

nism alone. The expression given for this ratio was  $\text{ArBr}/\text{ArOH} = (\text{Br}^-)[k_3/k_2 + k_4(\text{H}_2\text{O})/k_1 + k_3k_4(\text{Br}^-)/k_1k_2]/(\text{H}_2\text{O})$  in which  $k_1$  is the unimolecular rate constant,  $k_4$  is the bimolecular rate constant and  $k_2$  and  $k_3$  are the rate constants for the combination of the carbonium ion with water and bromide ion, respectively.

If the volume changes of activation for the two mechanisms should differ by more than 1–2 ml./mole, then the product composition would vary sensibly with pressure. The values of the rate constants are such that the product ratio is much less sensitive to changes in  $k_3/k_2$  than in  $k_4/k_1$ . The value of  $k_1$  is known from the present work to be decreased by one-third at 1360 atm., and it might be expected that  $k_4$  would be unaffected or even increased by pressure.

In order to shed light on the latter point, a preliminary experiment was performed on the reaction of N,N,N-trimethyl-*p*-nitroanilinium chloride with hydroxide ion which produces *p*-nitrophenol as the chief product. The reaction is bimolecular since its rate is proportional to the hydroxide ion concentration, and at 1360 atm. the rate is retarded by 4% which corresponds to a volume change of activation of 1 ml./mole. The fact that the volume change is not negative as in most bimolecular reactions is owing to the fact that it involves ions of opposite charge, and water of solvation is released as the transition state is formed.

If the volume change of activation for the bimolecular reaction of bromide ion with *p*-nitrobenzenediazonium ion were also 1 ml./mole, then the ratio of *p*-nitrobromobenzene to *p*-nitrophenol would change from  $0.259 \pm 0.012$  at 135 atm. to  $0.356$  at 1360 atm. The measured ratio at the upper pressure was  $0.240 \pm 0.015$ . Any evidence of simultaneous reactions having different pressure coefficients is therefore entirely lacking.

### Experimental

**Kinetic Measurements.**—The high pressure vessel and thermostat bath have been previously described.<sup>9</sup> A 2.5 ml.

sample of 0.04 *M* diazonium salt solution was inclosed in a small-mouthed glass bell of 6.5 ml. capacity together with a stirrer consisting of a small piece of iron wire sealed in glass. The remaining volume was filled with mercury, and the bell was pushed up inside an inverted test tube. The mouth of the bell was pressed against the end of the tube to effect a seal, and the apparatus was re-inverted. A few ml. of mercury was added to the test tube to allow for compression of the liquid. After a period of heating under pressure the sample holder was cooled to 20°, and dissolved nitrogen was expelled from the solution in the bell by agitating the stirrer with an external magnet. The bell was removed by reversing the procedure above after tipping the test tube to equalize the internal and external mercury levels. The volume of nitrogen was then measured by filling the bell with water from a 10 ml. buret. The average deviation of duplicate measurements was 2–3%.

Solutions of N,N,N-trimethyl-*p*-nitroanilinium chloride and sodium hydroxide were treated in the manner previously described.<sup>9</sup> The reaction mixture was analyzed for *p*-nitrophenol spectrophotometrically after extraction with chloroform to remove *p*-nitrodimethylaniline. A 1 ml. aliquot of a solution originally 0.04 *M* in quaternary salt was diluted to 250 ml. with water and diluted further 10:1 with 0.09 *N* sodium hydroxide. The concentration was calculated from the optical density at 399 m $\mu$  with a path length of 1 cm.

**Measurements of Product Composition.**—The mixture resulting from the decomposition of *p*-nitrobenzenediazonium fluoroborate in a solution 1.5 *M* in bromide ion was analyzed by the method of Lewis and Hinds.<sup>10</sup> The reaction was carried out in a glass tube fitted with a rubber piston and having dimensions such that the piston was not completely expelled by nitrogen gas when the pressure was released.

A solution of N,N,N-trimethyl-*p*-nitroanilinium chloride, 0.04 *M*, and sodium hydroxide, 0.89 *M*, was allowed to react for 96 hr. (10 half-lives) at 51.4° and was found to contain 86% of the theoretical amount of *p*-nitrophenol. A solution of 1 g. of the quaternary salt in 10 ml. of 1 *M* sodium hydroxide was placed in a sealed tube and heated for 2.5 hr. in boiling water. Extraction of the reaction mixture with chloroform and evaporation of the extract gave 0.24 g. (31%) of *p*-nitrodimethylaniline, m.p. 163–164°, which was identified by the undepressed m.p. of a mixture with an authentic sample. An aliquot of the aqueous layer was analyzed spectrophotometrically for *p*-nitrophenol and was found to contain 61% of the theoretical amount.

**Reagents.**—The diazonium fluoroborates were prepared by generalizing the method of Lewis and Hinds.<sup>10</sup> N,N,N-Trimethyl-*p*-nitroanilinium chloride was prepared by the method of Zaki and Fahim.<sup>11</sup>

(11) A. Zaki and H. Fahim, *J. Chem. Soc.*, 270 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY, STANFORD, CALIFORNIA]

## Peroxides. IX. The Kinetics of the Hydrogen Evolution from the Thermal Decomposition of 1-Hydroxyalkyl Alkyl Peroxides<sup>1</sup>

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The kinetics of the thermal decomposition of 1-hydroxy-*n*-butyl *n*-butyl peroxide and 1-hydroxyisobutyl isobutyl peroxide have been studied over the temperature range of 80–110° by following the rate of hydrogen evolution as a means of elucidating the mechanism of the decomposition of these compounds and the corresponding hydroperoxides from which they were derived.  $\alpha$ -Methylstyrene was used both as a solvent and as a trap for free-radicals. The Arrhenius energies of activation and frequency factors and the enthalpies of activation and entropies of activation were calculated from the rate data for both compounds. These data have been interpreted in terms of a concerted cyclic transition state.

### Introduction

Studies on the thermal decomposition of *n*-butyl hydroperoxide<sup>3</sup> led to the postulate that 1-

hydroxy-*n*-butyl *n*-butyl peroxide was the intermediate which was responsible for the formation of

(1) Previous communication, Paper VIII in this series, L. J. Durham, C. F. Wurster and H. S. Mosher, *THIS JOURNAL*, **80**, 332 (1958).

(2) Taken from the Ph.D. Dissertation of Lois J. Durham, Stanford University, 1959.

(3) H. S. Mosher and C. F. Wurster, *THIS JOURNAL*, **77**, 5451 (1955).

hydrogen, butyric acid and butyraldehyde.<sup>3,4</sup> It was further postulated that this intermediate decomposed *via* a cyclic concerted mechanism. This theory was compatible with all of the known evidence,<sup>1</sup> but kinetic data were not available. If this interpretation of the results was correct, the rate of hydrogen evolution would be expected to follow first order kinetic laws. This paper is a report of the kinetic studies on the hydrogen evolution reaction.

As a result of preliminary studies in which the conditions for the reaction were worked out, the isomeric 1-hydroxyisobutyl peroxide was found to be more favorable for a detailed investigation, and most of the kinetic studies were done with this compound.

It was found that the amount of gaseous products other than hydrogen was greatly decreased in the presence of inhibitors, thus simplifying the study of hydrogen evolution.  $\alpha$ -Methylstyrene proved to be unusually satisfactory as an inhibitor and also served as a convenient solvent for the reaction.

### Experimental

**Preparation of Peroxy-compounds.**—The preparation of *n*-butyl hydroperoxide,<sup>5</sup> isobutyl hydroperoxide<sup>4</sup> and 1-hydroxy-*n*-butyl *n*-butyl peroxide<sup>1</sup> have been described. The 1-hydroxyisobutyl isobutyl peroxide was prepared in the same manner as the normal isomer, yield 67%, b.p. 38–40 (0.6 mm.),  $n_D^{20}$  1.4166.

*Anal.* Calcd. for C<sub>8</sub>H<sub>18</sub>O<sub>3</sub>: C, 59.23; H, 11.18. Found: C, 59.20; H, 11.22.

**Reagents.**—Hydroquinone, di-*t*-butyl-*p*-cresol and dodecane (Eastman, Practical) were used without any further purification.  $\alpha$ -Methylstyrene (Matheson, C.P.) was redistilled, b.p. 163.5–164°.

**Preliminary Studies.**—Decompositions of both normal and isomeric 1-hydroxybutyl butyl peroxides were carried out under various conditions of solvents and inhibitors as indicated in Table I. No significant difference was observed between experiments conducted in Pyrex and Vycor vessels, so Pyrex was used in all subsequent work. The apparatus used in the preliminary studies was essentially the same as that used in the kinetic studies, although minor modifications were made which led to the final apparatus. In the preliminary work the samples were not degassed prior to decomposition.

**Kinetic Studies.**—The apparatus consisted of a reaction vessel connected to a manifold of six mercury-filled gas burets through a water condenser and a U-type trap cooled by Dry Ice–isopropyl alcohol. The reaction was stirred by means of a small Pyrex (or Vycor) covered magnetic stirring bar to prevent supersaturation of the liquid by the evolved gas. The reaction vessel was heated by an oil-bath in an aluminum container which was insulated by one inch of fiber glass. The temperature was controlled to better than  $\pm 0.1^\circ$  and was estimated to be within  $\pm 0.2^\circ$  of the reported values by comparison with a certified Bureau of Standards thermometer at 80 and 100° and with a calibrated copper-constantan thermocouple at 80 and 110°. In all kinetic studies the system was flushed thoroughly with nitrogen and the liquid degassed by freezing and thawing at reduced pressure. The volume of gas evolved was observed at short intervals, the length of the interval being determined by the rate of the reaction. The starting time was taken as the time of immersion of the reaction vessel in the constant temperature bath. For the faster reactions, readings were taken at 50 or 100 second intervals, while 200 or 300 second intervals were used in the slower reactions. Larger intervals were used near the completion of the reaction. Although the first reading could be taken within 50 seconds from the immersion time ( $T_0$ ), an inherent error due to warming of the vessel and contents made the assignment of the actual zero time in-

(4) C. F. Wurster, L. J. Durham and H. S. Mosher, *THIS JOURNAL*, **80**, 327 (1958).

(5) H. R. Williams and H. S. Mosher, *ibid.*, **76**, 2981 (1954).

TABLE I

EXPERIMENTAL DATA FROM PRELIMINARY STUDIES ON 1-HYDROXYALKYL ALKYL PEROXIDES<sup>a</sup>

Inhibitor and/or solvent	Inhib. concn. mole % <sup>b</sup>	$T_{1/2}$ min. <sup>c</sup>	H <sub>2</sub> purity % <sup>d</sup>	H <sub>2</sub> yield % <sup>e</sup>
1-Hydroxy- <i>n</i> -butyl <i>n</i> -butyl peroxide				
None		113 <sup>f</sup>	No analysis <sup>g</sup>	
None		60 <sup>f</sup>	No analysis <sup>g</sup>	
None <sup>h</sup>		78 <sup>f</sup>	63	48
H.Q. <sup>i</sup>	4.8	86	91 <sup>j</sup>	41
H.Q. <sup>i</sup>	7.0	67	94 <sup>j</sup>	36
H.Q. <sup>i</sup>	11.2	79	90 <sup>j</sup>	60
H.Q. <sup>i</sup>	11.6	85	92 <sup>j</sup>	60
H.Q. <sup>h,i</sup>	18.7	66	97	44
DTBC <sup>k</sup>	2.6	61 <sup>f</sup>	67 <sup>l</sup>	46
$\alpha$ -MS <sup>h,m</sup>	74.4 <sup>n</sup>	91 <sup>f</sup>	93	58
H <sub>2</sub> O <sup>h</sup>	78.3 <sup>p</sup>	155	94	54
1-Hydroxyisobutyl isobutyl peroxide				
None		47	38 <sup>q</sup>	54 <sup>r</sup>
DTBC <sup>k</sup>	1.1	37	76 <sup>l</sup>	83
DTBC <sup>h,k</sup>	1.5	39	80 <sup>l</sup>	73
DTBC, Do. <sup>k,r</sup>	1.4	86	58 <sup>l</sup>	86
DTBC <sup>k</sup>	0.91	. . <sup>s</sup>	67 <sup>l</sup>	81
H.Q. <sup>h,i</sup>	2.8	53	95	66

<sup>a</sup> All runs were made at approximately 100°. <sup>b</sup> Defined as moles inhibitor  $\times$  100/mole peroxide. <sup>c</sup> Half-life observed for over-all reaction taken as time at which one half total final volume of gas was evolved. <sup>d</sup> Per cent hydrogen in decomposition gas (exclusive of nitrogen added). <sup>e</sup> Mole hydrogen  $\times$  100 divided by mole peroxide. <sup>f</sup> Volume of decomposition gas was not adjusted to normal temperature before calculations. <sup>g</sup> Gas contained propane, identified by infrared analysis. <sup>h</sup> Decomposition vessel and stirrer made of Vycor. <sup>i</sup> Hydroquinone. <sup>j</sup> Gas contained only a trace of hydrocarbon residue insufficient for identification by infrared analysis. <sup>k</sup> Di-*t*-butyl-*p*-cresol. <sup>m</sup>  $\alpha$ -Methylstyrene. <sup>n</sup> Corresponds to 2.89 molal solution of peroxide. <sup>o</sup> Corresponds to 5.14 molal solution of peroxide. <sup>p</sup> Minimum value, possible leak in apparatus during analysis. <sup>q</sup> Dodecane was used as a solvent, 1.47 molal in peroxide. <sup>r</sup> Insufficient readings taken to determine half-life.

accurate. This resulted in rate plots which did not intersect the origin. The kinetic data are summarized in Table II.

**Analysis of Decomposition Gas.**—At the end of the reaction, all or part of the decomposition gas was transferred to an Orsat gas analysis unit. The gas was analyzed for carbon dioxide, oxygen, hydrogen and carbon monoxide in that order, using standard Orsat technique. The residual gas, containing nitrogen (added at the start of the reaction) and any hydrocarbons formed during the reaction, was subjected to infrared analysis. Propane was identified in runs which contained no inhibitors and in runs which contained di-*t*-butyl-*p*-cresol. Runs which contained hydroquinone or  $\alpha$ -methylstyrene gave too little hydrocarbon to identify by infrared analysis. In most cases samples which contained inhibitors yielded gas which was better than 90% in hydrogen. The hydrogen analyses are given in Tables I and II under the heading %H<sub>2</sub> purity. Analyses are given in greater detail in reference 2.

### Results

A first order kinetic plot of the data [ $\log(1 - V/V_f)$  vs. time, where  $V$  = volume at time  $t$  and  $V_f$  = final volume] gave a series of points which fell on a straight line very nicely in every case to at least 60% reaction and in some cases to 80 or 90% reaction. The order of the reaction was also checked by application of the methods of Powell<sup>6</sup>

(6) R. B. Powell in A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 14.

TABLE II  
DECOMPOSITION DATA FOR 1-HYDROXYALKYL ALKYL PEROXIDES IN  $\alpha$ -METHYLSTYRENE

Temperature, C. <sup>a</sup>	Weight sample mg.	Init. molal concn.	Total volume, ml.	H <sub>2</sub> Purity, % <sup>b</sup>	H <sub>2</sub> Yield, % <sup>c</sup>	T <sub>1/2</sub> , sec. <sup>d</sup>
1-Hydroxyisobutyl isobutyl peroxide						
79.42 ± 0.05	508	0.548	42.9	96	54	18500
79.32 ± .02	743	5.10	87.0	96	76	11400
99.40 ± .03	422	0.476	29.3	96	45	3280
99.41 ± .04	899	2.02	88.5	93 <sup>e</sup>	61	2700
99.44 ± .15	1267	3.74	143.8	97 <sup>e</sup>	74	2200
99.44 ± .03	1709	5.22	180.6	97 <sup>e</sup>	69	1840
109.9 ± .09	554	0.505	35.6	92	40	1580
110.0 ± .03	564	0.544	37.6	94	42	1590
109.6 ± .03	765	4.80	75.9	94	65	772
110.0 ± .03	910	5.05	88.7	94	64	773
1-Hydroxy- <i>n</i> -butyl <i>n</i> -butyl peroxide						
79.39 ± 0.02	1024	2.02	59.5	90	48	38500
99.39 ± .02	556	0.601	26.8	98	32	8600
99.43 ± .06	938	2.07	70.3	93	47	6400
109.9 ± .09	746	2.06	53.8	96	47	2400

<sup>a</sup> Corrected temperature. See experimental section for explanation of limits of error. <sup>b</sup> Purity refers to the mole per cent. hydrogen in the total gas evolved, exclusive of added nitrogen. <sup>c</sup> Expressed as moles H<sub>2</sub> per mole of peroxide initially present. <sup>d</sup> Half-life observed for the over-all reaction explained in footnote c, Table I. <sup>e</sup> Average of analyses on several fractions.

and of Wen-Hsuen Chang.<sup>7</sup> Because of a warm up period after T<sub>0</sub>, the first order plots did not always intersect the origin, causing some difficulties in the application of the latter method. However, when this was taken into consideration, both methods were compatible with first order kinetics.

The yield of hydrogen was not constant under varying conditions of temperature and concentration, suggesting that there were different effects on the competing reactions under the varying conditions. Thus the observed over all rate constant was not the rate constant for hydrogen formation. The rate constant for the formation of hydrogen was obtained from the over all rate constant and the yield of hydrogen by the relationship<sup>8</sup>:  $k_h = k_r \times (\text{yield H}_2)$ .

The data at any one concentration were quite reproducible as shown by the following two sets of duplicate runs which gave first order rate constants of  $1.95 \pm 0.05 \times 10^{-4}$  and  $5.45 \pm 0.05 \times 10^{-4}$  sec.<sup>-1</sup> at 0.5 and 5.0 molal concentrations, respectively, at 110°. In all four of the runs there was no observable deviation from the first order kinetic plot until after 80% of the hydrogen was evolved. However, there was a concentration effect which showed up as an approximate two-fold increase of the rate constant accompanying a ten-fold increase in concentration (Fig. 1).

Using the rate constants for hydrogen formation ( $k_h$ ) at different temperatures but always at the same concentration, the energy of activation ( $\Delta E_a$ ) was determined from an Arrhenius plot (Fig. 2) and the frequency factors (*A*) calculated (Table

(7) Wen-Hsuen Chang, *J. Phys. Chem.*, **61**, 819 (1957).

(8) The authors are indebted to Prof. R. Hardwick for the derivation of this relationship and for many enlightening discussions on the theoretical aspects of this work.

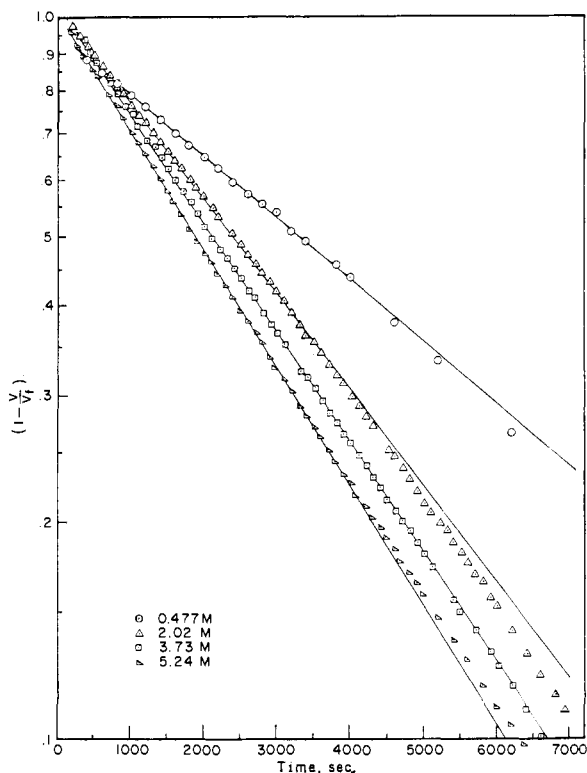


Fig. 1.—The effect of concentration on the decomposition of 1-hydroxy-iso-butyl iso-butyl peroxide at 99.4°.

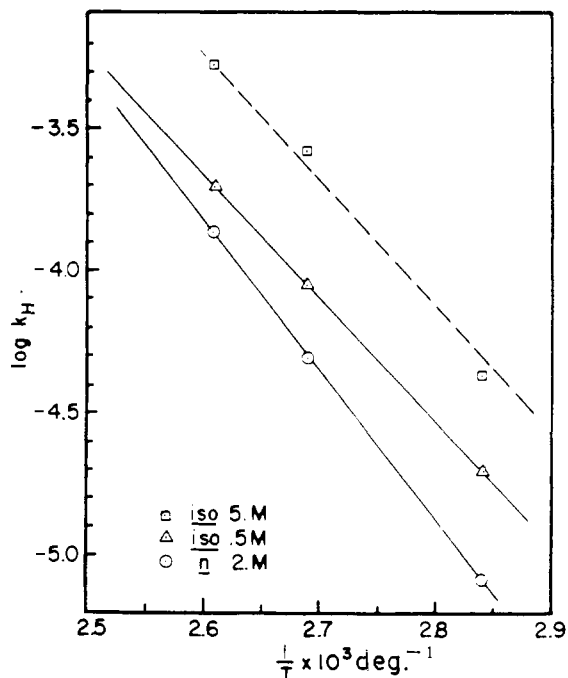


Fig. 2.—Arrhenius plot for the determination of activation energy for 1-hydroxybutyl butyl peroxides.

III). The results were also expressed in terms of the theory of absolute rates, the enthalpy of activation ( $\Delta H^*$ ) being determined from a plot of  $\log k_h/T$  vs.  $1/T$  (Fig. 3) and the entropy of activation ( $\Delta S^*$ ) being calculated from the Eyring equation (Table III).

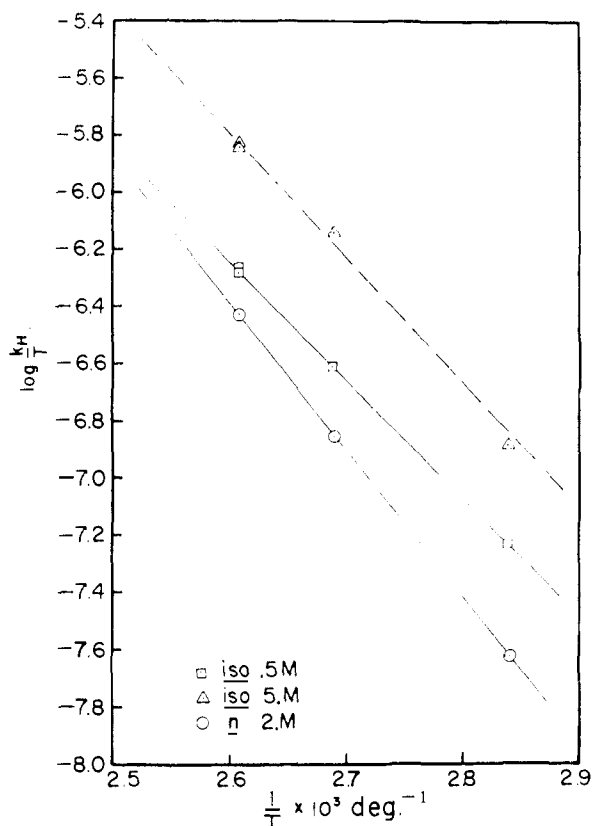


Fig. 3.—Determination of enthalpy of activation for 1-hydroxybutyl butyl peroxides.

#### Discussion

From the preliminary experiments it was found that the presence of inhibitors did not diminish the yield of hydrogen, but actually increased it in some cases (Table I, col. 5). At the same time, the amount of substances such as carbon monoxide and propane, which are undoubtedly of radical origin, was significantly decreased (indicated by increased purity of hydrogen in the presence of inhibitors (Table I, col. 4)), causing a net decrease in the total volume of gas evolved. A decrease in the over all rate of gas evolution was also observed in some cases. These observed results can be rationalized in terms of the efficiency of the inhibitor in trapping radicals. When the radicals which are formed in the competing homolytic cleavage of the peroxide bond are trapped by an efficient inhibitor, the products will be non-gaseous, thus resulting in a gas of higher hydrogen purity. Furthermore, these radicals are prevented from initiating an induced decomposition of the starting peroxide, with the over-all effect of giving a higher yield of hydrogen and a longer half-life. Exceptions to these generalizations probably represent contributions of other competing reactions which were not controlled and which contributed to the deviations from first order kinetics during the last 10–20% of the reaction. One such possibility is the slow formation of formic acid which is strong enough to cause acid catalyzed decomposition of the starting peroxide.

Of the inhibitors used,  $\alpha$ -methylstyrene was chosen as the most satisfactory because it not

TABLE III

RESULTS CALCULATED FROM DECOMPOSITION DATA FOR 1-HYDROXYALKYL ALKYL PEROXIDES IN  $\alpha$ -METHYLSTYRENE

Temp., $\times 10^3$ , $^{\circ}\text{C}$ .	$k_r$ , $\times 10^3$ , <sup>a</sup> sec. <sup>-1</sup>	$k_h$ , $\times 10^3$ , <sup>b</sup> sec. <sup>-1</sup>	$\Delta E_a$ , <sup>c</sup> kcal./mole	$A$ , <sup>d</sup> sec. <sup>-1</sup>	$\Delta H^*$ , <sup>e</sup> kcal./mole	$\Delta S^*$ , <sup>f</sup> cal./mole	$\Delta F^*$ , <sup>g</sup> kcal./mole
1-Hydroxyisobutyl isobutyl peroxide, 0.5 molal							
79.4	3.7	2.0	20.0	$5.1 \times 10^7$	19.0	-27.0	28.5
99.4	20	8.9		$4.7 \times 10^7$		-27.2	29.1
109.9	48	19		$4.9 \times 10^7$		-26.9	29.3
110.0	48	20		$5.1 \times 10^7$		-26.9	29.3
1-Hydroxyisobutyl isobutyl peroxide, 5.0 molal							
79.4	5.5	4.4	21.2 <sup>h</sup>	$2 \times 10^{10}$	20.5 <sup>h</sup>	-22 <sup>h</sup>	28 <sup>h</sup>
99.4	38	26		$2 \times 10^9$		-22 <sup>h</sup>	28 <sup>h</sup>
109.9	85	55		$2 \times 10^9$		-21 <sup>h</sup>	29 <sup>h</sup>
110.0	85	54		$2 \times 10^9$		-21 <sup>h</sup>	29 <sup>h</sup>
1-Hydroxy- <i>n</i> -butyl <i>n</i> -butyl peroxide, 2.0 molal							
79.4	1.7	0.81	24.6	$1.5 \times 10^{10}$	23.6	-15.7	29.1
99.4	10.6	5.0		$1.4 \times 10^{10}$		-15.9	29.5
109.9	29	14		$1.5 \times 10^{10}$		-16.1	29.8

<sup>a</sup> First order rate constant for all reactions combined. <sup>b</sup> First order rate constant for hydrogen evolution, derived from  $k_r$  and hydrogen yield. <sup>c</sup> Arrhenius energy of activation. <sup>d</sup> Arrhenius frequency factor. <sup>e</sup> Enthalpy of activation. <sup>f</sup> Entropy of activation. <sup>g</sup> Free energy of activation. <sup>h</sup> These figures contain a large uncertainty because the points in the determination of  $\Delta H^*$  and  $\Delta E_a$  did not fall on a straight line at 5 molal concentration. The maximum deviations are:  $\Delta E_a$ ,  $\pm 3.2$  kcal./mole;  $A$ , from  $3 \times 10^7$  to  $6 \times 10^{10}$  sec.<sup>-1</sup>;  $\Delta H^*$ ,  $\pm 3.1$  kcal./mole;  $\Delta S^*$ ,  $\pm 8$  cal./mole/deg.;  $\Delta F^*$ ,  $\pm 6$  kcal./mole. The results in the other two cases were exactly fitted by a straight line thus no range was obtained for them.

only acted effectively as an inhibitor (compared to hydroquinone, Table I, col. 4) but also served as a convenient solvent for the reaction. Because these studies were conducted above the "ceiling temperature" of the  $\alpha$ -methylstyrene,<sup>9</sup> the solvent remained a liquid and did not polymerize.<sup>10</sup>

The preliminary studies showed a higher hydrogen yield and a shorter reaction time for the 1-hydroxyisobutyl isobutyl peroxide than for the normal isomer. These results made the isobutyl compound more desirable for the detailed kinetic studies.

The fact that first order kinetic laws were followed at any one concentration but that these first order rate constants increased with increasing concentration requires further consideration. This dependence of the rate constant upon concentration approximated a linear function of the molar (not the molal) concentration within the range studied (0.5 to 5 molal). Studies were not carried out at lower concentrations, so it was not possible to tell whether a limit was being approached.<sup>11</sup> A variation of rate constant with concentration was reported in the thermal decomposition of diacetyl peroxide<sup>12</sup> resulting from an induced radical decomposition. While this effect was similar to the one observed here, the cause was undoubtedly not the same. An induced decomposition is possible in the absence of inhibitors, but it does not appear likely in their presence, especially when the

(9) H. W. McCormick, *J. Polymer Sci.*, **25**, 488 (1957).

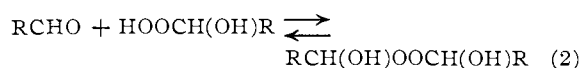
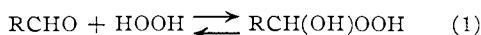
(10) We wish to thank Dr. Frank Mayo for the suggestion of using  $\alpha$ -methylstyrene as a radical trap and for many valuable discussions throughout the progress of this work.

(11) Certain limits were placed upon the ranges of concentration by practical sizes of decomposition vessels and minimum amounts of peroxides needed to obtain accurately measurable quantities of gas.

(12) M. Levy, M. Steinberg and M. Szwarc, *THIS JOURNAL*, **76**, 5978 (1954).

inhibitor is also the solvent. The formation of hydrogen was affected in a manner indicating that the induced decomposition had been minimized since conditions favorable to radical formation and hence induced radical decomposition (irradiation by ultraviolet light) actually caused a decrease in the amount of hydrogen formed and an increase in other products.

It has been reported that an equilibrium exists between hydrogen peroxide with aldehydes and a peroxyhemiacetal<sup>13</sup> (eq. 1,2).



Although a similar equilibrium exists between the hydroxyalkyl alkyl peroxide and the hydroperoxide and aldehyde,<sup>4,14</sup> (eq. 3) the equilibrium



is strongly in favor of the hydroxyalkyl alkyl peroxide. This is evidenced by the rapid exothermic reaction obtained upon mixing hydroperoxide with aldehyde and by the fact that the compound so formed may be distilled at reduced pressure, showing a much higher boiling point than its components. Also, the linearity of the data as shown in Fig. 1 indicates that the equilibrium must be established rapidly compared to the rate of decomposition. Thus the reaction represented by equation 3 can hardly be an important factor in the concentration dependence of the rate constant.

From earlier studies and product analysis,<sup>4</sup> other reactions were known to be competing with the one under study. If these other reactions were also first order, no deviations from the first order plots would have been observed on this account. The fact that the deviations observed were relatively small suggested that there was at the most a small second order contribution from one of the competing reactions.

We are left with the conclusion that a solvent effect<sup>15,16,17</sup> of unknown nature is contributing to the deviations of the first order rate constant with concentration. Neither the effect of the dielectric constant of the reaction medium nor the effect of association or hydrogen bonding was determined. The use of concentrations as approximations to the activities may also have contributed to the deviations. One observation of possible importance in this connection is the effect of water (Table I) in slowing down the hydrogen evolution reaction. Thus it appears that the reaction is sensitive to the type of solvent used, although it is premature to speculate on the nature of this dependence (*i.e.*, amount of association in ground *versus* transition state) at this time.

Almost every type of reaction mechanism has

(13) (a) A. Rieche, *Ber.*, **64B**, 2328 (1931). (b) C. N. Satterfield and C. Case, *Ind. Eng. Chem.*, **46**, 998 (1954).

(14) F. H. Dickey, J. H. Raley, F. F. Rust, R. S. Tresede and W. E. Vaughan, *ibid.*, **41**, 1673 (1949); F. H. Dickey, F. F. Rust and W. E. Vaughan, *THIS JOURNAL*, **71**, 1432 (1949).

(15) C. Walling and R. B. Hodgdon, *ibid.*, **80**, 228 (1958).

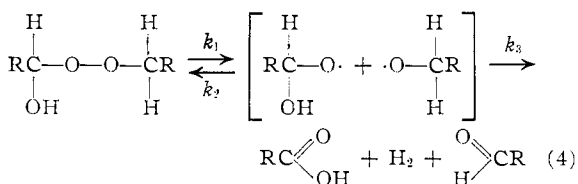
(16) W. E. Parker, L. P. Witnauer and D. Swern, *ibid.*, **80**, 323 (1958).

(17) P. D. Bartlett and R. Altschul, *ibid.*, **67**, 816 (1945).

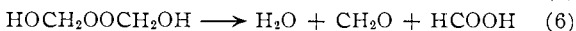
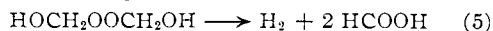
been proposed to explain the decomposition of various peroxidic materials. One of the most common mechanisms evoked is the homolytic cleavage of the O-O bond.<sup>18</sup> However, radical chain mechanisms,<sup>19</sup> cage mechanisms,<sup>12,20</sup> linear concerted mechanisms<sup>21</sup> and ionic mechanisms involving acid<sup>22</sup> and base<sup>23</sup> catalysis have all been proposed. The mechanism proposed by Wieland and Wingler<sup>24</sup> for the related decomposition by base of bis-(hydroxymethyl) peroxide has already been considered.<sup>1</sup>

In the present case, ionic mechanisms have already been eliminated.<sup>1</sup> Since the reaction producing hydrogen proceeds unhindered by the presence of radical inhibitors, while radical type side products are greatly affected, radical induced mechanisms are also unlikely. It has been demonstrated with considerable certainty that the hydrogen is evolved as molecular hydrogen and not as atomic hydrogen.<sup>1,4</sup> If the reaction is unimolecular, the two mechanisms remaining for consideration are the concerted cyclic process and a "cage" mechanism.

A "cage" mechanism<sup>25</sup> whereby radicals are formed but react with each other within a solvent cage can be represented as



where the species in the brackets represent the radicals which are trapped in the solvent cage. These radicals may react to either regenerate the starting peroxide ( $k_2$ ) or react irreversibly ( $k_3$ ) to give the products. Since a "cage" mechanism cannot operate in the gas phase, a definitive experiment would be a vapor phase decomposition study. Such a vapor phase decomposition of a hydroxyalkyl alkyl peroxide has not been carried out but the decomposition of a related peroxide, bis-hydroxymethyl peroxide has been reported to give hydrogen formic acid, formaldehyde and water<sup>26</sup> according to



Style and Summers reported that, in the photochemical reaction of formaldehyde with oxygen, a thermal reaction takes over above 275° in which

(18) J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 88 (1948). J. Murawski, J. S. Roberts and M. Szwarc, *J. Chem. Phys.*, **19**, 698 (1951). N. A. Milas and D. M. Surgenor, *THIS JOURNAL*, **68**, 205 (1946).

(19) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947). W. E. Cass, *ibid.*, **68**, 1976 (1946).

(20) A. Rembaum and M. Szwarc, *ibid.*, **76**, 5975 (1954); **77**, 3486 (1955). M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954).

(21) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

(22) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

(23) N. Kornblum and H. E. De la Mare, *THIS JOURNAL*, **73**, 880 (1951).

(24) H. Wieland and A. Wingler, *Ann.*, **431**, 301 (1923).

(25) J. E. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934); M. J. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

(26) A. D. Jenkins and D. W. G. Style, *J. Chem. Soc.*, 2337 (1953).

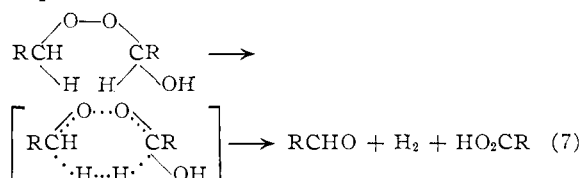
hydrogen is formed without hydrogen atoms.<sup>27</sup> They propose that bis-hydroxymethyl peroxide was the intermediate in this non-radical process. Since this was a gas phase reaction, a cage mechanism could not be involved. A concerted mechanism would explain these results in the gas phase as well as those in the present case in solution. Thus by analogy with this related reaction which does go in the gas phase, we may assume that the cage mechanism does not operate in the present reaction in solution. Furthermore, although a cage mechanism seems possible in an inert solvent, it hardly seems conceivable when the solvent is reactive towards the "caged" species as in the present case.

If in equation 4 the rate-determining step is  $k_1$ , then there would be no deuterium isotope effect when the corresponding deuterated compound was decomposed. As will be reported in the subsequent paper, there is such an isotope effect and thus this postulate is untenable. If one assumes that the recombination of the radicals within the cage to give starting material is such that the rate determining step is  $k_3$ , then an isotope effect would be anticipated. Under these circumstances one would expect the entropy of activation to be positive instead of negative as found.

(27) D. W. G. Style and D. Summers, *Trans. Faraday Soc.*, **42**, 388 (1946).

The large negative entropy of activation (Table III) found is compatible with a rigid transition state and has been repeatedly found for reactions postulated to proceed from non-cyclic reactants via a cyclic transition state.<sup>28</sup>

Thus the cage mechanism is untenable and the evidence in favor of the cyclic concerted mechanism for the formation of hydrogen, acid and aldehyde from the hydroxybutyl butyl peroxide is substantial. The mechanism proposed (eq. 7) is compatible with all the data obtained so far. No other mechanism has been proposed which explains all of the facts.



**Acknowledgment.**—We wish to thank the National Science Foundation for financial support of this investigation.

(28) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 106; J. F. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); E. G. Foster, A. C. Cope and F. Daniels, *THIS JOURNAL*, **69**, 1893 (1947); J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chapter 24.

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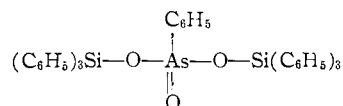
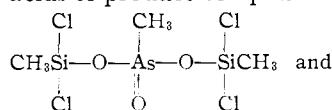
## Monomers and Polymers Containing Si-O-As Linkages<sup>1</sup>

BY BERTRAND L. CHAMBERLAND AND ALAN G. MACDIARMID

RECEIVED JANUARY 18, 1960

$[(\text{C}_6\text{H}_5)_3\text{SiO}]_3\text{As}$  was prepared by the interaction of  $\text{AsCl}_3$  with  $(\text{C}_6\text{H}_5)_2\text{SiONa}$  or with  $(\text{C}_6\text{H}_5)_3\text{SiOH}$  in the presence of  $\text{NH}_3$ . It was also prepared by the cohydrolysis of  $\text{AsCl}_3$  and  $(\text{C}_6\text{H}_5)_3\text{SiCl}$ .  $[(\text{C}_6\text{H}_5)_3\text{SiO}]_3\text{AsO}$  was prepared by the reaction of  $(\text{C}_6\text{H}_5)_3\text{SiCl}$  with  $\text{KH}_2\text{AsO}_4$ . The macro-molecular species,  $(\text{HO})_2\text{As}(\text{O})[\text{OSi}(\text{C}_6\text{H}_5)_2\text{OAs}(\text{O})\text{OH}]_2\text{OH}$  was prepared by the interaction of  $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$  with  $\text{KH}_2\text{AsO}_4$  at room temperature. This product slowly decomposed to give a material whose composition approached  $[\text{OSi}(\text{C}_6\text{H}_5)_2\text{OAs}(\text{O})\text{OH}]_x$ .  $\text{As}[\text{OSi}(\text{C}_6\text{H}_5)_2\text{O}]_3\text{As}$  was prepared by the cohydrolysis of  $\text{AsCl}_3$  and  $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$  and also by the interaction of  $\text{AsCl}_3$  with  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$  in the presence of either  $(\text{C}_2\text{H}_5)_3\text{N}$  or  $\text{NH}_3$ . The physical, thermal and hydrolytic properties of the compounds prepared were examined.

Compounds of pentavalent arsenic containing Si-O-As linkages have been prepared by Kary and Frisch<sup>2</sup> by the interaction of both alkyl- and aryl-chlorosilanes with either alkyl- or aryl-arsenic acids to produce compounds such as



Hydrolysis of compounds of the above type did not proceed in a simple manner to give polymers con-

(1) This report is based on portions of a thesis to be submitted by Bertrand L. Chamberland to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

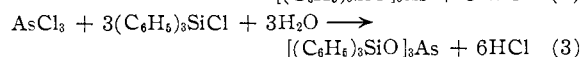
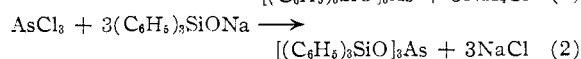
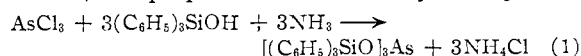
(2) (a) R. M. Kary and K. C. Frisch, *THIS JOURNAL*, **79**, 2140 (1957); (b) U. S. Patent 2,863,893 (1958).

taining alternating Si-O-As and O-Si-O linkages; instead, materials were obtained which had an arsenic to silicon ratio of only 1 to 12.

The present investigation was carried out for the purpose of preparing and characterizing monomers and polymers containing Si-O-As(III) or Si-O-As(V) linkages.

### Results and Discussion

Tris-(triphenylsilyl)-arsenite,  $[(\text{C}_6\text{H}_5)_3\text{SiO}]_3\text{As}$ , a colorless, microcrystalline substance melting at  $190.5^\circ$ , was prepared as indicated by the equations



Tris-(triphenylsilyl)-arsenate,  $[(\text{C}_6\text{H}_5)_3\text{SiO}]_3\text{AsO}$ , a colorless, crystalline substance melting at  $240-$