methyl-α-D-galactose; X-ray powder diffraction data[14,15] (identical with those of authentic 3-*O*-methyl-α-D-galactose): 8.85m, 6.93s, 5.74s, 4.98w, 4.56vs, 3.90vw, 3.76s, 3.62vw, 3.49m, 3.39s, 3.31m, 2.88w, 2.83w, 2.66m, 2.41w, 2.32w, 2.26w.

Tetra-*O*-acetyl-*O*-*p*-toluenesulfonyl-β-D-galactopyranose from Isomer A.—The general experimental procedure followed was that of Helferich and Klein.[16] An amount of 500 mg. of isomer A was treated with 200 mg. of *p*-toluenesulfonyl chloride in 3 ml. of dry pyridine. After 24 hr., the mixture was poured into ice and water. The precipitate that formed was filtered and dissolved in ethanol. Crystals appeared upon concentration of the solution; yield 500 mg., m.p. 153–155°. The product was recrystallized from an acetone–ether–petroleum ether (b.p. 30–60°) mixture; m.p. 154–155°, $[\alpha]^{25}\text{D}$ +43° (*c* 3, chloroform); X-ray powder diffraction data[14,15]: 10.52s, 8.44vw, 5.72m, 5.31w, 4.76w, 4.48m, 4.19vw, 4.00vw, 3.53w, 3.45m, 3.14w.

Anal. Calcd. for $C_{21}H_{26}O_{12}S$: C, 50.19; H, 5.21; S, 6.38. Found: C, 50.10; H, 5.30; S, 6.33.

Similar treatment of isomer B with *p*-toluenesulfonyl chloride and pyridine failed to yield a crystalline product.

The *p*-toluenesulfonate (150 mg.) from isomer A yielded a negligible precipitate (5 mg.) of sodium *p*-toluenesulfonate on heating at 100° with 70 mg. (1.5 molar ratio) of sodium iodide in 3 ml. of acetonylacetone for 48 hr. A like experiment utilizing 400 mg. of tetra-*O*-acetyl-6-*O*-*p*-toluenesulfonyl-β-D-glucopyranose, 180 mg. of sodium iodide and 8 ml. of acetonylacetone yielded 141.2 mg. (88%) of sodium *p*-toluenesulfonate.

Methyl Tri-*O*-acetyl-*O*-*p*-toluenesulfonyl-β-D-galactopyranoside from Isomer A.—The general procedure of Haworth, Jackson and Smith[7] was followed. An amount of 500 mg. of tetra-*O*-acetyl-*O*-*p*-toluenesulfonyl-β-D-galactopyranose (from isomer A) was treated for 1 hr. with 5 ml. of a solution containing 30% hydrogen bromide in anhydrous acetic acid:acetic anhydride (1:1 by vol.). Chloroform was then added to the solution and the extract was washed four times with water and dried over sodium sulfate. The dried solution was concentrated under reduced pressure, and the resulting sirup was dissolved in 25 ml. of dry methanol, and 10 g. of freshly prepared silver carbonate was added. The mixture was shaken for 5.5 hr. whereupon it was filtered, and the filtrate was concentrated under reduced pressure. Crystals of the methyl tri-*O*-acetyl-*O*-*p*-toluenesulfonyl-β-D-galactopyranoside appeared during the concentration; yield 240 mg., m.p. 129–130°, $[\alpha]^{25}\text{D}$ +24° (*c* 3, chloroform); X-ray powder diffraction data[14,15]: 9.77vs, 6.20w, 5.84m, 5.24s, 4.88m, 4.46w, 4.23w, 4.01s, 3.79vw, 3.65m, 3.51m, 3.37m.

Anal. Calcd. for $C_{20}H_{26}O_{11}S$: C, 50.62; H, 5.52; S, 6.77. Found: C, 50.42; H, 5.71; S, 6.67.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Deuterium-isotope Effects in the Autoxidation of Aralkyl Hydrocarbons. Mechanism of the Interaction of Peroxy Radicals[1]

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α-Phenethylperoxy radicals interact to form non-radical products 1.9 times as readily as their α-deutero derivatives. This is taken as evidence that the termination reaction is $2C_6H_5CH(D)CH_3COO\cdot \rightarrow C_6H_5COCH_3 + C_6H_5CH(D)OH(D)\text{-}CH_3 + O_2$. Yields of hydroperoxide and acetophenone produced in the autoxidation of ethylbenzene at various kinetic chain lengths are consistent with the indicated termination reaction. Evidence is presented that this reaction involves a cyclic transition state and excluding an alternate process proceeding by the formation and disproportionation of alkoxy radicals. The deuterium-isotope effect in the reaction of a peroxy radical with cumene and α-*d*-cumene is $k_H/k_D = 5.5$. The magnitudes of deuterium-isotope effects in the reactions of atoms and radicals with carbon–hydrogen and carbon–deuterium bonds are considered. Reactivities of the attacking atoms or radicals and polar effects in the reaction are discussed.

Despite the fact that the autoxidation of hydrocarbons has been studied intensively,[2] evidence is lacking as to the mechanism and products of the reaction wherein two peroxy radicals are converted to non-radical products. We have, therefore, investigated the products of this termination reaction in the oxidation of ethylbenzene and have demonstrated its detailed mechanism by a study of deuterium-isotope effects. The deuterium-isotope effect in the reaction of a peroxy radical with α-*d*-cumene has been measured, and its magnitude confirms our earlier conclusions in regard to the extent of bond-breaking in the transition state for this reaction.

Results

Autoxidations of cumene, ethylbenzene and various deuterated derivatives were performed at 60° in the liquid phase in the presence of α,α′-azodiisobutyronitrile (AIBN). The rates of oxidation were independent of the oxygen pressure over the range 200–760 mm. indicating that only peroxy radicals were involved in the termination reaction.[2] The kinetics of the reaction under these conditions indicate that the following sequence of events is involved.

$$\text{AIBN} \xrightarrow{k_d} (CH_3)_2\dot{C}CN \xrightarrow{O_2} \text{ROO}\cdot \ (\text{Rate} = R_i)$$

$$\text{ROO}\cdot + \text{RH} \xrightarrow{k_3} \text{ROOH} + \text{R}\cdot$$

$$\text{R}\cdot + O_2 \xrightarrow{\text{fast}} \text{ROO}\cdot$$

$$2\text{ROO}\cdot \xrightarrow{k_6} \text{non-radical products} + O_2$$

Under steady-state conditions the rate of oxygen consumption is calculated to be

$$-d[O_2]/dt = k_3[\text{RH}](R_i)^{1/2}/(2k_6)^{1/2} + R_i/2 \quad (1)$$

The rate of initiation, R_i, is equal to $2k_de[\text{AIBN}]^{1/2}$ where *e* represents the fraction of catalyst molecules that produce two free radicals. In Table I the rates of oxidation of cumene and ethylbenzene are presented as a function of hydrocarbon concentration, AIBN concentration and oxygen pressure. The data of column 6 indicate that (1) is obeyed and the rate of oxidation is independent of

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[1] Directive Effects in Aliphatic Substitutions. IX. Presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, September, 1956.

[2] J. L. Bolland, *Quart. Revs.*, **3**, 1 (1949); L. Bateman, *ibid.*, **8**, 147 (1954).

TABLE I

OXIDATION OF CUMENE AND ETHYLBENZENE AT 60.0°

Hydrocarbon	[RH], mole l.$^{-1}$	[AIBN], mole l.$^{-1}$	O_2 pressure, mm.	Rate of oxygen absorption,[a] mole l.$^{-1}$ sec.$^{-1}$ $\times 10^5$	(Rate—$R_i/2$)/[RH] [AIBN]$^{1/2}$ $\times 10^6$
Cumene	6.90	0.100	750	2.58	1.16
Cumene	6.90	.100	500	2.58	1.16
Cumene	6.90	.100	200	2.60	1.17
Cumene	6.90	.200	750	3.66	1.14
Cumene	6.90	.050	750	1.75	1.13
Cumene	4.00[b]	.100	750	1.53	1.15
Ethylbenzene	7.82	.100	750	0.58	0.207
Ethylbenzene	7.82	.100	500	.56	.199
Ethylbenzene	7.82	.100	200	.60	.214
Ethylbenzene	7.82	.150	750	.74	.211
Ethylbenzene	7.82	.200	750	.85	.203

[a] Corrected for nitrogen evolved in decomposition of AIBN. [b] Chlorobenzene used as an inert diluent.

the oxygen pressure and proportional to $k(R_i)^{1/2} + R_i/2$. The value of R_i used in the above calculations for 0.1 *M* AIBN has been taken as 1.38×10^{-6} mole l.$^{-1}$ sec.$^{-1}$ based on a value of 1.15×10^{-5} sec.$^{-1}$ for k_d at 60° and 0.60 for *e*. The value of k_d in an aromatic solvent was selected from a compilation of various literature references[3,4] while the value of *e* appears established from the work of Hammond, Sen and Boozer.[5]

Having thus established the course of the reaction, the deuterium-isotope effect in the slow propagation step (k_3) was investigated. α-Deuterocumene was prepared by the reaction of deuterium chloride with α,α-dimethylbenzylpotassium. Analysis by high resolution nuclear magnetic resonance spectroscopy indicated that 58.4% of the tertiary hydrogen atoms of cumene had been replaced by deuterium atoms. Aromatic deuterium atoms were present (0.24 atom/molecule) in the form of d_1-, d_2- and d_3-cumenes, but analysis by high resolution infrared absorption indicated that less than 3% of the molecules contained a β-deuterium atom.

This sample of α-*d*-cumene oxidized considerably less rapidly than cumene, even though 41.6% of the molecules had an α-hydrogen atom. Since, in the presence of 0.1 *M* AIBN, cumene was oxidized at a rate of 2.58×10^{-5} mole l.$^{-1}$ sec.$^{-1}$ and α-*d*-cumene (58.4% pure) at a rate of 1.38×10^{-5} mole l.$^{-1}$ sec.$^{-1}$, it can be calculated that in the slow propagation reaction the deuterium-isotope effect is $k_H/k_D = 5.5$. Based on possible errors in analysis, the isotope effect might be as low as 4.5 and as high as 7.2.

$$\mathrm{ROO\cdot} + \mathrm{RH} \xrightarrow{k_H} \mathrm{ROOH} + \mathrm{R\cdot}$$

$$\mathrm{ROO\cdot} + \mathrm{RD} \xrightarrow{k_D} \mathrm{ROOD} + \mathrm{R\cdot}$$

$$k_H/k_D = 5.5$$

There can be no deuterium-isotope effect in the termination reaction in the oxidation of α-*d*-cumene since both cumene and α-*d*-cumene yield the same α,α-dimethylbenzylperoxy radical.

The data of Table II demonstrate that the yields of hydroperoxide in the autoxidations of cumene and α-*d*-cumene were essentially quantitative irrespective of kinetic chain length (molecules oxidized per initiating fragment). This supports the conclusion of Boozer[6] that the interaction of cumylperoxy radicals should be formulated

$$2C_6H_5C(CH_3)_2OO\cdot \longrightarrow C_6H_5C(CH_3)_2OOH + C_6H_5CCH_3{=}CH_2 + O_2$$

The yield of hydroperoxide in the oxidation of ethylbenzene was neither quantitative nor independent of kinetic chain lengths (see Table II). The yield of hydroperoxide decreased with decreasing kinetic chain length suggesting that oxygen-containing non-peroxidic products were formed in the termination reaction. In the oxidation of ethylbenzene, under the conditions specified in Table II, an average of 4.2 molecules of oxygen were absorbed per initiating radical. If the termination reaction between two α-phenethylperoxy radical yields one molecule of oxygen and one molecule of oxygen combined in non-peroxidic products, the theoretical yield of hydroperoxide, based on oxygen absorbed, is 88%. The observed yield was 85%. In the oxidation of d_4-ethylbenzene (prepared by the addition of deuterium to phenylacetylene) the kinetic chain length was only 2.0 and the yield of hydroperoxide was 65%. The theoretical yield calculated on the basis of a termination reaction yielding a molecule of oxygen and a molecule of oxygen combined in non-peroxidic products is 75%.

A possible termination reaction, consistent with the above observations, is

$$2C_6H_5CHCH_3OO\cdot \longrightarrow C_6H_5COCH_3 + C_6H_5CHOHCH_3 + O_2$$

Hydroxylic and ketonic products are generally formed in small amounts in low-temperature autoxidations, but these products may represent only the decomposition of some of the initially formed hydroperoxide. However, the formation of exactly one mole of acetophenone per two kinetic chains would give considerable support to the above termination reaction. The oxidates of α-d_1-ethyl-

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(3) The following data were used: F. M. Lewis and M. S. Matheson, THIS JOURNAL, **71**, 747 (1949): 80°, xylene, 1.53×10^{-4} sec.$^{-1}$; 70°, xylene, 4.16×10^{-5} (unpublished); 90°, xylene, 5.0×10^{-4} (unpublished): L. M. Arnett, *ibid.*, **74**, 2027 (1952), 77°, xylene, 9.5×10^{-5}; 82°, xylene, 1.45×10^{-4}; M. Talat-Erben and S. Bywater, *ibid.*, **77**, 3712 (1955), 70°, toluene, 4.0×10^{-5}; 80.4°, toluene, 1.55×10^{-4}; 90°, toluene, 4.86×10^{-4}; 100°, toluene, 1.6×10^{-3}; G. S. Hammond, J. N. Sen and C. E. Boozer, ref. 5, 62.5°, benzene, 1.42×10^{-5}; 62.5°, chlorobenzene, 1.54×10^{-5}; C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949), 69.8°, toluene, 3.8×10^{-5}; 80.2°, toluene, 1.66×10^{-4}; G. A. Russell, *ibid.*, **78**, 1044 (1956), 80°, cumene, 1.67×10^{-4}: J. C. Roy, J. R. Nash, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **78**, 519 (1956), 80°, chlorobenzene, 1.50×10^{-4}: J. W. Breitenbach and A. Schindler, *Monatsh. Chem.*, **83**, 724 (1952), 50°, styrene, 2.97×10^{-6}; 70°, styrene, 4.72×10^{-5}. These data yield the expression $k_d = 1.78 \times 10^{15} \exp(-31{,}300/RT)$ with serious deviation for the 82° point of Arnett only. Interestingly, the decomposition rates of C. E. H. Bawn and S. H. Mellish [*Trans. Faraday Soc.*, **47**, 1216 (1951)], obtained by use of diphenylpicrylhydrazyl, which supposedly is a measure of k_de,[4,5] are in excellent agreement with this rate expression over the range 40–70°. Decomposition rate constants in nitrobenzene solution are consistently higher. The data of Hammond, ref. 5, 1.79×10^{-5} sec.$^{-1}$ at 62.5°, and of K. Ziegler, W. Deparade and W. Meye [*Ann.*, **567**, 141 (1950)], 2.0×10^{-4} at 80°, 2.25×10^{-3} at 100°, give the expression $k_d = 4.9 \times 10^{15} \exp(-31{,}200/RT)$.

(4) C. Walling, *J. Polymer Sci.*, **14**, 214 (1954); J. C. Bevington, *Nature*, **175**, 477 (1955), *J. Chem. Soc.*, 1127 (1956).

(5) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

(6) C. E. Boozer, B. W. Ponder, J. C. Trisler and C. E. Wrightman, *ibid.*, **78**, 1506 (1956).

TABLE II

OXIDATION OF ARALKYL HYDROCARBONS AT 60°, 0.1 *M* AIBN

Hydrocarbon (mole)	[RH], mole l.$^{-1}$	Rate[a] mole l.$^{-1}$ sec.$^{-1}$ × 10^5	Kinetic chain length[b]	Oxygen absorbed[a] mole × 10^3	Hydroperoxide found Iodimetric[c]	Hydroperoxide found Stannous chloride[d]	% Oxygen found as hydroperoxide[e]
Cumene (0.1380)	6.90	2.58	19	1.86	1.87	1.80	97
Cumene (0.1380)	6.90	1.75[f]	25	1.12	1.10	1.10	98
"α-d_1-Cumene" (0.0690)	6.90	1.38	10.0	0.90	0.88	0.86	96
Ethylbenzene (0.1562)	7.82	0.58	4.2	2.00	1.80	1.70	85
α-d_1-Ethylbenzene (0.0783)	7.83	0.47	3.4	0.915	0.75	0.72	79
d_4-Ethylbenzene (0.0785)	7.85	0.27	2.0	0.64	0.53	0.42	64

[a] Corrected for nitrogen evalued in decomposition of AIBN. [b] Based on oxygen consumed. [c] Reference 41. [d] Reference 42. [e] Calculated from hydroperoxide found by stannous chloride. [f] 0.05 *M* AIBN.

benzene and d_4-ethylbenzene were therefore analyzed for carbonyl content by infrared absorption. In the oxidation of d_4-ethylbenzene the kinetic chain length was only 2. Therefore, three molecules of hydroperoxide and one molecule each of acetophenone and α-phenethanol were expected per pair of initiating radicals formed. Of the total oxygen absorption of 0.64×10^{-3} mole, $^1/_8$ should be present as acetophenone if the suggested termination reaction occurs. By analysis 0.13×10^{-3} mole of acetophenone was found which is in fair agreement with the theoretical value of 0.16 $(2 \times 0.64/8) \times 10^{-3}$ mole. Based on a kinetic chain length of 3.4, 0.135×10^{-3} mole of acetophenone was expected in the oxidation of α-d_1-ethylbenzene wherein 0.915×10^{-3} mole of oxygen was consumed. The observation that 0.13×10^{-3} mole of acetophenone was formed lends strong support to the suggested termination reaction.

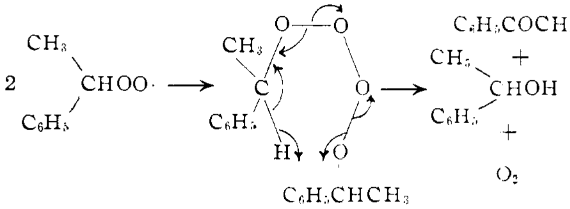
The mechanism of this termination reaction was investigated further by a study of deuterium-isotope effects in the oxidation of ethylbenzene. If there were no deuterium-isotope effect in the termination reaction of α-deutero-α-phenethylperoxy radicals, the ratio of $k_3/k_6^{1/2}$ for the oxidations of ethylbenzene and α-d_1-ethylbenzene[7] should be 1:0.60 provided that the deuterium-isotope effect in the propagation reaction is $k_H/k_D = 5.5$. The observed ratio was 1:0.78. This ratio would be consistent with a termination reaction involving no isotope effect only if the deuterium-isotope effect in the propagation reaction (k_3) was $k_H/k_D = 1.8$. This isotope effect is so inconsistent with the isotope effect of 5.5 determined in the oxidation of cumene that there must be a deuterium-isotope effect in the termination reaction of α-deutero-α-phenethylperoxy radicals.[8] Using an isotope effect in the propagation reaction of $k_H/k_D = 5.5$, it follows that α-phenethylperoxy radicals terminate 1.7 times as readily as the peroxy radicals formed in the oxidation of α-d_1-ethylbenzene. The peroxy radicals formed in the oxidation of α-d_1-ethylbenzene[7] should be 78.8% α-deutero-α-phenethylperoxy and 20.2% α-phenethylperoxy based on the magnitude of the isotope effect in the propagation reaction. If the crossed termination reaction (k_{HD}) is assumed to occur with a rate constant that is the geometric mean of the rate constants for the other two reactions,[9] $k_{HD} = (k_H k_D)^{1/2}$, it can be calculated that the deuterium-isotope effect in the termination reaction is $k_H/k_D = 1.9$. The magnitude of this deuterium-isotope effect, which occurs when a deuterium atom is substituted for an α-hydrogen

$$\left.\begin{array}{l} 2C_6H_5CHCH_3OO\cdot \xrightarrow{k_H} \\ C_6H_5CHCH_3OO\cdot + C_6H_5CDCH_3OO\cdot \xrightarrow{k_{HD}} \\ 2C_6H_5CDCH_3OO\cdot \xrightarrow{k_D} \end{array}\right\} \text{non-radical products}$$

atom in the α-phenethylperoxy radical, suggests that an α-carbon–hydrogen bond of the α-phenethylperoxy radical is broken in the rate-determining step of the termination reaction. This, of course, is in agreement with the termination reaction suggested wherein two α-phenethylperoxy radicals interact to form oxygen, acetophenone and α-phenethanol.

Discussion

Mechanism of Chain Termination.—The observation that α-phenethylperoxy radicals terminate more readily than their α-deutero derivatives allows the assignment of a detailed mechanism to this reaction. A reaction involving a cyclic transition state seems most likely.



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I may actually be an intermediate that is formed rapidly and reversibly and which decomposes slowly in an irreversible manner. The reaction path illustrated is consistent with the yield of hydroperoxide and acetophenone observed in the oxidation of ethylbenzene and in view of the exothermicity of the reaction,[10,11] is consistent with a low

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[7] Containing 1.1% ethylbenzene.

[8] Since a hydrogen atom of ethylbenzene is less reactive than a hydrogen atom of cumene toward a peroxy radical [G. A. Russell, THIS JOURNAL, **78**, 1047 (1956)], it is expected that if there is a difference in the deuterium-isotope effect in the propagation reaction, then the largest deuterium-isotope effect will occur in the attack of a peroxy radical on ethylbenzene.

[9] See for example, G. M. Burnett, "Mechanism of Polymer Reactions," Interscience Pub., Inc., New York, N. Y., 1954, p. 290.

[10] Using the bond dissociation energies of T. L. Cottrell ["The Strengths of Chemical Bonds," Academic Press, New York, N. Y., 1954] $D_{(-O-O-)}$, 35 kcal. mole^{-1}; $D_{(\equiv C-H,\ benzyl)}$, 78; $D_{(O_2)}$, 117; $E_{(=C=O,\ ketone)} - E_{(\equiv C-O-)}$, 87; $D_{(RO-H)}$, 100 [P. Gray, *Trans. Faraday Soc.*, **52**, 344 (1956)], it is calculated that 157 kcal. is liberated in the interaction of two moles of peroxy radicals. This estimate is high if the oxygen-oxygen bond dissociation energy of a peroxy radical is greater than 35 kcal. mole^{-1}. Since estimates of $D_{(RO-O\cdot)}$

deuterium-isotope effect ($k_H/k_D = 1.9$) when a deuterium atom is substituted for an α-hydrogen atom.[12]

Vaughan and co-workers have suggested that prim. and sec.-alkylperoxy radicals terminate by the formation and disproportionation of alkoxy radicals.[13]

$$2R_2CHOO\cdot \xrightarrow{k_f} O_2 + 2R_2CHO\cdot \xrightarrow{k_t} R_2CO + R_2CHOH$$

This suggestion lacks experimental verification, particularly in regard to the actual participation of alkoxy radicals in the reaction. However, in the liquid phase oxidation of ethylbenzene a termination reaction involving the formation and disproportionation of alkoxy radicals can be excluded. A deuterium-isotope effect of the magnitude observed would not be expected if alkoxy radicals were formed slowly and disproportionated rapidly ($k_f < k_t$). On the other hand, although a deuterium-isotope effect would be expected if $k_f > k_t$, this process can be eliminated on the basis of stoichiometry of the oxidation reaction, since, if alkoxy radicals were formed rapidly but disproportionated slowly, a majority of the alkoxy radicals would have to enter into chain propagation reactions, *e. g.*

$$C_6H_5CHCH_3O\cdot + RH \longrightarrow C_6H_5CHCH_3OH + R\cdot$$

The observation that only one molecule of oxygen was present in non-peroxidic products per two kinetic chains in the oxidation of ethylbenzene excludes this possibility.

The improbability of $k_f > k_t$ can be demonstrated by a somewhat less direct approach. We can write the following expressions for the oxidation of ethylbenzene performed in the presence of 0.1 *M* AIBN.[14]

$$k_p/k_t = \frac{\text{rate of chain propagation}}{\text{rate of chain termination}} = \frac{k_3[RH][ROO\cdot]}{2k_6[ROO\cdot]^2} = 7.4$$

Therefore, if $k_f > k_t$, $k_p/k_f < 7.4$. It would seem likely that cumylperoxy and α-phenethylperoxy radicals would interact to form alkoxy radicals at about the same rate. In this case, and at the *same* radical concentration, we could write for an oxidation of cumene

$$k_p/k_f < 7.4 \times \frac{6.90}{7.82} \times \frac{1}{1.20} = 5.6$$

where 6.90 and 7.82 are the concentrations of cumene and ethylbenzene, and the ratio 1:1.20 represents the relative reactivities of cumene and ethylbenzene towards a peroxy radical.[8] We have previously shown that α-phenethylperoxy radicals terminate more readily than cumylperoxy radicals.[8,15] Because of this, under conditions of constant rate of initiation, the concentration of peroxy radicals is greater in an oxidation of cumene than in an oxidation of ethylbenzene. It follows, from Table I, that the concentration of peroxy radicals in the oxidation of cumene (0.1 *M* AIBN, 6.90 *M* cumene) is 6.8 times the concentration of α-phenethylperoxy radicals in the oxidation of ethylbenzene (0.1 *M* AIBN, 7.82 *M* ethylbenzene). Therefore, for a 0.1 *M* AIBN-catalyzed oxidation of cumene, $k_p/k_f < 5.6/6.8 = 0.8$. This indicates that if $k_f > k_t$ and if k_f is the same for cumylperoxy and α-phenethylperoxy radicals, that cumylperoxy radicals formed in a 0.1 *M* AIBN-catalyzed oxidation would interact to yield alkoxy radicals more rapidly than they would react with cumene. Such a situation is unlikely in view of the essentially quantitative yield of hydroperoxide obtained in the oxidation of cumene (Table II).

Another possible termination reaction[16] can be

$$2ROO\cdot + R'C_6H_5 \longrightarrow ROOH + R'C_6H_4OOR$$

excluded on the basis of the observed deuterium-isotope effect in the termination reaction and also on the basis of the argument that this reaction should occur as readily for cumylperoxy radicals as for α-phenethylperoxy radicals. In this case the kinetic chain length observed in the oxidation of cumene (0.1 *M* AIBN) should be $^1/_{10}$ (6.90/7.82 × 1/1.20 × 1/6.8) that observed in the oxidation of ethylbenzene (0.1 *M* AIBN) whereas the kinetic chain length is actually much greater in the oxidation of cumene (Table II).

Finally, we would like to point out that the termination mechanism suggested for α-phenethylperoxy radicals is possibly general for prim. and sec.-alkylperoxy radicals. Previously we have demonstrated that most prim.- and sec.-peroxy radical terminate much more readily than sec.-alkylperoxy radicals.[8,15] This suggests that many prim.- and sec.-alkylperoxy radicals terminate in the same manner and that a different termination reaction is involved for ter.-alkylperoxy radicals. Such a circumstance is readily appreciated if prim.- and sec.-alkylperoxy radicals terminate by the cyclic interaction pictured wherein an α-carbon–hydrogen bond is ruptured. Ter.-alkylperoxy radicals, lacking an α-carbon–hydrogen bond, cannot undergo this termination reaction.[6]

Bolland and Cooper have suggested that in the photo-sensitized oxidation of ethanol acetic acid is formed in a termination reaction involving peroxy radicals.[17] In the absence of any data to the contrary, and in view of the present findings, we would prefer to formulate the reactions as shown.

Deuterium-isotope Effects in Aliphatic Substitutions.—The observation that the deuterium-isotope effect observed in the attack of a peroxy radical upon an α-hydrogen atom of an aralkyl hydrocarbon has the magnitude $k_H/k_D = 5.5$ is in

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in the range 45–55 are not unreasonable (see footnote 22). Δ*H*, may be as low as 59 kcal. per mole of peroxy radical.

[11] C. H. Bamford and M. J. S. Dewar [*Proc. Roy. Soc.* (*London*), **198A**, 252 (1949)] have assigned an energy of activation of about 1. kcal. mole^{-1} to the termination reaction between two α-tetralylperoxy radicals.

[12] K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[13] E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, *Disc. Faraday Soc.*, **10**, 242 (1951); F. H. Seubold, Jr., F. F. Rust and W. E. Vaughan, THIS JOURNAL, **73**, 18 (1951).

[14] In the oxidation of ethylbenzene 4.2 molecules of oxygen was consumed per initiating radical. One molecule of oxygen was consumed in the initiating step and one molecule of oxygen was liberated in the termination of two kinetic chains. Therefore, on the average, an α-phenethylperoxy radical abstracted a hydrogen atom 3.7 times before it entered into a termination reaction.

[15] G. A. Russell, THIS JOURNAL, **77**, 4583 (1955).

[16] This reaction is similar to the termination reaction that occurs in peroxidations inhibited by phenols or substituted-anilines [C. E. Boozer and G. S. Hammond, *ibid.*, **76**, 3861 (1954), **77**, 3233, 3238 (1955)].

[17] J. L. Bolland and H. R. Cooper, *Proc. Roy. Soc.* (*London*), **225A**, 405 (1954); *Nature*, **172**, 413 (1953).

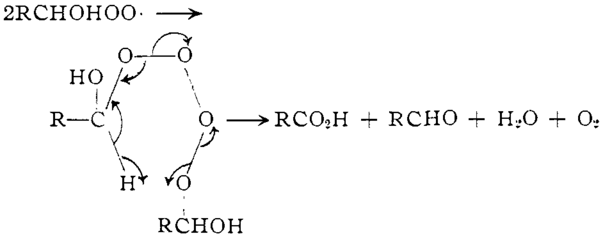
TABLE III

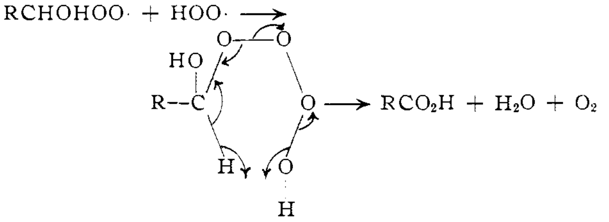
DEUTERIUM-ISOTOPE EFFECT, ENERGY OF ACTIVATION, EXOTHERMICITY AND SELECTIVITY OF ATOMS AND RADICALS IN THE REACTION $X\cdot + RH \rightarrow XH + R\cdot$

X	RH	Exothermicity[a]	Energy of activation	k_H/k_D	Relative reactivity of toluene (prim.-hydrogen) to cumene (ter.-hydrogen)
$Cl\cdot$	$C_6H_5CH_3$	24.7	2–3[b]	2.0 (80°)[c]	1:4 (80°)[d]
$(CH_3)_3CO\cdot$	$C_6H_5CH_2CH_3$	25.0[e]	. .	3.7 (107–116°)[f]	1:5 (135)[g]
$Br\cdot$	$C_6H_5CH_3$	9.0	7.2[h]	4.8 (77°)[i]	. . . .
$ROO\cdot$	$C_6H_5C(CH_3)_2H$	16–26	6.7[j]	5.5 (60°)	1:13 (90°)[k]
$CH_3\cdot$	$C_6H_5CH_3$	23.5	8.3[l]	5.5 (125°)[m]	1:12.5 (91.5°)[m]

[a] Based on bond dissociation energies listed by Cottrell (ref. 10). [b] H. O. Prichard, J. B. Pyke and A. F. Trotman-Dickenson, THIS JOURNAL, **77**, 2629 (1955). [c] H. C. Brown and G. A. Russell, *ibid.*, **74**, 3995 (1952). [d] Ref. 24. [e] $D_{(RO-H)}$ taken as 100 kcal. mole^{-1}, P. Gray, ref. 10. [f] E. L. Eliel, F. T. Fang and S. H. Wilen, *Preprints of General Papers, Div. Pet. Chem.*, 1, 195 (1956). [g] A. L. Williams, G. A. Oberright and J. W. Brooks, THIS JOURNAL, **78**, 1190 (1956). [h] H. R. Anderson, Jr., H. A. Scheraga and E. R. VanArtsdalen, *J. Chem. Phys.*, 21, 1258 (1953). [i] Ref. 12. [j] H. W. Melville and S. Richards, *J. Chem. Soc.*, 944 (1956). [k] Ref. 8. [l] A. F. Trotman-Dickenson and E. R. Steacie, *J. Chem. Phys.*, 19, 329 (1951), this energy of activation may be largely a measure of the reactivity of aromatic hydrogen atoms, see reference cited in footnote [f]. [m] Toward the trichloromethyl radical, E. C. Kooyman, *Disc. Faraday Soc.*, 10, 163 (1951).

excellent agreement with an isotope effect of about 5 reported by Max and Deatherage for the relative rates of autoxidation of *cis*-9-octadecene and its 8,8,11,11-tetradeutero derivative.[18] The isotope effect reported here has more significance, however, because in the case of the octadecenes isotope effects in both propagation and termination reactions may have been present as well as uncertainties in regard to the rates of initiation.





Wiberg has discussed the correlation between the magnitude of the deuterium-isotope effect in free radical substitution reactions and the reactivity of the attacking radical or atom.[12] In Table III are listed a compilation of data concerning the isotope effect and the reactivity of chlorine atoms, alkoxy radicals, bromine atoms, peroxy radicals and methyl radicals. The exothermicities listed in Table III were calculated assuming a bond dissociation energy for an α-carbon–hydrogen bond of toluene of 77.5 kcal. mole^{-1}.[19] This may be as much as 10 kcal. too low.[20] The exothermicity of the reaction between a peroxy radical and cumene listed in Table III has been calculated assuming $D_{(ROO-H)}$ to be 90–100 kcal. mole^{-1}. This estimate is based on the comments of Vaughan[21] and the recently determined value of $D_{(R_O-H)}$ as 100 kcal. mole^{-1}.[10,22]

From Table III it is apparent that the deuterium-isotope effect increases with the energy of activation of the reaction and with the selectivity of the attacking atom or radical. We believe that in reactions involving a low energy of activation and a low deuterium-isotope effect, the carbon–hydrogen (or deuterium) bond is only slightly broken in the transition state. As the atom or radical becomes more selective, the energy of activation increases, the deuterium-isotope effect increases and the transition state for the reaction involves a greater amount of bond breaking. The argument that the transition state in these hydrogen-abstraction reactions varies between one resembling the reactants and one involving a carbon–hydrogen (or deuterium) bond that has been extensively ruptured can be placed on a more quantitative basis. Evans and Polanyi suggested that for processes such as

$$AB + C \longrightarrow A + BC \qquad (1)$$

$$DB + C \longrightarrow D + BC \qquad (2)$$

involving similar A and D that $\Delta E_1^{\ddagger} - \Delta E_2^{\ddagger} = \alpha(\Delta H_1 - \Delta H_2)$ where α can vary between 0 and 1 and decreases with an increase in the reactivity of the attacking radical or atom.[23] It now appears

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(18) R. A. Max and F. E. Deatherage, *J. Am. Oil Chem. Soc.*, **28**, 110 (1951).

(19) From the pyrolysis of toluene, M. Szwarc [*J. Chem. Phys.*, **16**, 128 (1948)]. From electron-impact measurements a value of 77 ± 3 has been obtained [D. O. Schissler and D. P. Stevenson, *ibid.*, **22**, 151 (1954)].

(20) The following bond dissociation energies for a benzyl hydrogen atom have been recently reported: electron-impact, 95 kcal. mole^{-1}, [J. B. Farmer, I. H. S. Henderson, C. A. McDowell and L. P. Lossing, *ibid.*, **22**, 1948 (1954), J. B. Farmer, F. P. Lossing, O. G. H. Marsden and C. A. McDowell, *ibid.*, **24**, 52 (1956)]: bromination of toluene, 88 kcal. mole^{-1} [H. R. Anderson, Jr., H. A. Scheraga and E. R. Van Artsdalen, *ibid.*, **21**, 1258 (1953)]: pyrolysis of toluene, 90 kcal. mole^{-1} [H. Blades, A. T. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 298 (1954)].

(21) W. E. Vaughan, *Disc. Faraday Soc.*, **10**, 314 (1951).

(22) Recently published heats of hydroperoxidation of a number of hydrocarbons [W. Pritzkow and K. A. Miller, *Ber.*, **89**, 2318 (1956)] are not in disagreement with a bond dissociation energy of 90–100 kcal. if the reaction $R\cdot + O_2 \rightarrow ROO\cdot$ is exothermic by 20–30 kcal. mole^{-1}. For example, the reaction $C_5H_{12} + O_2 \rightarrow C_6H_{11}OOH$ is exothermic by 28 kcal. mole^{-1} while the bond dissociation energy of a cyclohexane carbon–hydrogen bond is about 92 kcal. mole^{-1} [J. L. Franklin, *J. Chem. Phys.*, **21**, 2029 (1953)]. If $D_{(ROO-H)}$ is 90–100 kcal., it follows that $D_{(RO-O)\cdot)}$ is in the range 45–55 kcal. since $D_{(R-O\cdot)}$ is 92 kcal. [P. Gray, ref. 10].

(23) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938): E. C. Baughan and M. G. Polanyi, *Nature*, **146**, 685 (1940); E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943); M. G. Evans, *Disc. Faraday Soc.*, **2**, 271 (1947).

that the value of α can be used not only as a measure of the reactivity of the atom but also as a measure of the extent of bond breaking in the transition state. We have shown previously that in photochlorination α is 0.1 and suggested that this should be interpreted as meaning that the carbon–hydrogen bond is only about 10% broken in the transition state for the attack of a chlorine atom on a branched-chain hydrocarbon.[24] On the other hand, α is 0.5 for the attack of a methyl radical on an aliphatic hydrocarbon indicating that in this case the original carbon–hydrogen bond is half broken in the transition state.[25] For peroxidation a value of α of 0.39 has been found.[26,27] Values of the deuterium-isotope effect (Table III) are in agreement with these conclusions. The deuterium-isotope effect is small for the reactive chlorine atom and large for the less reactive peroxy or methyl radicals. The deuterium-isotope effect, which occurs because of the freezing out of certain vibrational frequencies in the transition state, should be 1.4 at $\alpha = 0$ and, although temperature dependent, can be calculated at $\alpha = 0.5$ (*e.g.*, $k_H/k_D = 4.7$ at 100°).[12,28] Attempts have been made to calculate α from the values of k_H/k_D by assuming a linear relationship between these quantities over the range $\alpha = 0$ to $\alpha = 0.5$ (reactions of the type under discussion with $\alpha > 0.5$ proceed with great difficulty). From the data of Table III the following values of α were calculated, $Cl\cdot$ (80°), $\alpha = 0.08$; $(CH_3)_3CO\cdot$, (120°), $\alpha = 0.43$; $Br\cdot$ (77°), $\alpha = 0.44$; $ROO\cdot$ (60°), $\alpha = 0.50$; $CH_3\cdot$ (125°), $\alpha = 0.50$. These values of α are in surprisingly good agreement with the experimental values.

Polar Effects in Aliphatic Substitutions.—Table III demonstrates that there is not a direct relationship between the reactivity of an atom or radical and the exothermicity of its reaction with a carbon–hydrogen bond. The value of α is a far better measure of the reactivity of an atom or radical than is the heat of the reaction. Chlorine atoms and methyl radicals react with a hydrocarbon with nearly equal exothermicity, but chlorine atoms ($\alpha = 0.1$) are far more reactive than methyl radicals ($\alpha = 0.5$), as judged from the energy of activation or deuterium-isotope effect, and less selective.[29] This is due undoubtedly to stabilization of transition states by polar resonance forms.[8,24,30] For example, transition state resonance forms such as

$$R\cdot{}^{+}H\bar{:}X \quad R\cdot{}^{+}H\bar{:}OR \quad R\cdot{}^{+}H\bar{:}OOR$$

should be important in the attack of atoms or radicals having a high electron affinity on a carbon–hydrogen bond. Of course, the exothermicity of the reaction cannot be completely ignored. For example, when the polar effect is held constant, such as in alkoxy and peroxy radicals, the more exothermic reaction (attack by alkoxy radical) proceeds more readily and with a lower selectivity.

Experimental

Materials.—Cumene and ethylbenzene (Phillips 99 mole % minimum) were rectified in a large Podbielniak column (>50 plates) and middle fractions having constant refractive index and boiling point selected. These fractions were combined, chromatographically filtered through activated silica gel (Davidson, 80–100 mesh) and stored under nitrogen at 0°. Cumene, b.p. 69–69.5 at 42 mm., n^{20}_D 1.4912; ethylbenzene, b.p. 138.5–139°, n^{20}_D 1.4959.[31]

α-d_1-Ethylbenzene was prepared by the reaction of lithium aluminum deuteride (Metal Hydrides Corp.) with α-phenethyl chloride.[32] The α-d_1-ethylbenzene was purified by rectification through a spinning-band Podbielniak column (*ca.* 50 plates) and chromatographically filtered through silica gel, b.p. 133–133.5°, n^{20}_D 1.4954. Analysis was performed by mass spectrometry at an ionizing voltage sufficiently low that the ratio of peak heights for mass numbers 106 and 105 was $>10^4$.[33] After correcting for the presence of isotopic carbon, the following analysis was obtained, ethylbenzene, 1.1%, d_1-ethylbenzene, 98.8%, d_2-ethylbenzene, 0.1%.

d_4-Ethylbenzene was prepared by the addition of deuterium (Stuart Oxygen Co.) to purified phenylacetylene (b.p. 64.5 at 48 mm., n^{20}_D 1.5489) at 25° in the presence of a platinum oxide catalyst. The product was rectified through a spinning-band Podbielniak column and chromatographically filtered through silica gel, b.p. 136–136.5°, n^{20}_D 1.4943. Analysis by mass spectrometry at reduced ionizing potential indicated the following composition, ethylbenzene, 0.05%, d_1-ethylbenzene, 0.8%, d_2-ethylbenzene, 5.2%, d_3-ethylbenzene, 20.5%, d_4-ethylbenzene, 41.5%, d_5-ethylbenzene, 31.9%. Extensive shuffling of hydrogen and deuterium atoms in the presence of a hydrogenation catalyst was expected.[34]

α-d-Cumene was prepared by the addition of deuterium chloride to the organometallic compound formed by the reaction of sodium–potassium alloy with α,α-dimethylbenzyl methyl ether.[35,36] The α,α-dimethylbenzyl methyl ether was prepared by the addition of hydrogen chloride to purified α-methylstyrene (b.p. 81.5–82° at 40 mm., n^{20}_D 1.5382) followed by methanolysis in the presence of potassium hydroxide. The ether was rectified through a small packed column (*ca.* 10 plates), b.p. 84.5–85°, n^{20}_D 1.4958, d^{20}_4 0.946. α,α-Dimethylbenzyl methyl ether (100 g.) was added to 1.77 equivalents of potassium in the form of the sodium-potassium alloy (Na:K = 1:5, 54.5 g.) in 5 l. of ether. The deep red solution of the organometallic compound was stirred for 24 hr. under a dry nitrogen atmosphere before neutralization with 1.9 equivalents of deuterium chloride (prepared from benzoyl chloride and 11.3 g. of 99.5+% deuterium oxide).[37] The deep red color of the

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(24) G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4031, 4578 (1955).

(25) A. F. Trotman-Dickenson, *Quart. Revs.*, **7**, 198 (1953).

(26) J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950).

(27) α, of course, is not necessarily a constant for a given atom or radical but may increase with a decrease in the reactivity of the carbon–hydrogen bond involved. For this discussion we will consider α to be nearly independent of the reactivity of the hydrocarbon.

(28) This calculation assumes that at $\alpha = 0.5$ all zero point energy differences in the transition states have been lost. This is thus a maximum deuterium-isotope effect.

(29) The energy of activation for attack of a chlorine atom and a methyl radical on methane are 3.8 and 14.3 kcal. mole^{-1}, respectively [H. O. Prichard, J. B. Pyke and A. F. Trotman-Dickenson, THIS JOURNAL, **77**, 2629 (1955); J. R. McNesby and A. S. Gordon, *ibid.*, **76**, 4196 (1954).

(30) Other independent evidence for polar effects in radical–hydrocarbon reactions has been presented [E. C. Kooyman, R. Van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **B56**, 75 (1953); R. Van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954); C. Walling and E. McElhill, THIS JOURNAL, **73**, 1927 (1951); C. Walling and B. Miller, *ibid.*, in press.

(31) All boiling points were determined with uncalibrated iron–constantan thermocouples.

(32) E. L. Eliel, THIS JOURNAL, **71**, 3970 (1949); J. E. Johnson, R. H. Blizzard and H. C. Carhart, *ibid.*, **70**, 3664 (1948).

(33) D. P. Stevenson and C. D. Wagner, *ibid.*, **72**, 5612 (1950); R. E. Honig, *Anal. Chem.*, **22**, 1474 (1950); F. H. Field and S. H. Heatings, *ibid.*, **28**, in press (1956). All mass spectra were obtained at the General Engineering Laboratory of the General Electric Company by Mr. G. Schachter.

(34) R. L. Burwell, Jr., and A. B. Littlewood, *ibid.*, **78**, 4170 (1956).

(35) W. G. Brown, C. J. Mighton and M. Senkus, *J. Org. Chem.*, **3**, 62 (1938).

(36) K. Ziegler and B. Schnell, *Ann.*, **437**, 222 (1934).

(37) H. C. Brown and C. Groot, THIS JOURNAL, **64**, 2223 (1942).

organometallic compound was discharged completely by the first equivalent of deuterium chloride. The solution of α-d-cumene in ether was filtered and rectified in the spinning-band Podbielniak column, b.p. 70–70.5° at 47 mm., n^{20}_{D} 1.4908. The product was analyzed after chromatographic filtration by high resolution nuclear magnetic resonance spectroscopy, high resolution infrared spectroscopy and by mass spectrometry.

The high resolution NMR analysis was performed and interpreted by Dr. J. N. Shoolery of Varian Associates. Three different peaks in the spectra of cumene and α-d-cumene, each a measure of the concentration of tertiary hydrogen atoms, were compared. The relative heights of all three peaks in the spectra of α-d-cumene and cumene (run under comparable conditions) was 1:2.4 ± 0.1. Thus, 41.6% of the cumene molecules contained an α-hydrogen atom and 58.4% of the cumene molecules contained an α-deuterium atom in the sample of α-d-cumene. A possible error of ±3% seems possible in this analysis.

Analysis by mass spectrometry at low ionizing voltages (ratio of mass numbers 120 to 119 $> 10^4$) indicated that 0.85 deuterium atoms were present per molecule of cumene and that the distribution of deuterium was as follows, cumene, 32.8%, d_1-cumene, 52.0%, d_2-cumene, 14.0%, d_3-cumene, 1.2%.

The high resolution infrared absorption spectra were obtained and interpreted by Dr. R. S. McDonald of this Laboratory using a Perkin-Elmer Model 13U spectrometer with a lithium fluoride prism. The spectrum in the 3–4 μ region was resolved into absorption bands for carbon–hydrogen stretching vibrations which are characteristic for aromatic, methyl and tertiary hydrogen atoms. Carbon–deuterium stretching frequencies were resolved in the 4–5 μ region without resort to high resolution techniques. The assignment of frequencies is given in Table IV.

TABLE IV

ASSIGNMENT OF C–H AND C–D STRETCHING FREQUENCIES IN CUMENE AND "α-d-CUMENE"

R	R–H stretching frequency, cm.$^{-1}$	R–D frequency, cm.$^{-1}$	Deuterium-isotope shift
C_6H_5–	3100(weak)	..	..
	3080	2280	1.35
	3040	2250	1.35
$C_6H_5CHCH_3CH_2$–	2960	2220	1.345
	2920(weak)	..	..
$C_6H_5C(CH_3)_2$–	2880	2145	1.34

Assuming that $C_6H_5CHCH_3CH_2$–D and $C_6H_5C(CH_3)_2$–D have similar extinction coefficients, it is calculated that not more than 3% of the cumene molecules contained a β-deuterium atom.

From these observations we conclude that 0.24 (0.85 − 0.58 − 0.03) deuterium atoms were present as aromatic deuterium atoms per cumene molecule in the sample of α-d-cumene. This is in agreement with the observation that in the NMR spectra the area of the aromatic-hydrogen peak was slightly reduced for the sample of α-d-cumene. The neutralization of α,α-dimethylbenzylpotassium is being investigated further in an attempt to prepare pure α-d-cumene and to elucidate the mechanism of the formation of ring-deuterated cumenes.

AIBN was recrystallized twice from acetone, m.p. 104–105°. The AIBN was used as a 0.01 M solution in benzene which was stored at 0°. The oxygen was 99.3–99.5% pure, the principal impurities being nitrogen and hydrogen.

Procedure.—Oxidations were performed in the general manner described previously.[38] The desired amount of 0.1 M AIBN solution was first pipetted into the oxidation flask and the benzene removed under reduced pressure at 0°. The desired amount of hydrocarbon was then weighed into the flask (±0.001 g.) and the oxidation flask attached to a gas buret. The flask, which was a modified 50-ml. erlenmeyer flask, was evacuated at Dry Ice temperature and filled with oxygen five times. After warming to room temperature in the presence of an atmosphere of oxygen, the flask was placed in a shaking rack in a thermostated oil-bath and vigorously shaken while the absorption of oxygen was followed by manual control of the mercury level in a gas buret.

The densities of the deuterated hydrocarbons at 60° were calculated from the densities of cumene, d^{60}_4 0.830,[39] and ethylbenzene, d^{60}_4 0.831,[39] by the equation of McLean and Adams.[40]

Analytical.—The analyses of the deuterated hydrocarbons have been discussed already. The oxidates were analyzed for peroxidic oxygen by the iodimetric procedure of Kokatnur and Jelling[41] and the stannous chloride procedure of Hargrave and Morris.[42] The iodimetric procedure involved the addition of 1 ml. of oxidate to 25 ml. of 99% isopropyl alcohol containing 1 ml. of glacial acetic acid and 1 ml. of saturated potassium iodide solution. This solution was refluxed for 5 minutes under an atmosphere of carbon dioxide, diluted with 25 ml. of water and titrated with 0.1 N sodium thiosulfate. There was no blank correction. The stannous chloride procedure used consisted of the reaction of 1 ml. of the oxidate with a mixture of 10 ml. of glacial acetic acid and 10.0 ml. of 0.05 M stannous chloride. After 1 hr. at room temperature under a nitrogen atmosphere, the solution was titrated with 0.1 N potassium triiodide solution. In this analysis a blank was always run and the concentration of hydroperoxide in the oxidate was proportional to the difference between the blank titer and the titer of the reaction containing the oxidate. The agreement between the two methods (Table II) is somewhat better than expected from the data of Hargrave and Morris.[42]

Analyses for acetophenone in oxidized ethylbenzene were performed by infrared absorption. An appropriate series of standards were prepared and the absorption at 5.9 μ measured by a Perkin-Elmer model 21 spectrometer and plotted as a function of concentration. Attempts to analyze for α-phenethanol by a similar procedure were not successful because of the lack of strong and unique absorption in α-phenethanol.

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[38] G. A. Russell, THIS JOURNAL, **78**, 1041 (1956).

[39] G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Pub. Corp., New York, N. Y., 1946.

[40] A. McLean and R. Adams, THIS JOURNAL, **58**, 804 (1936).

[41] V. R. Kokatnur and M. Jelling, *ibid.*, **63**, 1432 (1941).

[42] K. R. Hargrave and A. L. Morris, *Trans. Faraday Soc.*, **52**, 89 (1956).