with a background of 40. This indicated that the DBPO contained less than 0.3% *t*-butyl peroxide.

Yields of Products. The absolute yield of *t*-butyl alcohol was estimated from total oxygen evolution. However, the ratio of alcohol to peroxide, which is important to our radiochemical results, is obtained by measuring the area under the g.l.c. curves obtained by injecting 2 μl. of either the original product containing unreacted DBPO or product which had been vacuum distilled away from the DBPO onto an 8 ft. × 1/8 in. column as described above. By comparison with synthetic mixtures they gave weight ratios of 10.5:1 and 11.2:1, respectively. Added DBPO did not affect the results. This indicates about 21 moles of alcohol per mole of di-*t*-butyl peroxide, representing an average chain length of 10.5.

Thus $t\text{-BuOH}/2(t\text{BuO})_2 = 10.5$, O_2/DBPO used = 10.5, and average $2d(O_2)/d(CO_2) = 10.5$. The composition of products can therefore be calculated from the DBPO which was used. Alcohol = 21 × DBPO used = 32 mmoles, di-*t*-butyl peroxide = DBPO used = 1.54 mmoles, *t*-butyl hydroperoxide = (initial *t*-BuOOH) − (*t*-BuOH) = 8.0 mmoles.

Calculation of Activities. Of the 10.700 g. total weight used in run 9, 0.094 g. of DBPO remained behind, and 0.138 g. of CO_2 and 0.515 g. of O_2 were evolved, leaving 9.935 g. of volatile products of which 9.136 g. were used for dilution with alcohol, peroxide, and hydroperoxide. The activity in the alcohol product based on a chain length of 10.5 is therefore

$$\frac{(52.6 \text{ mmole} + 32.4)\,(0.92 \text{ mmole})}{(32.4)(0.92 \text{ mmole})} \times 18{,}800 \text{ c.p.m./mmole diluted} = 52{,}000 \text{ c.p.m./mmole}$$

The activity in the peroxide is

$$\frac{(32.4)(0.92/10.5 + 26.92 \text{ mmole})}{(32.4)(0.92/10.5)} \times 2803 = 56{,}050 \text{ c.p.m./mmole}$$

This represents

$$\frac{(56{,}050)(1)}{(56{,}050 + 21.0)(52{,}000)} \times 100 = 4.8\% \text{ of DBPO activity}$$

Decomposition of Cumene Hydroperoxide. A solution of 4.00 ml. of cumene hydroperoxide (2.79 *M*) purified by the method of Kharasch[20] in 6.00 ml. of chlorobenzene was decomposed at 45.0° in the kinetic apparatus described above. As initiator 0.125 g. (0.055 *M*) of radioactive DBPO was used. The DBPO gave a net count of 5230/mg. The average chain length was 7.8 by kinetic measurement and 8.0 over-all (see Table II). The final solution was cooled to −80° to condense any volatile materials, and 1.00 ml. (0.793 g.) of di-*t*-butyl peroxide was added. About 6 ml. of liquid was distilled at 25° under high vacuum and a small amount of lithium aluminum hydride was added to the distillate and then redistilled. The peroxide was separated by g.l.c. fractionation as described above, shown to contain negligible *t*-butyl alcohol, and counted. For 84.4 mg. the activity was 4765 c.p.m. This represents a 6.8% yield of di-*t*-butyl peroxide from DBPO.

Acknowledgment. We wish to thank the Academic Senate Committee on Research of the University of California for a grant, and the National Institutes of Health for a Fellowship (A. F.). We are also grateful to Dr. Paul D. Bartlett, Dr. Charles Perrin, and especially to Dr. Richard Hiatt for helpful advice.

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Mechanisms of Autoxidation. Terminating Radicals in Cumene Autoxidation

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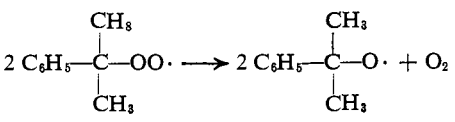
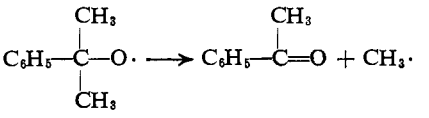
The effect of t-butyl hydroperoxide on the rate of cumene autoxidation has been studied. Although t-butyl hydroperoxide does not initiate cumene autoxidation, it accelerates the autoxidation initiated by α,α-azobisisobutyronitrile (AIBN). Furthermore, the rate of autoxidation depends directly on the ratio of cumene hydroperoxide to t-butyl hydroperoxide. These and other data, combined with previous studies, strongly indicate the following termination mechanism for autoxidation of cumene and other tertiary hydrocarbons. The CH_3





$$CH_3\cdot + O_2 \longrightarrow CH_3OO\cdot$$

$$ROO\cdot + CH_3OO\cdot \longrightarrow CH_2O + (ROOH \text{ or } ROH) + O_2$$

deuterium isotope effect found by Boozer, et al., is also explained by this scheme.

Introduction

The autoxidations of hydrocarbons at moderate temperatures and oxygen pressures display kinetic

behavior requiring that these chain processes terminate by a bimolecular reaction of peroxy radicals.[1,2]

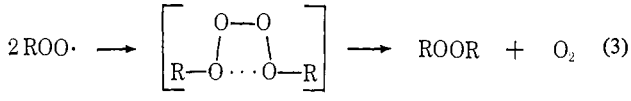
$$2\mathrm{ROO}\cdot \longrightarrow \text{nonradical products} \quad (1)$$

The nature of this termination reaction has been the subject of several investigations,[3–7] and several mechanisms have been proposed.

In the case of secondary peroxy radicals, which terminate 100–500 times faster than do tertiary peroxy radicals,[4a] the α-hydrogen has been implicated in the termination step by its isotope effect.[4b] This termination has been written as a direct one-step reaction.

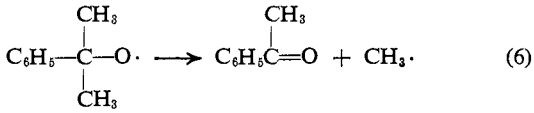
$$2\mathrm{R_2CHOO}\cdot \longrightarrow \mathrm{R_2C{=}O} + \mathrm{R_2CHOH} + \mathrm{O_2} \quad (2)$$

Since tertiary peroxy radicals cannot undergo this mechanism, other mechanisms have been proposed.[5,6a]



$$2\mathrm{ROO}\cdot \longrightarrow \mathrm{2RO}\cdot + \mathrm{O_2} \quad (4)$$

$$2\mathrm{RO}\cdot \longrightarrow \mathrm{ROOR} \quad (5)$$

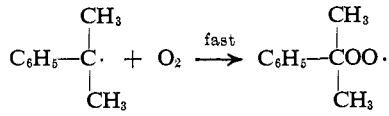


$$\mathrm{CH_3}\cdot + \mathrm{O_2} \longrightarrow \mathrm{CH_3OO}\cdot \quad (7)$$

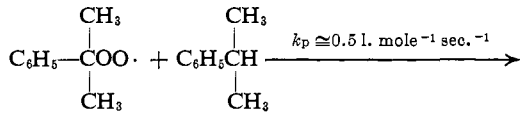
Blanchard[5] has related the amount of acetophenone produced during autoxidation of cumene to the chain length and has concluded that, although a certain fraction of cumylperoxy radicals decomposes by reaction 4, the termination step is either reaction 3 or reaction 5. Bartlett and Traylor[6a] confirmed the occurrence of reaction 4 using oxygen tracers but suggested that, reaction 5 being a poor process in cumene, termination might involve methylperoxy radicals produced by the sequence of reactions 4, 6, and 7.

The purpose of the present work is to determine which of these sequences actually constitutes termination of cumene autoxidation. Since the rate of hydrogen abstraction by ROO· is little dependent on the structure of R,[4c] it is reasonable to assume that interaction of ROO· by reaction 3 or 4 followed by reaction 5 would be similarly independent of the structure of R. In this event, the rate of autoxidation of cumene is expected to be almost independent of the structure of R in ROO·. On the other hand, the rate of autoxidation of cumene should depend on the structure of R in ROO· if the rapid termination reaction 2 is preceded by the slower reaction 6. For example, cumyloxy radicals are known to undergo reaction 6 in cumene[5,6] to give methyl radicals. In contrast to this behavior, *t*-butoxy radicals exclusively abstract hydrogen in cumene[8] or in hydroperoxides,[7,9] producing a negligible amount of methyl radicals. Thus, if the chain in cumene autoxidation could be carried by *t*-butylperoxy instead of by cumylperoxy radicals, or if cumyloxy radicals could be rapidly trapped in another way, any termination of methylperoxy radicals could be prevented, resulting in an increase in the rate of oxidation.

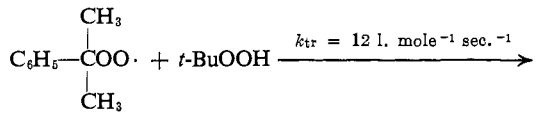
The possibility of changing the chain-carrying radical has been realized recently by Thomas and Tolman,[10] who indicated that reaction 10 has a rate constant of about 12 l. mole^{-1} sec.$^{-1}$. The following sequence is a very likely one. At equal concentrations of cumene



(8)



(9)



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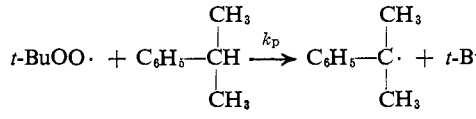

(11)

$$2t\text{-BuOO}\cdot \longrightarrow 2t\text{-BuO}\cdot + \mathrm{O_2} \quad (12)$$

and *t*-butyl hydroperoxide, cumylperoxy radical abstracts hydrogen from *t*-butyl hydroperoxide about 24 times faster than from cumene, and therefore the chain would be carried and terminated by *t*-butylperoxy radicals. For the same reasons, any effect *t*-butyl hydroperoxide has on autoxidation rate should be decreased by adding excess cumene hydroperoxide. Thus, if termination is occurring through methyl radicals, the addition of a small amount of *t*-butyl hydroperoxide should give an accelerated initial rate which decreases with time. This and other effects have been observed and are discussed below.

Results

We have designed a continuous recording gasometer for measuring oxygen absorption or evolution. This apparatus allows accurate instantaneous oxygen absorption rates to be measured even though the rate is changing with time. Furthermore, we obtain a continuous recording of total oxygen absorbed and from this can calculate the concentration of cumene hydroperoxide as a function of time. (The oxygen absorbed is nearly equal to cumene hydroperoxide formed at the long chain lengths occurring in this study.)

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(7) (a) R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem.*, **42**, 2754 (1964); (b) R. Hiatt, private communication.
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(9) A. Factor, C. A. Russell, and T. G. Traylor, *ibid.*, **87**, 3692 (1965).
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Table I. Changes in Rates of Autoxidation of Cumene with Time in the Presence of *t*-Butyl Hydroperoxide in Chlorobenzene at 60°[a]

Run	Concn. of *t*-BuOOH, *M*	Time, sec.	Concn. of of $C_6H_5CMe_2OOH$,[b] *M*	Mole fraction of $C_6H_5CMe_2$-OOH[c]	$10^5 \times$ rate O_2 absorption, mole l.$^{-1}$ sec.$^{-1}$	$10^5 \times$ rate[d]/ cumene sec.$^{-1}$
2	0	...	...	1.00	1.53	0.425
3	0	...	...	1.00	1.45	0.403
4	0.500	0	0.0	0.0	...	...
4	0.500	360	0.0124	0.024	4.75	1.32
4	0.500	1260	0.0540	0.0976	4.33	1.21
4	0.500	3000	0.128	0.204	3.50	0.97
4	0.500	4500	0.175	0.259	2.88	0.80
4	0.500	5400	0.203	0.288	2.98	0.82
14	0.250	0	0	0	...	...
14	0.250	240	0.011	0.043	4.77	1.33
14	0.250	840	0.0467	0.158	4.70	1.31
14	0.250	1680	0.0752	0.231	4.26	1.19
14	0.250	3000	0.126	0.335	3.62	1.01
14	0.250	4440	0.173	0.430	3.12	0.87
20	2.25	0	0	0.0	...	...
20	2.25	780	0.047	0.02	6.06	1.69
20	2.25	1380	0.085	0.037	6.24	1.74
20	2.25	2040	0.125	0.053	6.24	1.74
20	2.25	2580	0.159	0.066	6.16	1.72
24	0.100	0	0.0379	0.275	...	...
24	0.100	900	0.088	0.469	4.06	1.13
24	0.100	1560	0.110	0.529	3.79	1.06
24	0.100	2280	0.143	0.590	3.35	0.932
24	0.100	3840	0.191	0.656	3.01	0.838
24	0.100	5040	0.226	0.694	2.75	0.764

[a] [Cumene] = 3.59 *M*, [AIBN] = 0.100 *M*. [b] Including that produced by autoxidation. [c] Of total ROOH. [d] Observed rate divided by cumene concentration.

The effect of added *t*-butyl hydroperoxide on the rates of cumene autoxidation can be seen in Table I and Figure 1. The plot of rate ($d[O_2]/dt$) against time in Figure 1 shows the usual zero-order reaction in the absence of *t*-butyl hydroperoxide (D) or in the presence of large concentrations of *t*-butyl hydroperoxide (A). Furthermore, a large quantity of *t*-butyl hydroperoxide causes the zero-order rate to increase by a factor of 4.0, even though no reaction occurs until the initiator, AIBN, is added. When a small amount of *t*-butyl hydroperoxide is used, the rate is initially high but rapidly decreases (B). It is also demonstrated in Figure 1 that addition of cumene hydroperoxide to solutions containing *t*-butyl hydroperoxide decreases the rate acceleration (C).

The rate of cumene autoxidation as a function of *t*-butyl hydroperoxide concentration was determined by measuring initial oxidation rates at concentrations of *t*-butyl hydroperoxide from 0 to 10 *M* (pure *t*-butyl hydroperoxide). The data are shown in Table II and plotted in Figure 2. Although the rate acceleration for small concentrations of *t*-butyl hydroperoxide is difficult to obtain because of the rather rapid rate decrease with time (see Figure 1), reasonable estimates are available by extrapolation to zero time as shown in Figure 1.

It is immediately apparent from Figure 2 that small concentrations (0.1 *M*) of *t*-butyl hydroperoxide bring about a fourfold increase in autoxidation rate, but that this does not increase further with more *t*-butyl hydroperoxide even up to 80% hydroperoxide. At 9 *M* *t*-butyl hydroperoxide (90% concentration) oxygen evolution competes with oxidation, and the rate of oxygen absorption decreases.[11]

Table II. Effect of *t*-Butyl Hydroperoxide on Rates of Autoxidation of Cumene in Chlorobenzene at 60.0°[a]

Run	Concn. of cumene, *M*	Concn. of *t*-BuOOH, *M*	$10^5 \times$ $d[O_2]/dt$, mole l.$^{-1}$ sec.$^{-1}$	($10^5 \times d[O_2]/dt$)/cumene, sec.$^{-1}$
2[b]	3.59	0	1.527	0.425[c]
14	3.59	0.250	4.79	1.4[c]
4	3.59	0.500	4.79	1.4
5	3.59	1.00	5.58	1.56
6	3.59	1.50	5.92	1.65
20	3.59	2.25	6.17[d]	1.72[d]
7	3.59	3.00	5.98	1.67
8	3.59	4.00	5.94	1.65
25	3.59	4.50	6.14	1.71
9	3.59	5.00	6.00	1.67
10	2.87[e]	6.00	4.72	1.65
11	2.15[e]	7.00	4.02	1.87
17	1.795[e]	7.50	2.95	1.70
12	0.718[e]	9.00	0.96	1.50
16	0.359[e]	9.50	<0.2	<0.6

[a] Initiator, 0.100 *M* AIBN; vol. 20 ml. [b] Several runs such as 2 gave constant oxidation rates duplicating published values. [c] Extrapolated to zero time. See Figure 1. Other runs did not change with time. [d] Average value from Table I. [e] No chlorobenzene. These solutions were mixtures of cumene, *t*-butyl hydroperoxide, and initiator.

An interesting situation develops at 9.5 *M* *t*-butyl hydroperoxide. Rather rapid cumene autoxidation occurs without oxygen uptake.[11] In fact the kinetic run 16 of Table II showed oxygen absorption for several minutes and then began to slowly evolve gas.

(11) These conditions correspond to the terminal oxidation rates discussed by Tobolsky, Metz, and Mesrobian.[12] However, their kinetic treatment cannot be correct at these temperatures because they assumed a bimolecular thermal decomposition of hydroperoxide rather than the zero-order chain process which occurs.[7,9]

(12) A. V. Tobolsky, D. J. Metz, and R. B. Mesrobian, *J. Am. Chem. Soc.*, 72, 1942 (1950).

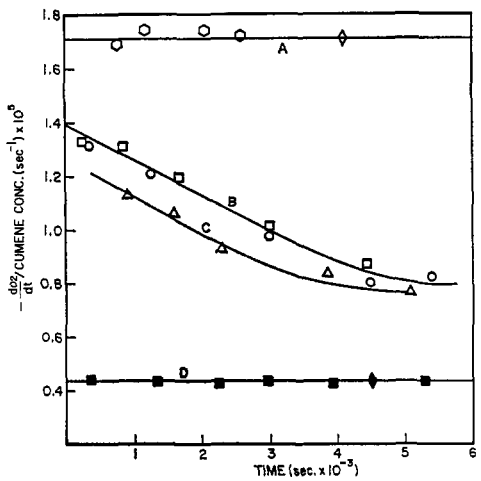


Figure 1. Rates of cumene autoxidation *vs.* time with zero, low and high concentrations of *t*-butyl hydroperoxide, data from Table I: ○, run 20, 2.25 *M* *t*-BuOOH; ■, run 2, no *t*-BuOOH; □, run 14, 0.250 *M* *t*-BuOOH, no cumene hydroperoxide; ○, run 4, 0.500 *M* *t*-BuOOH, no cumene hydroperoxide; ◇, a composite of a number of runs at high [*t*-BuOOH] in which the recorder plotted a straight line ($d[O_2]/dt$) for 3000–6000 sec.; ◆, all runs without *t*-BuOOH; these gave straight lines ($d[O_2]/dt$); △, run 24, 0.100 *M* *t*-BuOOH, 0.0379 *M* cumene hydroperoxide.

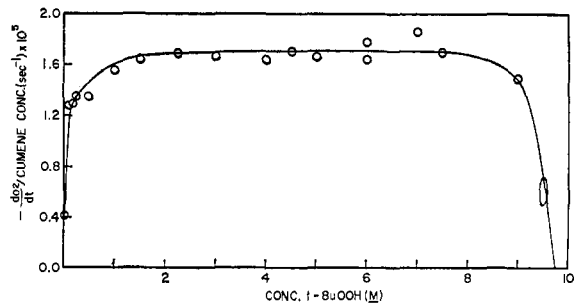


Figure 2. Effect of added *t*-butyl hydroperoxide on the rate of cumene autoxidation at 60.0°. Data are from Table II.

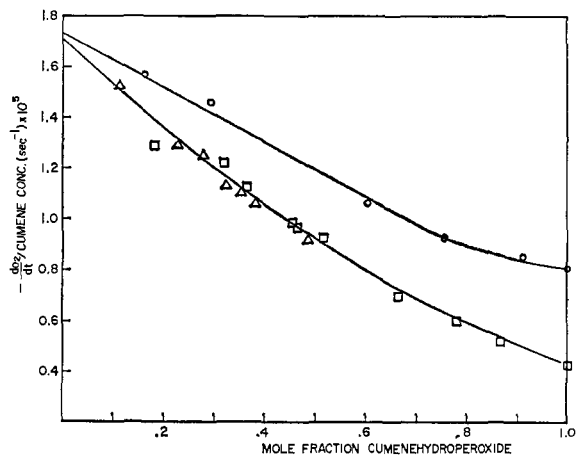


Figure 3. Rate of cumene autoxidation at 60.0° in chlorobenzene with 0.100 *M* AIBN as a function of the mole fraction of cumene hydroperoxide (cumene hydroperoxide/(cumene hydroperoxide + *t*-butyl hydroperoxide)). The data are from Table III: □, rates of separate runs with various amounts of added *t*-butyl hydroperoxide, cumene concentration 5.98 *M*; △, run T24, *t*-butyl hydroperoxide concentration 0.271 *M* and cumene concentration 5.82 *M*; ○, large concentrations of both cumene hydroperoxide and *t*-butyl hydroperoxide, cumene concentration 3.59 *M* (note that the intercept corresponds to the average maximum value of rate/cumene concentration from Figure 1).

This peculiar behavior is the expected result because of depletion of cumene by autoxidation.

For reasons presented below, the rate of cumene autoxidation should be related to the ratio of *t*-butyl hydroperoxide to cumene hydroperoxide. For convenience the rate of autoxidation is plotted as a function of mole fraction of cumene hydroperoxide in Figure 3 from data in Table III. The data are obtained both by adding cumene hydroperoxide and by calculating the mole fraction of the cumene hydroperoxide produced by autoxidation in the presence of *t*-butyl hydroperoxide and are similar by either method. The upper curve represents rates in the presence of large concentrations of both hydroperoxides. It is especially significant that cumene hydroperoxide itself causes cumene autoxidation to increase. This has not been noticed previously because large concentrations of cumene hydroperoxide are not usually obtained in kinetic studies.

Discussion

Source of Rate Acceleration. Although the results presented are predicted by the proposed termination mechanism involving methyl radicals, we must exclude other equally reasonable sources of the effect of *t*-butyl hydroperoxide on cumene autoxidation rates before discussing the mechanistic implications of this study.

The addition of *t*-butyl hydroperoxide, a known initiator, to the system cumene–solvent–oxygen–initiator could bring about a rate increase by causing additional chain initiation. Three observations exclude this possibility. The addition of ~0.2 *M* of *t*-butyl hydroperoxide causes the rate to increase fourfold whereas the addition of 0.2 *M* cumene hydroperoxide is without effect. Second, above 0.5 *M* *t*-butyl hydroperoxide the rate of autoxidation does not increase with increasing concentrations of *t*-butyl hydroperoxide (Figure 2). Finally, in each run, the solution containing hydroperoxide, cumene, and oxygen was attached to the gasometer and showed no oxidation until the AIBN was added. Then oxidation began immediately. Therefore, it is clear that the observed effects at 60° are not associated with initiation by *t*-butyl hydroperoxide.

A second possibility which has been suggested is a solvent effect.[9] The constancy of oxidation rate per mole of cumene from 5 to 90% *t*-butyl hydroperoxide and the absence of any effect of cumene hydroperoxide below about 5% concentration make it unlikely that the change in rate is caused by a solvent effect.

It is also conceivable that reactions 3, 4, and 5 or the propagation reaction 9 might have different rates when cumylperoxy radical is replaced by *t*-butylperoxy radical. However, Russell and Williamson[4c] have already shown that the rate of reaction 9 is virtually independent of the structure of ROO·, and we can expect the rates of reactions 3, 4, and 5 to be similarly unaffected by changing the structure of ROO·.

We therefore conclude that *t*-butyl hydroperoxide increases the rate of autoxidation of cumene mainly by decreasing the rate constant for termination. In the absence of *t*-butyl hydroperoxide, cumylperoxy radicals must terminate rapidly by some mechanism not avail-

Table III. Rates of Autoxidation of Cumene in the Presence of *t*-Butyl Hydroperoxide and Cumene Hydroperoxide in Chlorobenzene at 60°[a]

Run	Concn. of cumene, *M*	Concn. of *t*-BuOOH, *M*	Time, sec.	Concn.[b] of $C_6H_5CMe_2$-OOH, *M*	Mole fraction[c] of $C_6H_5CMe_2$-OOH	Rate × 10^5, mole $l.^{-1}$ $sec.^{-1}$	Rate × 10^5/cumene[d], $sec.^{-1}$
T13	5.98	0	0	0	0	2.43	0.416
T16	5.98	0	0	0	0	2.49	0.417
T23	5.98	0	0	0	0	2.67	0.446
T17	5.98	0.0167	4200	0.104	0.866	3.11	0.520
T18	5.98	0.0667	6000	0.171	0.780	3.58	0.598
T19	5.98	0.183	7500	0.231	0.665	4.17	0.698
T20	5.98	0.167	480	0.037	0.18	7.67	1.28
T20	5.98	0.167	1020	0.0767	0.32	7.31	1.22
T21	5.98	0.366	1560	0.114	0.364	6.67	1.12
T21	5.98	0.366	2220	0.166	0.456	5.93	0.99
T22	5.98	0.660	2940	0.201	0.464	5.76	0.964
T24	5.82	0.271	300	0.0315	0.105	8.90	1.52
T24	5.82	0.271	900	0.0760	0.220	7.48	1.29
T24	5.82	0.271	1200	0.1025	0.276	7.26	1.25
T24	5.82	0.271	1620	0.127	0.324	6.60	1.13
T24	5.82	0.271	1920	0.147	0.354	6.38	1.10
T24	5.82	0.271	2220	0.166	0.382	6.20	1.06
T24	5.82	0.271	3660	0.254	0.486	5.32	0.912
C19	3.59	1.80	0	0.34	0.16	5.63	1.57
C21	3.59	0.45	0	1.36	0.752	3.30	0.920
C22	3.59	1.50	0	0.620	0.292	5.23	1.46
C23	3.59	0.75	0	1.13	0.603	3.82	1.07
T25	3.59	0	...	1.90	1.00	2.88	0.80

[a] Initiator, 0.100 *M* AIBN. [b] Cumene hydroperoxide added plus that which formed during autoxidation (total O_2 absorbed). [c] Of total ROOH. [d] $(d[O_2]/dt)$/concentration of cumene.

able to *t*-butylperoxy radicals. Such a mechanism can be formulated as a sequence of individually known reactions 4,[5,6a] 6,[5] 7,[3] and 2.[4b,13] This sequence would not be possible for *t*-butylperoxy radicals since, under the conditions of cumene autoxidation, *t*-butoxy radicals do not fragment in the manner of reaction 6.

It is reasonable to assume that cumylperoxy radicals undergo such a sequence involving cleavage to acetophenone with ultimate termination by methylperoxy radicals. Russell[4a] has shown that secondary or primary radicals terminate several hundred times faster than do tertiary peroxy radicals, and, since methyl radicals are known to react very rapidly with oxygen,[3] there is a rapid termination process available once methyl radicals are formed. During cumene autoxida-

$$CH_3OO\cdot + ROO\cdot \longrightarrow ROH \text{ (or ROOH)} + CH_2O + O_2 \quad (13)$$

tion, methyl radicals are produced simultaneously with the cleavage to acetophenone. The constant yield of acetophenone per termination reaction, observed by Blanchard,[5] is consistent with methylperoxy radical termination.

Relative Termination Rate Constants for t-BuOO· and $C_6H_5CMe_2OO\cdot$. The extent to which the two kinds of termination occur can be established if it is assumed that reactions 3, 4, and 9 are independent of the structure in R. Writing the over-all rate equation (14) and concluding, as we have done, that the change

$$-\frac{d[O_2]}{dt} = \frac{k_I^{1/2} I^{1/2} RH k_p}{k_t^{1/2}} \quad (14)$$

is in the termination step, then the rate change is given by eq. 15 where the subscripts refer to rates and

$$\left(\frac{d[O_2]}{dt}\right) \Big/ \left(\frac{d[O_2]}{dt}\right)_0 = \frac{k_{t_0}^{1/2}}{k_t^{1/2}} \quad (15)$$

terminations with and without *t*-butyl hydroperoxide. It can be seen that a fourfold increase in rate requires a 16-fold decrease in k_t, and termination by cumylperoxy radicals is 16 times faster than that by *t*-butylperoxy radicals.

Nature of the Rate Acceleration. The fourfold increase in rate of cumene autoxidation upon addition of small quantities of *t*-butyl hydroperoxide has been attributed to differences in behavior of *t*-butylperoxy and cumylperoxy radicals. The major known difference between these radicals is that, subsequent to reaction 4, cumyloxy radicals cleave to give methyl radicals much more rapidly than do *t*-butoxy radicals. However, there remains the possibility that *t*-butylperoxy radicals may abstract from cumene somewhat faster than do cumylperoxy radicals or that *t*-butylperoxy radicals undergo reaction 5 more slowly than do cumylperoxy radicals. Either of these differences would contribute to the observed rate increase.

Let us therefore consider the effect of adding large concentrations of cumene hydroperoxide which does not introduce the complications mentioned above. The propagation reaction (9) and reaction 5 are not changed. What is changed may be seen from a comparison of the DBPO-induced decomposition of *t*-butyl hydroperoxide and cumene hydroperoxide discussed in the previous paper.[9] When cumene hydroperoxide in high concentration is decomposed in a chain initiated by DBPO, less than 1 molecule of acetophenone is produced for 50 cumyl alcohol molecules. This contrasts the results in low concentrations of cumene hydroperoxide in cumene solvent where large amounts of acetophenone are produced.[5,14]

(13) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discussions Faraday Soc.*, 10, 242 (1951).

Therefore large concentrations of cumene hydroperoxide prevent cumyloxy radical cleavage by chain transfer (reaction 16) just as do small concentrations of *t*-butyl hydroperoxide.

$$C_6H_5C(CH_3)_2OOH + C_6H_5C(CH_3)_2O\cdot \longrightarrow C_6H_5C(CH_3)_2OO\cdot + C_6H_5C(CH_3)_2OH \quad (16)$$

We may now compare the quantitative effects predicted by the assumption of methyl radical termination with those found in this work. The previous paper[9] indicated that, of every eleven bimolecular interactions of either *t*-butylperoxy or cumylperoxy radicals, reaction 3 occurred once and reaction 4 occurred ten times.[15] Termination by reaction 3 should therefore result in the evolution of 11 molecules of oxygen per termination step. Bartlett and Traylor[6a] have shown that only 1.5 to 3 oxygen molecules are evolved for each termination. Reaction 3 thus accounts for only one-tenth to one-third of total termination in cumene autoxidation. The remaining two-thirds to nine-tenths of total termination must occur by another mechanism. At chain lengths of interest in this work (12–15), 3 oxygen molecules are evolved per termination step under conditions where eight-tenths acetophenone molecule is formed for each termination. Addition of 2 *M* cumene hydroperoxide prevents acetophenone (and $CH_3\cdot$) formation and increases the rate by a factor of 2. A factor of 2 in rate corresponds to a fourfold decrease in termination rate constant k_t (eq. 15), which is exactly that predicted if termination were forced to proceed through reaction 3. Under these conditions 11 oxygen molecules will be evolved for each termination rather than 3. That is, rather than one interaction of peroxy radicals in three leading to termination, only one interaction in 11 will lead to termination when large concentrations of cumene hydroperoxide are present. Since the rates of reactions 3 and 4 are unchanged, this means that k_t will decrease to $^3/_{11} \cong {}^1/_4$ its original value when cumene hydroperoxide is added and methyl radical formation is prevented.

Therefore the effect of adding either a little *t*-butyl hydroperoxide (0.1 *M*) or a lot of cumene hydroperoxide (2 *M*) is best explained in terms of methyl radical termination. The rate increase in excess of a factor of two which added *t*-butyl hydroperoxide causes must be attributed to small differences between *t*-butylperoxy radicals and cumylperoxy radicals in reaction 4 or in abstraction from cumene (reaction 9).

The Termination Process. We may now write an essentially complete mechanism for termination of cumene autoxidation and make certain predictions about the autoxidation of other tertiary hydrocarbons. The termination begins with reaction 17.[9] Reaction

$$2ROO\cdot \longrightarrow [RO\cdot O_2\cdot OR]^{cage} \xrightarrow{9\%} ROOR + O_2 \quad (17a)$$

$$[RO\cdot O_2\cdot OR]^{cage} \xrightarrow{91\%} 2RO\cdot + O_2 \quad (17b)$$

17b is then followed by reactions 18 through 22.

$$RO\cdot \longrightarrow CH_3\cdot + R'_2C{=}O \quad (18)$$

$$CH_3\cdot + O_2 \xrightarrow{rapid} CH_3OO\cdot \quad (19)$$

$$CH_3OO\cdot + ROO\cdot \longrightarrow CH_2O + O_2 + ROH \quad (20)$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot \quad (21)$$

$$RO\cdot + ROOH \longrightarrow ROO\cdot + RO\cdot \quad (22)$$

The amount of each kind of termination depends on the competition between reaction 18 and the sum of reactions 21 and 22. Because hydroperoxide is a better hydrogen atom source than cumene, reaction 22 can be caused to compete successfully with reaction 18 whereas reaction 21 cannot. However, at the low concentrations of cumene hydroperoxide encountered in usual kinetic and product studies even reaction 22 does not completely prevent reaction 18.

With the assumption that only reactions 17a and 20 terminate chains, we may now relate the amount of each kind of termination to the number of oxygens[6a] and acetophenones[5] evolved per termination reaction. Every 11 peroxy radical interactions produces one termination by reaction 17a, 11 oxygen molecules, and 20 cumyloxy radicals. If we let X be the number of these 20 cumyloxy radicals which cleave to give methyl radicals and assume that these rapidly terminate through reactions 19 and 20, then $0 \lesssim X \lesssim 20$; the number of oxygens evolved per termination step[6a] is

$$\beta = \frac{11 + X}{1 + X} \quad (23)$$

and the number of acetophenone molecules produced per termination step is given by

$$Ac = \frac{X}{1 + X} \quad (24)$$

Table IV lists values of β, X, and chain lengths calculated from eq. 23 and 24 and observed in this and other works.

Table IV. Correlation of Chain Length, Oxygen Evolution, and Acetophenone Production with Methylperoxy Radical Termination of Cumene Autoxidation[a]

Concn. of cumene, *M*	Chain length	β	X	% of $CH_3OO\cdot$ termination	Acetophenones per termination Calcd.	Found[d]
3.59[b]	24	11[c]	0	0	0	0
6.90[d]	20	4	2.3	70	0.7	0.75
3.59	12	2.9[e]	4.2	80	0.8	0.8
2.72	7.8	2.5[e]	5.7	85	0.85	0.75
0	0	1.5[e]	20	95	0.95	...

[a] Initiator, 0.1 *M* AIBN. [b] Containing 1.9 *M* cumene hydroperoxide, Table III. [c] Based on chain length for cumene hydroperoxide decomposition; ref. 9. [d] See ref. 5. [e] See ref. 6a. The value of 1.5 is that obtained by extrapolating to zero chain length.

The data in Table IV afford an explanation of three published observations which were not previously understood. The extrapolation of β to 1.5 rather than 1.0 at zero chain length[6a] is predicted by eq. 23. The requirement of 1.5 oxygens derives from the fact that each cumylperoxy radical pair produces two methyl radicals, stopping two chains and evolving three oxygen molecules. The apparent constancy of acetophenone production per termination[5] is also explained in Table IV as a result of the predominance of methylperoxy radical termination under most conditions. Finally,

(14) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **16**, 105 (1951).

(15) This chain length has been corrected for viscosity effect and for temperature change to that which occurs at 60° in chlorobenzene.

the effect of methyl deuterium substitution on termination of cumene autoxidation, observed by Boozer, *et al.*,[16] and much discussed,[2,5,6] is clarified by the proposed methylperoxy radical termination. The rate constant for termination of cumene autoxidation is given by eq. 25 where the subscripts refer to reaction

$$k_{\text{term}} = k_{17b}F + k_{17a} \tag{25}$$

numbers and F, the fraction of cumyloxy radicals which terminate, is given by eq. 26. The propaga-

$$F = \frac{k_{18}k_{20}(\text{ROO}\cdot)}{[k_{18} + k_{21}(\text{RH}) + k_{22}(\text{ROOH})]\,[k_{20}(\text{ROO}\cdot) + k_{27}(\text{RH})]} \tag{26}$$

tion reaction (eq. 27) is included. At either very short

$$\text{CH}_3\text{OO}\cdot + \text{RH} \longrightarrow \text{R}\cdot + \text{CH}_3\text{OOH} \tag{27}$$

chain lengths where concentrations of RH and ROOH are small and $F = 1$ or in the presence of hydroperoxide where $F = 0$, there should be no methyl isotope effect because

$$k_{\text{term}} = k_{17b} + k_{17a}$$

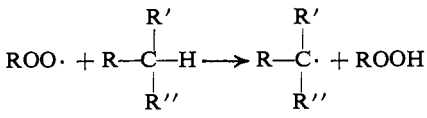
or

$$k_{\text{term}} = k_{17a}$$

However, at intermediate chain lengths where eq. 26 does not simplify, there are isotope effects introduced through k_{18} which has a secondary isotope effect and k_{20} in which a primary isotope effect is known.[4a] It is in these intermediate chain lengths where Boozer, *et al.*,[16] report a methyl isotope effect.

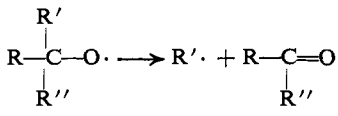
Remaining Problems in Cumene Autoxidation. We have not described the mechanism of reaction 20. Several mechanisms have been proposed,[2-4] none of which explains all the observed facts. Except for this reaction we believe that all the major processes occurring in cumene autoxidation have been described.

Application to Other Tertiary Hydrocarbons. A major deciding factor in the mechanism of autoxidation of a tertiary hydrocarbon is the competition between propagation (*e.g.*, reaction 9) and cleavage (reaction 18) rates. Propagation rates depend on stability of the radical formed



(28)

whereas cleavage rates depend on stabilities of the ketone and the radical R′· (eq. 29). Resonance



(29)

effects in R, R′, and R″ which stabilize the radical in reaction 28 also stabilize the ketone in reaction 29. Therefore ketone formation is difficult to avoid. The formation of ketone also increases with increasing stability in R′·. Because alkylbenzenes of the type C_6H_5CHRR' where R = Et, Pr, etc. split off these radicals faster than Me· all other tertiary aralkyl hydrocarbons of this type will undergo the secondary termination process involving ROO· or R′OO·. Similarly, diaryl hydrocarbons of the type Ar_2CHR will yield stable ketones $Ar_2C{=}O$ and tend to undergo the secondary termination to a greater extent than does cumene.

Because this alkoxy radical splitting usually introduces compounds containing the R_2CHO– group which readily oxidize further, it is a source of many and varied by-products and is to be avoided. A means of preventing this splitting is suggested by reaction 22. If a chain-transfer agent is introduced to react rapidly with RO· then the only by-products will be 20 ROH and 1 ROOR per chain. The use of HBr in autoxidation of isobutane[17a] is such an example. Although the mechanism written for this reaction involved Br· abstraction from isobutane, the prevention of *t*-

$$\text{ROO}\cdot + \text{HBr} \longrightarrow \text{ROOH} + \text{Br}\cdot \tag{30}$$

$$\text{Br}\cdot + \text{RH} \longrightarrow \text{R}\cdot + \text{HBr} \tag{31}$$

butoxy radical cleavage is undoubtedly also very important. This transfer increases chain length and

$$\text{RO}\cdot + \text{HBr} \longrightarrow \text{ROH} + \text{Br}\cdot \tag{32}$$

prevents formation of methyl radicals[17b] and their oxidation products.

In summary, the autoxidation of tertiary hydrocarbons is terminated by peroxide formation (reaction 17a) only in the presence of good chain-transfer agents, never by reaction 5, and usually by reactions of the products of alkoxy radical cleavage.

Experimental

Reagents. Cumene was distilled at atmospheric pressure through a 10-plate column under nitrogen and stored at 0° under nitrogen. *t*-Butyl hydroperoxide and chlorobenzene were purified as previously described.[9] Cumene hydroperoxide was distilled at 45° at 0.1 mm. α,α-Azobisisobutyronitrile (AIBN) was recrystallized from methanol, dried, and stored at −20°.

Kinetic Measurements. We have assembled from commercially available units an automatic recording gasometer for evolution or absorption.[18] This apparatus consists of a portable vacuum line shown in Figure 4 and a recording solenoid-operated buret shown in Figure 5.

The vacuum line is about 12 × 12 in. in over-all dimensions and is mounted on a rack by a clamp around the water jacket B so that it can be raised and lowered. This allows the reaction flask Y, attached at G, to be lowered into a thermostated oil bath at the desired time without otherwise disturbing the system.

The recording mercury supply of Figure 5 is mounted on a ring stand which is in turn either placed on the floor below the manifold for gas evolution or clamped on the rack above the manifold for gas absorption. To maintain constant pressure, mercury is gravity fed

(16) C. E. Boozer, B. W. Ponder, J. C. Trisler, and C. E. Wrightman, *J. Am. Chem. Soc.*, 78, 1506 (1956).

(17) (a) E. R. Bell, F. H. Dickey, J. H. Raley, F. F. Rust, and W. E. Vaughan, *Ind. Eng. Chem.*, 41, 2597 (1949); (b) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, *Discussions Faraday Soc.*, 10, 246 (1953).

(18) A constant volume recording device has been described by L. R. Mahoney, *J. Am. Chem. Soc.*, 86, 448 (1964).

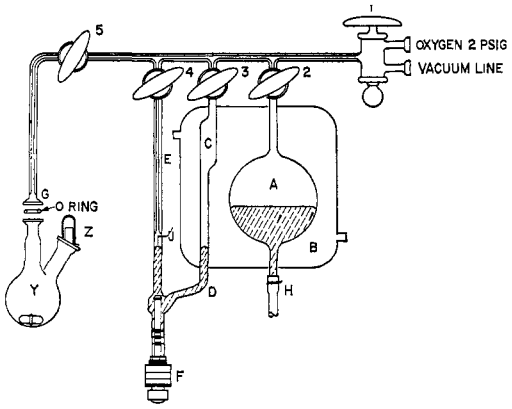


Figure 4. Reactor and vacuum line for automatic recording of gas evolution or absorption. This manifold consists of the following: 1, a water-jacketed (B) 250-ml. gas supply (A), which is attached from point H through about 3 ft. of $^3/_{16}$-in. tygon tubing to the solenoid valve (V_1) in Figure 5; 2, a 20-ml. reference pressure reservoir (C) in which the desired pressure is set; a column of mercury (D) only 2 in. high to reduce inertia attaches this reference to the manifold through (E), which contains a sealed-in tantalum contact wire (J); this contact wire is attached to the actuating post on the thermocap relay; the relay can be switched to open the solenoid valve (V_1) either on making or breaking contact at (J) depending on whether gas absorption or gas evolution is being measured; 3, a mercury level adjusting valve (Delmar-Urry Needle Valve, Delmar Scientific Laboratories, Inc., Maywood, Ill.) is used to accurately position the mercury for each run; the glass tubing is 3-mm. capillary wherever possible.

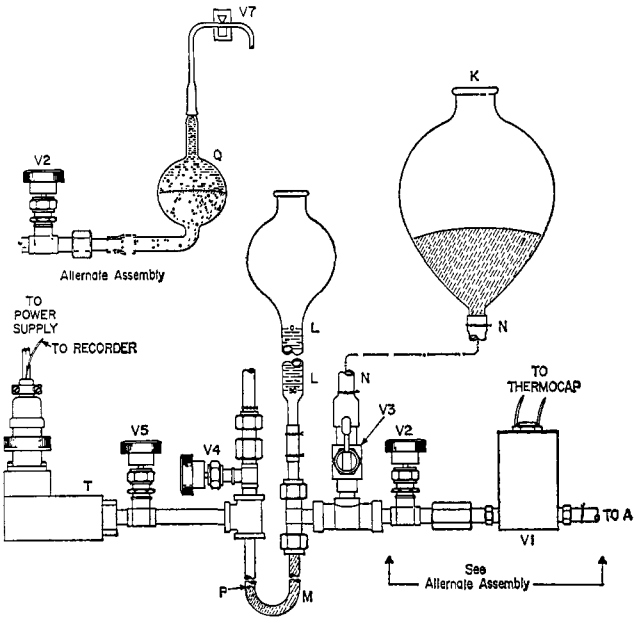


Figure 5. Solenoid-controlled automatic recording buret. This was assembled from the following components: relay (not shown), Niagara Electron Laboratories, Andover, N. Y.; thermocap relay; solenoid valve (V_1), Model V52DA1200 stainless steel valve with $^1/_{16}$-in. orifice, from Skinner Electric Valve Division, New Britain, Conn.; needle valve (V_2), a Whitey $^1/_8$-in. pipe valve of 316 stainless steel No. ORM2; toggle valve (V_3), a Whitey No. 1GF2 toggle valve in $^1/_8$-in. pipe thread; brass Hoke valves (V_4 and V_5), $^1/_8$-in.; connections of 316 stainless steel in either $^1/_4$-in. Swagelok or $^1/_8$-in. pipe; pressure transducer (T), Statham Instruments Inc., Model PM6TC ± 15-350 (power supply for transducer (not shown) from Sorenson, Richards Avenue, South Norwalk, Conn., Model QR40-0.75A); and recorder, Sargent Model SR. The inset shows the attachment which replaces the valve (VI) and the gas manifold of Figure 4 to convert the apparatus for automatic recording of kinetic data from pH-Stat or intermittent titration. The 30-ml. Pyrex bulb (Q) contains the titrating solution supported by mercury from the buret (L) which is, for this purpose, a 5-ml. buret. The valve (V_7) (Radiometer magnetic valve) is operated either by a push-button switch or by a pH meter such as the Radiometer TTT1. Rates with half-lives of less than 60 sec. are easily and accurately recorded if a Vibromix stirrer is used to stir the reaction solution.

either into or out of the bulb A from the buret L by opening solenoid valve V_1. The rate of flow through the open solenoid valve is adjusted with the needle valve V_2. The buret can be quickly emptied or filled with the mercury supply K by opening the toggle valve V_3 while holding K at the proper level. The tubing N is Tygon. The apparatus described to this point would serve for kinetic runs by reading the buret. However, by connecting a pressure transducer T at the base of the buret and feeding the output of this transducer to a 10–30-mv. recorder the mercury height can be recorded *vs.* time. By reading the buret at two or three levels and observing the recorder values the chart paper can be quickly calibrated to read volume *vs.* time. The glass tube M and valves V_4 and V_5 are necessary to protect the brass parts of the transducer against mercury. The tube M is filled on the transducer side from P upwards with heptane or other noncorrosive liquids by pouring such liquids in through V_4. The valve V_5 is added for safety and is closed when the apparatus is not in use. All valves which contact mercury must be stainless steel. The two T-joints which M connects are bolted together for rigidity.

When properly adjusted, this apparatus will actuate every 0.5 sec. in fast reactions (*e.g.*, 0.05 ml./sec.), giving essentially continuous recording of volume. The advantage over other positive-drive-type devices is the simplicity and ease of calibration. Thus, if three or four points are taken by reading the buret and a stopwatch during each or some of the runs, an immediate check is obtained on the whole apparatus. This apparatus is optimum for 40 ml. total gas evolution during a run and probably requires at least 10 ml. for accurate rate recordings. However, slight changes in the manifold and buret would allow accurate measurements of smaller total volume changes. For example, to measure small volume changes, the bulb A is kept almost filled with mercury.

If constant volume operation is desired, the transducer T is simply attached to the manifold through capillary tubing.[16] Adaptation of the recording part of this apparatus to pH-Stat kinetic recordings using titrating liquids instead of mercury is also straightforward.

Technique. In a typical run for cumene autoxidation the mercury supply is mounted so that the bottom of the 50-ml. buret will be about 1 ft. above A. The thermocap relay is turned to neutral. The reaction flask Y is charged with cumene and solvent. The catalyst, *e.g.*, AIBN, is weighed into a 9 × 25 mm. test tube Z, which is placed in the $^{18}/_9$ ball joint cap as shown in Figure 4. When the ball joint is properly aligned this test tube slips into the reaction flask. However, by tilting the cap slightly, the test tube containing catalyst can be prevented from falling in until the rest of the solution is in thermal equilibrium with the bath. The reaction flask is then attached to the manifold with an O-ring joint at G, immersed in Dry Ice–acetone, and, after stopcocks 2, 3, and 4 are

closed and 5 opened, pumped at about 1 mm. for a few minutes. Stopcock 1 is then turned to admit 2 p.s.i.g. of oxygen and the flask is warmed until the solution melts, is recooled, and re-evacuated. This process is carried out twice, then stopcock 5 is closed and the reactor is warmed to room temperature while maintaining 2 p.s.i.g. of oxygen pressure. Stopcocks 2, 3, and 4 are opened, the manifold is evacuated and then filled with oxygen, and stopcock 5 is opened. The buret L is filled and the recorder adjusted to near 100% and started. The apparatus is then lowered so that the reactor sits in the bath over a rotating magnet. By adjusting the valve F the mercury is brought as close as possible to J without actual contact. With stopcocks 2, 3, 4, and 5 open, the vacuum line is disconnected and stopcock 1 is opened briefly to the atmosphere or to some desired pressure for the reaction, and then closed. Stopcock 3 is then closed and the Thermocap turned to "high." The mercury in D will now show the reactor gases expanding slightly, or the recorder will show any uncatalyzed autoxidation. Usually no volume change occurred. After sufficient warm-up time the ball joint cap is adjusted so that the catalyst tube falls into the solution. The rapid stirring by the $^3/_4$-in. magnetic bar[19] quickly brings about catalyst dissolution, and the recorder shows an immediate beginning of an accurate zero-order plot. The buret is read and the volume and time are marked on the recorder chart at the proper point. This is repeated when the buret is nearly empty. Valve V_3 is opened to allow the buret to fill quickly and recording is continued until sufficient data are obtained. We usually excite the transducer with 12 v. d.c. (an automobile battery can be used), which produces about 25 mv. from a 50-ml. buret filled with mercury. The transducer tends to produce a current even when the buret reads empty, and a negative zero adjust on the recorder is required. If the recorder is not so equipped, a small bucking voltage can be put in reverse series with the transducer by using a 1.5-v. battery and two resistors of about 1000 ohms and 1–2 ohms.

(19) See ref. 6b for stirrer description.

Using the technique described, as many as six cumene autoxidation runs can be carried out in 8 hr. The results are in very good agreement with published rates of cumene autoxidation.[5]

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The Relation of Proton Exchange to Tautomerism in Unsaturated Ethers

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Deuterium exchange experiments with alkyl allyl ethers, using potassium t-butoxide in refluxing t-butyl alcohol-d for 10 days, have shown that isomerization to alkyl cis-propenyl ethers occurs with incorporation of a deuterium atom in the methyl position of the propenyl group as the major process. Approximately 30% of the product does not contain deuterium. Alkyl cis-propenyl ethers, under the same conditions, undergo very little if any exchange. At higher temperatures, 175° for 24 hr., the cis-propenyl isomer undergoes exchange at the methyl position of the propenyl group. These results are interpreted in terms of a common allyl anionic intermediate which protonates more rapidly to produce the more stable isomer, i.e., alkyl cis-propenyl ethers.

Introduction

The role of carbanionic intermediates in base-catalyzed reactions of allylic systems is an area of high current interest. Reaction systems which have been investigated employing deuterium exchange techniques include vinylacetic acid,[1] cyclohexenylnitriles,[2] cyclohexenones,[3] unsaturated sulfoxides,[4] indene,[5] and aliphatic olefins.[6,7] Also studies have been conducted utilizing optically active compounds in conjunction with deuterium exchange.[8–10] Ingold[9] originally proposed that those systems involving relatively stable ionic intermediates isomerized through the formation of a common allylic anion while with less acidic compounds a concerted transition state was realized. Cram's[8c] very recent work with methylenazomethine equilibria demonstrates that the operation of concerted processes in these reactions has not been established. In several cases[5–8] intramolecular hydrogen transfer has been demonstrated.

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(5) G. Bergson, *Acta Chem. Scand.*, 17, 2691 (1963).
(6) S. Bank, C. A. Rowe, and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 2115 (1963).
(7) (a) For studies with dienes see R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3032 (1963). (b) Exchange with cycloheptatriene has also been reported: W. von E. Doering and P. P. Gaspar, *ibid.*, **85**, 3043 (1963).
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(9) C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 1493 (1933); 93 (1934).
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