Kinetics and Mechanism of the Oxidation of p,p'-Dichlorobenzyl Sulfide by Hydrogen Peroxide[1]

BY C. G. OVERBERGER AND R. W. CUMMINS[2]

A kinetic study was made of the oxidation of p,p'-dichlorobenzyl sulfide to sulfoxide by hydrogen peroxide in isopropyl alcohol. Activation energies, frequency factors and entropies of activation were obtained for the uncatalyzed and for the sulfuric acid-catalyzed oxidation. The rate data followed the second order rate law provided a minimum molar ratio of water to sulfoxide of 4–5 was maintained. The specific rate constant for the uncatalyzed oxidation ($19.1 \pm 0.4 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$ at 49.8° was independent of initial water concentration in the range 0.06 to 2.53 M. The dependence of rate on sulfuric acid concentration was found to be given by the relation $k(30.2°) = 3.1 \times 10^{-5} + 3.0 \times 10^{-1}$ [H_2SO_4]. Rate data obtained with two alcohols, two nitriles and one ether indicate that the oxidation is independent of dielectric constant but is promoted by solvents capable of hydrogen bonding with hydrogen peroxide. Large differences in activation energies and entropies found for the acid-catalyzed and uncatalyzed oxidations suggest that two mechanisms are operative. The activation entropy for the hydrogen peroxide oxidation was found to be equal to that for the peroxybenzoic acid oxidation within experimental error.

In conjunction with a kinetic study of the peroxybenzoic acid oxidation of p,p'-dichlorobenzyl sulfide in isopropyl alcohol and toluene[3] some parallel work was conducted with hydrogen peroxide in isopropyl alcohol to obtain comparative activation energies and entropies in the hope that the results would be helpful in clarifying the mechanisms of organic peroxyacid and hydrogen peroxide oxidations.

Although the kinetics of hydrogen peroxide oxidation of organic compounds in aqueous solution have been studied,[4,5] apparently no kinetic data are available for anhydrous organic solvent systems. In 1941, Stoner and Dougherty[4] reported that the oxidation of disulfide acids, such as dithiodiacetic acid, to sulfonic acids by hydrogen peroxide in dioxane–water mixtures was an acid-catalyzed process with the oxidation rate increasing with decreasing proportion of water to dioxane in the solution, presumably due to reduction of the catalytic activity of the protons by water solvation. Ross,[5] in 1946, showed that the oxidation of thiodiglycol in aqueous hydrogen peroxide was bimolecular and subject to acid catalysis. The effect of acid on rate was explained by supposing that $H_2{}^+OOH$ can donate an ^+OH ion easier than neutral HOOH can. Edwards[6] recently summarized available information on the kinetics and mechanism of the reaction of hydrogen peroxide with inorganic donor particles.

The present work was limited largely to the determination of specific rate constants for the acid-catalyzed and uncatalyzed hydrogen peroxide oxidation of p,p'-dichlorobenzyl sulfide in isopropyl alcohol at three different temperatures to provide data for calculation of activation energies and entropies for comparison with the peroxybenzoic acid oxidation. The effects of water, acid and solvent type on oxidation rate were also investigated.

Experimental

Materials.—p,p'-Dichlorobenzyl sulfide, m.p. 41.5–42.0° uncor., was prepared as described by Overberger, Ligthelm and Swire[7] who reported a m.p. of 40.5–41.0°; hydrogen peroxide C.P. 90% (Buffalo Electro-Chemical Company, Inc.); sulfuric acid 96% ("Baker Analyzed" Reagent); isopropyl alcohol ("Baker Analyzed" Reagent) was purified as described previously.[3]

Ethyl alcohol (Commercial Solvents Corporation, Gold Shield Label) $n^{20.5}{}_D$ 1.3610 [$n^{20.5}{}_D$ 1.3610[8]] was used without further purification.

Diisopropyl ether (Matheson Chemical Company) was purified by the method of Vogel[9] and fractionated from sodium using a 100 by 2 cm. column packed with $^1/_8$ inch, single-turn glass helices. A middle one-third cut was collected, b.p. 68.5–68.9° (760 mm.), $n^{20}{}_D$ 1.3689 (b.p. 68.3° (760 mm.), $n^{20}{}_D$ 1.3689[10]).

Acetonitrile (Matheson Chemical Company) was fractionated and a middle one-third cut collected, b.p. 81.4–81.8° (760 mm.), $n^{16.5}{}_D$ 1.3460 (b.p. 81.6–82.0° (760 mm.), $n^{16.5}{}_D$ 1.3460[8]).

Propionitrile (Eastman Kodak Co. yellow label) was fractionated and a middle one-half cut collected, b.p. 97.2–97.4° (760 mm.), $n^{20}{}_D$ 1.3663 (b.p. 97.4° (760 mm.), $n^{20}{}_D$ 1.3664[10]).

Kinetic Measurements.—The rate of hydrogen peroxide consumption by sulfide for the uncatalyzed reactions was followed by iodometric titration by the Nozaki[11] peroxide method. The Nozaki method was unsatisfactory for following the acid-catalyzed oxidations, apparently because of reaction between isopropyl alcohol and acetic anhydride, and the Kokatnur and Jelling[12] method was substituted.

A 12 by 16 inch water-bath equipped with motor-driven stirrer, low-drift immersion heating units, and a merc-to-merc thermoregulator capable of temperature control to ±0.05° was employed. Glassware was cleaned with cleaning solution, rinsed with water followed by acetone and air-dried with filtered compressed air.

p,p'-Dichlorobenzyl sulfide stock solution (0.2000 M) was prepared by weighing 2.830 g. of p,p'-dichlorobenzyl sulfide into a 50-ml. glass-stoppered volumetric flask followed by dissolution and dilution to the mark with fractionated solvent.

Hydrogen peroxide stock solution ($ca.$ 0.2000 M) was prepared immediately before use by diluting 0.27 ml. of 90% hydrogen peroxide in a 50-ml. volumetric flask to the mark with fractionated solvent.

For the acid-catalyzed rate runs isopropyl alcohol con-

(1) This is the second of two papers concerned with the kinetics and mechanism of oxidation by hydrogen peroxide and organic peroxy acids. For the first paper see C. G. Overberger and R. W. Cummins, THIS JOURNAL, **75**, 4250 (1953).

(2) A portion of a thesis by R. W. Cummins submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) C. G. Overberger and R. W. Cummins, THIS JOURNAL, **75**, 4250 (1953).

(4) G. G. Stoner and G. Dougherty, $ibid.$, **63**, 1291 (1941).

(5) S. D. Ross, $ibid.$, **68**, 1484 (1946).

(6) J. O. Edwards. $J. Phys. Chem.$, **56**, 279 (1952).

(7) C. G. Overberger, S. P. Ligthelm and E. A. Swire, THIS JOURNAL, **72**, 2856 (1950).

(8) N. A. Lange, "Handbook of Chemistry," Sixth Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1946.

(9) A. I. Vogel, $J. Chem. Soc.$, 618 (1948).

(10) R. R. Dreisbach and R. A. Martin, $Ind. Eng. Chem.$, **41**, 2875 (1949).

(11) K. Nozaki, $Ind. Eng. Chem., Anal. Ed.$, **18**, 583 (1946).

(12) V. R. Kokatnur and M. Jelling, THIS JOURNAL, **63**, 1432 (1941).

taining the desired concentration of sulfuric acid was used for preparing both the sulfide and peroxide stock solutions.

In a typical rate run the stock solutions and an empty 50-ml. glass-stoppered volumetric flask were thermostated at 49.8°. After about 30 minutes a 20-ml. aliquot of the sulfide stock solution was transferred to the empty flask by means of a pipet, followed by an equal volume of hydrogen peroxide stock solution while swirling vigorously. A 2-ml. aliquot of the reaction mixture was taken for analysis at once and similar aliquots taken hourly thereafter. Liberated iodine was titrated with 0.01 N thiosulfate. The thermostated hydrogen peroxide stock solution was likewise analyzed hourly (1-ml. aliquots) to determine its stability. Since the hydrogen peroxide stock solutions were stable over the entire reaction periods in all cases it was not necessary to correct titrations. A water analysis was made during the first hour by the Karl Fischer visual end-point method[13] employing a 5-ml. sample.

Uncatalyzed oxidations were followed over 6 to 7 hour periods at temperatures of 30, 40 and 50° providing coverage of 10 to 30% of the reaction, while acid-catalyzed rate runs extended over 5-minute periods with 20 to 60% completion of reaction depending on temperature and acid concentration.

In a typical experiment in isopropyl alcohol 1 molar in water at 49.8°, the sulfoxide was isolated in 91% yield after a 67-hour reaction period, m.p. 162-164°. Recrystallization from ethanol gave a m.p. 164-165°. The reported[7] m.p. of p,p'-dichlorobenzyl sulfoxide is 164.8-165.1°.

Results and Discussion

General.—Rate data were obtained in isopropyl alcohol at 30, 40 and 50° for the uncatalyzed and sulfuric acid-catalyzed hydrogen peroxide oxidations of p,p'-dichlorobenzyl sulfide. The dependence of oxidation rate on both water and sulfuric acid concentrations was determined. Oxidation rates were also determined in ethyl alcohol, diisopropyl ether, acetonitrile and propionitrile. All runs were made with initial sulfide and peroxide concentrations at 0.1 M.

The second order rate law was found to be obeyed accurately with the exceptions noted below. Rate constants were calculated using the second order rate equation and activation energies, and frequency factors were obtained from the variation of ln k with $1/T$, the method of least squares being used in all cases. The entropy of activation, $\Delta S^{\ddagger}$, was calculated from the frequency factor A by means of the equation[14]

$$A = e\,(k'T/h)e^{\Delta S^{\ddagger}/R}$$

The rate constants for both the catalyzed and uncatalyzed oxidations in isopropyl alcohol at 30, 40 and 50°, E, ln A and $\Delta S^{\ddagger}$, are presented in Table I. Some typical second order rate plots are shown in Figs. 1 and 2, while Arrhenius plots are set forth in Fig. 3.

Data for establishing over-all order of the uncatalyzed oxidation by the differential method[15] will be found in Table V, while Fig. 4 shows a plot of log $\Delta(b - x)/\Delta t$ vs. log $(b - x)$ from which a reaction order of 1.97 was obtained. Application of the differential method to two additional sets of rate data gave comparable results.

The indicated uncertainties in k, E, ln A and $\Delta S^{\ddagger}$

(13) J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

(14) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

(15) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1940, p. 1047.

are indeterminate errors estimated[16] from relative errors in the experimental measurements. The largest errors originated in the determination of hydrogen peroxide concentration and time. The precision of the specific rate constants, as estimated from the standard deviations of the slopes[17] of representative rate plots, amounted to approximately half of the uncertainty values reported in Table I.

TABLE I

SPECIFIC RATE CONSTANTS, ACTIVATION ENERGIES, FREQUENCY FACTORS AND ACTIVATION ENTROPIES FOR THE OXIDATION OF p,p'-DICHLOROBENZYL SULFIDE IN ISOPROPYL ALCOHOL BY HYDROGEN PEROXIDE[a] OVER TEMPERATURE RANGE DISCUSSED

Isopropyl Alcohol

Temp., °C.	k(l. mole^{-1} sec.$^{-1}$) × 10^5	E(kcal. mole^{-1})	ln A	$\Delta S^{\ddagger}$ (cal. mole^{-1} deg.$^{-1}$) (40°)
30.2	3.0, 3.1 ± 0.1			
39.8	7.6, 7.6 ± 0.2			
49.8	18.5, 19.3, 19.1,			
	19.3 ± 0.4	17.2 ± 0.3	18.3 ± 0.5	−24.2 ± 0.7

Isopropyl Alcohol, 0.0245 M in Sulfuric Acid

	k(l. mole^{-1} sec.$^{-1}$) × 10^2			
30.2	1.16 ± 0.03			
40.0	1.68 ± .04			
49.8	2.68 ± .07	8.9 ± 0.2	10.0 ± 0.4	−40.7 ± 1.4

[a] The indicated uncertainties in the experimental values are estimated indeterminate errors.

Effect of Water.—Oxidation rates were determined in isopropyl alcohol at 49.8° with initial water concentrations at 0.06, 0.09, 1.26 and 2.53 M. The specific rate constants obtained, summarized in Table II, were independent of initial water concentration within the estimated limit of uncertainty, the average rate being 19.1 ± 0.4 × 10^{-5} l. mole^{-1} sec.$^{-1}$. It was concluded that any attempt to prepare isopropyl alcohol solutions of hydrogen peroxide less than about 0.05 M in water would not be justified.

TABLE II

EFFECT OF WATER ON THE RATE OF OXIDATION OF p,p'-DICHLOROBENZYL SULFIDE BY HYDROGEN PEROXIDE IN ISOPROPYL ALCOHOL AT 49.8°

Initial water, M	k(l. mole^{-1} sec.$^{-1}$) × 10^5
0.06	18.5 ± 0.4
0.09	19.3 ± .4
1.26	19.1 ± .4
2.53	19.3 ± .4

For initial water concentrations of 0.06 and 0.09 M the kinetics were without complication during the first 20% of the oxidations. Thereafter the reaction rates accelerated, as indicated by deviations of the second order rate plots from a straight line in the direction of decreasing slope. The effect is illustrated in Fig. 1 where it will be noted that at an initial water concentration of 0.06 M a considerable deviation from second order kinetics occurred after 3 hours; at 0.09 M initial water concentration a deviation was first apparent after 5 hours, while at 1.26 M no deviation was observed

(16) A. A. Benedetti-Pichler, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 376 (1936).

(17) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 42.
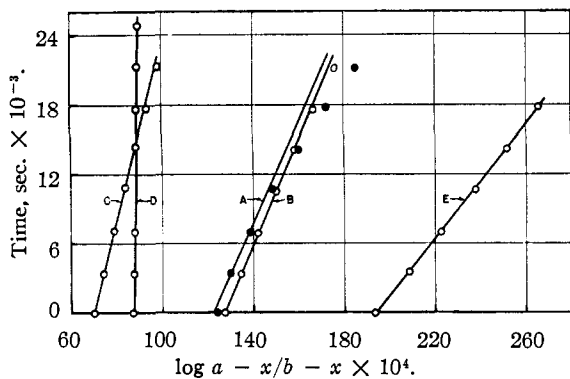
Fig. 1.—Second order rate plots for uncatalyzed hydrogen peroxide oxidation of p,p'-dichlorobenzyl sulfide at 49.8°: A, isopropyl alcohol 0.06 M in water; B, isopropyl alcohol 0.09 M in water; C, isopropyl alcohol 1.26 M in water; D, acetonitrile 0.05 M in water; E, ethyl alcohol 0.21 M in water.
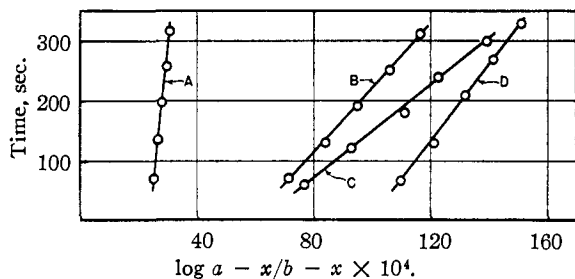

Fig. 2.—Second order rate plots for the sulfuric acid-catalyzed hydrogen peroxide oxidation of p,p'-dichlorobenzyl sulfide in isopropyl alcohol at 30.2°: A, 0.0245 M; B, 0.0955 M; C, 0.1490 M; D, 0.0500 M.

during a total reaction period of 6 hours. A similar effect was observed in isopropyl alcohol

Fig. 3.—Arrhenius plots for hydrogen peroxide oxidation of p,p'-dichlorobenzyl sulfide in isopropyl alcohol: A, uncatalyzed; B, 0.0245 M in sulfuric acid.

at 39.8° where, at initial water concentrations of 0.03 and 0.04 M, deviations occurred after about 10% completion of reaction; no deviations were noted for oxidations at 30.2°, which is in accord with the fact that the small temperature differences do not affect the strength of the bond solvating the sulfoxide.
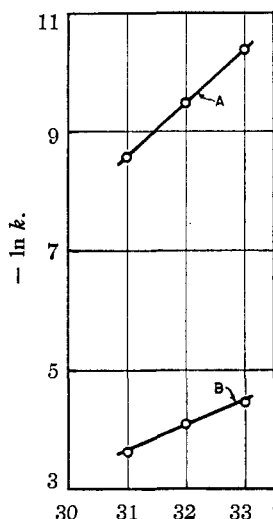
A possible explanation for accelerating reaction rates at low water concentrations is that the sulfoxide, normally the sole oxidation product other than water, is further partly oxidized to sulfone if a sufficiently large excess of water is not present to solvate the sulfoxide. This explanation receives support from the observation that a certain minimum molar ratio of water to sulfoxide appears to be required to prevent deviation from
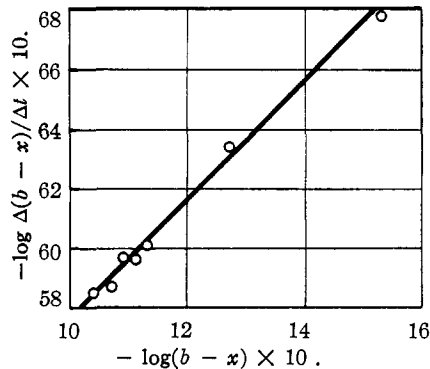

Fig. 4.—Determination of reaction order; see Table V.

second order kinetics. At 49.8 and 39.8° the second order rate law applied accurately until the molar ratio of water to sulfoxide decreased to values of 4 to 5. Absence of deviations from second order kinetics at 30.2° was presumably due to termination of the oxidations before the water to sulfoxide ratio had reached the critical range. Solvation of sulfoxide by water should result in a negative charge displacement toward the solvation site with reduction in the nucleophilicity of the sulfur atom and decreased oxidation of sulfoxide to sulfone. Water may be able to solvate sulfoxide more effectively than isopropyl alcohol because of its smaller size and larger dipole.[18]

Effect of Sulfuric Acid.—Specific rate constants for hydrogen peroxide oxidations in isopropyl alcohol at 30.2° increased linearly with sulfuric acid concentration, as shown in Table III and Fig. 5, from 1.16 × 10^{-2} 1. mole^{-1} sec.$^{-1}$ at 0.0245 M in acid to 4.80 × 10^{-2} 1. mole^{-1} sec.$^{-1}$ at 0.1490 M. The dependence of the specific rate constant for the over-all reaction on acid concentration may be expressed by the relation

$$k (30.2°) = 3.1 \times 10^{-5} + 3.0 \times 10^{-1} [\text{H}_2\text{SO}_4]$$

where 3.1 × 10^{-5} is the specific rate constant for the uncatalyzed oxidation and 3.0 × 10^{-1} is the catalytic constant for the acid-catalyzed reaction as obtained from the slope of the plot of k vs. H₂SO₄.
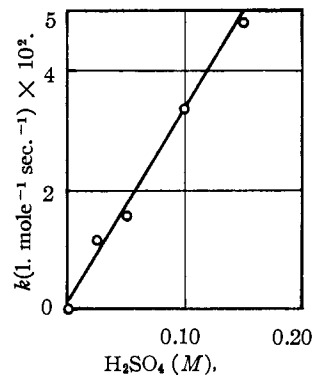

Fig. 5.—Effect of sulfuric acid on the rate of oxidation of p,p'-dichlorobenzyl sulfide by hydrogen peroxide in isopropyl alcohol at 30.2°.

TABLE III

EFFECT OF SULFURIC ACID ON THE RATE OF OXIDATION OF p,p'-DICHLOROBENZYL SULFIDE BY HYDROGEN PEROXIDE IN ISOPROPYL ALCOHOL AT 30.2°[a]

Sulfuric acid, M	k (1 mole^{-1} sec.$^{-1}$) × 10²
0.0245	1.16 ± 0.03
.0500	1.56 ± .04
.0955	3.36 ± .08
.1490	4.80 ± .12

[a] The initial water concentration was 0.24 M in each case.

(18) J. Hine and M. Hine, THIS JOURNAL, **74**, 5266 (1952).

At 0.1 M acid concentration the oxidation rate was 3 powers of 10 faster than for the uncatalyzed oxidation. The experimental activation energy for the catalyzed reaction was 8.9 kcal. mole^{-1} as against 17.2 kcal. mole^{-1} for the uncatalyzed oxidation; activation entropies were -24.2 and -40.7 cal. mole^{-1} deg.$^{-1}$, respectively, for the uncatalyzed and catalyzed processes. The difference in rates between the acid-catalyzed and uncatalyzed oxidations was estimated[19] to be about 60% dependent on the difference in activation energies and 40% on the difference in activation entropies.

Effect of Solvent.—Specific rate constants obtained at 49.8° in ethyl and isopropyl alcohol, diisopropyl ether, acetonitrile and propionitrile are compared in Table IV. The rates of oxidation in the two alcohols were not significantly different, but in propionitrile the rate was only 4% of that in isopropyl alcohol notwithstanding that the dielectric constants of the two solvents are nearly the same. In diisopropyl ether, with a dielectric constant of about 4, the oxidation rate was 8% of that in isopropyl alcohol.

TABLE IV

EFFECT OF SOLVENT ON THE RATE OF OXIDATION OF p,p'-DICHLOROBENZYL SULFIDE BY HYDROGEN PEROXIDE AT 49.8°

Solvent	Dielectric constant (20°)	k (l. mole^{-1} sec.$^{-1}$) $\times 10^5$
Ethyl alcohol	25.7	20.2 ± 0.4
Isopropyl alcohol	26	$19.1 \pm .4$
Acetonitrile	38.8	$1.8 \pm .03$
Propionitrile	27.7	$0.7 \pm .01$
Diisopropyl ether	$ca.$ 4	$1.6 \pm .03$

The data indicate that the oxidation is independent of the dielectric constant of the solvent but is promoted by solvents capable of hydrogen bonding with hydrogen peroxide. The higher dielectric constants of the nitriles than of the ether might be expected to promote dissociation of the O–O bond and increase the reaction rate, but apparently solvation is a more important consideration.

TABLE V

DETERMINATION OF THE OVER-ALL ORDER OF THE OXIDATION OF p,p'-DICHLOROBENZYL SULFIDE BY HYDROGEN PEROXIDE IN ISOPROPYL ALCOHOL 1.86 M IN WATER AT 49.7° BY THE DIFFERENTIAL METHOD^a

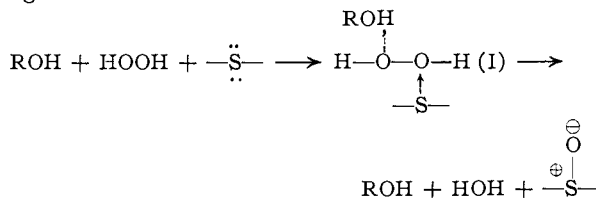| Time, kilosecs.	$b - x$	$\frac{\Delta(b-x)/}{\Delta t \times 10^6}$	$\frac{\log \Delta(b-x)/}{\Delta t}$	$b - x^b$	$\log (b-x)^c$
0.09	0.0930	...	.....	.....	......
3.72	.0879	1.405	-5.852	0.0905	-1.043
7.39	.0830	1.335	-5.875	.0855	-1.068
10.92	.0792	1.077	-5.968	.0811	-1.091
14.46	.0753	1.102	-5.958	.0773	-1.112
18.13	.0717	0.981	-6.008	.0735	-1.134
97.56	.0353	.458	-6.339	.0535	-1.272
163.92	.0244	.164	-6.785	.0299	-1.524

^{a} $a = 0.1011$, $b = 0.0946$; 70% of reaction covered. ^{b} Average of the first and second, second and third, etc., values of the molar hydrogen peroxide concentrations. ^{c} The slope of the plot of $\log \Delta(b-x)/\Delta t$ vs. $\log (b-x)$ was found to be 1.97 by the method of least squares.

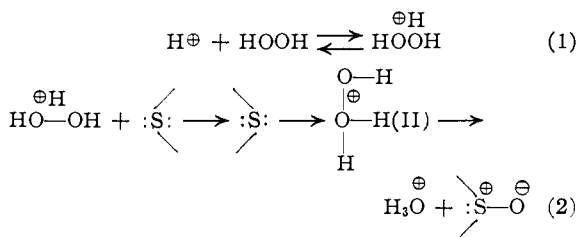(19) E. G. Foster, A. C. Cope and F. Daniels, THIS JOURNAL, 69, 1893 (1947).

Oxidation Mechanism.—The appreciable differences in activation energies and entropies for the catalyzed and uncatalyzed reactions suggest that two mechanisms are operative. The uncatalyzed process may be a termolecular displacement with solvent the electrophilic and sulfide the nucleophilic agent

$$\text{ROH} + \text{HOOH} + -\overset{..}{\underset{..}{\text{S}}}- \longrightarrow \text{H}-\overset{\overset{\text{ROH}}{|}}{\text{O}}-\text{O}-\text{H (I)} \longrightarrow$$

$$\text{ROH} + \text{HOH} + \overset{\overset{\ominus}{\text{O}}}{\underset{\oplus|}{-\text{S}-}}$$

It is not clear why water should not be more effective in solvating the hydrogen peroxide as specified by the lack of effect of water on rate in the range 0.6 to 2.53 M. It is conceivable that alcohol and water may be equally effective in solvating hydrogen peroxide. The termolecular mechanism is in agreement with the observed effects of solvent type on oxidation rate. From the non-dependence of rate on dielectric constant it may be inferred that the transition state I is non-ionic. The hydrogen peroxide may be largely solvated by alcohol before any oxidation occurs so that the observed activation entropy is a measure of the change

$$\text{H}-\overset{\overset{\text{ROH}}{|}}{\text{O}}-\text{O}-\text{H} + -\overset{..}{\underset{..}{\text{S}}}- \longrightarrow \text{I}$$
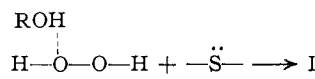
The acid-catalyzed transformation may be represented by the bimolecular process

$$\text{H}^\oplus + \text{HOOH} \rightleftharpoons \overset{\oplus\text{H}}{\text{HOOH}} \qquad (1)$$

$$\overset{\oplus\text{H}}{\text{HO}}-\text{OH} + :\text{S}: \longrightarrow :\text{S}: \longrightarrow \overset{\overset{\text{O}-\text{H}}{|\oplus}}{\underset{|}{\text{O}}}-\text{H(II)} \longrightarrow$$

$$\text{H}_3\text{O}^\oplus + :\overset{\oplus}{\text{S}}-\overset{\ominus}{\text{O}} \qquad (2)$$

in which only a small fraction of the hydrogen peroxide is presumed to be in the form of $\text{H}_2\text{-}\overset{\oplus}{\text{O}}\text{-O-H}$ ions[20] before reaction. It is accordingly postulated that proton addition to hydrogen peroxide constitutes an essential part of the formation of the transition state and that greater restriction in the several degrees of freedom of the hydrogen peroxide molecule is thereby imposed in the acid- than in the uncatalyzed process, resulting in a more rigid structure for state II than for I with a consequent larger decrease in entropy for the acid-catalyzed oxidation.

Comparison of Hydrogen Peroxide and Peroxybenzoic Acid as Oxidants.—The specific rate con-

(20) M. G. Evans and N. Uri, Trans. Faraday Soc., 45, 224 (1949), have estimated that the equilibrium constant for the reaction

$$\text{H}^\oplus + \text{HOOH} \rightleftharpoons \text{H}_2\overset{\oplus}{\text{O}}\text{OH}$$
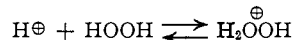
should have a value of the order of 10^{-3}. From this value it is computed that in a solution 0.1 M in respect to both hydrogen peroxide and sulfuric acid the concentration of $\text{H}_2\overset{\oplus}{\text{O}}\text{OH}$ would be 10^{-5} M, disregarding the effect of the relatively basic isopropyl alcohol (pK_a isopropyl alcohol, 18; pK_a hydrogen peroxide, 12) in reducing the proton concentration.

stant for the peroxybenzoic acid oxidation of p,p'-dichlorobenzyl sulfide in isopropyl alcohol was previously reported[3] to be 0.26 ± 0.01 l. mole^{-1} sec.$^{-1}$ at 35°. The corresponding rate constant for the hydrogen peroxide oxidation, as obtained by extrapolation of the data of Table I using the relation $\ln k = \ln A - E/RT$, was $1.45 \pm 0.03 \times 10^{-8}$ l. mole^{-1} sec.$^{-1}$ so that the rate of oxidation by peroxybenzoic acid is 7 powers of 10 faster than by hydrogen peroxide. However, at the same temperature the peroxybenzoic acid oxidation was only 3 powers of 10 faster than the sulfuric acid-catalyzed hydrogen peroxide oxidation, at 0.0245 M acid concentration. The activation entropies for the hy-

drogen peroxide and peroxybenzoic acid oxidations were found to be equal within experimental error while the experimental energies of activation were 17.2 ± 0.3 and 9.6 ± 0.5 kcal. mole^{-1}, respectively. Thus, the difference in oxidation rates between the uncatalyzed hydrogen peroxide and peroxybenzoic acid oxidations was almost entirely dependent on the difference in energies of activation of the two processes, whereas the spread in oxidation rates between the acid-catalyzed hydrogen peroxide and the peroxybenzoic acid oxidations was about 85% the result of the difference in activation entropies.

BROOKLYN, N. Y.

Synthesis and Physical Properties of Some C₁₂ and C₁₃ Phenylalkane and Cyclohexylalkane Hydrocarbons

BY JOSEPH M. LAMBERTI AND PAUL H. WISE

The synthesis, purification and some of the physical properties, including heats of combustion and viscosities, of four phenylalkanes and three cyclohexylalkanes are reported. Melting points for 3-phenylhexane and 2,4-dimethyl-3-phenylpentane, which were prepared in a purity of 99 mole % or better, were determined. The synthesis and properties of 2-ethyl-1-cyclohexylbutane and 2,4-dimethyl-3-cyclohexylpentane are reported for the first time.

As part of a systematic study directed toward correlating hydrocarbon structure and physical properties, this Laboratory has synthesized and purified representative homologs in several series of dicyclic hydrocarbons: alkyldiphenylmethane,[1] 2-alkylbiphenyl,[2] 2-alkylbicyclohexyl,[3] and the di-phenyl- and dicyclohexylalkane.[4] In order to make this evaluation of structural effects more comprehensive, several hydrocarbons have been synthesized which contain one phenyl or one cyclohexyl group attached to a side chain of six or more carbon atoms. The present paper describes the synthesis, characterization and purification of four aromatic hydrocarbons: 3-phenylhexane, 2-ethyl-1-phenylbutane, 2,4-dimethyl-3-phenylpentane and 2,4-dimethyl-1-phenylpentane; and three cyclohexyl compounds: 3-cyclohexylhexane, 2-ethyl-1-cyclohexylbutane and 2,4-dimethyl-3-cyclohexylpentane.

Although several of these hydrocarbons have been prepared previously, some of the physical properties desired for the correlation studies were not determined.[5] It was also desirable in synthesizing these compounds to choose methods that would lead to an unequivocal structure for each hydrocarbon. Of the aromatic hydrocarbons, 3-phenylhexane has been previously prepared by Levene and Marker.[6] The preparations of 2-ethyl-1-phenylbutane,[7] 2,4-dimethyl-3-phenylpen-

tane[8] and 2,4-dimethyl-1-phenylpentane[9] have also been described. Of the cyclohexyl hydrocarbons reported in this paper, only the synthesis of 3-cyclohexylhexane[10] has been reported.

In the present investigation, the four aromatic hydrocarbons were synthesized by preparing phenyl-substituted alkylcarbinols by means of the Grignard reaction, dehydrating the carbinols over alumina to the corresponding olefins, then hydrogenating the olefins to the desired aromatic hydrocarbons. The three cyclohexyl compounds were prepared by either completely hydrogenating the olefins or saturating the aromatic ring of the purified aromatic hydrocarbons. The reactions were carried out on a scale sufficient to yield at least 500 ml. of the final hydrocarbons.

The phenylalkylcarbinols prepared in the present work were found to dehydrate when fractionated even at reduced pressure, so the crude Grignard reaction products were rapidly distilled at 20 mm. pressure to remove gross impurities. The carbinols were then dehydrated over alumina at temperatures between 220–260°, and the resulting olefins were hydrogenated to the desired phenyl or cyclohexyl hydrocarbons. The hydrocarbons were characterized by ozonolysis of the intermediate olefins.

The final hydrocarbon products were purified by fractional distillation in 6-ft. Podbielniak columns at 100 mm. pressure, followed by repeated percolation through silica gel; fractions that had constant indices of refraction and densities were combined for the determinations of physical properties. Examination of the infrared spectra of the phenylalkanes did not indicate the presence of any olefinic

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