

endo- and *exo*-dehydronorbornyl and *endo*- and *exo*-norbornyl halides have been determined in aqueous ethanol solution.

The *exo*-isomers solvolyze considerably more readily than the *endo*-isomers. The double bond in the dehydronorbornyl halides appears to contribute less "driving force" in the ionization of the C-X bonds than does the 5,6-double bond in the solvolysis of cholesterol derivatives.

Nortricyclyl bromide appears to be singularly unreactive relative to other substances containing the cyclopropylcarbinyl grouping. The cyclopropane ring in the nortricyclyl cation does not appear to contribute significantly to the stabilization of the ion. It is suggested that "steric inhibition of hyperconjugative-type resonance" may be involved.

CAMBRIDGE 39, MASS.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, THE BARRETT DIVISION, ALLIED CHEMICAL & DYE CORPORATION]

The Decomposition of Cyclohexyl Hydroperoxide and the Peroxide-catalyzed Polymerization of Styrene*

BY ADALBERT FARKAS AND ELIO PASSAGLIA

Heretofore, most peroxide-catalyzed polymerization experiments have been carried out with benzoyl peroxide or derivatives of benzoyl peroxide.¹ In view of the rather complicated processes involved in the decomposition of benzoyl peroxide,² in the present work the polymerization of styrene was studied in the presence of cyclohexyl hydroperoxide since earlier experiments indicated that organic hydroperoxides are active polymerization catalysts.³

Preparation and Identification of Cyclohexylhydroperoxide.—The presence of a peroxide among the oxidation products of cyclohexane was reported by Mittag.⁴ Cyclohexyl hydroperoxide was isolated and purified according to the method used by Farkas and Stribley⁵ for the preparation of methylcyclohexyl hydroperoxide. The pure peroxide is a colorless liquid with a slight garlic-like odor. It is converted to 62.3 mole per cent. of cyclohexanol and 37.4 mole per cent. of cyclohexanone when reduced with aqueous solution of ferrous sulfate. The reduction with hydrogen in the presence of platinum oxide produces substantially pure cyclohexanol with a yield of 90 mole per cent.

Thermal Decomposition of Cyclohexyl Hydroperoxide.—The thermal decomposition of cyclohexyl hydroperoxide was investigated in various solvents at various concentrations and temperatures. Figure 1 shows the decomposition of cyclohexyl hydroperoxide in cyclohexane solu-

tion at 150° at two concentrations, the logarithm of the peroxide concentration being plotted against the time. At a low peroxide concentration, the decomposition proceeds according to a first order law. This law is, however, not obeyed at the higher concentration. The initial rate appears to be the same at both concentrations and it is possible that the acceleration observed at the higher concentration is due to the effect of the decomposition products of the peroxide on the rate of its decomposition.

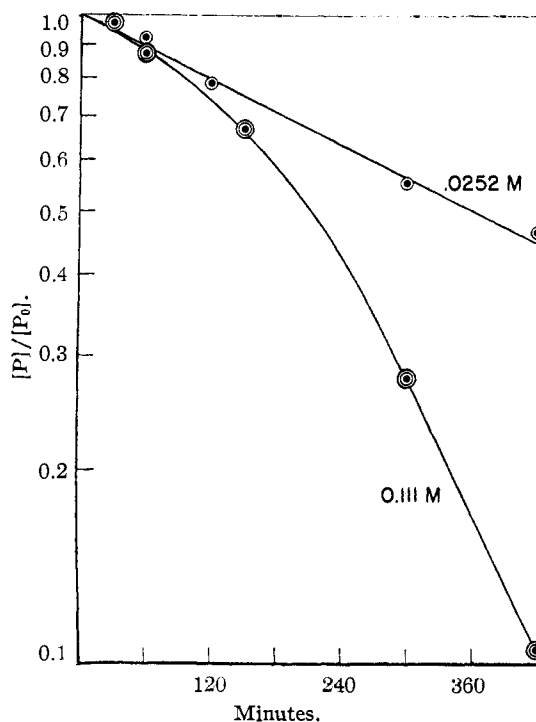


Fig. 1.—Decomposition of cyclohexyl hydroperoxide in 0.0252 and 0.111 *M* solutions in cyclohexane at 150°.

The first order velocity constants for the decomposition in cyclohexane are given in Table I

* This paper was presented before the Organic Division of the American Chemical Society in Atlantic City, New Jersey, September, 1949.

(1) See, *e. g.*, (a) S. G. Cohen, *THIS JOURNAL*, **67**, 17 (1945); (b) Price and Kell, *ibid.*, **63**, 2798 (1941); Redington, *J. Polymer Sci.*, **3**, 503 (1948).

(2) (a) Nozaki and Bartlett, *THIS JOURNAL*, **68**, 1686 (1946); (b) Barnett and Vaughn, *J. Phys. Colloid Chem.*, **51**, 927 (1947); **51**, 942 (1947); (c) D. J. Brown, *THIS JOURNAL*, **62**, 2657 (1940).

(3) A. Farkas, A. F. Stribley and A. I. Smith, Petroleum Division, Am. Chem. Soc. Meeting at Atlantic City, New Jersey, April, 1946.

(4) Mittag, Scientific Zetko Exchange, "Catalytic Oxidation with Air in Liquid Phase. IV. Oxidation of Cyclohexane," P. B.-566, Department of Commerce, Office of Technical Services.

(5) A. Farkas and A. F. Stribley, U. S. Patents 2,430,864 and 2,430,865.

for three temperatures. From these data, the activation energy for the decomposition was calculated to be 34 kcal. per mole.

The data of Table I show that cyclohexyl hydroperoxide is a relatively stable peroxide. This stability is very striking if the rate of decomposition of cyclohexyl hydroperoxide is compared with the decomposition rate of benzoyl peroxide. At 70°, cyclohexyl hydroperoxide showed no decomposition in benzene solution after 270 hours. Benzoyl peroxide under similar conditions of concentration and temperature decomposed to an extent of 50% in about twenty hours. Consequently, under these conditions, benzoyl peroxide decomposes at least 1,000 times as fast as cyclohexyl hydroperoxide.

TABLE I
DECOMPOSITION OF 0.0252 M CYCLOHEXYL HYDROPEROXIDE IN CYCLOHEXANE

Temp., °C.	Time, minutes	First order velocity constant, $k \times 10^4, \text{min.}^{-1}$
150	420	1.92
140	420	0.696
130	420	0.143

The decomposition of cyclohexyl hydroperoxide was studied also in the presence of styrene after it was ascertained that the rate of decomposition observed in cyclohexane or benzene was insuffi-

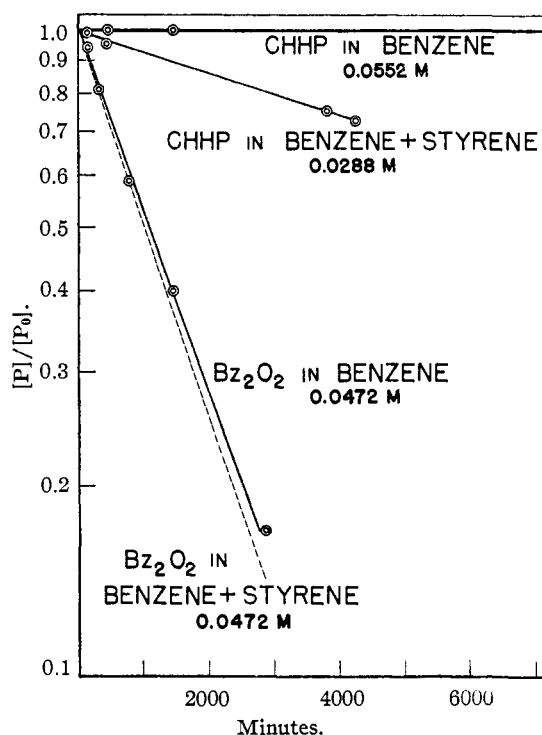


Fig. 2.—Decomposition of cyclohexyl hydroperoxide (CHHP) and benzoyl peroxide (Bz_2O_2) in benzene and in 50/50 by volume benzene-styrene solution at 70°. The peroxide concentrations are as indicated.

cient to account for the rate of the catalyzed polymerization of styrene in the presence of cyclohexyl hydroperoxide. The results obtained at 70° in a 50/50 volume per cent. styrene-benzene mixture containing 0.0288 mole of peroxide per liter are shown in Fig. 2 together with data for the decomposition of cyclohexyl hydroperoxide in benzene and for the decomposition of benzoyl peroxide in benzene and benzene-styrene mixture. The broken line for the decomposition of benzoyl peroxide in benzene-styrene mixture is based on data of Cohen.^{1a} It will be seen that both benzoyl peroxide and cyclohexyl hydroperoxide followed first order decomposition in benzene-styrene mixture, and that while the decomposition of benzoyl peroxide was only slightly affected by the addition of styrene, the decomposition of cyclohexyl hydroperoxide was considerably accelerated by the presence of styrene. The first order velocity constants for the runs shown in Fig. 2 are summarized in Table II.

TABLE II
DECOMPOSITION OF CYCLOHEXYL HYDROPEROXIDE (CHHP) AND BENZOYL PEROXIDE (Bz_2O_2) AT 70°

Peroxide	Molarity	Solvent	First order velocity constant, $k \times 10^4, \text{min.}^{-1}$
CHHP	0.0552	Benzene	0
CHHP	.0288	Benzene-styrene	0.76
Bz_2O_2	.0472	Benzene	6.17
Bz_2O_2	.0472	Benzene-styrene	6.90

Polymerization of Styrene in the Presence of Cyclohexyl Hydroperoxide.—The polymerization experiments were designed to show the effect of peroxide concentration, and the effect of time. All experiments were carried out in sealed evacuated glass ampules using a 50/50 by volume styrene-benzene solution at $70 \pm 0.1^\circ$.

The results on the effect of the peroxide concentration are given in Fig. 3 and indicate that the fraction of styrene polymerized increases with the peroxide concentration. If these results are com-

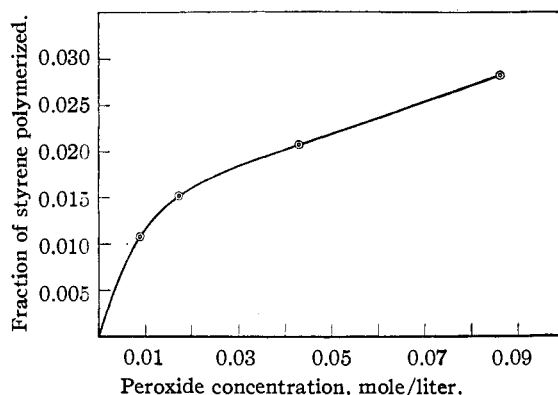


Fig. 3.—Effect of cyclohexyl hydroperoxide concentration on the polymerization of styrene at 70° in ninety minutes.

pared with the data of Cohen,^{1a} it is found that the benzoyl peroxide catalyzed polymerization occurred only about five times as fast as the cyclohexyl hydroperoxide catalyzed polymerization under similar conditions of concentration and temperature in spite of the fact that in the absence of styrene, benzoyl peroxide decomposed at least 1,000 times as fast as cyclohexyl hydroperoxide.

The progress of the polymerization of styrene in the presence of cyclohexyl hydroperoxide is shown in Fig. 4.

Since both the rate of polymerization of styrene and the rate of decomposition of peroxide have been measured, it is possible to determine the number of styrene molecules polymerized for each peroxide molecule decomposed at different stages of the reaction. These data are given in Table III. It will be seen that the ratio styrene polymerized to peroxide decomposed is fairly constant and has the value of about 328. This value was compared with the average degree of polymerization (D.P.) of the polymer as determined by viscosity measurements. As shown by the data of Table III, the degree of polymerization is about three times larger than the value 328. While the detailed discussion of this relation is outside the scope of this paper, it may be said that the results obtained are compatible with a polymerization mechanism in which one decomposing peroxide molecule starts on the average one growing polymer chain and in which these chains are preferentially terminated by recombination.

TABLE III

DECOMPOSITION OF CYCLOHEXYL HYDROPEROXIDE AND POLYMERIZATION OF STYRENE

Time, minutes	Moles of peroxide decomposed per kg. (P)	Moles of styrene polymerized per kg. (S)	Ratio S/P	D. P. by viscosity
120	0.000544	0.179	329	1370
420	.00129	0.407	316	1103
3827	.00789	2.54	323	1083
4242	.00877	3.00	342	1010

Discussion

The most striking property of cyclohexyl hydroperoxide is its stability. This stability is worth noting in view of the fact that this peroxide is a secondary hydroperoxide and as such could be expected to undergo ready decomposition by dehydration.

While it was found that the first order law is followed in the decomposition of cyclohexyl hydroperoxide at low concentration, it is not certain that a mechanism involving free radicals as found in the case of benzoyl peroxide^{2a} is absent in this case. It is planned to investigate this point more fully.

The other striking feature of cyclohexyl hydroperoxide is its accelerated decomposition in the presence of styrene. Since styrene is polymerized in the presence of cyclohexyl hydroperoxide, it is

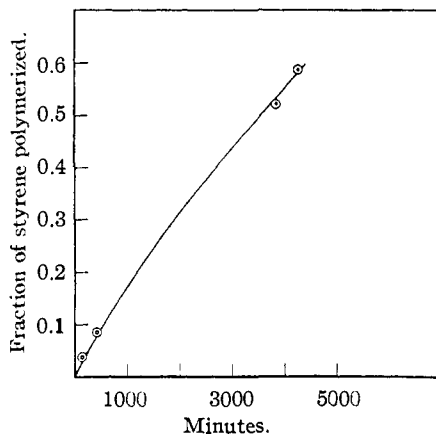


Fig. 4.—Effect of time on the polymerization of styrene at 70° in the presence of 0.0288 *M* cyclohexyl hydroperoxide.

very likely that the two reactions occur simultaneously, and the decomposition of cyclohexyl hydroperoxide and the polymerization of styrene, are coupled in some way. At the present time, it is not possible to give a definite explanation for this effect.

One possible explanation is the "cage" effect discussed by Matheson.⁶ According to this view, the two fragments of an undissociated peroxide molecule are held in a "cage" of solvent molecules,⁷ and recombine before they can diffuse apart. In the presence of an unsaturated molecule such as styrene, however, the fragments can add to the monomer and are thus prevented from recombining.

Another explanation for the behavior of cyclohexyl hydroperoxide involves an electron transfer mechanism similar to the one proposed for the photochemical decomposition of hydrogen iodide⁸ and to the mechanism suggested by Haber and Weiss⁹ for the catalyzed decomposition of hydrogen peroxide. According to this concept, the activation preceding the decomposition of the peroxide molecule consists in the shifting of an electron within the peroxide molecule so that a certain polarization occurs. If the structure of the peroxide permits sufficient mobility due to the presence of an aromatic ring, double bond or polar group, this electron shift can be stabilized and decomposition will occur. If no such polarizable features are present in the peroxide molecule, the electron shift will not remain permanently established but the electron will return to its original position without any chemical change. This seems to occur in the case of cyclohexyl hydroperoxide and possibly in the case of the alkyl and naphthenic hydroperoxides. On the other hand, peroxides like benzoyl peroxide are not intrinsi-

(6) Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

(7) Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(8) Farkas and Farkas, *ibid.*, **34**, 1113 (1938).

(9) Haber and Weiss, *Proc. Roy. Soc. (London)*, **A147**, 332 (1939).

cally stable because of the presence of the mentioned groups. The stable cyclohexyl hydroperoxide will undergo decomposition in solvents like styrene which have electron donating or accepting properties. Thus, the electron transfer necessary for the decomposition of cyclohexyl hydroperoxide occurs between the hydroperoxide and styrene.

The progress of the polymerization as shown by Fig. 4 can be represented mathematically by following the procedure used by Price and Kell^{1b} and allowing for the change in the peroxide concentration in the course of the polymerization.

Since the peroxide concentration $[P]$ as a function of time t is given by the equation

$$[P] = [P_0]e^{-k_1 t} \quad (1)$$

the rate of polymerization is given by

$$-d[M]/dt = k_2[P]^{1/2}[M] = k_2[P_0]^{1/2}e^{-k_1 t/2}[M] \quad (2)$$

where $[P_0]$ is the initial peroxide concentration and $[M]$ the monomer concentration. On integrating equation (2), equation (3) is obtained

$$-\ln \frac{[M]}{[M_0]} = \frac{2k_2}{k_1} \left([P_0]^{1/2} - [P]^{1/2} \right) = \frac{2k_2}{k_1} [P_0]^{1/2} \left(1 - \frac{[P]^{1/2}}{[P_0]^{1/2}} \right) \quad (3)$$

$[M_0]$ being the initial concentration of the monomer.

In Fig. 5 the logarithm of the ratio of the monomer concentration was plotted against the quantity $1 - ([P]/[P_0])^{1/2}$. It will be seen that the experimental points can be represented satisfactorily with a straight line in agreement with equation (3).

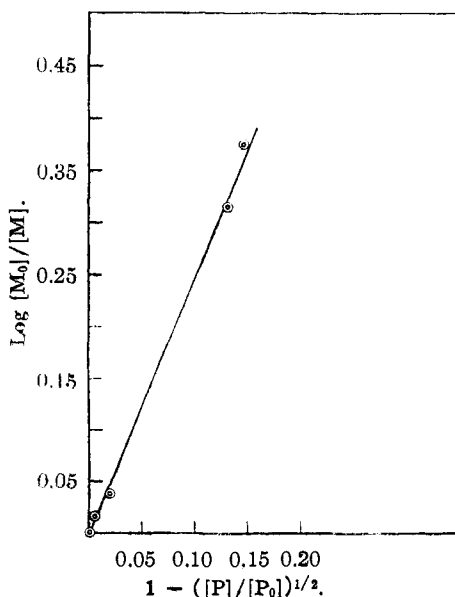


Fig. 5.—Relation between styrene polymerization and cyclohexyl hydroperoxide decomposition.

Experimental

Isolation of Cyclohexyl Hydroperoxide.—Air-oxidized cyclohexane (6400 g.) containing 1.91% cyclohexyl hy-

droperoxide was washed with 10% sodium carbonate solution to remove acids. The neutralized material was cooled to 6°, stirred vigorously, and 40% sodium hydroxide solution in 100% excess of that required by the equation $C_6H_{11}OOH + NaOH \rightarrow C_6H_{11}OONa + H_2O$ added dropwise, the whole addition taking approximately thirty minutes. The precipitated peroxide salt was filtered on a large Buchner funnel fitted with glass cloth. The salt was dissolved in ice water, the resulting hydrocarbon layer was separated, and carbon dioxide slowly blown into the aqueous layer. The peroxide separated all at once, the solution turning suddenly from clear to milky. The crude peroxide oil was separated and traces of hydrocarbon and water were removed by distillation at room temperature under a pressure of 0.1 mm. The peroxide was then distilled at room temperature under a pressure of 10^{-4} mm., and collected in a Dry Ice trap. The yield on the first precipitation was 85.8 g. with a peroxide concentration of 89.0%.

The distilled peroxide was dissolved in cyclohexane to make a 2% solution and the whole procedure of precipitation, separation and distillation repeated; final yield, 46.8 g. (38.3%), 97.2% purity.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.05; H, 10.42. Found: C, 60.58; H, 10.60; d_4^{25} , 1.018; n_D^{25} , 1.4638; f. p. -20° ; molar refractivity, observed, 31.50; calculated¹⁰ 31.40.

Reduction of Cyclohexyl Hydroperoxide with Ferrous Sulfate.—Cyclohexyl hydroperoxide (4.86 g., 95.8% pure) was added slowly to 39.2 g. of ferrous ammonium sulfate in 125 ml. of water. The resulting deep brown solution was acidified with dilute sulfuric acid and extracted twice with ether. The ether was evaporated and a clear oil resulted; yield, 4.18 g. The cyclohexanone content of the oil was determined by the 2,4-dinitrophenylhydrazine method.¹¹ The 2,4-dinitrophenylhydrazone had a m. p. of 160.2° . The same derivative of pure cyclohexanone (Eastman Kodak Company) melted at 160.3° ; mixed m. p. was 160.3° . The concentration of cyclohexanone was 36.7%. Cyclohexanol was determined by acetylation and saponification of the ester and was identified by the 3,5-dinitrobenzoate derivative which had a m. p. of 112.3° as compared to the reported value of $112-113^\circ$ ¹² for the derivative of genuine cyclohexanol. The concentration of cyclohexanol was 62.3%.

Reduction of Cyclohexyl Hydroperoxide with Hydrogen and Platinum Oxide Catalyst.—Five grams of cyclohexyl hydroperoxide (95.6% pure) dissolved in 100 ml. of cyclohexane was reduced with hydrogen in the presence of 0.2 g. of platinum oxide catalyst, at a pressure of 3.5 atm. After a reaction time of fifteen minutes at room temperature, the hydrogenated solution was found to be free of acid, peroxide and cyclohexanone. After removing most of the cyclohexane, an oil was obtained which contained 53.7% cyclohexanol, corresponding to 90.7% of the theoretical amount; m. p. of the 3,5-dinitrobenzoate was 112.6° .

Thermal Decomposition of Cyclohexyl Hydroperoxide.—Cyclohexane from E. I. du Pont de Nemours & Co., Inc., of better than 99% purity, was redistilled and the middle fraction was used as the solvent.

Initial concentrations of the peroxide were determined in ten-ml. portions as described below (see Analytical). Twenty-five-ml. portions of cyclohexyl hydroperoxide solution were placed in individual glass ampules, which had been washed in sulfuric acid-chromic acid solution, rinsed with distilled water and dried overnight at 110° . The ampules were equipped with ground glass joints for connection to a vacuum system. They were placed in a Dry Ice-acetone bath and after freezing were evacuated to 10^{-4} mm. The vacuum pumps were disconnected by means of a stopcock and the cooling bath removed. When

(10) Milas, Surgenor and Perry, *Trans JOURNAL*, **68**, 1617 (1946).

(11) Iddles, Low, Rosen and Hart, *Ind. Eng. Chem., Anal. Ed.*, **11**, 102-103 (1939).

(12) Huntress and Mulliken, "Identification of Pure Organic Compounds, Order 1," John Wiley and Sons, New York, N. Y., 1941.

all the solid had melted, the cooling bath was replaced and the evacuation was resumed. After all traces of air had been removed, the samples were sealed, and placed in an oil-bath, maintained at a predetermined temperature with an accuracy of $\pm 0.1^\circ$. At intervals, one ampule was removed from the oil-bath, chilled quickly and a 10-ml. sample of its contents was withdrawn and titrated.

Polymerization of Styrene—Raw Materials.—Styrene was obtained from The Dow Chemical Company and was distilled at room temperature immediately prior to use. The material boiled at 74° at 73 mm. and had d_{20}^{20} 0.907 and n_D^{20} 1.5468. Baker and Adamson thiophene-free reagent grade benzene from The General Chemical Division of Allied Chemical & Dye Corp. and Eastman Kodak Co. white label benzoyl peroxide of 98.8% purity were used without further purification. E. I. du Pont de Nemours & Co., Inc., reagent grade methanol was distilled over solid sodium hydroxide and the portion boiling at 64.5° (90%) was collected.

Polymerization of Styrene by Cyclohexyl Hydroperoxide.—A stock solution of cyclohexyl hydroperoxide in benzene having at least twice the final desired maximum concentration was made. This was diluted with styrene so that the final solution contained 50% by vol. of benzene-peroxide solution and 50% by vol. styrene. The peroxide concentration was checked by titration and 25-ml. samples were sealed in glass ampules as described above. The filled ampules were placed in a water-bath at $70 \pm 0.1^\circ$, removed after ninety minutes and quickly chilled. The ampules were then broken and weighed amounts of the solution were added to excess methanol. The precipitated polystyrene was allowed to settle overnight, then filtered on sintered glass crucibles, washed five times with methanol and dried at 70° to constant weight.

Rate Measurements in Benzene-Styrene.—The procedure used here was the same as in the polymerization experiment above except that only one concentration of cyclohexyl hydroperoxide was used. It was found more convenient to express the concentration as weight per cent. cyclohexyl hydroperoxide, since the polymerized styrene became quite viscous. For this reason, weighed samples of solution were used for analysis. The ampules were removed from the water-bath at various times and chilled. One weighed portion was analyzed for peroxide and the polystyrene precipitated from another weighed portion. Since some of these samples were quite viscous and a great deal of polystyrene was obtained, the polystyrene was re-dissolved in benzene and re-precipitated after the first

drying and weighing. Surprisingly little occlusion was found.

Viscosity Measurements.—Approximately 0.06 base molar solutions of polystyrene were made up in benzene. These were then diluted so that at least two concentrations were available for each sample of polystyrene. Viscosity was measured at $25 \pm 0.1^\circ$ with an Ostwald viscosimeter having a flow time for benzene of 59.4 sec. The molecular weights and degrees of polymerization were then calculated using the method of Gregg and Mayo.¹³

Analytical.—The method used was similar to that described by Wheeler.¹⁴ The sample to be analyzed for peroxide was placed in a 250-ml. iodine flask. To it was added 20 ml. of 50/50 acetic acid-chloroform solution and a few pieces of Dry Ice to sweep out air. After the Dry Ice had vaporized, 2 ml. of saturated potassium iodide was added quickly, admitting as little air as possible. The flasks were shaken for ten minutes, water was added, and the solutions titrated with standard thiosulfate. Blanks usually amounted to one or two drops of 0.1 *N* thiosulfate.

Summary

1. Cyclohexyl hydroperoxide was isolated in substantial purity from the oxidation products of cyclohexane and its structure was ascertained.

2. The rate of decomposition of cyclohexyl hydroperoxide was measured in various solvents. This decomposition was found to follow a first order law at low concentrations and had an activation energy of 34 kcal. per mole. In the presence of styrene the decomposition of cyclohexyl hydroperoxide was accelerated very considerably.

3. The rate of polymerization of styrene was studied in the presence of cyclohexyl hydroperoxide. The degree of polymerization of the polymer formed as determined by viscosity measurements was found to be about three times larger than the number of styrene molecules polymerized per peroxide molecule decomposed.

(13) Gregg and Mayo, *THIS JOURNAL*, **70**, 2373 (1948).

(14) Wheeler, *Oil and Soap*, **9**, 89 (1932).

PHILADELPHIA 37, PENNSYLVANIA

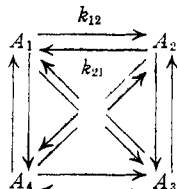
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PHYSICS, THE UNIVERSITY OF TEXAS, AND TECHNICAL AND RESEARCH DIVISIONS, HUMBLE OIL AND REFINING CO.]

A General Theory of Coupled Sets of First Order Reactions

BY F. A. MATSEN AND J. L. FRANKLIN

The most general form for a coupled set of first order reactions is the one in which every component is reacting to form every other component. For four components



From the general form any simpler set may be obtained by setting certain of the rate constants equal to zero.

Application of the law of mass action to the

general *m*-component system yields the following set of rate equations

$$\dot{A}_i + \sum_{j=1}^m K_{ij}A_j = 0 \quad (i = 1, 2, \dots, m) \quad (1)$$

where $K_{ij} = -k_{ij}$ and $K_{ii} = \sum_p k_{ip}$ ($p = 1, 2, \dots, m$).

Equations of this form have been integrated by a number of authors¹ and the integral shown to be

$$A_i = \sum_{r=1}^m B_{ir}e^{-\lambda_r t}$$

(1) (a) Picard, "Traité d'Analyse," Paris, 1928; (b) Rakowski, *Z. physik. Chem.*, **67**, 321 (1907); (c) Zwolinski and Eyring, *THIS JOURNAL*, **69**, 2702 (1947); (d) Denbigh, Hicks and Page, *Trans. Faraday Soc.*, **44**, 479 (1948).