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Acid-catalyzed Decomposition of Cumene Hydroperoxide

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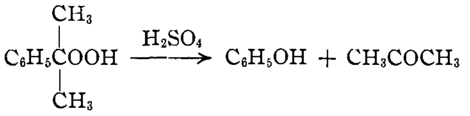
Investigation of the kinetics of the acid-catalyzed, degradative rearrangement of cumene hydroperoxide to phenol and acetone in aqueous acetic acid containing varying amounts of *p*-toluenesulfonic acid has shown the reaction to be first order with respect both to the hydroperoxide and to hydronium ion. It is not catalyzed by molecular acetic acid. The over-all activation energy for the decomposition in fifty weight per cent. acetic acid at unit ionic strength is 21.3 kcal./mole.

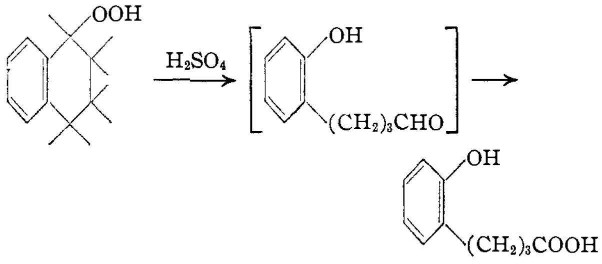
The acid-catalyzed decomposition of cumene hydroperoxide was first reported by Hock and Lang,[1] who employed boiling 10% aqueous sulfuric acid to effect the conversion to phenol and acetone. The yield of phenol was 75%; only a qualitative test



$$C_6H_5\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}OOH \xrightarrow{H_2SO_4} C_6H_5OH + CH_3COCH_3$$

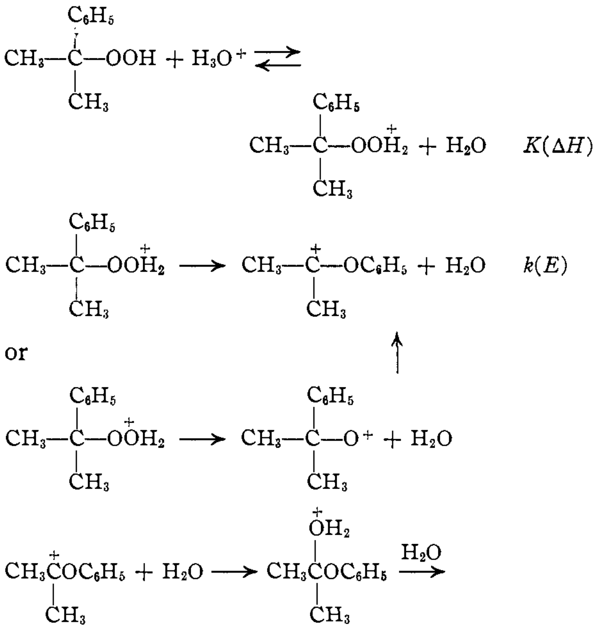
was made for acetone. More recently, Armstrong, Hall and Quin[2] have reported yields of phenol and acetone of 82 and 74%, respectively, as well as minor amounts of acetophenone and α-methylstyrene, using essentially the same procedure. In the present study yields of 92% of phenol and 81% of acetone were obtained by operation in a homogeneous medium at 60°. This type of decomposition appears to be general for organic hydroperoxides, certainly so for those which contain an aromatic nucleus bonded to the carbon atom holding the hydroperoxide group as in the following examples.[1]

$$(C_6H_5)_2CHOOH \xrightarrow{H_2SO_4} C_6H_5OH + C_6H_5CHO$$



The kinetics of the degradative rearrangement of cumene hydroperoxide in fifty weight per cent. aqueous acetic acid containing varying amounts of *p*-toluenesulfonic acid has now been investigated. Acetic acid was chosen as a component to determine the catalytic effect of a weak acid as well as to increase the solubility of the peroxide. In all cases the ionic strength was maintained at unity by the addition of lithium chloride whenever necessary. Two experiments in which the initial peroxide concentration was varied fivefold were conducted at each acid concentration. The first-order rate constants, k_1, for peroxide disappearance in each pair of decompositions were in good agreement. These were averaged (Table I) for the determination of the order of the reaction with respect to hydronium ion by plotting k_1 against hydronium ion concentration. Since this plot is precisely linear, the decomposition is first order in hydronium ion, as well as in cumene hydroperoxide. The fact that the curves at the various temperatures pass through the origin shows that catalysis by molecular acetic acid is negligible. Thus the reaction exhibits specific acid catalysis,[3] and the correct rate expression is $-d(ROOH)/dt = k_2(H_3O^+)(ROOH)$. Values of k_2 determined from the slopes of the curves described above are presented in Table I.

The activation energy for the decomposition under these conditions was calculated to be 21.3 kcal./mole from the conventional plot, the points falling beautifully on a straight line. This value cannot be attributed to a single process, *e.g.*, the fission of the oxygen–oxygen bond, since it is a compound function as shown by consideration of the most probable mechanism for the reaction.



$$CH_3-\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{C}}-OOH + H_3O^+ \rightleftarrows CH_3-\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{C}}-\overset{+}{O}OH_2 + H_2O \qquad K(\Delta H)$$

$$CH_3-\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{C}}-\overset{+}{O}OH_2 \longrightarrow CH_3-\overset{+}{\underset{\displaystyle CH_3}{C}}-OC_6H_5 + H_2O \qquad k(E)$$

or

$$CH_3-\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{C}}-\overset{+}{O}OH_2 \longrightarrow CH_3-\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{C}}-O^+ + H_2O \quad \uparrow$$

$$CH_3\overset{+}{\underset{\displaystyle CH_3}{C}}OC_6H_5 + H_2O \longrightarrow CH_3\overset{\displaystyle \overset{+}{O}H_2}{\underset{\displaystyle CH_3}{C}}OC_6H_5 \xrightarrow{H_2O}$$

$$C_6H_5OH + CH_3COCH_3 + H_3O^+$$

$$-\frac{d(ROOH)}{dt} = k(RO\overset{+}{O}H_2) = kK(H_3O^+)(ROOH) = k_2(H^7O^+)(ROOH)$$

As usual, then, in cases in which a preliminary equilibrium is involved, it is the logarithm of kK rather than of a simple second-order rate constant which was plotted so that the slope yields $E + \Delta H$ rather than E alone. Lack of knowledge of ΔH per-

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[1] H. Hock and S. Lang, *Ber.*, **77B**, 257 (1944).

[2] G. P. Armstrong, R. H. Hall and A. C. Quin, *J. Chem. Soc.*, 666 (1950).

[3] This observation of specific acid catalysis in the decomposition of cumene hydroperoxide is in contrast to the general acid catalysis found by P. D. Bartlett and J. E. Leffler (THIS JOURNAL, **72**, 3030 (1950)) for the acid-catalyzed decomposition of bis-phenylacetyl peroxide in toluene.

TABLE I

RATE CONSTANTS FOR THE DECOMPOSITION OF CUMENE HYDROPEROXIDE IN 50% W. ACETIC ACID

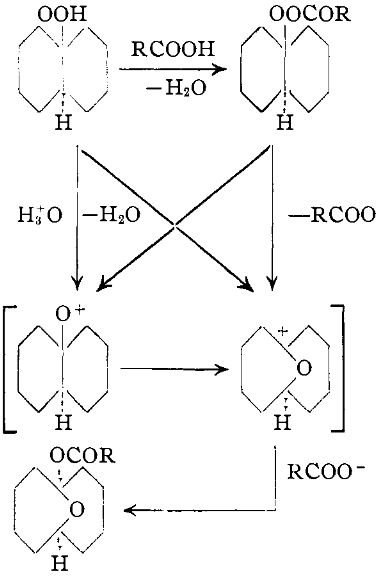
(Ionic strength = 1.0)

p-$CH_3C_6H_4SO_3H$- (moles/kg.)	$10^5 k_1$ (sec.$^{-1}$) 0.00	0.02	0.05	0.10	0.20	$10^4 k_2$ (kg. moles^{-1} sec.$^{-1}$)
40°	...	....	1.72 ± 0.01	3.26 ± 0.07	7.12 ± 0.13	3.42
50°	1.07[a]	2.40 ± 0.0	....	1.00 ± 0.02	21.0 ± 1.0	10.1
60°	...	6.91 ± 0.33	13.7 ± 0.3	27.1 ± 0.7	....	26.4

[a] Single determination only.

mits no estimate of the actual value of either the energy or entropy of activation for the reaction.

The mechanism here proposed is similar to that of Criegee for the rearrangement of certain peresters.[4] Indeed in the reaction of hydroperoxides with strong organic acids, he was able to isolate the peresters only in low yields, a large fraction of the hydroperoxide undoubtedly first rearranging by the mechanism proposed here before reacting with the acid or its anion to yield the final product. Insufficient evidence is at hand to determine whether this rearrangement is a concerted or a two-step process. In view of recent work on the effect of neighboring groups in displacement reactions[5] and of the great electron affinity of cationic oxygen, a concerted rearrangement appears to be the more probable.



Experimental

Materials.—Cumene hydroperoxide was prepared by the liquid phase oxidation of cumene with molecular oxygen at 120°. The sodium salt was precipitated by shaking the solution with 25% aqueous sodium hydroxide, filtered off, washed with acetone, and dissolved in water. The solution was acidified with carbon dioxide, and the upper layer extracted with petroleum ether, dried over anhydrous potassium carbonate, filtered and concentrated at 50° and 1 mm. The clear, colorless residue was found to contain 95.6 weight per cent. cumene hydroperoxide by the following analytical method. An aliquot of *ca.* 0.2 g. was refluxed with 50 ml. of isopropyl alcohol, 5 ml. of glacial acetic acid and 2 ml. of saturated aqueous sodium iodide for five minutes; 50 ml. of water was added, and the liberated iodine titrated with standard sodium thiosulfate.

p-Toluenesulfonic acid monohydrate, glacial acetic acid and anhydrous lithium chloride were reagent grade chemicals used without further purification.

Procedure for Rate Measurements.—Solutions of the desired acidity were prepared gravimetrically, using fifty parts of glacial acetic acid, the desired weight of *p*-toluenesulfonic acid, sufficient lithium chloride to obtain an ionic strength of unity, and distilled water to one hundred parts. The hydronium ion concentration of each solution at each temperature was calculated approximately from the data of Harned and Ehlers[6], for the ionization constant of acetic acid under varying conditions of temperature and ionic strength.

HYDRONIUM ION CONCENTRATION OF SOLUTIONS OF *p*-TOLUENESULFONIC ACID IN 50% W. ACETIC ACID

(ionic strength = 1.0)

(p-$CH_3C_6H_4SO_3H$) (moles/kg.)	$10^2(H_3O^+)$ (moles/kg.) 40°	50°	60°
None	...	1.16	...
0.02	...	2.53	2.51
.05	5.27	...	5.24
.10	10.1	10.1	10.1
.20	20.1	20.1	...

Cumene hydroperoxide was weighed from a Lunge pipet into a 100-ml. volumetric flask in an amount sufficient to provide 50 ml. of an approximately 0.2 or 0.05 mole/kg. solution. The acid solution to be employed was brought to temperature in a tared flask in the thermostat which was regulated to ±0.1°, and poured into the volumetric flask which was then stoppered, swirled to dissolve the peroxide, and immersed in the thermostat. Timing was started when

TABLE II

DECOMPOSITION OF CUMENE HYDROPEROXIDE IN 50% W. ACETIC ACID

(p-$CH_3C_6H_5SO_3H$) = 0.05 mole/kg.; t = 40°; ionic strength = 1.0.

Time (min.)	Titer[a]	(ROOH), moles/kg.	$10^5 k_1$ (sec.$^{-1}$)[b]	
1. $C_6H_5C(CH_3)_2OOH$ = 0.2 mole/kg.				
5	20.86	0.195	2.30	
30	20.32	.190	1.81	1.72 ± 0.04
60	19.75	.185	1.65	
120	18.57	.174	1.68	
180	17.45	.163	1.72	
240	16.42	.153	1.73	
2. $C_6H_5C(CH_3)_2OOH$ = 0.04 mole/kg.				
5	4.10	0.0384	1.84	1.72 ± 0.04
30	4.01	.0375	1.62	
62	3.87	.0362	1.73	
120	3.65	.0341	1.72	
180	3.42	.0320	1.74	
240	3.23	.0302	1.70	

[a] Ml. of 0.0996 N $Na_2S_2O_3$ required for a 5.323_6-g. sample.
[b] Rate constants calculated from the equation $\ln c = k_1 t + b$ in which b is the intercept calculated by the method of least squares. The rate constant was calculated to be 1.72 × 10^{-5} sec^{-1} from the least squares slope, and 1.73 × 10^{-5} sec.$^{-1}$ from the graphical slope.

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[4] R. Criegee, *Ann.*, **560**, 127 (1948).

[5] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

[6] H. S. Harned and R. W. Ehlers, *ibid.*, **54**, 1350 (1932); **55**, 652 (1933).

half the acid solution had been added. At measured intervals 5-ml. aliquots of the reaction mixture were removed for analysis with a pipet calibrated by weight with the acid solution at the desired temperature. Each sample was run directly into 50 ml. of isopropyl alcohol containing 2 ml. of saturated aqueous sodium iodide under carbon dioxide. The analysis was continued as described above. Data for a typical pair of measurements at 40° in a mixture containing 0.05 mole of *p*-toluenesulfonic acid per kilogram of solution are given in Table II. Because of the greater ease of the graphical method, it was generally employed for the calculation of the rate constants. Occasional checks with the least squares method showed excellent agreement.

Stoichiometry of the Reaction.—Because of interference in the phenol determination due to acetylation in the acetic acid solution, aqueous ethanol was employed as solvent for quantitative determination of the phenol and acetone formed in the reaction. A solution of 7.3707 g. (0.0464 mole) of 95.6% w. cumene hydroperoxide in fifty weight per cent. aqueous ethanol containing 0.5 mole of *p*-toluenesulfonic acid per kilogram of solution was maintained at 60 ± 1° for 80 minutes. An equal volume of distilled water was added, the pressure was reduced to 125 mm., and the mixture was distilled through a ten-inch, helices-packed column. Analysis showed the distillate to contain 0.0260 mole of acetone[7] (2,4-dinitrophenylhydrazone m.p. 125–126°; lit. m.p. 126°) and 0.0052 mole of phenol[8] (2,4,6-tribromo derivative, m.p. 95.5–6.0°; lit. m.p. 96°); and the residue to contain 0.0246 mole of phenol and 0.0141 mole of unreacted peroxide. The yield of phenol was 92.3% and of acetone, 80.5%.

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(7) This procedure, a modification of the hydroxylamine hydrochloride method of M. Marasco (*Ind. Eng. Chem.*, **18**, 701 (1926)), is described in "Methyl Ethyl Ketone, Its Uses and Data on Its Properties," Shell Chemical Corp., San Francisco, California, 1938, p. 45.

(8) L. Lykken, R. S. Treseder and V. Zahn, *Ind. Eng. Chem., Anal. Ed.*, **18**, 103 (1946).

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Gas Production in the Photolysis of Liquid Methyl Iodide[1]

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The importance of "Hot Radical" processes in the photolysis of liquid methyl iodide is further evidenced in the formation of methane and ethane as gaseous products. For the reactions induced by light at 2537 Å. the quantum yield for the formation of methane is 0.023, while that of ethane is 0.007. Although the iodine concentration is increasing during the course of the reaction, the ethane and methane yields are found to be independent of the extent of irradiation. The gas yields are dependent upon iodine concentration only at very high iodine concentrations. At room temperature, these yields are independent of the temperature of the sample. Methylene iodide is shown to be a product of the photolysis, while little or no hydrogen, ethylene, or acetylene formation is observed.

Previously Hamill and Schuler[3] and Schultz and Taylor[4] have concluded from studies, respectively, of the liquid and vapor phase photolysis of methyl iodide that it is necessary to assume as part of the mechanism certain reactions which are independent of the iodine concentration and of the temperature of the system. This led to a proposed mechanism which bases the net observed products on reactions occurring as a result of the excess kinetic energy given to the methyl radicals in the photolytic step. These hot radical processes must take place before this excess energy has been entirely redistributed by collision with the surrounding molecules.

This investigation was undertaken in order to determine the effect of iodine on the production of methane and ethane in the liquid phase photolysis. Since iodine does not interfere with the required analyses, investigation of the gas production reactions allows a study of the iodine dependence of the processes over a much wider range of iodine concentrations than was possible in the iodine production measurements. This work also serves as the basis for a comparative study of gas production in the X-ray decomposition of methyl iodide.[5]

Experimental

Methyl Iodide.—Both commercially obtained C.P. methyl iodide and a laboratory preparation (from methanol, phosphorus and iodine) were used in this investigation. The samples were washed with thiosulfate and water, dried with silica gel, and carefully fractionated through a three-foot helix-packed column. The center cut boiling at 42.4° was taken and, when kept in the dark, found to be without decomposition over periods of many months. All samples were found to have a refractive index ($n^{25}\text{D}$) of 1.5271–1.5272. A total of 9 different fractions from 5 preparations was used with no apparent discrepancies being traceable to the individual samples.

Ultraviolet Source.—A 50-watt Hanovia SC-2537 helical low pressure mercury discharge lamp was used. This was operated from the laboratory a.c. line through a variac and high voltage transformer. The intensity was monitored in terms of a constant lamp current of 50 ma. The input to the transformer at this setting was 3.3 amperes at 97–98 volts. A small centrifugal blower was used to circulate air over the sample tube and lamp in order to keep these at room temperature and remove any ozone formed. There was very little increase in the temperature of the system with this arrangement.

Cells.—The cell used for a major part of the work consisted of a 12-mm. quartz tube with a graded seal to Pyrex and an attached high vacuum stopcock. Five ml. of methyl iodide was placed in this tube, the sample degassed, the vapor region masked to restrict the activation to the liquid phase, and the sample irradiated for the desired period in the center of the lamp helix.

A second cell, which permitted thermostating of the sample during the irradiation, consisted of a jacketed tube to which a quartz window was cemented with silver chloride and the seal made vacuum tight with Glyptal. A side tube and stopcock, through which the tube could be evacuated, were arranged at angles of 120° to the cell axis. By rotating the assembly, the side arm could be employed in the freezing of the sample during the degassing and measuring operations. The sample was irradiated with the cell in a vertical position and with the window facing the end of the

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(1) This work was supported, in part, under Contract AT(30-1)-1084 with the U. S. Atomic Energy Commission. Presented at the 121st Meeting of the American Chemical Society in Buffalo, N. Y., March 25, 1952.

(2) Brookhaven National Laboratory, Upton, N. Y.

(3) W. H. Hamill and R. H. Schuler, THIS JOURNAL, **73**, 3466 (1951).

(4) R. D. Schultz and H. A. Taylor, *J. Chem. Phys.*, **18**, 194 (1950).

(5) R. C. Petry and R. H. Schuler, THIS JOURNAL, **75**, 3796 (1953).