH}] \qquad (18)$$

close analog for the interaction of cumylperoxy and methylperoxy radicals (reaction 12), we have chosen $k_{12} = 10^6$ for our calculations. From the Russell[21] cyclic mechanism, this is probably a maximum possible value since the cumylperoxy radical can appear only as cumyl alcohol and since the hydrogen atoms in methylperoxy may be relatively unreactive. The propagation constant $k_{11}$ is taken as unity, the approximate value of $k_p$ for cumene from Table II at 60°. Since $R_i = 2k_t[\text{CuO}_2\cdot]^2 = 2.56 \times 10^{-8}$ $M$ sec$^{-1}$ (experimental value in 55° experiment in Table II), and since $k_t = 2.5 \times 10^4$ at 60° (Table II), the effective value of $[\text{CuO}_2\cdot] = 0.7 \times 10^{-6}$ $M$. Thus the ratio of termination to propagation reactions of methylperoxy radicals = rate$_{12}$/rate$_{11}$ = $[(10^6)(0.7)(10^{-6})]/[(1)(6.9)] = 0.10$ at 60°. Since the activation energy for reaction 11 is about 8 kcal/mole higher than for reaction 12, rate$_{12}$/rate$_{11}$ = 0.40 at 25°. Thus the maximum value of the fraction of methylperoxy radicals reacting by reaction 12 is estimated to be 0.09 at 60° and 0.29 at 25°.

Substitution of the necessary numbers in eq 16 for neat cumene at 25° gives

$$k_t = k_6 + 2k_7(0.05)(0.29)$$

Since $k_7 = (5\text{–}8)k_6$ at 25°,[22] the second term is 0.14–0.23 the value of the first term and methylperoxy radicals account for a maximum of 12–19% of the total termination reactions under these conditions. Substitution of the data for 60° in eq 16 indicates that methylperoxy radicals account for a maximum of about 24% of the terminations at our rates of initiation. Thus our values of $k_t$ overestimate $k_6$ by not more than 12–24%; however, correction of the values does not significantly change the frequency factor or activation energy for the interaction of two cumylperoxy radicals.

Traylor[6] has found that 1.90 $M$ cumene hydroperoxide accelerates the oxidation of cumene by a factor of 1.86 ± 0.07 after correction for difference in hydrocarbon concentrations. This enhancement results from trapping the cumyloxy radical and preventing the formation of methyl radicals. The effect of hydroperoxide on the apparent termination constant may be calculated using the rate expression[10]

$$-\text{d}[\text{O}_2]/\text{d}t = k_p[\text{RH}](R_i/2k_t)^{1/2} + R_i/2a$$

The term $a$ equals the fraction of peroxy radical interactions which result in termination (and is equal to the reciprocal of $\beta$ as defined by Traylor). Traylor estimates it to be 0.3 in oxidation of pure cumene under his conditions and 0.1 in the presence of cumene hydroperoxide. Substitution of the data into this expression indicates that termination ($k_t$) is 170% larger in the absence of hydroperoxide. Thus 63% [170(100/270)] of the termination in the absence of hydroperoxide is due to methylperoxy termination in his experiments. Applying the expression we have derived above gives 56% methyl termination, in good agreement considering the uncertainty associated with the estimate of $a$ in the oxidation of pure cumene.

Traylor[6] has generally concluded that methylperoxy radicals terminate once they are formed; thus acetophenone formed was equated to termination by methylperoxy. According to eq 16, this assumption will be approximately true at low cumene concentrations and high rates of initiation, the conditions where Blanchard and Traylor have obtained information on the reaction, but it is inadequate at long chain lengths.

Equation 16 indicates that $F$ should vary inversely with hydrocarbon concentration and that the rate of oxidation of cumene would therefore be greater than first order in cumene concentration; however, Blanchard[5] has shown that the reaction is close to first order in hydrocarbon. His data for the formation of hydroperoxide are also approximately first in hydrocarbon dependence above 1.7 $M$ and slightly higher below. The unusual feature of these data is that the rate is independent of solvent; this is not the case with other hydrocarbons that have been studied.[23] Thus it appears that the solvent effect due to dilution with chlorobenzene has largely compensated the effect of the change in $F$ with hydrocarbon.

**Other Data on Cumene Termination.** Melville and Richards[1] performed their rotating sector experiments with initiation rates near $10^{-6}$ $M$ sec$^{-1}$; we calculate that at these rates reaction 12 should account for about 50% of the termination. Despite this relatively large amount of methylperoxy termination, our data agree with their data within experimental error. There is poor agreement with the data of Thomas,[4] who measured radical concentration in oxidizing cumene and in decomposing cumyl hydroperoxide, and with the data of Howard and Robb,[2] who monitored the photochemical aftereffects by following the decrease of heat evolution. However, for Thomas' data $k_t$ appears to be accurate to no more than ±75% in the radical concentration measurements, since $k_t$ depends on $[\text{RO}_2\cdot]^2$ and $[\text{RO}_2\cdot]$ does not appear to be more accurate than ±50%. The lower limit of the error is in the range of our data. The precision of Howard and Robb's data was not reported.

Vichutinskii[3] has studied the termination reaction for cumene by following chemiluminescence of the reaction, and reports data which give both an activation energy and frequency factor for the termination lower than ours. However their experimental values and ours agree within a factor of 2.

**Effect of Added *t*-Butyl Hydroperoxide.** In the presence of *t*-butyl hydroperoxide, the following reaction is important.

$$\text{CuO}_2\cdot + t\text{-BuO}_2\text{H} \longrightarrow \text{CuO}_2\text{H} + t\text{-BuO}_2\cdot \qquad (19)$$

For the corresponding reaction with tetralin hydroperoxide, Thomas and Tolman[24] have evaluated the rate

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(21) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

(22) The high value is obtained by assuming a temperature dependence found for $2t\text{-BuO}_2\cdot$[12] and the low value is obtained from the data of Thomas.[4]

(23) See Hendry and Russell, footnote *b*, Table II.

(24) J. R. Thomas and C. A. Tolman, *J. Am. Chem. Soc.*, **84**, 2079 (1962).

constant as 12 $M$ sec$^{-1}$ at 57°. Thus under the conditions where $t$-butyl hydroperoxide was added to the cumene oxidation, rate$_{19}$ = $12(1.95[\text{CuO}_2\cdot]) = 23.4\cdot[\text{CuO}_2\cdot]$, approximating $k_{19}$ with Thomas and Tolman's value.[24] The competing propagation reaction has a rate = $k_\text{p}[\text{CuH}][\text{CuO}_2\cdot] = 1(5.7[\text{CuO}_2\cdot])$. Therefore cumylperoxy radicals are generally converted to $t$-butylperoxy radicals, and the propagation and termination reactions are largely

$$t\text{-BuO}_2\cdot + \text{CuH} \longrightarrow t\text{-BuO}_2\text{H} + \text{Cu}\cdot \tag{20}$$

$$2t\text{-BuO}_2\cdot \longrightarrow t\text{-Bu}_2\text{O}_2 \tag{21}$$

Also occurring are

$$2t\text{-BuO}_2\cdot \longrightarrow 2t\text{-BuO}\cdot + \text{O}_2 \tag{22}$$

$$t\text{-BuO}\cdot + t\text{-BuO}_2\text{H} \longrightarrow t\text{-BuOH} + t\text{-BuO}_2\cdot \tag{23}$$

The measured termination constant $k_{21}$, 700 $M$ sec$^{-1}$ in this system at 35°, is $^1/_{14}$ that found for cumene. Interpolation of the data of Thomas gives a value of 450, in agreement.[4] From the induced decomposition of $t$-butyl hydroperoxide,[12] $k_{22}/k_{21} = 8.8$ at 35°. Thus the rate constant for peroxy–peroxy interaction (reactions 21 plus 22) is $9.8k_{21}$ or $6.9 \times 10^3$. Using the same frequency factor found for cumylperoxy interaction, this value for the interaction gives 8.6 kcal/mole for $E_\text{a}$ compared to 7.0 for cumylperoxy interaction.

**Comparison of Mechanisms of Termination for Tertiary $\text{RO}_2\cdot$ and Primary or Secondary $\text{RO}_2\cdot$.** Previously the low termination rate constant for cumene could have been explained by the indirect mechanism requiring methylperoxy radicals, but our results show that the activation energy of 7 kcal/mole to form the caged pair of alkoxy radicals is responsible for the slow reaction and not the complexities of the reaction. Thus it may be argued that primary and secondary peroxy radicals do not terminate by disproportionation of first formed alkoxy radicals. If this were the case, one would expect an activation energy for termination similar to alkoxy radical formation by tertiary peroxy radicals rather than the much lower value of 2 ± 2 kcal/mole. The only mechanism for the termination of primary and secondary peroxy radical that is consistent with product analysis and observed deuterium isotope effects is the cyclic mechanism originally proposed by Russell.[21] It was earlier felt that the specific configuration required for the cyclic mechanism would make the reaction too slow to complete with alkoxy radical formation. However, since alkoxy radical formation has a significant activation energy, the reaction is retarded sufficiently to favor the cyclic reaction. At higher temperatures the difference in activation energies will be less important and alkoxy formation may predominate.

**Propagation Constants.** The difference between the rate expression for $k_\text{p}$ in Table III and that obtained from the data of Howard and Robb[2] results largely from the value assigned to the activation energy of termination. Our value for the frequency factor is $10^2$ times larger than that obtained from Howard's and Robb's data and is of the same order as that found for propagation in polymerization.[14] In fact, these data agree well with the expression for transfer to cumene in polymerizing styrene [$\log k = 6.1 - (12.8/4.576T)$].[25] In general, assuming termination energies of activation of 1–2 kcal/mole for the secondary systems leads to more reasonable frequency factors for propagation and better agreement with the cumene data.

There has been considerable interest in evaluating the effect of the organic portion of a peroxy radical on the reactivity of the radical.[26] However, this question to date has been attacked by comparing the relative reactivities of a series of hydrocarbons with various peroxy radicals. Any effect of organic structure of the peroxy radical on the reaction with the hydrocarbons in the series tends to cancel and remain undetected. We have measured the rate of attack of cumene by both cumyl and $t$-butylperoxy radicals. The data in Table II show that these rate constants are essentially identical. Thus the $t$-butyl and cumyl groups have the same effect on the reactivity of the peroxy radical. Howard and Ingold[27] have reported some effect of structure on the reaction of $\text{RO}_2\cdot$ with 2,6-di-$t$-butyl-4-phenol in dimethyl sulfoxide and suggest a steric effect as an explanation.

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(25) R. A. Gregg and F. R. Mayo, *Discussions Faraday Soc.*, **2**, 328 (1947); M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, **73**, 1700 (1951).

(26) G. A. Russell and R. C. Williamson, *ibid.*, **86**, 2364 (1964).

(27) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **44**, 1119 (1966).