[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Ferrous Iron and Peroxides. III. Reaction with Cumene Hydroperoxide, in Aqueous Solution[1]

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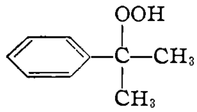
In previous publications[2,3] the authors have presented the results of an experimental study of the reaction between hydrogen peroxide and ferrous iron, in very dilute aqueous solution, in the presence of various compounds. In the absence of oxygen, it has been shown[2] that the peroxide–iron reaction induces the oxidation of certain organic compounds (termed "promoters") by hydrogen peroxide; several compounds (termed "suppressors") suppress this induced reaction. In the presence of oxygen,[3] induced oxygen oxidation of ferrous iron occurs in the presence of various organic compounds, apparently through the intermediate formation of organic peroxides; this induced oxygen oxidation is suppressed by chloride ion, but not by any of the organic compounds studied. Mechanisms for these reactions were presented in these papers, and in a review paper[4] on the reaction between ferrous iron and peroxides. It is likely that in the reaction between ferrous iron and organic peroxides, particularly hydroperoxides, active intermediates are formed, through mechanisms similar to that of the ferrous iron–hydrogen peroxide reaction. The present paper deals with a study of the reaction between ferrous iron and a hydroperoxide, under conditions similar to those used with hydrogen peroxide.[2,3] The results obtained are of particular importance in view of the wide use of the reaction between ferrous iron and organic hydroperoxides in the determination of these hydroperoxides, and in the initiation of the polymerization of vinyl monomers.

The hydroperoxide chosen for the present study is cumene hydroperoxide (phenyldimethyl methyl hydroperoxide), designated below as CHP. This compound is a typical organic hydroperoxide, of structure



The preparation of this compound from cumene (isopropylbenzene) by photochemical autoxidation at 60–70° has been described by Hock and Lang.[5] Cumene hydroperoxide is an oily liquid which is quite stable at room temperature. As shown below, its solubility in water is sufficient (0.09 *M*) to permit study of its reactions in dilute aqueous solutions. CHP is used in oxidation–reduction polymerization recipes which have proved to be of considerable practical importance.[6,7] Determination of CHP by both ferrous and iodometric methods has been studied recently.[8]

Experimental

Reagents.—The reagents used were as described previously.[2,3] The water used in all experiments was purified by distillation from alkaline permanganate. Benzene (Mallinckrodt reagent grade) and CHP (purified as below) were also used.

Purification of CHP.—A sample of CHP (Sample No. X5557–47) prepared from cumene was kindly furnished by the Hercules Powder Co. Iodometric analysis of this sample by a macro procedure (*v. i.*) corresponded to 71.4% pure CHP. It has been pointed out by Hock and Lang[5] that the impurities in a sample of cumene hydroperoxide prepared by autoxidation of cumene may consist largely of the decomposition products of cumene hydroperoxide, namely, dimethylphenylcarbinol, phenol, and acetone, in addition to the unchanged cumene.

Purification of the Hercules sample of cumene hydroperoxide was carried out by the alkali extraction procedure of Hock and Lang,[5] with the omission of the final vacuum distillation used by these authors. Iodometric analysis by the above procedure corresponded to 94.2% pure CHP. It should be pointed out that both Hock and Lang[5] and Wagner, *et al.*,[8] obtained samples of 95% purity. Further purification does not seem feasible by this method.

Iodometric Analysis of CHP.—Two methods of iodometric analysis have been investigated for use with CHP. The first of these is a macro method, developed in this Laboratory[9] for determination of *t*-butyl hydroperoxide.

Procedure.—Accurately weigh a 1.2 to 1.6 g. sample into a weighing bottle, transfer the sample to a 100-ml. volumetric flask and dilute to the mark with glacial acetic acid. Pipet a 25-ml. aliquot into a 125-ml. iodine flask, and then bubble nitrogen through the solution for five minutes. Add 2 g. of finely divided sodium iodide, flush the air space above the solution with nitrogen, and stopper the flask. Allow the solution to stand in the dark at room temperature for twenty minutes. Add 50 ml. of water, and titrate with 0.1 *N* thiosulfate solution, using starch indicator near the end-point. A blank solution should require less than about 0.02 ml. of thiosulfate solution. The reaction time of twenty minutes was found to be sufficient, by comparison with determinations carried out in sealed flasks at 100°.

The method of Kokatnur and Jelling[10] was used for the

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[1] This investigation was started under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Synthetic Rubber Program of the United States Government. From a thesis submitted by A. I. Medalia to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the doctor's degree, 1948.

[2] I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3777, (1949).

[3] I. M. Kolthoff and A. I. Medalia, *ibid.*, **71**, 3784 (1949).

[4] A. I. Medalia and I. M. Kolthoff, *J. Polymer Sci.*, **4**, 377 (1949).

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

[6] E. J. Vandenberg and G. E. Hulse, *Ind. Eng. Chem.*, **40**, 932 (1948).

[7] W. A. Schulze, W. B. Reynolds, C. F. Fryling, L. R. Sperberg and J. E. Troyan, *India Rubber World*, **117**, 739 (1948).

[8] C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976, 982 (1947); C. D. Wagner, H. L. Clever and E. D. Peters, *ibid.*, **19**, 980 (1947).

[9] I. M. Kolthoff and T. S. Lee, private communication.

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

determination of small amounts of cumene hydroperoxide. In this method the peroxide is dissolved in about 75 ml. of boiling absolute ethanol in a 150-ml. beaker; after addition of 1 ml. each of glacial acetic acid and saturated aqueous potassium iodide, boiling is continued for five minutes, and then the iodine formed is titrated immediately with 0.005 *N* thiosulfate. The accuracy of the method was improved by amperometric determination of the end-point, using the procedure developed by the late Dr. L. S. Guss of this laboratory. In this procedure a rotating platinum microelectrode at the potential of a saturated calomel electrode serves as an indicator of the iodine concentration; titration is continued until the current, which is due to reduction of iodine at the microelectrode, decreases to zero. With amounts of CHP as small as 5 mg. (0.03 millimole) in 75 ml., the accuracy and precision were found to be of the order of 2%.

Results and Discussion

Solubility of Purified Cumene Hydroxide in Water.—The solubility in water of the purified sample of cumene hydroperoxide, and its distribution between benzene and water and between benzene and aqueous alkali, have been determined. The method used was to shake various amounts of water, cumene hydroperoxide, and (in some cases) benzene for two minutes in an ungreased separatory funnel; 2-ml. portions of the filtered aqueous layer were then analyzed by the method of Kokatnur and Jelling. The results are given in Table I.

Table I.

Solubility of Cumene Hydroperoxide in Water and Aqueous Alkali at 25°

Benzene taken,[a] ml.	Concn. of NaOH in aqueous phase initially, *N*	CHP[b] taken,[a] g.	CHP[b] diss. in 100 ml. of aqueous phase, g.	Mole % CHP in aqueous phase	Mole % CHP in organic phase[c]
..	....	2.60	1.36	0.161	(95)
..	....	13.0	1.35	.160	(95)
2.0	....	2.60	0.731	.0865	36.3
6.0	....	2.60	.441	.0522	17.6
14.0	....	1.95	.238	.0282	6.67
28.0	0.0506	3.91	.466	.0551	6.70
28.0	.253	3.91	1.11	.132	5.51

[a] Per 100 ml. of water. [b] Based on 100% purity. [c] Corrected for the solubility of benzene in water.

The solubility of the sample of purified CHP in water does not depend upon the amount of CHP taken; this is indicative of the purity of this sample. The data for the distribution of CHP between benzene and water show that the behavior does not follow the ideal distribution equation

$$(\text{Mole \% in water}) = K\ (\text{mole \% in benzene}) \quad (1)$$

Graphical extrapolation of the data to 100% purity gives for the solubility of pure CHP in water a value of 0.165 mole %, or 0.0914 molar, or 1.39 g. per 100 ml. of solution.

From the data for the distribution of CHP between benzene and aqueous alkali the ionization constant, K_a, is calculated to be 2.6×10^{-13} (0.0506 *N* alkali) and 2.4×10^{-13} (0.253 *N* alkali), respectively, at 25°. By way of comparison, the ionization constant of hydrogen peroxide is given[11] as 2.4×10^{-12} at 25°.

Approximate Determination of the Rate of Reaction between Ferrous Iron and CHP. Procedure.—Solutions of CHP and ferrous iron in 1.5 *N* sulfuric acid (total volume, 120 ml.) were mixed in the absence of air, in a reaction vessel with two compartments, described in a previous publication.[2] After the desired time of reaction 20 ml. of air-free benzene was added to the inner compartment and the mixture was shaken for ten seconds. After standing for one to two minutes to allow separation of the phases, a 15-ml. aliquot of the benzene phase was analyzed by the procedure of Kokatnur and Jelling,[9] and 50-ml. portions of the aqueous phase were titrated with ceric sulfate. The results of experiments carried out as above are given in Table II.

Table II

Reaction between Ferrous Iron and Purified CHP in 1.5 *N* H_2SO_4 at 27°, in the Absence of Oxygen. Initial Concentrations: $(Fe^{++})_0 = 5.31 \times 10^{-4}\ M$; $(CHP)_0 = 2.21 \times 10^{-4}\ M$

Time of reaction, sec.	Concn. remaining at given time ($M \times 10^4$)		Molar reaction ratio $\frac{\Delta(Fe^{++})}{\Delta(CHP)}$	Approximate rate constant, k_1 (l. mole^{-1}sec.$^{-1}$)
	Fe^{++}	CHP		
30	4.52	1.38	0.95	30
40	4.36	1.36	1.15	28
75	4.10	1.00	1.00	22

In Table II the reaction times given are from the instant of mixing the ferrous iron and CHP to the midpoint of the period of shaking with benzene. In calculating the rate constant, it was assumed that, as in the reaction between hydrogen peroxide and ferrous iron, the rate-determining step is first-order in both reactants. The calculation of the rate constant is complicated by the fact that the reaction between ferrous iron and CHP is not stoichiometric, as is evident from Table II; the average reaction ratio under the experimental conditions is 1.05. The calculation of the approximate rate constant has been based upon the rate of disappearance of ferrous iron only, taking an average value of the concentration of CHP. Thus if

$$-\,d(Fe^{++})/dt = k_1(Fe^{++})(CHP) \quad (2)$$

then

$$\int_0^t \frac{-d(Fe^{++})}{(Fe^{++})} = -\ln\left[\frac{(Fe^{++})}{(Fe^{++})_0}\right] = k_1t(CHP)_{\text{average}} \quad (3)$$

The values of k_1 given in Table II were calculated on the basis of equation (3). The agreement between the values obtained is probably as good as can be expected in view of the inaccuracy of the reaction times and the large changes in the concentrations of CHP over the ranges in which average values were taken. The average value of k_1 is 27 l. mole^{-1} sec.$^{-1}$, or slightly less than half the

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(11) R. A. Joyner, *Z. anorg. Chem.*, **77**, 103 (1912).

value (62) given by Baxendale, Evans and Park[12] for the corresponding rate constant in the hydrogen peroxide–ferrous iron reaction.

Reaction in the Absence of Oxygen: Determination of Over-all Reaction Ratios.—The experiments described below were carried out using the reaction vessels and technique described previously. After rapid mixing of the ingredients, the reaction was allowed to go to completion, and then aliquots were removed after twenty and forty minutes and titrated with ceric sulfate. It was not necessary to extract the reaction mixture with benzene before the titration, since the CHP was completely consumed. Purified (94%) CHP was used throughout. Results obtained in the presence and absence of various added substances are given in Table III. Reactions were carried out at room temperature.

TABLE III

REACTION BETWEEN FERROUS IRON AND PURIFIED CHP IN 1.5 N H_2SO_4, IN THE ABSENCE OF OXYGEN

Initial concentrations				Molar ratios	
Ethanol, M	Acetic acid, M	Acetone, M	Fe^{++} ($M \times 10^3$)	Initial $\frac{(Fe^{++})}{(CHP)}$ taken	$\frac{(Fe^{++}) \text{ reacted}}{(CHP) \text{ taken}}$
..	..	..	0.53	2.41	1.15
..	..	..	1.9	3.28	1.12
10^{-2}	..	..	1.9	3.28	1.06
10^{-1}	..	..	1.9	3.28	0.76
..	10^{-1}	..	1.9	3.28	1.40
..	10	..	1.9	3.28	1.92
10^{-1}	10	..	1.9	3.28	1.79
..	..	10	1.9	3.28	1.93

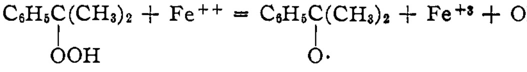
In the absence of added substances, the molar reaction ratio is considerably less than the stoichiometric value of 2.00 (see also Table II). It is of interest that the same reaction ratio of 1:1 is found with two different initial concentrations of reactants. The results indicate that the reaction between ferrous iron and CHP induces the decomposition of CHP. In this respect the behavior is similar to that of hydrogen peroxide in its reaction with ferrous iron in the presence of an organic compound of the "promoting" type.[2]

Addition of ethanol increases the extent of the induced decomposition of CHP. The reaction ratios found with the concentrations of ethanol employed in the experiments of Table III are higher than those found in the hydrogen peroxide–ferrous iron reaction when carried out in the presence of these concentrations of ethanol, under comparable conditions.[2]

Addition of acetic acid diminishes the extent of induced decomposition of CHP, both in the presence and absence of ethanol. Qualitatively, acetic acid exerts the same "suppressing" action on the ferrous iron–CHP systems as was found in the hydrogen peroxide–ferrous iron–ethanol system.[2] With 0.1 M acetic acid, the induced decomposition of CHP is only partially suppressed, while with 10 M acetic acid (62% by weight) suppression is virtually complete, in the absence of ethanol, but only partially complete in the presence of 0.1 M ethanol. Similarly, suppression is virtually complete with 10 M acetone, in the absence of ethanol. The importance of these results from the standpoint of peroxide analysis is obvious, as will be demonstrated in a subsequent paper.

In the experiments carried out in 10 M acetic acid, it was necessary to dilute the solutions with approximately an equal volume of water before titrating, in order to obtain a sharp end-point. In the experiment with acetone, a sharp end-point was obtained by diluting the 50-ml. aliquot with 100 ml. of water before titrating. In this experiment, correction was made for loss of acetone by volatilization during the hour-long flushing with nitrogen, by weighing the vessel before and after flushing.

As has been discussed elsewhere,[4] the mechanism of the reaction between ferrous iron and hydrogen peroxide is not known with certainty, despite the extensive studies of this reaction. Much less study has been devoted to the reaction between hydroperoxides and ferrous iron, and the possible reaction steps are much more numerous. Presentation of such speculative mechanisms would be premature at this time. The course of the reaction cannot be established definitely without determination of the products. However, it is certain on the basis of the above data, together with results of reactions carried out in the presence of oxygen (*v. i.*), that in the course of the reaction between CHP and ferrous iron, some active intermediate is formed. By analogy with the mechanism of Haber and Weiss[13,14] for the reaction between hydrogen peroxide and ferrous iron, it is likely that the first step of the reaction is as shown below



$$\underset{\displaystyle \text{OOH}}{C_6H_5\overset{|}{C}(CH_3)_2} + Fe^{++} = \underset{\displaystyle \text{O}\cdot}{C_6H_5\overset{|}{C}(CH_3)_2} + Fe^{+3} + OH^- \qquad (4)$$

resulting in formation of a reactive organic radical. In the absence of oxygen this free radical can react with CHP resulting in a decomposition of the hydroperoxide by a chain reaction, and also with ethanol, acetic acid, acetone, etc. The free radicals formed play a part in the induced decomposition of the CHP. In the presence of oxygen the various organic free radicals react with oxygen, giving rise to induced oxygen oxidation of ferrous iron.

Reaction in the Presence of Oxygen.—The reaction between ferrous iron and CHP in aqueous solution has been studied in the presence of oxygen by the "shaking" and "stirring" techniques described previously.[2,3] In the "shaking" technique, the same apparatus and procedure were

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[12] J. H. Baxendale, M. G. Evans and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946).

[13] F. Haber and J. Weiss, *Naturwiss.*, **20**, 948 (1932).

[14] F. Haber and J. Weiss, *Proc. Roy. Soc.* (*London*), **A147**, 332 (1934).

used as in the experiments of Table III, except that the solutions were flushed with air or oxygen rather than nitrogen. In the "stirring" technique, one reactant is added by pipet to a solution of the other reagents, with vigorous stirring. In each experiment carried out by the "shaking" technique, the vessel was shaken for eighty seconds, to allow access of the solution to the oxygen of the gas phase during the greater part of the reaction. Aliquots of the reaction mixture were titrated with ceric sulfate after ten and twenty-five minutes reaction time. The titrations agreed closely, showing that under the conditions used, the CHP had been completely reduced within ten minutes. The results are given in Table IV.

Table IV

Reaction between Ferrous Iron and Purified CHP, in 1.5 *N* H_2SO_4, in the Presence of Oxygen. Experiments Carried Out by "Shaking" Technique

Initial concentrations				Molar ratios	
Ethanol, *M*	Acetic acid, *M*	Fe^{++} ($M \times 10^3$)	Gas	Initial $\frac{(Fe^{++})}{(CHP)}$ taken	$\frac{(Fe^{++})\text{ reacted}}{(CHP)}$ taken
..	..	0.51	Air	3.82	3.50
..	..	.51	Air	7.64	4.64
..	..	.51	Air	12.7	4.70
..	..	.51	Oxygen	12.7	4.70
10^{-4}	..	.51	Air	12.7	4.90
10^{-}[illegible]	..	.51	Air	12.7	6.50
..	..	1.9	Oxygen	3.28	3.05
..	10	1.9	Oxygen	3.28	2.94

The results of Table IV show that considerable induced oxygen oxidation of ferrous iron takes place during the course of the reaction between ferrous iron and CHP, in the presence of oxygen. With a given initial concentration of ferrous iron, the reaction ratio is practically independent of the initial ratio of reactants, provided that ferrous iron is in sufficient excess over CHP. With 0.51×10^{-3} *M* ferrous iron and 0.40×10^{-4} *M* CHP, the same results were obtained in air as in oxygen. Addition of ethanol has a definite effect in increasing the induction factor. The addition of acetic acid (10 *M*) does not materially affect the extent of the reaction, in the single experiment performed. The results found for the reaction between CHP and ferrous iron in the presence of oxygen are qualitatively similar to those found for the reaction between hydrogen peroxide and ferrous iron in the presence of both oxygen and an organic compound.[3]

Results obtained by the "stirring" technique are given in Table V. The "reverse" mode of addition was used (CHP added to ferrous iron). Titrations carried out on duplicate reaction mixtures after ten and twenty minutes agreed closely; only the average values are given.

Table V

Reaction between Ferrous Iron and Purified CHP, in 1.5 *N* H_2SO_4. Experiments Carried Out by "Stirring" Technique in the Presence of Air

	Molar ratios	
Initial concn. of Fe^{++} ($M \times 10^3$)	$\frac{\text{Initial }(Fe^{++})}{(CHP)\text{ taken}}$	$\frac{(Fe^{++})\text{ reacted}}{(CHP)\text{ taken}}$
1.0	2.97	2.45
2.0	2.97	1.83

With 10^{-3} *M* ferrous iron, induced air oxidation of ferrous iron is found, while with 2×10^{-3} *M* ferrous iron, induced decomposition of CHP predominates over the induced air oxidation, in the experiments of Table V. This behavior is similar to that found with hydrogen peroxide in the presence of ethanol.[3]

Summary

The solubility of cumene hydroperoxide (CHP) in water at 25° is 0.0914 *M*. The distribution ratio of CHP between water and benzene is a function of the concentration of CHP. The ionization constant (acid dissociation constant) of CHP is 2.5×10^{-13} at 27°. The rate constant of reaction between CHP and ferrous iron in aqueous solution (1.5 *N* sulfuric acid) at 27°, taken as first order in each reactant, is roughly 27 l. $mole^{-1}$ $sec.^{-1}$.

The behavior of cumene hydroperoxide in its reaction with ferrous iron is qualitatively similar to that of a mixture of hydrogen peroxide and an organic compound such as ethanol. Thus, the reaction between cumene hydroperoxide and ferrous iron in pure aqueous solution leads to considerable induced decomposition of the peroxide, in the absence of oxygen, and to considerable induced oxidation of ferrous iron, in the presence of oxygen. Addition of ethanol to the system increases the extent of both induced reactions; while addition of acetic acid suppresses the induced decomposition of peroxide in the absence of oxygen, but does not suppress the induced oxidation in the presence of oxygen.

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