[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Kinetics of the Decomposition of Tertiary Hydroperoxides in Solvents[1,2]

BY VIVIAN STANNETT AND ROBERT B. MESROBIAN

Introduction.—The reactions which occur during the decomposition of hydroperoxides are of particular interest because of their connection with the processes of hydrocarbon oxidation and olefin polymerization. It is very generally accepted that during the course of hydrocarbon autoxidation, hydroperoxides appear as one of the first products of reaction, and that the further progress of oxidation is greatly affected by the nature of the hydroperoxide formed. In principle it might be expected that from studies of hydroperoxide decomposition in hydrocarbon solvents in the *absence* of oxygen, it should be possible to specify in greater detail the secondary stages of oxidation where hydroperoxides play an important role.

In this article, studies are presented on the kinetics of the decomposition of two common tertiary hydroperoxides—*t*-butyl hydroperoxide and dimethylphenyl methyl (cumene) hydroperoxide—in several organic solvents and in the temperature range 50–150°.

Several earlier workers have discussed the mechanism of the decomposition of these two hydroperoxides on the basis of the type of end-products formed after breakdown at high temperatures. Hock and Lang[3] report that cumene hydroperoxide yields phenol and acetone when heated at elevated temperature in the presence of acids, and Milas and Surgenor[4] have observed the formation of mostly methanol and acetone in the decomposition products of *t*-butyl hydroperoxide after heating the vapors at 250°. On the basis of these investigations, and particularly from the latter case, the decomposition of tertiary hydroperoxides has been postulated by the latter authors and also by George and Walsh[5] to occur by initial homolytic fission of the peroxy linkage, followed by cleavage of the resultant alkoxy radical and subsequent termination of the radical intermediates (Equations A)

$$\begin{array}{lll} (1a) & R_2R'C\cdot OOH \longrightarrow R_2R'CO\cdot + HO\cdot & \\ (2a) & R_2R'CO\cdot \longrightarrow R_2C{=}O + R'\cdot & (A) \\ (3a) & R'\cdot + HO\cdot \longrightarrow ROH & \end{array}$$

where $R' = CH_3-$ or C_6H_5- and $R = CH_3-$

In addition to their studies at 250° Milas and Surgenor also note that *t*-butyl hydroperoxide undergoes a quite different mode of decomposition when heated alone at lower temperatures (Equation B)

$$(CH_3)_3COOH \xrightarrow{95°} (CH_3)_3COH + {}^1/_2O_2 \qquad (B)$$

The over-all reaction noted above is also typical of the peracids, but no mechanism for this type of process is known.[4] Recently, Kharasch[6] has called attention to the fact that hydroperoxides may undergo decomposition according to three possible types of reaction, *viz.*, free radical, ionic and loss of molecular oxygen.

Under the conditions employed in our studies on hydroperoxide decomposition in solvents, a breakdown reaction involving free radicals is believed to occur which resembles in some ways the decomposition of potassium persulfate in methanol solution as reported by Bartlett and Cotman.[7] Furthermore, at the temperatures of measurement, the initiation step for the decomposition of the two hydroperoxides appears to occur by bimolecular reaction of the hydroperoxide with the solvent rather than by a unimolecular reaction. The rates of decomposition of the two hydroperoxides in solution are found to vary greatly with the solvent employed. The free radical nature of the decomposition in solvents is suggested by the type of end-products formed (*e. g.*, benzaldehyde from benzyl alcohol) and by the reactions of the hydroperoxides with vinyl monomers.

Experimental

Reagents.—The *t*-butyl hydroperoxide was obtained 60% pure from the Lucidol Co. It was purified to about 95% by fractional distillation *in vacuo* followed by fractional crystallization. The cumene hydroperoxide was obtained 70% pure from the Hercules Powder Co. and was purified to 95.6% by the formation and purification of the sodium salt followed by regeneration of the hydroperoxide and its separation and fractional distillation *in vacuo*. The various solvents employed were taken from freshly opened bottles of reagent grade materials and distilled before use. The vinyl monomers were freed from inhibitor by distillation *in vacuo* and the middle fraction taken for use. The sodium iodide, sodium thiosulfate and isopropyl alcohol used in the analytical procedure were of reagent grade.

Procedure.—Samples of the hydroperoxide solution were pipetted into small reaction tubes (between 1 and 10 cc. samples were used as required), flushed with nitrogen and the tubes sealed. Comparison of data obtained from samples sealed under vacuum after several freezing and melting operations with samples sealed under nitrogen showed identical results. The analytical procedure used for the hydroperoxide estimations was that described by Wagner, Smith and Peters.[8] The amount of water in solutions in which the hydroperoxide had been totally decomposed was estimated by Karl Fischer titration. The determination of aldehyde content in solutions in which the hydroperoxide had decomposed completely by reaction with benzyl alcohol solvent was carried out according to

---

[1] This work was carried out with the support of the Office of Naval Research.

[2] Presented before the Division of Organic Chemistry during the American Chemical Society Meeting in Atlantic City, September 19–23, 1949.

[3] Hock and Lang, *Ber.*, **77**, 257 (1944).

[4] Milas and Surgenor, THIS JOURNAL, **68**, 205 (1946).

[5] George and Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946).

[6] Kharasch, 11th National Organic Symposium of the American Chemical Society, Madison, Wisconsin, June, 1949.

[7] Bartlett and Cotman, THIS JOURNAL, **71**, 1419 (1949).

[8] Wagner, Smith and Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).

the method of Bryant and Smith.[9] The first results obtained for aldehyde content were checked, using the procedure of Ripper.[10] The aldehyde obtained in the above reaction was identified as benzaldehyde, both from its odor and from the melting point of its 2,4-dinitrophenylhydrazone.

Experimental Results

The Decomposition of Hydroperoxides in Solvents at 73.5°.—The effect of solvent on decomposition rate is summarized in Table I for *t*-butyl hydroperoxide at 73.5°. The concentration of hydroperoxide in solvent was in all cases 0.2 molar and the data tabulated as per cent. decomposition of hydroperoxide after heating for the indicated times. The more effective solvents were found to be the alcohols, phenols, vinyl monomers and esters. It should be added, however, that while little decomposition occurred at this temperature with the other classes of solvents listed in Table I, at higher temperatures (of the order of 120°) decomposition occurs at experimentally measurable rates. In general, the same order of solvent activity was observed in studies on cumene hydroperoxide decomposition as with *t*-butyl hydroperoxide, differing only in that the corresponding rates of decomposition were appreciably less with cumene hydroperoxide. The extent of decomposition of cumene hydroperoxide at 73.5° in four vinyl monomers and some of the polymerization effects noted are given in Table II.

TABLE I

DECOMPOSITION OF *t*-BUTYL HYDROPEROXIDE AT 73.5°

Concentration of ROOH = 0.2 *M*

Solvent	Decomposition, % 1 hr.	3 hr.	5 hr.
Benzene			0
Pyridine			0
Xylene			0
Anisole			0
Carbon tetrachloride			0
Chloroform			0
Cyclohexane			0
Chlorobenzene			0
Methyl alcohol			0.9
Cyclohexene			3.0
Glacial acetic acid			3.5
Dioxane			4.0
Di-*n*-butyl ether			4.3
Nitrobenzene			7.0
Cyclohexanone	4.1		
Styrene	9.0	25.1	
Ethyl benzoate	9.2		
Aniline	10.0		
Ethyl acetate	17.8		
Isopropyl alcohol	20.5		
t-Butyl alcohol	26.8		
o-Cresol	27.9		
n-Butyl alcohol	31.3		
Benzyl alcohol	41.1	79.7	92.1
Ethyl alcohol	45.3		

TABLE II

DECOMPOSITION OF CUMENE HYDROPEROXIDE AT 73.5°

Concentration of ROOH = 0.2 *M*

Solvent	Decomposition, % 1 hr.	3 hr.	5 hr.
Styrene	4.0	11.1	17.2
Vinyl acetate	0.0	0.0	<1.0
Acrylonitrile	14.4	Solid polymer formed	
Methyl methacrylate	18.2	Solid polymer formed	
Methyl methacrylate (ROOH omitted)		Mobile liquid	

The Effect of Chemical Agents on *t*-Butyl Hydroperoxide Decomposition in Benzene at 73.5°.—It was noted from Table I that no appreciable decomposition of *t*-butyl hydroperoxide occurs during heating in benzene at 73.5°. When, however, free radical forming chemical agents such as azo-bis-(α-methylpropionitrile) are added to the solution of hydroperoxide in benzene, a definite amount of decomposition is found to occur (Table *III*). Gaseous oxygen, on the other hand, as noted from the data in Table IV appears to slightly retard the decomposition in benzyl alcohol.

TABLE III

THE EFFECT OF RADICALS ON THE DECOMPOSITION OF *t*-BUTYL HYDROPEROXIDE IN BENZENE AT 73.5°

Concentration of ROOH = 0.2 *M*

Added chemical agent	Concn., m./l.	Decomposition of ROOH, % 20 hr.	40 hr.
None		0	<1.0
Azo-bis-(α-methylpropionitrile)	0.04	8.7	11.6

TABLE IV

THE EFFECT OF OXYGEN ON THE DECOMPOSITION OF *t*-BUTYL HYDROPEROXIDE IN BENZYL ALCOHOL AT 73.5°

Concentration of ROOH = 0.9 *M*

	Decomposition, % 1 hr.	2 hr.
Oxygen	24.8	44.1
Air	27.0	45.7
Vacuum	32.2	50.2
Nitrogen	31.9	50.0

The Decomposition of Hydroperoxides in Benzyl Alcohol.—Among the various solvents listed in Table I, the effect of benzyl alcohol solvent on hydroperoxide decomposition was first studied in an attempt to specify the over-all stoichiometry of the decomposition process as well as the kinetic order of reaction. The total decomposition of dibenzoyl peroxide in isobutyl alcohol has been reported by Gelissen and Hermans[11] to yield about 0.24 mole of isobutyraldehyde per mole of initial peroxide, along with several other end-products. In our studies of hydroperoxide decomposition in benzyl alcohol the formation of as high as 0.88 mole of benzaldehyde per mole of initial hydroperoxide has been noted. Furthermore, water is formed during decomposi-

---

(9) Bryant and Smith, THIS JOURNAL, **57**, 57 (1935).

(10) Ripper, *Monatsh.*, **21**, 1079 (1900); *Sitzungsber Akad. Wiss. Wien*, **109**, (IIb), 854 (1900).

(11) Gelissen and Hermans, *Ber.*, **58**, 765 (1925).

tion, the total amount of which may be estimated by Karl Fischer titration, provided all the hydroperoxide has decomposed. In Table V are listed the data on the amounts of water and benzaldehyde formed from the total decomposition of the two hydroperoxides in benzyl alcohol. It is apparent that for each mole of decomposed hydroperoxide one mole of water and between 0.6 and 0.88 mole of aldehyde are formed. It is known that hydroperoxides[4,12] react with alcohols in the presence of strong mineral acids to form dialkyl peroxides and water.

TABLE V

SOME PRODUCTS OF THE TOTAL DECOMPOSITION OF HYDROPEROXIDES IN BENZYL ALCOHOL

Initial peroxide content, m./l.	Temp., °C.	Moles H_2O Mole ROOH	Moles benzaldehyde Mole ROOH
	Cumene Hydroperoxide		
1.03	73.5	1.09	0.7
0.22	73.5	1.05	.6
.66	110.0	1.10	.74
	t-Butyl Hydroperoxide		
.66	73.5	1.18	.88
.66	110.0	1.03	.82

$$R_3COOH + R'OH \xrightarrow{\text{Acid}} R_3COOR' + H_2O \quad (C)$$

This type of reaction could account for the formation of equivalent amounts of water from hydroperoxide decomposition in benzyl alcohol solvent, but it is not consistent with the previously noted result that appreciable quantities of benzaldehyde are formed. An alternative process for hydroperoxide decomposition in benzyl alcohol, represented as an over-all equation, but which may involve several steps is

$$R_3COOH + C_6H_5CH_2OH \longrightarrow R_3COH + H_2O + C_6H_5CHO \quad (D)$$

Accordingly, hydroperoxides can oxidize primary alcohols to the corresponding aldehyde.

The rates of decomposition of the two hydroperoxides in benzyl alcohol have been measured under a variety of conditions. The data for two typical runs made at 73.5° with cumene hydroperoxide are summarized in Table VI, and the rate curves are shown in Fig. 1.

TABLE VI

THE DECOMPOSITION OF CUMENE HYDROPEROXIDE IN BENZYL ALCOHOL AT 73.5°

Run 1		Run 2	
Time, hours	ROOH, m./l.	Time, hr.	ROOH, m./l.
0.0	0.248	0.0	0.0525
1.0	.214	1.0	.0375
2.0	.177	2.0	.0252
4.0	.124	3.0	.0168
6.0	.092	4.0	.0121
8.0	.067		
11.0	.045		

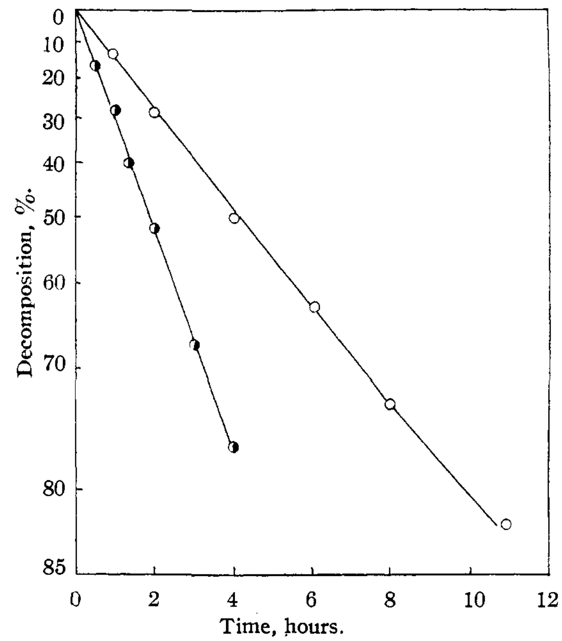

Fig. 1.—The decomposition of cumene hydroperoxide in benzyl alcohol at 73.5°: ○, 0.248 m./l.; ◑, 0.053 m./l.

It may be seen that while the decomposition rate followed a pseudo-unimolecular plot, the order of reaction must be complex insofar as the apparent rate constant for the reaction increased as the initial hydroperoxide concentration decreased. This observed increase of the rate constant with dilution may be due to the fact that either the decomposition mechanism involves certain ionic factors or that the products of reaction act as inhibitors, although in neither case would the logarithmic dependence of the over-all rate be anticipated except possibly as a fortuitous occurrence. The decomposition of cumene hydroperoxide in benzyl alcohol in the presence of small amounts of dilute sulfuric acid was noted to proceed very rapidly at 73.5°, demonstrating that this reaction can be subject to acid catalysis. In this case, however, no benzaldehyde could be detected. On the other hand the addition of water or benzoic acid was found to have little effect on the decomposition rate and on the extent of formation of benzaldehyde. In further attempts to specify the decomposition reaction, measurements of the initial rates were made, it being considered that during the initial stages of reaction the formation of inhibitory reaction products are not important. It was found that even for initial rate measurements the kinetic results were similar to those obtained from measurements of the total decomposition of hydroperoxide. Further details concerning the mechanism of this reaction are being studied and will be the subject of a later communication.

The Decomposition of Cumene Hydroperoxide in Styrene Monomer.—The rate of decomposition of cumene hydroperoxide in xylene is quite

---

[12] Dickey, Raley, Rust, Tresede and Vaughan, *Ind. Eng. Chem.*, **41**, 1673 (1949).

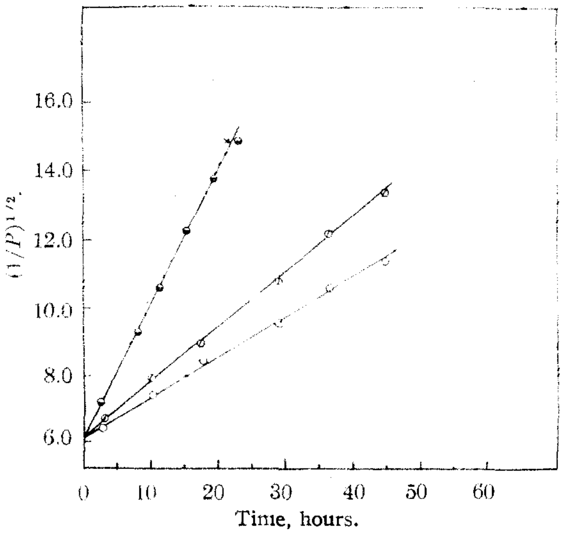

Fig. 2.—The decomposition of cumene hydroperoxide (0.0265 M) in xylene at various concentrations of monostyrene, 110°: ○, 0.44 M styrene; ⊘, 1.32 M styrene; ◒, 2.20 M styrene.

slow at 110°. When styrene monomer is present in the solution, however, the decomposition is greatly accelerated. In Fig. 2 are plotted the data on the decomposition of cumene hydroperoxide (0.0265 molar) in xylene at three concentrations of monostyrene. For these runs logarithmic plots of per cent. decomposition were not linear with time but linear relationships were obtained from plots of the reciprocal of the square root of the hydroperoxide concentration against time. The arrow in Fig. 2 represents 90% decomposition. The three-halves-order rate constants for the runs made in xylene containing styrene are listed in Table VII. The rate constants for several other runs made at the same temperature are also listed in this Table. The latter two runs (5 and 6) were made in monomer alone, and were carried out to only 40% decomposition since the solutions after long times of heating became extremely viscous. Analyses for water formed after the total decomposition of hydroperoxide in styrene–xylene solutions were negative. It was also found that the $^3/_2$ order rate constants for hydroperoxide decomposition in monomer are proportional to the square root of the initial monomer concentration as may be seen by comparing the constancy of the numbers in the last two columns of Table VII.

TABLE VII

THE DECOMPOSITION OF CUMENE HYDROPEROXIDE IN XYLENE AT VARIOUS CONCENTRATIONS OF MONOSTYRENE AT 110°

Run	Concentrations m./l. ROOH	Styrene	$K_{3/2}$(m./l.)$^{1/2}$ hr.$^{-1}$	$K_{3/2}$/(Styrene)$^{1/2}$
1	0.0265	0.44	0.11	0.17
2	.0265	1.32	.15	.16
3	.0265	2.20	.37	.24
4	.118	1.73	.33	.25
5	.332[a]	8.32[a]	.75	.23
6	.640[a]	7.95[a]	.68	.24

[a] No xylene present.

In order to confirm the dependence of the over-all rate on (ROOH)$^{3/2}$ and (Styrene)$^{1/2}$ the initial rates of reaction (up to 5%) were measured. This was considered to be particularly necessary in this reaction in view of the fact that the styrene component was being progressively removed to some extent by secondary polymerization effects. The results of the initial rate measurements are shown in Figs. 3 and 4 and it may be seen that the slopes for the log (Initial Rate) *vs.* log (ROOH) at constant styrene concentration and for log (Initial Rate) *vs.* log (Styrene) at constant hydroperoxide concentration indicate the $^3/_2$ and $^1/_2$ order dependence upon hydroperoxide and styrene concentrations, respectively. The over-all energy of activation for the decomposition of cumene hydroperoxide in monostyrene in the temperature range 73.5° to 110° was found to be 24.2 ± 0.3 kcal.

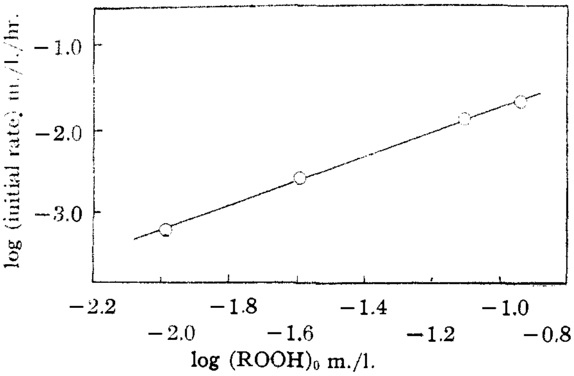

Fig. 3.—Dependence of initial rate of cumene hydroperoxide decomposition on the initial hydroperoxide concentration at 110° and at a constant initial styrene concentration of 1.74 m./l.; slope of line calculated to be 1.43.

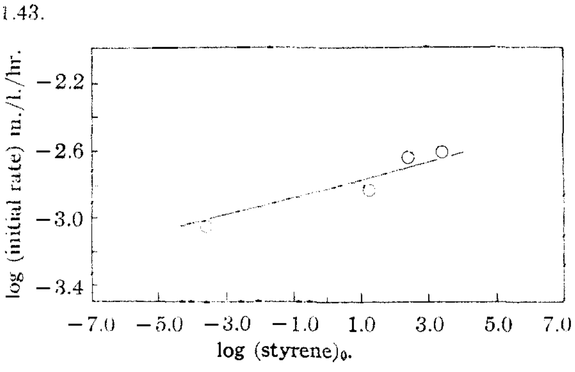

Fig. 4.—Dependence of initial rate of cumene hydroperoxide decomposition on the initial styrene concentration at 110° and at a constant initial hydroperoxide concentration of 0.026 m./l.; slope of line calculated to be 0.5.

The Decomposition of Cumene Hydroperoxide in Di-*n*-butyl Ether at 117°.—Di-*n*-butyl ether was investigated as a solvent for the decomposition of cumene hydroperoxide. As shown in Figure 5 the nature of the decomposition curves appears to be quite complex. None of the ordinary methods of plotting gave linear relationships for decomposition *vs.* time. In general, it appears that the decomposition is greatly accelerated by the products of reaction. This result is evidenced by the nature of the decomposition curves and from the rate measurements of two runs at the concentration of 0.44 molar, wherein the solvent for the second run consisted of the solution resulting from the total decomposition of hydroperoxide in the first run.

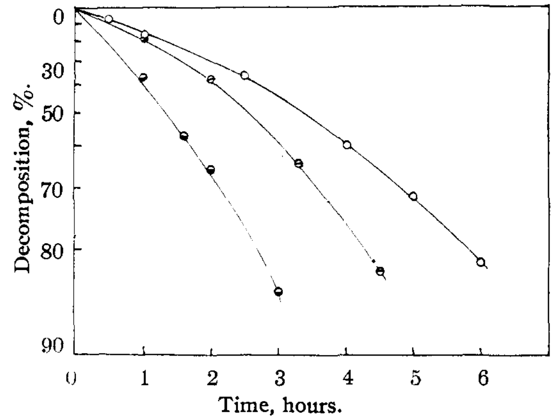

Fig. 5.—The decomposition of cumene hydroperoxide in di-*n*-butyl ether at 117°: O, 0.08 *M*; ⊘, 0.44 *M*; ●, 0.44 *M* (solvent contains decomposition products).

The Decomposition of Cumene Hydroperoxide in Mesitylene at Various Temperatures.—The rates of decomposition of cumene hydroperoxide in mesitylene at 138° and at various initial concentrations of hydroperoxide are shown in Fig. 6. The plots, as such, are in accordance with either a unimolecular or pseudo-unimolecular reaction since the reactions were carried out at high concentration ratios of mesitylene to hydroperoxide. Concentration effects apparently complicate the decomposition, since linear relationships are obtained only at hydroperoxide concentrations less than 0.027 molar. It is not unlikely that at higher concentrations, an appreciable amount of hydroperoxide decomposes by chain induced reactions. In order to specify the temperature dependence of the reaction in mesitylene, measurements of the decomposition rate were made at several temperatures using only solutions of low initial hydroperoxide concentration. The results of these studies are shown in Fig. 7 and the over-all energy of activation is calculated to be 23.6 ± 0.2 kcal.

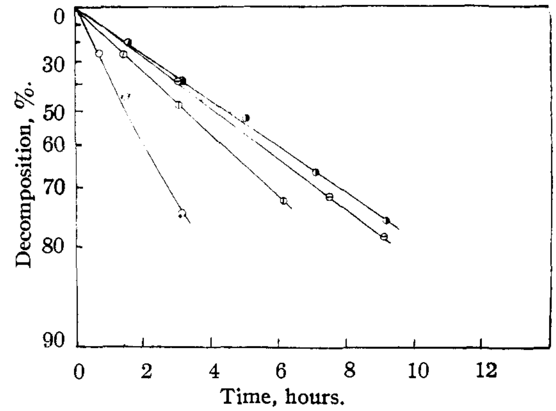

Fig. 6.—The decomposition of cumene hydroperoxide in mesitylene at 138°: O, 0.26 *M*; ⊘, 0.065 *M*; ⊗, 0.027 *M*; ◑, 0.013 *M*.

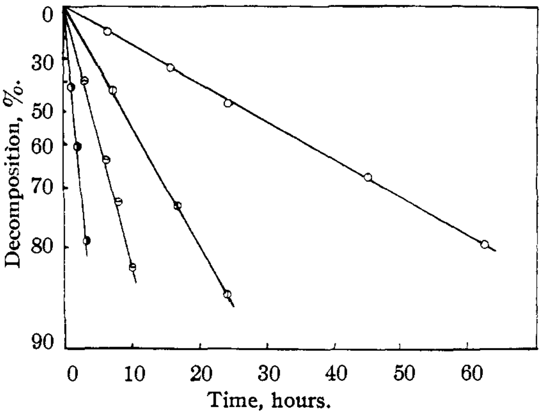

Fig. 7.—The decomposition of cumene hydroperoxide in mesitylene at various temperatures: $(ROOH)_0 = 0.034$ *M*; $E_{act.} = 23.6$ kcal.; O, 113°; ⊘, 128°; ⊖, 138°; ◑, 154.5°.

Discussion

The following conclusions concerning the nature of tertiary hydroperoxide decomposition in solvents, based on the above results may be listed. (It is assumed here that the decomposition mechanism in the various fast and slow solvents is similar, although this may not necessarily be the case.)

(1) The decomposition reaction involves free radical intermediates. This is evidenced by the polymerization effects produced during decomposition of the hydroperoxides in monomers and from the kinetic order of the decomposition reaction in xylene containing styrene monomer. Also the formation of benzaldehyde from benzyl alcohol is difficult to explain without postulating a free radical mechanism. The small amount of retardation of the decomposition in benzyl alcohol by oxygen is not sufficiently pronounced to warrant particular emphasis in this respect.

(2) Decomposition of the hydroperoxides in benzene may be induced to some extent by radicals formed from the decomposition of azo-bis-(α-methylpropionitrile). The decomposition of cumene hydroperoxide at high concentrations in mesitylene suggests that chain-induced decompositions may occur in this case as well as in the styrene reaction. Other evidence for the occurrence of chain-induced decomposition of hydroperoxide

has been presented recently by Kolthoff and Medalia[13] from studies of the reaction of ferrous iron and cumene hydroperoxide in the absence of oxygen.

(3) The kinetic order of the decomposition reaction as regards the initial step is believed to be bimolecular with the solvent. In the one pertinent reaction studied, of hydroperoxide decomposition in xylene containing styrene, the initial step of the decomposition was difficult to specify directly in view of the fact that important subsidiary reactions occur which lead to the $^3/_2$-order dependence on hydroperoxide and $^1/_2$-order dependence on styrene.

In order to explain the large accelerating effect of methanol on the decomposition of potassium persulfate in buffered aqueous solution, Bartlett and Cotman[7] arrived at the conclusion that a radical chain reaction was operative in which solvent radicals were formed by bimolecular reaction of methanol with persulfate ion and that these solvent radicals effected considerable induced decomposition of persulfate ion. By analogy, one may derive an expression for hydroperoxide decomposition in xylene containing styrene as

$$-d(\text{ROOH})/dt = K'(\text{ROOH})(\text{Styrene}) + K''(\text{ROOH})^{3/2}(\text{Styrene})^{1/2} \quad (E)$$

If the induced effect predominates, then only the second term on the right side of equation (E) is important. This type of kinetic behavior appears to occur in the case of styrene and is evidenced in the Figs. 2–4.

Under conditions where chain-induced decompositions are not important, then the rate of decomposition of hydroperoxide is bimolecular with the solvent as represented by the first term on the right side of equation (E). This may be the case for the decomposition in mesitylene at low concentrations of hydroperoxide.

Summary

Studies are presented on the kinetics of the decomposition of *t*-butyl hydroperoxide and dimethylphenyl methyl (cumene) hydroperoxide in several organic solvents and in the temperature range 50 to 150°.

BROOKLYN, NEW YORK RECEIVED DECEMBER 14, 1949

[13] Kolthoff and Medalia, THIS JOURNAL, **71**, 3789 (1949).

[CONTRIBUTION FROM THE SUGAR RESEARCH FOUNDATION LABORATORY, DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Stability of Carbonate Buffered Cupritartrate Reagents of Low *p*H for Estimating Micro and Macro Quantities of Reducing Sugars

BY LAWRENCE J. HEIDT AND KENNETH A. MOON

Recent studies in this Laboratory[1] of the method devised by P. A. Shaffer, A. F. Hartman and M. Somogyi for estimating reducing sugars have led to improvements in the reliability of the method and in the yield of cuprous oxide, and to the adaptation of the method to the estimation of macro as well as micro quantities of reducing sugars. The best results are obtained when the carbonate buffered cupritartrate micro and macro reagents are at *p*H 9.0 and 8.7, respectively. It was pointed out, however, that the reagents at these *p*H values sometimes deposit an azure blue crystalline precipitate, and that when this occurs, the supernatant solutions give lower yields of cuprous oxide.

The present study was made primarily to determine the effect of the accumulation of the precipitate upon the yield of cuprous oxide produced by the supernatant solution and upon the *p*H and optical density of the solution. The composition of the precipitate and the effect of *p*H upon the reproducibility of the results were also determined. In the remainder of this article the copper reagent will be called reagent and the mildly alkaline solution of sodium thiosulfate will be called thio.

Materials, equipment and procedures were for the most part the same as in the earlier work.[1]

All measurements were made at 24 ± 1°. The temperature of the vigorously boiling water-bath, in which the reagent was reduced by sugar, was 100 ± 0.5°.

The *p*H measurements were made with a Cambridge Electron Ray Research Model *p*H Meter equipped with the Standard Electrode ensemble. The *p*H values were reproduced to ±0.005 unit.

Optical densities, $D = \log_{10} (I_0/I)$, were measured with the Beckman DU quartz spectrograph serial 3249. The light source was a tungsten lamp. The wave length scale was calibrated with a mercury arc lamp and with a didymium glass filter previously calibrated. The transmission and optical density scales were calibrated with mildly alkaline solutions of potassium chromate. The length of the light path in the solutions was in all cases 1.000 cm. The measurement of optical densities was confined to the region between $D = 0.4$ and 1.2 unless otherwise noted. The densities are referred to an equal depth of water.

[1] (a) L. J. Heidt, F. W. Southam, J. D. Benedict and M. E. Smith, THIS JOURNAL, **71**, 2190 (1949); (b) L. J. Heidt and F. W. Southam, *ibid.*, **72**, 589 (1950).