

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA, AND OF BROOKHAVEN NATIONAL LABORATORIES, UPTON, NEW YORK]

Reaction of Cumene Hydroperoxide with Hydrazine Induced by the Reaction Between Iron(III)EDTA and Hydrazine^{1,2}

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The direct reaction between cumene hydroperoxide (CHP) and hydrazine is negligibly slow at 0° and pH 9. Upon the addition of the ethylenediaminetetraacetate (EDTA) complex of iron(III) a pronounced reaction occurs at 0° in which the CHP is transformed quantitatively into acetophenone. From an analysis of the kinetic results it appears that the first step is the relatively slow reaction between iron(III) EDTA and hydrazine, forming iron(II) EDTA and hydrazyl radicals. Both iron(II)EDTA and hydrazyl are oxidized by hydroperoxide, forming acetophenone (AP) and methyl radicals. The acceleration is probably due to the chain reaction $\text{CH}_3\cdot + \text{N}_2\text{H}_4 \rightarrow \text{CH}_4 + \text{N}_2\text{H}_3\cdot$ and $\text{N}_2\text{H}_3\cdot + \text{ROOH} \rightarrow \text{N}_2\text{H}_2 + \text{AP} + \text{CH}_3\cdot$. The effect of the EDTA complex of iron(III) is markedly suppressed by sodium acrylate (M), which can be accounted for by the competitive reaction $\text{CH}_3\cdot + \text{M} + (n-1)\text{M} \rightarrow \text{CH}_3\text{M}_n\cdot$, the latter itself being terminated by reaction with $\text{CH}_3\cdot$.

Introduction

In emulsion polymerization at low temperature the initiating free radicals generally are produced by the interaction of a hydroperoxide and iron(II), the latter being formed continually by reaction of iron(III) with a reducing agent. As an example, hydrazine is a suitable reductant for the ethylenediaminetetraacetate complex of iron(III), denoted as iron(III)EDTA.³ In order to interpret the involved kinetics of emulsion polymerization, the kinetics of radical formation in homogeneous medium must be known. The mechanisms of the reactions between iron(III)EDTA and hydrazine⁴ and between iron(II)EDTA and hydroperoxide⁵ have been established. The present paper deals with the system iron(III)EDTA-hydrazine-cumene hydroperoxide (CHP) in aqueous solution, in the absence and presence of sodium acrylate.

Experimental

Most of the experimental procedures and the chemicals have been described.⁴ CHP (Hercules Powder Co.) was purified by the method of Hock and Lang.⁶ The purity was found to be 90.5% by the arsenious⁷ and iodometric methods⁸ Acetophenone and acrylic acid were Eastman products. Each was purified by fractional distillation before use.

The rate of disappearance of CHP from solutions containing iron(III)EDTA and hydrazine at pH 9 was measured polarographically with the dropping mercury electrode at -0.9 v. vs. the s.c.e., using a Leeds and Northrup Electrochromograph Type E. This potential is in the diffusion current region of both iron(III)EDTA and CHP. After correction for the residual current the diffusion current was found proportional to the concentration in solutions of either CHP or iron(III)EDTA over a range between 3×10^{-4} and 2×10^{-3} M. In a mixture 0.05 M in borax and containing both electroactive species the observed diffusion current at -0.9 v. was smaller than the sum of the individual diffusion currents of each species. This is caused by reaction of iron(II)EDTA formed upon reduction of iron(III)EDTA with some CHP at or near the electrode with formation of the RO· free radical, which rapidly disproportionates into acetophenone and the $\text{CH}_3\cdot$ free radical.

(1) This investigation was carried out under a grant from the National Science Foundation.

(2) Initial experiments are described in the M.S. Thesis of H. Minato, University of Minnesota, July, 1958.

(3) I. M. Kolthoff and E. J. Meehan, *J. Polymer Sci.*, **9**, 343 (1952).

(4) H. Minato, E. J. Meehan, I. M. Kolthoff and C. Auerbach, *J. Am. Chem. Soc.*, **81**, 6168 (1959).

(5) W. L. Reynolds and I. M. Kolthoff, *J. Phys. Chem.*, **60**, 996 (1956).

(6) H. Hock and S. Lang, *Ber.*, **77B**, 257 (1944).

(7) D. C. Walker and H. S. Conway, *Anal. Chem.*, **25**, 923 (1953).

(8) V. R. Kokatnur and M. Jelling, *J. Am. Chem. Soc.*, **63**, 1432 (1941).

Acetophenone yields a wave with a diffusion current at -1.7 v. which is proportional to the acetophenone concentration. This wave was not found in solutions of pure CHP but was observed in mixtures of iron(III)EDTA and CHP. The current giving rise to the wave at -1.7 v. is kinetic in nature. The height of this wave gives a measure of the rate of reaction between iron(II)EDTA and CHP and is determined more accurately than the "negative kinetic current" at -0.9 v. which is equal to the difference between the current calculated, assuming no reaction occurs, and the observed current. When the effect of drop time upon the diffusion currents was taken into account, the sum of the diffusion currents at -0.9 and -1.7 v. was found equal to the calculated sum of the diffusion currents at -0.9 v. In mixtures which were 0.001 M in iron(III)EDTA and 0.3 to 1.1×10^{-3} M in CHP the observed current at -0.9 v. corresponded to an apparent decrease of the CHP concentration of 10% both at 0° and 25°. This decrease was found proportional to the CHP concentration under the above conditions. Thus, the current at -0.9 v. serves as a reliable indicator of the concentration of CHP in solutions containing iron(III)EDTA. In blank experiments it was shown that hydrazine is polarographically inactive in the voltage range used.

Results

Reaction Between CHP and Hydrazine.—The direct uncatalyzed reaction is negligibly slow. For example in a solution 0.001 M in CHP, 0.05 M in hydrazine, 0.006 M in EDTA and 0.05 M in borax (pH 9), only 5% of the CHP was found to react in 30 minutes at 25°. The reaction was much faster in the absence of EDTA, the half-time being a few minutes. This large increase in rate could be attributed to a trace of copper which catalyzes the reaction and which is made harmless by EDTA. This effect is so great that the catalysis could be made use of analytically for the determination of traces of copper. The reaction at 25° was found practically instantaneous in the presence of 5×10^{-5} M copper(II), but with an excess of EDTA this concentration of copper had no effect on the rate. Oxygen also exerts a pronounced accelerating effect on the reaction of CHP in the presence of EDTA. The reaction between CHP and hydrazine has not been studied further, but it has been established that under all the conditions used in the present work (particularly presence of EDTA, absence of oxygen) the reaction is slower by several orders of magnitude than the iron(III)EDTA-hydrazine reaction.⁴

Disappearance of CHP in Presence of Iron(III)EDTA and Hydrazine.—The reaction rate was measured at 0° and 25° in solutions 0.05 M in

borax, $0.5-1 \times 10^{-3} M$ in iron(III)EDTA and $0.01-0.05 M$ in hydrazine. The solutions contained about $10^{-3} M$ free EDTA and sufficient sodium sulfate to make the ionic strength unity. Separate experiments showed that variation of the ionic strength from 0.2 to 1 did not affect the rate appreciably. Results of typical experiments at $5 \times 10^{-4} M$ iron(III)EDTA and three concentrations of hydrazine at 0° are shown in Fig. 1. Brief induction periods, possibly due to traces of oxygen, were observed both at 0° and 25° . Initial reaction rates (v_0) are given in Table I. These were obtained graphically allowing for the induction periods.

TABLE I
DISAPPEARANCE OF CHP IN PRESENCE OF IRON(III)EDTA
AND HYDRAZINE, $pH = 9.0$

(1) 0°						
Molar CHP	concn. $\times 10^4$ FeY^-	Molar N_2H_4	concn. NaA^a	$v_0 \times 10^5$	$k_0 \times 10^{5c}$	$k_1[FeY^-][N_2H_4] \times 10^5$
7.2	5.38	0.01	..	1.2	0.19	0.05
7.2	5.38	.02	..	2.3	.14	.11
7.2	5.38	.05	..	3.6	.13	.27
8.0	10.0	.01	..	2.7	.29	.10
8.8	5.00	.01	0.1	0.4 ^d	.11	.05
8.8	5.00	.02	0.1	0.7 ^d	.28	.10
(2) 25°						
7.1	5.17	0.01	..	5.3	..	1.2
7.1	5.17	.02	..	9.4	..	2.4
7.1	5.17	.05	..	12	..	6.0
6.0	4.83	.01	..	5.4	..	1.1
6.0	4.83	.02	..	7.6	..	2.2
6.0	4.83	.05	..	13	..	5.6

^a Sodium acrylate. ^b Initial rate of reaction, mole $l^{-1} min^{-1}$. ^c Limiting zero order reaction rate, mole $l^{-1} min^{-1}$. ^d Obtained by extrapolation to zero time.

Under the experimental conditions at 25° , the rate was practically zero order with respect to CHP until 60-70% had reacted. From then on there was a gradual decrease in rate. In the experiments at 0° the reaction was between zero order and first order with respect to CHP. For such kinetics, $-dc/dt = k_0 + k_1c$, and a plot of $\log(c + k_0/k_1)$ vs. t should yield a straight line of slope k_1 . By trial it was found that such linear plots could be obtained with values of k_0/k_1 of the order of 10^{-4} . The corresponding values of the zero order constant k_0 are given in Table I.

In a number of instances the amount of acetophenone (AP) was measured polarographically at the end of the reaction. Within the experimental error (5%) the CHP was converted quantitatively to AP. Application of the chromotropic acid test for formaldehyde,⁹ modified to include the determination of methanol, showed that no detectable amount of either substance was present at the end of the reaction.

Sodium acrylate has a pronounced retarding effect at 0° . While in its absence the reaction at 0° was 90% complete in 100 minutes, in the presence of $0.1 M$ acrylate only 45% reaction occurred in 126 minutes ($5 \times 10^{-4} M$ iron(III)EDTA, $0.01 M$ hydrazine). Reacted CHP was converted quantitatively to AP. During the first

(9) C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945).

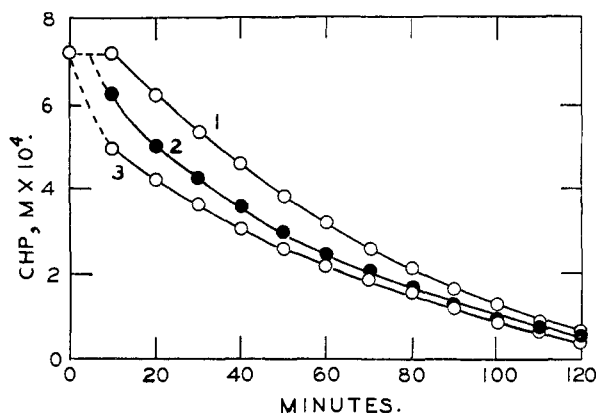


Fig. 1.—Reaction of CHP at 0° , $pH 9.0$; $Fe(III)EDTA = 5.17 \times 10^{-4} M$; hydrazine concentration: curve 1, $0.01 M$; curve 2, $0.02 M$; curve 3, $0.05 M$.

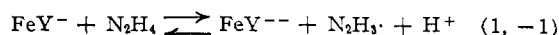
few minutes of each experiment in the presence of acrylate the reaction rate was relatively larger than the subsequent rate, undoubtedly due to a trace of a reducing impurity in the acrylate. After this brief initial period the reaction showed the same kinetic behavior as in the absence of acrylate, with the values of k_0 given in Table I.

In separate experiments it was shown that addition of $0.1 M$ sodium acrylate had no effect on the rate of reaction of iron(III)EDTA and hydrazine at 0° , $pH 9$.

Stoichiometry of CHP-Iron(II)EDTA Reaction.—When the concentrations of iron(II)EDTA and CHP (absence of hydrazine) in the reaction mixture are of the same order of magnitude, the molar reaction ratio is about unity. No induced decomposition occurs and the reaction products are AP and ethane. Under the conditions described in this paper, iron(II)EDTA is formed slowly and its concentration is small compared to the initial concentration of CHP. The following experiment was carried out to see whether any induced decomposition of CHP occurs under such conditions. To 20 ml. of an air-free solution $7 \times 10^{-3} M$ in CHP, $0.05 M$ in borax was added 5.0 ml. of air-free $5.3 \times 10^{-3} M$ iron(II)EDTA in $0.05 M$ borax. The addition was carried out continuously by means of a syringe over a period of five minutes. The concentration of unreacted CHP was determined polarographically. Duplicate experiments yielded a reaction ratio, moles iron(II) consumed/moles CHP consumed, of 1.09 ± 0.04 , which is the same as found when equivalent concentrations of CHP and iron(II)EDTA are mixed rapidly.

Discussion

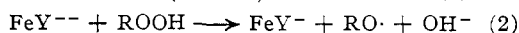
The first step in the reaction between iron(III)EDTA (FeY^-) and hydrazine is the reversible reaction



In a medium 9.3% in ethanol the bimolecular rate constant of the forward reaction 1 is 0.090 and $2.3 l.-mole^{-1} min^{-1}$ at 0° and 25° , respectively, the hydrazine concentration being that of the free base.⁴ Ethanol reduces the rate somewhat, and the value of the rate constant in the absence of

ethanol is estimated to be about 0.1 and 2.5 l.-mole⁻¹ min.⁻¹ at 0 and 25°, respectively. Thus in a solution 5×10^{-4} M in iron(III)EDTA and 10^{-2} M in hydrazine the rate of formation of iron(II)-EDTA and hydrazyl radicals in reaction 1 is 0.5×10^{-6} mole l.⁻¹ min.⁻¹ at 0°. Values of $k_1[\text{FeY}^-][\text{N}_2\text{H}_4]$ for other experimental conditions are given in Table I. Iron(II)EDTA is produced also in the subsequent fast oxidations of $\text{N}_2\text{H}_3\cdot$, $\text{N}_2\text{H}_2\cdot$ and $\text{N}_2\text{H}\cdot$, so the maximum rate of formation of iron(II)EDTA is four times the rate of reaction 1.

The rate constant for reaction 2 between iron(II)-EDTA and CHP (ROOH) at 0° is 1.44×10^4 l.

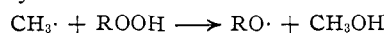


mole⁻¹ min.⁻¹, independent of pH over a wide range.⁵ It is known that k_{-1} is smaller than k_1 , so in the presence of sufficient CHP all the iron(II)-EDTA produced in (1) reacts with CHP and the back reaction (-1) does not occur. No induced decomposition of CHP occurs in mixtures of CHP and iron(II)EDTA (molar reaction ratio is unity), and the direct reaction between CHP and hydrazine is negligibly slow. Therefore if CHP disappeared only by reaction with iron(II)EDTA, the maximum rate of disappearance would be four times the rate of (1). Also, the reaction would be zero order with respect to CHP, when sufficient CHP is present. This situation appears to be approached at 25°. The decrease in rate after 60% of the CHP has reacted may be attributed to the fact that the back reaction (-1) can no longer be neglected.

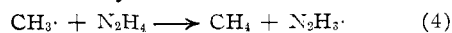
The most interesting results are obtained at 0°, at which temperature the values of v_0 are from 13 to 29 times the rate of (1), and the reaction appears to be between zero and first order with respect to CHP. Various mechanisms to account for the accelerated reaction have been considered. Both the acceleration and the kinetics could be accounted for by the reaction



followed by



However, no methanol could be detected in the reaction mixture and, in addition, the slow addition of iron(II)EDTA to CHP did not lead to any autocatalytic decomposition. The following mechanism appears plausible. Iron(II)EDTA formed in (1) reacts with CHP (2) and $\text{RO}\cdot$ thus formed decomposes (3). In the absence of hydrazine the methyl radicals self-terminate to form ethane. In the presence of hydrazine reaction 4 is assumed



This is analogous to the abstraction of hydrogen by methyl radical from dimethylhydrazine, which has been postulated to occur in the photolysis of the latter substance.¹⁰ Since hydrazyl radical is easily oxidized by the weak oxidizing agent

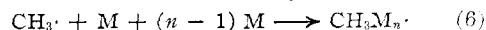
iron(III)EDTA,⁴ it may be expected to be oxidized more easily by the strong oxidizing agent hydroperoxide



Reactions 3, 4 and 5 constitute a chain reaction between hydroperoxide and hydrazine. Undoubtedly $\text{N}_2\text{H}_2\cdot$ and $\text{N}_2\text{H}\cdot$ radicals can also be oxidized by hydroperoxide.

The above mechanism corresponds to two simultaneous modes of disappearance of hydroperoxide: (a) a direct reaction with iron(II)EDTA and hydrazyl radicals produced in (1), zero order with respect to CHP at sufficiently high concentration of CHP, the maximum rate of the zero order reaction being $4 \times$ the rate of (1), and (b) a chain reaction 3, 4, 5. It is impractical to attempt to derive the kinetics in the general case, in which allowance is made for the oxidation of the three hydrazine-derived radicals ($\text{N}_2\text{H}_3\cdot$, $\text{N}_2\text{H}_2\cdot$ and $\text{N}_2\text{H}\cdot$) by two oxidants, and for the possibility of the back reaction -1 at low concentrations of hydroperoxide. Because of experimental difficulties it was not possible to use the polarographic method at much higher concentrations of CHP than used in the present work. For this reason no attempt has been made to analyze the kinetics in detail. Qualitatively it is plausible that the chain sequence should be first order with respect to hydroperoxide, so the combined zero-first order kinetics observed at 0° may be understood. Allowing for the uncertainty in deriving k_0 from the rate data, the agreement in order of magnitude between k_0 and $k_1[\text{FeY}^-][\text{N}_2\text{H}_4]$ at 0° is entirely satisfactory. The chain initiating reaction 4 is competitive with the dimerization of $\text{CH}_3\cdot$ to ethane. From the experimental results it appears that at 25° the dimerization is favored over reaction 4.

As mentioned in the Experimental part sodium acrylate does not affect the rate of reaction of iron(III)EDTA and hydrazine. This is conclusive proof that acrylate does not react with either iron(II)EDTA or with $\text{N}_2\text{H}_3\cdot$; if such reaction occurred, the back reaction -1 would be suppressed and the over-all reaction rate would be increased. The suppressing effect of acrylate (M) on the induced reaction of hydroperoxide with hydrazine can be accounted for by



which is competitive with (4).

The present research has been discontinued. The experimental results reported in this paper are new and unexpected. However, more work would be desirable to substantiate the above interpretation.

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(10) W. L. Kay and H. A. Taylor, *J. Chem. Phys.*, **10**, 497 (1942).