structure is probably disrupted in favor of strong bonds to the base molecules, so that one would not expect the lithium alkyls to exist as hexamer or tetramer in basic solvents. Halogen-metal interchange or metalation reactions[20] in hydrocarbon solvents presumably occur through initial coördination of the halogen (or basic atom, in the case of metalations) to the lithium. The reaction following initial coördination may be either the exchange reaction or (in the case of alkyl or aryl halides) coupling.

Acknowledgment.—This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

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[20] G. E. Coates, "Organometallic Compounds," 2nd Ed., Methuen, London, 1960, pp. 9–17.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER COMPANY, WILMINGTON, DELAWARE]

The Mechanism of Oxidation of *p*-Cymene

BY HAROLD BOARDMAN

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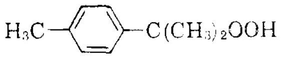
The kinetics of the oxidation of *p*-cymene, catalyzed by several initiators, has been investigated by measuring the instantaneous rate of oxygen uptake as a function of initiator concentration and by following the rate of hydroperoxide formation to low conversions. The major product of the oxidation, *p*,α,α-trimethylbenzyl hydroperoxide (I), is accompanied by minor amounts of *p*-isopropylbenzyl hydroperoxide (II), *p*-methylacetophenone (III) and 8-*p*-cymenol (IV). Evidence is given for the formation of II and IV in co-oxidation reactions and of I and III in the termination reaction.

It has been known for some time that *p*-cymene can be oxidized with molecular oxygen to give a variety of products, depending upon the experimental conditions. Thus, at temperatures of 140 to 170° in the presence of metal oxides, *p*-toluic acid and *p*-methylacetophenone were isolated from a *p*-cymene oxidate.[1] The use of a lead–manganese acetate catalyst permitted *p*-cymene to be oxidized at about 50° and the oxidate contained cumic acid, 8-*p*-cymenol and *p*-methylacetophenone.[2] The autoxidation of *p*-cymene in an aqueous alkaline medium produced *p*,α,α-trimethylbenzyl hydroperoxide which was identified through its reduction products.[3] Helberger, *et al.*,[4] presented evidence that a primary hydroperoxide, *p*-isopropylbenzyl hydroperoxide, was produced by the autoxidation of *p*-cymene at 60° in sunlight for ten days. Weber[5] was unable to confirm this but found that the ultraviolet-catalyzed oxidation proceeded at 90° to give a mixture of primary and tertiary hydroperoxide.

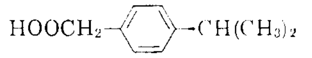
The object of this work was to make a detailed study of the mechanism of oxidation of *p*-cymene. The oxidations were conducted at temperatures below 85° to avoid initiation of oxidation by the hydroperoxide products. The rate of initiation can then be controlled by the use of initiators with known rates of decomposition.

Under these conditions the major products are: *p*,α,α-trimethylbenzyl hydroperoxide (I) (symbolized as ROOH), *p*-isopropylbenzyl hydroperoxide (II) (symbolized as R'OOH), *p*-methylacetophenone (III) and 8-*p*-cymenol (IV). Under the conditions of these experiments no *p*-methyl-α,α-dimethylbenzyl peroxide was formed.

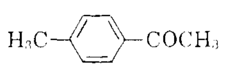
It was felt that a detailed kinetic study of this oxidation, particularly at low kinetic chain lengths, might indicate how these products are formed. A further objective was to elucidate the nature of the chain terminating step, essentially by comparing rate of oxygen uptake with rate of formation of oxygen-containing products.



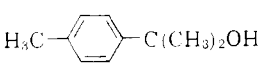
I



II



III



IV

Experimental

Materials. *p*-Cymene.—A commercial sample of *p*-cymene was washed with $^1/_4$ portions of concentrated sulfuric acid until the acid layer was clear. It was then washed with 10% sodium hydroxide solution and then with distilled water, dried and fractionally distilled through a 2-ft. glass helices-packed column. The hydrocarbon was stored under a nitrogen atmosphere until used. Ultraviolet analysis indicated it to be >99% pure.

1,1'-Azodicyclohexanecarbonitrile.—This initiator was prepared by dissolving 65 g. of potassium cyanide and 65 g. of hydrazine sulfate in 1,250 ml. of water, adding 600 ml. of dioxane and 98 g. of cyclohexanone and stirring at room temperature for 41 hr. The crystals that formed were filtered and washed with 2 liters of water and 200 ml. of cold ethanol. The crystals were placed in a 4-liter beaker and 1000 ml. of absolute ethanol, saturated with hydrogen chloride gas, was added. The mixture was cooled in an ice bath and a solution of 157 g. of bromine in 1000 ml. of alcohol was added dropwise until the solution remained yellow. The alcohol solution was poured into 4 liters of ice water and the crystals that separated were filtered and recrystallized from 500 ml. of alcohol containing enough water to cause incipient crystallization. After two recrystallizations, 18 g. of white crystals, m.p. 113°, was obtained.

Anal. Calcd. for $C_{14}H_{20}N_4$: N, 22.9; C, 68.9; H, 8.2. Found: N, 21.7; C, 68.6, 68.7; H, 8.1, 8.2.

Potassium Persulfate.—This initiator was used to initiate the oxidation of *p*-cymene in an emulsion system. It has been shown that the rate of decomposition of potassium persulfate in water solution is not affected by the presence of dissolved oxygen[6]; the rate is, however, greatly affected by the presence of dissolved organic materials. Consequently, the rate constant for the decomposition of potas-

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[1] C. E. Sensemann and J. J. Stubbs, *Ind. Eng. Chem.*, **24**, 1184 (1932).

[2] R. C. Palmer and C. H. Bibb, U. S. Patent 2,302,466 (1941).

[3] E. J. Lorand and J. E. Reese, U. S. Patent 2,438,125 (1948).

[4] J. H. Helberger, A. von Rebay and H. Fettback, *Ber.*, **72**, 1643 (1939).

[5] H. Weber, *Angew. Chem.*, **62**, 450 (1950).

[6] P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

sium persulfate was determined in the same medium as that used for the oxidation but in the absence of oxygen. The method of analysis was that used by Bartlett and Cotman.[7]

The emulsifier solution consisted of 25 g. of Duponol C, 6 g. of potassium hydrogen phosphate, 61 ml. of 0.437 *N* NaOH, and water to 882 g. of Baker's C.P. potassium persulfate was dissolved in the emulsifier solution which was saturated with *p*-cymene and the rate of decomposition was followed at 71.1°.

The rate of decomposition is first order and the rate constant is 0.0127 min.$^{-1}$. It is noteworthy that the persulfate decomposes eight times faster in this medium than it does in water.

The rate studies in the emulsion system were carried out on a mixture consisting of 30 ml. of the Duponol C emulsifier containing the potassium persulfate and 20 ml. of *p*-cymene.

Rate Studies.—The apparatus used for measuring the rate of oxygen consumption consisted of a vessel of about 200-ml. capacity attached to a jacketed gas buret. Water, kept at 26.4°, was circulated through the jacket from a constant-temperature bath. The oxygen pressure was kept constant with the air of an electrolytic cell, containing an aqueous solution of hydrazine sulfate, which was controlled by a manometer attached to the buret. The contents of the reaction vessel were stirred during a run by a magnetic stirrer. Twenty grams of hydrocarbon, with dissolved initiator, was introduced and all air was displaced by oxygen. The vessel, immersed up to the neck in a constant-temperature oil bath, was attached, stirring was begun, and oxygen was passed through the equipment by suitable manipulation of stopcocks. The stopcocks were closed and readings were begun after temperature equilibrium was reached.

It was determined that the rate of oxygen uptake (ml. of oxygen per gram of *p*-cymene per minute) was independent of the total amount of *p*-cymene, showing that diffusion of oxygen was not a rate-controlling factor. The rate of oxygen consumption is readily converted into moles per 1000 gram per minute knowing the temperature of the gas buret.

The dependence of the rate of oxygen consumption upon *p*-cymene concentration was obtained by diluting the *p*-cymene with *t*-butylbenzene.

The rate of hydroperoxide formation was followed by oxidizing *p*-cymene, containing initiator, in a small tower oxidizer. Oxygen was passed through the hydrocarbon as a fine stream of bubbles from a sintered glass inlet tube. In the emulsion oxidation the mixture was agitated in a flask and oxygen was bubbled through as before.

Analyses. Hydroperoxide.—The total hydroperoxide content was determined by iodometric analysis. A sample of the oxidate was added to 20 ml. of 2-propanol containing 9% of acetic acid, and 10 ml. of 2-propanol saturated with sodium iodide was added. The mixture was boiled for 10 to 15 minutes, 5 ml. of water was added and the solution was titrated with standard thiosulfate. Peroxides such as bis-(*p*,α,α-trimethylbenzyl)-peroxide do not react under these conditions. Peroxides of this type will release iodine on reflux in glacial acetic acid containing sodium iodide.

The primary hydroperoxide was determined in the following manner: The hydroperoxide concentrate, obtained by removing volatiles under reduced pressure, was added to 50 ml. of water and stirred thoroughly. A little over an equivalent of ferrous sulfate solution was added slowly while the solution was blanketed with nitrogen. This converts the tertiary hydroperoxide to *p*-methylacetophenone and the primary hydroperoxide to cumaldehyde. The water suspension was extracted with ether. The ether was replaced by ethanol and an aliquot of the ethanol solution, sparged with nitrogen, was analyzed polarographically for cumaldehyde. The wave height was previously standardized with an authentic sample of cumaldehyde.

By-products.—By-products III and IV were determined by infrared and ultraviolet absorption, the absorption spectra being previously standardized with authentic samples.

Kinetics of Oxidation.—The kinetics of oxidation were obtained by two methods. In the first, which is a differential method, the initial rates of oxygen uptake by samples of *p*-cymene containing known amounts of initiator were measured. In the second, or integral method, a stream of oxygen was passed through a sample of *p*-cymene containing initiator, and the build-up of hydroperoxide concentration was followed by iodometric titrations. The differential method is completely free of interference by any product, and if the over-all rate constant obtained by the two methods agree with each other, one may infer that by-products do not interfere kinetically with the oxidation chain.

Under the conditions of these experiments the kinetic chain length is 5 to 13. At this low chain length it becomes possible to determine, by comparison of the integral and differential methods, whether or not hydroperoxide is produced in the termination reaction.

Differential Rate Study.—The data obtained from the differential rate study showed that, like many hydrocarbon oxidations, the rate of oxygen uptake is proportional to the product of the hydrocarbon concentration and the square root of the initiator concentration. This is consistent with the generally accepted scheme of oxidation in which termination by two *p*,α,α-trimethylbenzylperoxy radicals takes place.

$$\mathrm{PN{=}NP} \longrightarrow \mathrm{N_2 + 2P\cdot} \qquad k_1$$

$$\mathrm{P\cdot + O_2} \longrightarrow \mathrm{POO\cdot} \qquad k_2$$

$$\mathrm{POO\cdot + RH} \longrightarrow \mathrm{POOH + R\cdot} \qquad k_3$$

$$\mathrm{R\cdot + O_2} \longrightarrow \mathrm{ROO\cdot} \qquad k_4$$

$$\mathrm{ROO\cdot + RH} \longrightarrow \mathrm{ROOH + R\cdot} \qquad k_5$$

$$\mathrm{2ROO\cdot} \longrightarrow \text{products} \qquad k_6$$

For the azo initiators it is assumed that all the initiator radicals react with oxygen. The efficiency of initiation, α, is defined as the fraction of radicals arising from the dissociating initiator, which initiate oxidation chains. By the use of inhibitors the efficiencies of initiation of α,α'-azodiisobutyronitrile and benzoyl peroxide were each found to be 0.50 in the oxidation of tetralin.[8]

The initiators used in this work were benzoyl peroxide, 1,1'-azodicyclohexanecarbonitrile, α,α'-azodiisobutyronitrile and, in an emulsion system, potassium persulfate. The rate constants of these initiators are tabulated in Table I.

TABLE I

DISSOCIATION CONSTANTS OF INITIATORS

Initiator	k_1 (min.$^{-1}$)	Ref.
Benzoyl peroxide	$7.37 \times 10^{17} \exp(-33{,}300/RT)$	(9)
1,1'-Azodicyclohexanecarbonitrile	$1.12 \times 10^{21} \exp(-39{,}900/RT)$	(10)
α,α-Azodiisobutyronitrile	$1.84 \times 10^{17} \exp(-31{,}300/RT)$	(10)
Potassium persulfate	1.27×10^{-2} min.$^{-1}$ at 71.1°	Exptl.

Since the number of moles of oxygen reacting in unit time under steady state conditions are: $2k_1P$ with initiator radicals, $2\alpha k_1P$ in the terminating reaction, and $\gamma 2\alpha k_1P$ (where γ is the chain length) in the chain, then

$$-\frac{\mathrm{d(O_2)}}{\mathrm{d}t} = 2k_1P + 2\alpha k_1P + \surd 2\alpha k_1P \qquad (1)$$

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(7) P. D. Bartlett and J. D. Cotman, *J. Am. Chem. Soc.*, **71**, 1419 (1949).

(8) L. Bateman and A. L. Morris, *Trans. Faraday Soc.*, **48**, 1149 (1952).

(9) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

(10) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

But since

$$\nu = \frac{k_5}{k_6}\frac{(\mathrm{RH})}{(\mathrm{ROO\cdot})}$$

and $M = -\frac{\mathrm{d(O_2)}}{\mathrm{d}t} - k_1P$ (correction for N_2 evolution) where M is the measured rate of oxygen consumption, then

$$M = k_1P + 2\alpha k_1P + \sqrt{2\alpha k_1P}\,K(\mathrm{RH}) \qquad (2)$$

where $K = k_5/k_6^{1/2}$. Let $C^2 = 2\alpha$ and $x^2 = k_1P$; after substituting these into eq. 2, transposing and dividing by x^2 we get

$$\frac{M}{x^2} - 1 = C^2 + \frac{CK(\mathrm{RH})}{x} \qquad (3)$$

Since the values of M and x are known, if the left side of eq. 3 is plotted against the reciprocal of x, it is possible to obtain K as well as the efficiency of initiation from the slope and intercept.

If the initiator radicals do not react with oxygen and no gas is evolved by the initiator, instead of eq. 3 we get

$$\frac{M}{x^2} = C^2 + \frac{CK(\mathrm{RH})}{x} \qquad (4)$$

The data relating to the differential rate study for the various initiators are tabulated in Table II. The plots of eq. 3 or 4 are shown in Fig. 1 and the values of α and K obtained from these plots are presented in Table II.

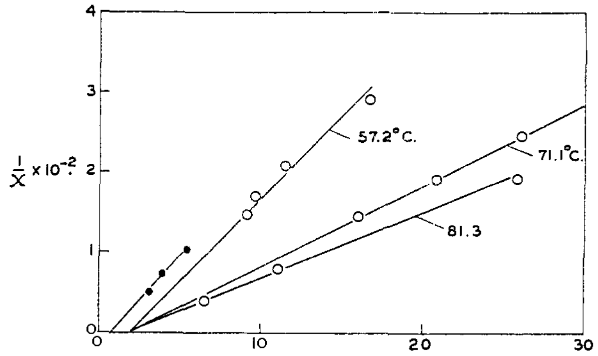


Fig. 1.—Plot of data from differential rate study: ○, α,α'-azodiisobutyronitrile initiator (eq. 3); ●, potassium persulfate initiator in emulsion (eq. 4).

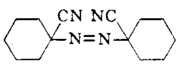
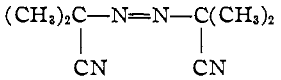
The rate of oxygen consumption was measured at 71.1°, using α,α'-azodiisobutyronitrile initiator, as a function of the concentration of p-cymene by dilution with t-butylbenzene. In order to plot the data, it was assumed that α, which from the data of Table II is 1 in pure p-cymene, remains at the value of 1 on lowering the p-cymene concentration; eq. 3 was then rearranged to give

$$\frac{M}{x} - 3x = 1.64\,K(\mathrm{RH}) \qquad (5)$$

By plotting the left side of eq. 5 against (RH) a straight line, of slope 1.64 K, should result providing that the efficiency of initiation remains 1. The data are given in Table III and the plot in Fig. 2. Figure 2 shows that although almost a linear relationship holds, the curve deviates from the ideal, represented by the dotted line. We interpret this deviation on the reasonable basis that the efficiency of initiation decreases as the hydrocarbon concentration decreases. Certainly the initiator radicals will have a higher probability of undergoing side reactions such as disproportionation, rather than hydrogen abstraction, as the concentration of p-cymene decreases. The efficiency of initiation was calculated for each hydrocarbon concentration by solving for C in eq. 3 using the

TABLE II

DATA RELATING TO DIFFERENTIAL RATE STUDY

Initiator	Temp., °C.	$x\cdot10^3$	$M\cdot10^4$	$K\cdot10^4$	α^a
$K_2S_2O_8$	71.1	9.56[b]	4.90		
		13.5	6.86		
		19.1	11.4	6.6	0.4
	71.1	0.766	1.138		
		1.041	1.568		
		1.510	2.28	9.8	1
 $(CH_3)_2\underset{\mathrm{CN}}{\underset{\vert}{C}}-N{=}N-\underset{\mathrm{CN}}{\underset{\vert}{C}}(CH_3)_2$	57.2	3.42	2.07		
		4.81	2.90		
		5.85	3.68		
		6.75	4.62	4.6	1
	71.1	6.94	8.19		
		4.10	4.56		
		5.24	5.98	7.6	1
	81.3	5.22	7.32		
		12.5	18.7		
		24.8	46.2	11.3	1
Mixed hydroperoxides of p-cymene	81.3	($k_1^{1/2} \times 0.301$)	1.79		

[a] α = Efficiency of initiation. [b] The concentration of potassium persulfate is its concentration in the aqueous phase. $x^2 = k_1P$; M = measured rate of oxygen uptake in mole/1000 g./min. $K = k_5/k_6^{1/2}$ mole$^{-1/2}$ 1000 g.$^{1/2}$ min.$^{-1/2}$.

TABLE III

RATE OF OXYGEN CONSUMPTION AS A FUNCTION OF p-CYMENE CONCENTRATION. TEMPERATURE 71.1°. INITIATOR α,α'-AZODIISOBUTYRONITRILE

(RH)	$x\cdot10^3$	$M \times 10^3$ (mole/1000 g./min.)	α
7.46	0.410	0.456	1
6.01	1.24	1.19	0.90
3.74	1.25	0.735	.61
2.24	1.25	0.463	.39

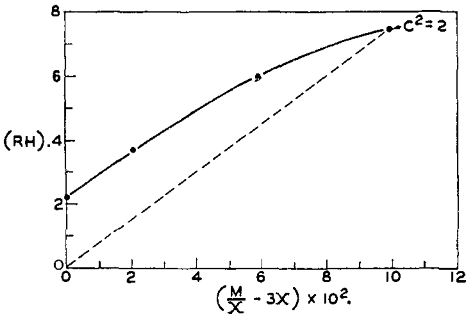


Fig. 2.—Rate of oxygen consumption as a function of p-cymene concentration at 71.1°: Dotted line represents ideal slope if efficiency of initiation remains 1 at all p-cymene concentrations.

value of K previously determined. The values of α are included in Table III; they are such that $\alpha \cong 0.15\,(\mathrm{RH})$.

In this work, the efficiency of initiation of α,α'-azodiisobutyronitrile was kept at 1 by the use of pure p-cymene and by keeping conversions to hydroperoxide at low values.

The data relating to benzoyl peroxide are not presented. Although the data did fit eq. 5 the intercept had a negative value. This is not surprising since the rate of decomposition of peroxide is very dependent upon environment. The agreement of K at 71.1° among the other three initiators is good, particularly since a small error in k_1 will produce a larger error in K. The somewhat larger value of K determined with 1,1'-azodicyclohexanecarbonitrile may be caused by the value of k_1 being a little low; however, this initiator also decomposes a little too slowly at this temperature to plot eq. 5 accurately.

The low initiating efficiency of potassium persulfate is related to the fact that the initiator radicals originate in the aqueous phase and must diffuse into the organic phase before oxidation chains can be initiated; doubtless, the interfacial area is a factor which affects the value of α. The agreement of the rate constant K with that obtained in the homogeneous system implies that an emulsion system merely changes the source of the initiator radicals and the oxidation chains proceed in the hydrocarbon phase exactly as they do in a homogeneous system. This is important in interpreting the autoxidation of p-cymene in which we have found that the presence of water changes the nature of the initiation step.

The Arrhenius plot of the rate constant obtained with α,α'-azodiisobutyronitrile at 57.2, 71.1 and 81.3° is given in Fig. 3, from which is obtained

$$K = \frac{k_5}{k_6^{1/2}} = 2.15 \times 10^3 \exp(-8600/RT) \qquad (6)$$

The activation energy for the termination of oxidation chains by two peroxy radicals, determined by intermittent photochemical initiation, has been found to be practically independent of the type of organic radical to which the oxygen is attached.[11] The value is less than 5 kcal. and probably 2 to 4 kcal. per mole. If we assume that E_6 is in the same range then E_5 = 10 to 11 kcal.

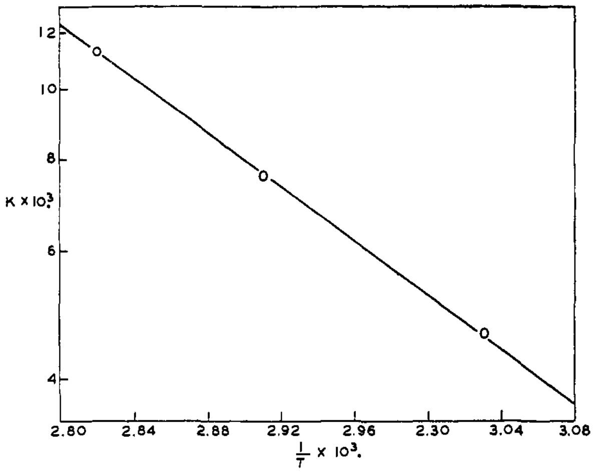


Fig. 3.—Temperature dependence of rate constant.

Integral Rate Study.—p-Cymene was oxidized at 71° in a homogeneous system with α,α -azodiisobutyronitrile initiator as well as in an emulsion system with potassium persulfate initiator. The data are plotted in Fig. 4. It should be remembered that the hydroperoxide concentration plotted is total hydroperoxide; the kinetic equations require the p,α,α-trimethylbenzyl hydroperoxide concentration, which was, by analysis, 86% of the total hydroperoxide. The data relative to the emulsion oxidation are significant. The oxidation proceeds at a much faster rate than theoretical and continues after all the initiator is used up. Since the differential method showed that the presence of an aqueous phase did not interfere with the oxidation chains then one or both of the hydroperoxides formed must be initiating oxidation by virtue of the presence of the aqueous phase.

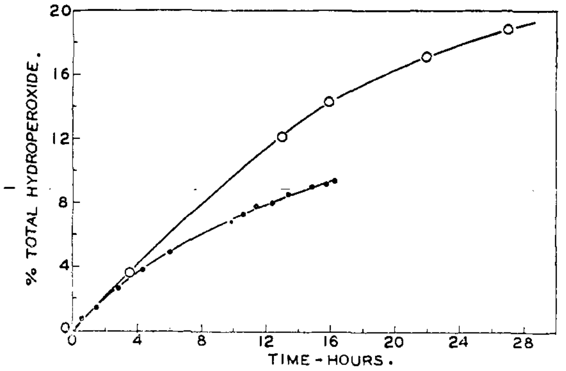


Fig. 4.—Oxidation of p-cymene at 71°: ●, α,α'-azodiisobutyronitrile initiator $P_0 = 4.58 \times 10^{-2}\,M$; ○, potassium persulfate initiator in an emulsion system $P_0 = 0.10\,M$.

Application of the steady state approximation to the oxidation scheme will give different expressions for the rate of hydroperoxide formation depending on whether or not hydroperoxide is formed in the termination step.

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[11] L. Bateman and G. Gee, *Proc. Roy. Soc.* (*London*), **A195**, 391 (1948).

A. No hydroperoxide in termination

$$\frac{\mathrm{d(ROOH)}}{\mathrm{d(P)}} = -2\surd \tag{7}$$

where P is PN=NP, but because

$$\surd = \frac{K(\mathrm{RH})}{\sqrt{2k_1P}}$$

and (RH) = $(\mathrm{RH})_0$ − 1.26 (ROOH) and letting (ROOH) = y, $x = 2k_1P = 2k_1P_0e^{-k_1t}$ eq. 7 becomes

$$2k_1\frac{\mathrm{d}y}{\mathrm{d}x} = -\frac{2K(\mathrm{RH})_0}{x^{1/2}} + \frac{2.52\,Ky}{x^{1/2}} \tag{8}$$

$$\text{Let } A = -\frac{1.26\,K}{k_1} \text{ and } B = \frac{K(\mathrm{RH})_0}{k_1}$$

then we have the first order differential equation

$$\frac{\mathrm{d}y}{\mathrm{d}x} + Ax^{-1/2}y + Bx^{-1/2} = 0 \tag{9}$$

Integration of this, using the integrating factor $e^{2Ax^{1/2}}$, gives

$$y + B/A = C_1e^{-2Ay^{1/2}} \tag{10}$$

The constant C_1 is easily evaluated knowing that the hydroperoxide concentration levels out at 0.68 M at $t = \infty$, *i.e.*, when all the initiator is used up. Evaluating the constants and rearranging gives the equation

$$\ln\,[5.92 - (\mathrm{ROOH})] = \ln 5.24 - 0.11e^{-k_1t/2} \tag{11}$$

B. Hydroperoxide in termination

$$\frac{\mathrm{d(ROOH)}}{\mathrm{d}(P)} = -2\surd - 1 \tag{12}$$

Using the same constants and substitutions as in the last derivation gives the first order differential equation

$$\frac{\mathrm{d}y}{\mathrm{d}x} + Ax^{-1/2}y + Bx^{-1/2} + \frac{1}{2k_1} = 0 \tag{13}$$

Integration of this, using the integrating factor $e^{2Ax^{1/2}}$, gives

$$y + \frac{B}{A} + \frac{x^{1/2}}{2k_1A} - \frac{1}{4k_1A^2} = C_2e^{-2Ax^{1/2}} \tag{14}$$

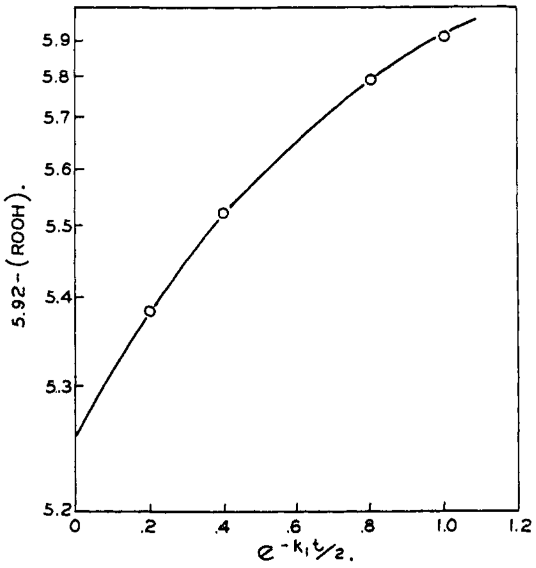

Fig. 5.—No hydroperoxide in termination reaction (eq. 11).

The constant C_2 is easily evaluated as before, giving

$$(\mathrm{ROOH}) = 13.82 - \frac{x^{1/2}}{2k_1A} - 13.1\,e^{-2Ax^{1/2}} \tag{15}$$

The last term of this equation is almost constant over the range of conversion in these experiments so that eq. 15 becomes

$$(\mathrm{ROOH}) \cong 0.68 - \frac{(2k_1P_0)^{1/2}}{2k_1A}\,e^{-k_1t/2} \tag{16}$$

Equations 11 and 16 are plotted in Figs. 5 and 6, respectively. The data evidently are in better agreement with eq. 16 than eq. 11 which is evidence for the formation of hydroperoxide in the termination reaction.

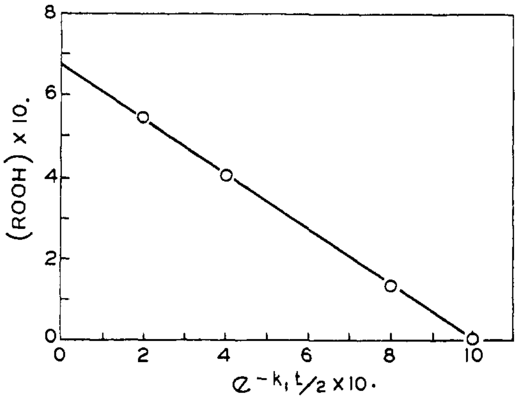

Fig. 6.—Hydroperoxide in termination reaction (eq. 16).

The over-all rate constant K can be evaluated from the slope of the plot of eq. 16 and the known values of k_1 and P_0. Such an evaluation gives K = 9.5 × 10^{-3}. This is in fair agreement with the value of 7.6 × 10^{-3} obtained by the differential method.

By-Product Formation.—The production of ketone, alcohol and primary hydroperoxide was investigated at 71.1° by dissolving known amounts of α,α'-azodiisobutyronitrile in samples of *p*-cymene which were then oxidized until all the initiator was used up, as evidenced by the levelling off of the rate of hydroperoxide formation. Formaldehyde was detected in the effluent gas. The oxidation products were concentrated by distilling off the hydrocarbon at 40° and 1–2 mm. pressure. The concentrated samples were analyzed with the results shown in Table IV. It is important to note that only a very minor proportion of these products appear through the thermal decomposition of the hydroperoxide which is quite stable at these temperatures.

***p*-Isopropylbenzyl Hydroperoxide (II).**—This primary hydroperoxide is the most abundant by-product in the oxidation. It can be isolated from the tertiary hydroperoxide in 80 to 90% purity by chromatographic absorption on alumina. Its identification relies on the fact that reduction with catalytic amounts of ferrous sulfate gives cumaldehyde

$$(\mathrm{CH_3})_2\mathrm{CH\text{-}C_6H_4\text{-}CH_2OOH} \longrightarrow (\mathrm{CH_3})_2\mathrm{CH\text{-}C_6H_4CHO} + \mathrm{H_2O}$$

a reaction which was utilized to analyze for the hydroperoxide. The data of Table IV show that

TABLE IV

PRODUCTS IN THE OXIDATION OF *p*-CYMENE

Temp., °C.	$(AZ)^a$ × 10^3	Total Hydroperoxide Initial	Final	(R'-OOH)^b	$\frac{(\text{R'OOH})^b}{(\text{ROOH})^c}$	(ROH) × 10^2	AP^d × 10^3
70	5.2	0	0.49	0.067	0.14	2.4	..
70	10.4	0	.53	.072	.14	3.2	..
70	20.8	0	.65	.12	.15	6.5	..
70	21.3	0.45	1.1	.18	.16	15.0	..
70	10.4	0	0.58	.085	.15	3.9	5.2
83	10.4	0	.60	.097	.16	4.5	6.5
83	20.8	0	.75	.12	.16	8.6	11.1
60	10.4	0	.47	.08	.17	4.5	8.2
60	20.8	0	.65	.12	.18	7.5	9.9

[a] α,α'-Azodiisobutyronitrile. [b] R' is $(CH_3)_2CH-C_6H_4-CH_2-$. [c] R is $H_3C-C_6H_4-C(CH_3)_2$. [d] $H_3C-C_6H_4-COCH_3$.

the total hydroperoxide contains about 14% primary hydroperoxide over a temperature range of 60 to 83° and a conversion range of 8 to 18%. The most plausible mechanism whereby this hydroperoxide is formed appears to be that of a co-oxidation, in which a tertiary peroxy radical (*p*,α,α-trimethylbenzylperoxy radical) occasionally abstracts a hydrogen atom from the methyl group. The benzylperoxy radical then abstracts a tertiary hydrogen

$$\text{ROO}\cdot + \text{R'H} \longrightarrow \text{ROOH} + \text{R'}\cdot \qquad k_7$$

$$\text{R'}\cdot + \text{O}_2 \longrightarrow \text{R'OO}\cdot \qquad k_8$$

$$\text{R'OO}\cdot + \text{RH} \longrightarrow \text{R'OOH} + \text{R}\cdot \qquad k_9$$

With such a co-oxidation mechanism the rate of formation of II will be given by

$$\frac{\text{d(R'OOH)}}{\text{d}t} = \frac{k_7}{k_5}\frac{\text{d(ROOH)}}{\text{d}t} \qquad (17)$$

In other words, if k_7 and k_5 have approximately the same temperature coefficients, the primary hydroperoxide will be a constant proportion of the tertiary hydroperoxide. The data of Table IV support this and indicate that $k_7/k_5 \cong 0.16$, so that the reactivity of the *p*,α,α-trimethylbenzylperoxy radical toward the primary hydrogen is 0.16 of its reactivity toward the tertiary hydrogen.[12]

An interesting confirmation of the formation of this primary hydroperoxide by a co-oxidation is presented in the next section.

8-*p*-Cymenol (IV).—The production of this alcohol is definitely associated with the hydroperoxide concentration (compare Run No. 4, Table IV) and doubtless arises by radical attack on the hydroperoxide. The attacking radicals could not be *p*,α,α-trimethylbenzylperoxy radicals since, as shown later, the generation of such peroxy radicals in the presence of the hydroperoxide and an inert solvent does not lead to alcohol; nor could the attacking radicals be initiator radicals since such a process would not lead to the correct kinetic dependence of alcohol concentration upon hydroperoxide concentration. The postulated radical transfer mechanism is

$$\text{R}\cdot + \text{ROOH} \longrightarrow \text{ROH} + \text{RO}\cdot \qquad k_{10}$$

$$\text{RO}\cdot + \text{RH} \longrightarrow \text{ROH} + \text{R}\cdot \qquad k_{11}$$

If this is true, then the rate of formation of IV must be given by

$$\frac{\text{d(ROH)}}{\text{d}t} = 2k_{10}\,(\text{R}\cdot)(\text{ROOH}) \qquad (18)$$

Applying the steady-state approximation to the chain oxidation the concentration of 8-*p*-cymyl radicals is given by

$$(\text{R}\cdot) = \frac{2k_1\alpha\text{P} + k_5(\text{RO}_2\cdot)(\text{RH})}{k_4(\text{O}_2)} \qquad (19)$$

$$\therefore (\text{ROH})_t = \frac{C}{\sqrt{k_t} + (\text{O}_2)}\,[(\text{ROOH})_t^2 - (\text{ROOH})^2]_0 \quad (20)$$

where subscripts *t* and 0 refer to final and initial concentrations, respectively, and *C* is a constant.

In Fig. 7 the data from Table IV for 70° have been plotted according to eq. 20. The data fit the postulated mechanism quite well. For comparison, a plot of alcohol concentration *versus* the concentration of hydroperoxide formed is shown. Equation 20 implies that an increase in the oxygen pressure will decrease the production of alcohol. If the oxygen pressure is decreased sufficiently a termination reaction of the following type can take place

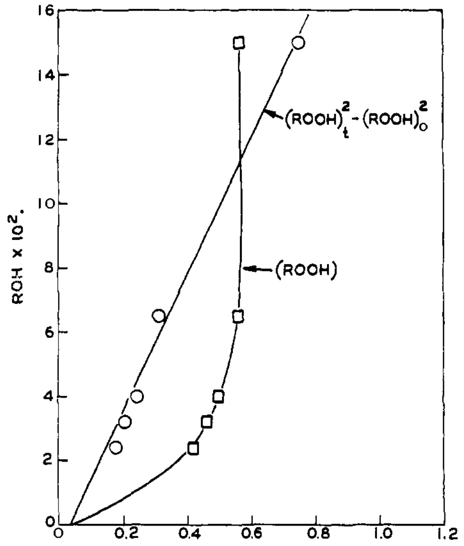

Fig. 7.—Dependence of 8-*p*-cymenol formation on tertiary hydroperoxide concentration at 70°.

$$\text{R}\cdot + \text{ROO}\cdot \longrightarrow \text{ROOR}$$

However, the radical transfer reaction can, apparently, take place with ease, so that this termination reaction may not take hold until quite low oxygen pressures are reached. As the oxygen pressure is lowered, the net effect may be that the kinetics do not change but alcohol production increases. This factor has not been recognized in the literature on oxidation kinetics. It is interesting to note that the methyl radical, in contrast with the 8-*p*-cymyl radical, breaks the oxygen–hydrogen rather than the oxygen–oxygen bond.[13]

Termination Reaction.—The nature of the termination reaction in oxidations of this kind has only recently been investigated. Boozer and co-

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[12] The relative reactivity of the benzylperoxy radical may be of the same order of magnitude. However, the concentration of this radical is so low that no oxidation chain involving the primary hydrogen is noticeable.

[13] Unpublished results from this Laboratory.

workers,[14] using cumene deuteriated in the methyl positions, showed that the chain-terminating step probably involves scission of a β-carbon–hydrogen bond and suggested the reaction

$$2C_6H_5C(CH_3)_2OO\cdot \longrightarrow C_6H_5C(CH_3)_2OOH + C_6H_5C(CH_3){=}CH_2 + O_2$$

Russell,[15] on the basis that the yield of hydroperoxide, based on the oxygen consumed, remained high in spite of low chain length (97, 98 and 96% yields at 19, 25 and 10 chain lengths, respectively) adduced this as supporting evidence for Boozer's termination reaction. It should be pointed out, however, that at a chain length of 10, if the termination reaction produces one mole of hydroperoxide, the yield should be 89 mole %.

Under the conditions of the oxidations reported here the p,α-dimethylstyrene would be easily detected. Since none was detected, Boozer's termination reaction is unlikely. However, his evidence that scission of the β-carbon–hydrogen bond is involved, places this requirement on any proposed reaction.

p-Methylacetophenone is postulated to arise in the termination reaction of the oxidation chain, which consists of the disproportionation of two p,α,α-trimethylbenzylperoxy radicals. The ketone has a sufficient concentration to be detected under the conditions of these experiments because of the low chain length. A radical transfer reaction which would give rise to the ketone can be written

$$p\text{-}CH_3\text{–}C_6H_4C(CH_3)_2OH + ROO\cdot \longrightarrow p\text{-}CH_3\text{–}C_6H_4C(CH_3)_2O\cdot + ROOH$$

$$p\text{-}CH_3\text{–}C_6H_4C(CH_3)_2O\cdot \longrightarrow \cdot CH_3 + p\text{-}CH_3C_6H_4COCH_3$$

This, however, seems unlikely—first because of the low concentration of alcohol, and secondly because of the known proclivity of the alkoxy radical to abstract tertiary hydrogen thereby regenerating the alcohol.

The following chemical evidence lends support to the postulate that the ketone arises in the termination reaction. When diacetyl peroxide is added slowly to a heated solution of α,α-dimethylbenzyl hydroperoxide in an aromatic hydrocarbon with a side chain capable of reacting readily with radicals (*e.g.*, ethylbenzene), one of the products is unsymmetrical peroxide; no symmetrical peroxide is detected.[16] Evidence has been obtained that such a radical attack on the hydroperoxide involves abstraction of hydrogen from the hydroperoxy group to generate a peroxy radical.[13] The formation of unsymmetrical peroxide is then readily explained by the following sequence of reactions

$$C_6H_5C(CH_3)_2OOH + \cdot CH_3 \longrightarrow CH_4 + C_6H_5C(CH_3)_2OO\cdot$$

$$C_6H_5CH_2CH_3 + \begin{cases} \cdot CH_3 \\ \text{or} \\ C_6H_5C(CH_3)_2OO\cdot \end{cases} \longrightarrow C_6H_5\underset{\cdot}{C}HCH_3 + \begin{cases} CH_4 \\ \text{or} \\ C_6H_5C(CH_3)_2OOH \end{cases}$$

$$C_6H_5\underset{\cdot}{C}HCH_3 + C_6H_5C(CH_3)_2OO\cdot \longrightarrow C_6H_5C(CH_3)_2OOCH(CH_3)C_6H_5$$

On the other hand, if diacetyl peroxide is added slowly to a heated solution of cumene hydroperoxide in an unreactive solvent like benzene, the only decomposition product of the hydroperoxide is acetophenone.[18] Since peroxy radicals must have been generated, and kinetic studies of oxidation definitely show that two peroxy radicals interact, then the termination must lead to acetophenone.

The data of Table I show that from 0.5 to 0.8 mole of *p*-methylacetophenone per mole of initiator was detected. Accuracy is difficult because of the low concentration of ketone. However, the data are consistent with a termination reaction in which one mole of *p*-methylacetophenone is produced for each pair of peroxy radicals. This fact, together with the kinetic evidence that a mole of hydroperoxide is produced in the termination reaction suggest

$$2H_3CC_6H_4C(CH_3)_2OO\cdot \longrightarrow H_3CC_6H_4C(CH_3)_2OOH + H_3CC_6H_4COCH_3 + CH_2O$$

The reaction can be rationalized on the basis that one peroxy radical abstracts a hydrogen from the α-methyl group of the other (perhaps through the agency of an unstable diperoxy compound). The resulting diradical stabilizes itself by decomposing to acetophenone and formaldehyde.

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[14] C. E. Boozer, B. W. Ponder, J. C. Trisler and C. E. Wightman III, *J. Am. Chem. Soc.*, **78**, 1506 (1956).

[15] G. A. Russell, *ibid.*, **79**, 3871 (1957).

[16] M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 753 (1950).