was found to be 97% *cis*-propenyl phenyl ether (**19**) and 3% *trans*-propenyl phenyl ether (**20**). Spectral evidence for **19** is the following: ir (film) 8.00 (Ph–O–R), 13.28, 14.50 μ (Ph); nmr (CCl_4) δ 1.70 (d of d, 3, J = 7.0 Hz, J = 1.5 Hz, CH_3), 4.75 (p, 1, J = 7 Hz, =C*H*CH_3), 6.30 (d of d, 1, J = 6.3 Hz, J = 1.5 Hz, –OCH=), 6.80–7.30 (m, 5, Ph) [lit.[31] **19**, J = 6.0 Hz for *cis*-CH=CH–].

Allyl Phenyl Ether and Potassium Amide in Liquid Ammonia. To a grey solution of approximately 50 mmol of KNH_2 in liquid ammonia—prepared by dissolving 2.24 g (57 mg-atoms) of potassium in 120 ml of liquid ammonia containing a pinch of hydrated ferric nitrate—was rapidly added 2.5 g (18.6 mmol) of APE. A red color developed immediately. The solution was stirred for 3 hr and then, while the ammonia evaporated, 40 ml of ether was added. After the ammonia had all evaporated, the ether solution was worked up[23] to afford 1.0 g of liquid, bp 50–55° (2.0 mm). By nmr and vpc (SE30) the product was found to be a mixture of 68% phenol and 32% of a mixture of 65% *cis*-propenyl phenyl ether (**19**) and 35% *trans*-propenyl phenyl ether (**20**). The nmr evidence for **20** is the following: (CCl_4) δ 1.48 (d of d, 3, J = 7.0 Hz, J = 1.5 Hz, CH_3) and 5.28 (d of q, 1, J = 11.0 Hz, J = 7.0 Hz, =C*H*-CH_3); the other protons were obscured by phenol peaks [lit.[31] for *trans*-CH=CH– of **20** is J = 11.3 Hz].

Isomerization of Allyl Phenyl Ether with Allyllithium. In a completely dry apparatus and under nitrogen atmosphere, 3.5 ml (9.8 mmol) of *n*-butyllithium in hexane was mixed with 1.34 g (4.7 mmol) of tetraallyltin.[18] The solution was stirred at room temperature for 45 min and then the precipitated allyllithium was filtered under nitrogen, washed twice with pentane, and dissolved in about 20 ml of anhydrous THF. By titration, this solution was found to contain 9 mmol of base (allyllithium). To the solution was added 0.5 g (3.8 mmol) of APE. After stirring at room temperature for 2 hr and at reflux for 1.5 hr, the reaction was worked up[23] to give an ether residue of 78% APE, 13% propiophenone (**2**), and 9% α-vinyl benzyl alcohol (**3**), by vpc (DEGS). Similarly, with DME as the solvent, the ether residue was found to contain 90% APE, 4% **1**, and 6% **3**.

Acknowledgments. We wish to thank Research Corporation and the Marquette University Committee on Research for their financial support. We are also indebted to Research Corporation for their aid in the purchase of the mass spectrometer used in this work. Thanks are also extended to Mr. James O'Kane for laying some of the groundwork of the work reported herein.

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(31) P. W. Jolly, F. G. A. Stone, and K. MacKenzie, *J. Chem. Soc.*, 6419 (1965).

The Neighboring Peroxide Anion and the 1,2-Dioxetane Intermediate. A Kinetic and Product Study of the Basic Decomposition of Chloro-*tert*-butyl Hydroperoxide

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Abstract: A kinetic and product study of the basic decomposition of chloro-*tert*-butyl hydroperoxide (**1**) in aqueous methanol suggests a neighboring peroxide anion reaction (ND_I-($^-$OO-4)). Based on this mechanism, the pK_a of **1**, obtained from kinetic data, is in good agreement with predicted values. Anchimeric assistance in the ND_I-($^-$OO-4) reaction is estimated to be approximately 10^4 and the α effect is 37 relative to the ND_I($^-$O-4) reaction. The products and light emission from the basic decomposition of **1** are in accord with a 1,2-dioxetane intermediate (**5**). Spectral data and light emission from an isolated sample of **5** provide further support. A kinetic treatment, which draws on iodometric and light emission data, allows the calculation of rate coefficients for the reactions of **5**. Activation parameters for unimolecular decomposition of **5** in 60% aqueous methanol with 1.58 *M* ionic strength are: E_a = 19.1 ± 0.3 kcal/mol and log A = 10.9. The products of this reaction are acetone and formaldehyde. A base-catalyzed decomposition of **5** also occurs to give, in part, 2-methyl-1,2-propanediol (**4**). A combination of kinetic and product data suggests that the initial product of the basic decomposition of **5** is α-hydroxyisobutyraldehyde. The latter compound, with formaldehyde and base, is proposed to give **4**. Activation parameters for the basic decomposition of **5** are: E_a = 16.3 ± 0.3 kcal/mol and log A = 9.42. Direct reaction of bromide ion and formaldehyde (at high concentration) with **5** is observed and rate coefficients are calculated.

The synergetic relationship between a functional group and the reaction site has fascinated chemists for a number of years. Although numerous groups are reported to enter into neighboring group reactions,[1] little is known about peroxy group participation in these reactions. For this reason, we have undertaken a comprehensive study of neighboring peroxide group reactions.[2] Our study was begun with a search for a four-ring peroxide anion ND$_I$ reaction ($^-$OO-4), which employed the basic decomposition of chloro-*tert*-butyl hydroperoxide (**1**).[4] This hydroperoxide fulfilled the requirements of avoiding complicating basic elimination reactions which

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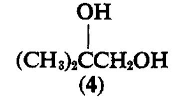
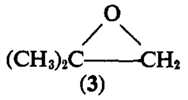
(1) For reviews see: (a) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969); (b) G. D. Sargent, *ibid.*, **20**, 301 (1966); (c) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965; (d) B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964); (e) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; (f) W. Lwowski, *Angew. Chem.*, **70**, 483 (1958).

(2) This type of neighboring group reaction is defined by Traylor[3] as "internal nucleophilic displacement" and abbreviated as ND$_I$.

(3) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970).

(4) For preliminary reports see: (a) W. H. Richardson, J. W. Peters, and W. P. Konopka, *Tetrahedron Lett.*, 5531 (1966); (b) W. H. Richardson, "Internationales Symposium, Chemie der Organischen Peroxide," Berlin, DDR, Sept 1967, Abstracts, p 81; (c) W. H. Richardson and V. F. Hodge, *Tetrahedron Lett.*, 2271 (1970).

Table I. Products from the Basic Decomposition of **1** in 60% Aqueous Methanol at 30° with Equimolar Reactant Concentrations[a]

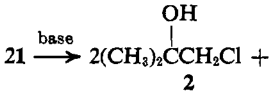
[**1**], *M*	[NaOH],[b] *M*	% yield[c] $(CH_3)_2CO$	 $(CH_3)_2C(OH)CH_2OH$ (**4**)	 (**3**)	% product balance
0.180	0.180	85.5	12.5	0	98.0
0.0900	0.0900	88.3	12.3	0	100.6
0.0450	0.0450	95.5	3.2	0	98.7
0.00900	0.00900	97.5	0	0	97.5
0.180 (+ 0.100 *M* NaBr)	0.180	58.9	29.7	12.5	101.1

[a] With 2 mol % EDTA based on sodium hydroxide. [b] The base is introduced as sodium hydroxide. [c] Based on reacted **1**.

occur with primary or secondary alkyl hydroperoxides[5,6] as well as β elimination of the elements of hydrogen halide. The N_{D_I}-($^{-}$OO-4) reaction is of particular interest, since one may assess the importance of the α effect[7-9] in intramolecular reactions and the properties of the 1,2-dioxetane intermediate[4] which may be generated in the reaction.

Results

Products. Aqueous methanolic solvent was used in order to facilitate ionic reactions and minimize radical reactions. To scavenge any trace amounts of transition metal ions, and thus prevent radical chain reactions, EDTA was incorporated into the reaction mixture.[10] Analysis of a typical sample of chloro-*tert*-butyl hydroperoxide (**1**) showed 89% **1** (by iodometric titration), 5% 1-chloro-2-methyl-2-propanol (**2**) (by glc with iodometric titration for **1**), 3% bischloro-*tert*-butyl peroxide (by glc), and 3% of an unknown compound (by glc). The latter two compounds were carried through the basic decomposition of **1** unchanged. The chlorohydrin (**2**) is converted to isobutylene oxide (**3**) and no 2-methyl-1,2-propanediol (**4**) is observed under the reaction conditions. The yields of products are based on the per cent **1** in the sample and the yields of **3** are corrected for initial amounts of **2**. The products from the basic decomposition of **1** depend on the concentrations of the reactants. With moderate to low equimolar reactant concentrations, the primary products are acetone and formaldehyde with smaller amounts of glycol **4** (Table I). Quantitative yields of acetone are approached at low reactant concentrations, but as the concentrations are increased, the yield of glycol increases at the expense of acetone. Decomposition of **1** by the reaction below[10a,11] is ruled out, since no epoxide



$$2\mathbf{1} \xrightarrow{\text{base}} 2(CH_3)_2C(OH)CH_2Cl + O_2 \quad (1)$$

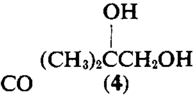
2

was observed, which would result from **2** under the basic conditions. Furthermore, no oxygen was observed (a maximum yield of 0.4% could pass undetected) with initial concentrations of **1** and sodium hydroxide as 0.146 and 0.150 *M*, respectively. The same gas analysis showed that isobutene was absent. In the presence of sodium bromide, the yield of epoxide is significantly increased. This can be attributed to a redox reaction between the hydroperoxide and bromide ion to give chlorohydrin, which is finally converted to epoxide. The formation of epoxides from the basic decomposition of β-bromohydroperoxides[12] can be explained by such a redox reaction, which results from the bromide that is produced in the primary reaction.

Formaldehyde, which is expected to accompany acetone, was detected as the dimedon derivative. At higher reactant concentrations ([**1**] = [NaOH] = 0.250 *M*) and with slow addition of base to the hydroperoxide, a 53.3% yield of formaldehyde was obtained. Since the product balance is excellent at equimolar reactant concentrations, the decreased yield of formaldehyde must be associated, in part, with the formation of the reduced glycol product.

At high base concentrations relative to hydroperoxide concentrations, a dramatic change in product yields results, as seen from Table II. Although high

Table II. Products from the Basic Decomposition of **1** in 60% Aqueous Methanol at 30° at High Base Concentrations[a]

[NaOH],[b] *M*	Added reactant	% yield[d] $(CH_3)_2CO$	 $(CH_3)_2C(OH)CH_2OH$ (**4**)
0.200[c]		42	38
1.58		28	32
1.58	0.01 *M* Br⁻	23	37
1.58	1.0 *M* Br⁻	0	81
1.58	0.01 *M* CH_2O	30	48
1.58	1.0 *M* CH_2O	0	62

[a] With 1.00 × 10^{-2} *M* **1**. [b] With 2 mol % EDTA. [c] μ = 1.58, maintained with sodium perchlorate. [d] With 1.6 *M* NaOH, **3** (10^{-2} *M*) undergoes reaction to give 1-methoxy-2-methyl-2-propanol, but **4** is not observed.

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[5] S. S. Medewedew and E. N. Alexejewa, *Chem. Ber.*, **65**, 133 (1932).

[6] For similar elimination reactions of dialkyl peroxides, see (a) N. Kornblum and H. E. De La Mare, *J. Amer. Chem. Soc.*, **73**, 880 (1951); (b) R. P. Bell and A. O. McDougall, *J. Chem. Soc.*, 1697 (1958); (c) W. H. Richardson and R. S. Smith, *J. Amer. Chem. Soc.*, **91**, 3610 (1969).

[7] J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 18 (1962).

[8] For reviews see (a) T. C. Bruice, A. Donzel, R. W. Huffman, and A. R. Butler, *ibid.*, **89**, 2106 (1967); (b) J. Hine and R. D. Weimer, Jr., *ibid.*, **87**, 3387 (1965); (c) C. A. Bunton, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience, New York, N. Y., 1962, p 24.

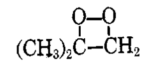
[9] The α effect may be interpreted in terms of the Hard-Soft-Acid-Base (HSAB) concept: (a) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963); (b) G. Klopman, *ibid.*, **90**, 223 (1968).

[10] (a) D. B. Denny and J. D. Rosen, *Tetrahedron*, **20**, 271 (1964); (b) for the effect of EDTA on the cobalt salt decomposition of *tert*-butyl hydroperoxide, see W. H. Richardson, *J. Amer. Chem. Soc.*, **87**, 247 (1965).

[11] (a) M. S. Kharasch, A. Fono, W. Nudenberg, and B. Bischof, *J. Org. Chem.*, **17**, 207 (1952); (b) V. A. Belyaev and M. S. Nemtsov, *J. Gen. Chem., SSR*, **31**, 3594, 3599 (1961); **32**, 3420 (1962).

[12] (a) M. Schulz, A. Rieche, and K. Kirschke, *Chem. Ber.*, **100**, 370 (1967); (b) K. R. Kopecky, J. H. van de Sande, and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968).

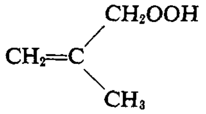
yields of acetone are obtained with moderate and equimolar reactant concentrations (Table I), the acetone yields fall to low levels with large base to hydroperoxide concentration ratios. In part, the decreased yield in acetone can be explained in terms of condensation reactions. With equimolar concentrations (1.00×10^{-2} *M*) of acetone and formaldehyde, a 6.5% loss of acetone results when the base concentration is 1.6 *M* under the reaction conditions of Table II. All of the acetone undergoes reaction when the formaldehyde concentration is increased to 1.0 *M*. A large array of condensation products results from such a reaction, where more than one formaldehyde molecule is condensed with one acetone molecule.[13] Condensation reactions do not entirely explain the effect of increasing base/**1** concentration ratios, since an increase in this ratio also increases the yield of glycol. Considering the effect of base on the yields of acetone and glycol as given in Tables I and II, a common intermediate is suggested from which acetone and glycol result, where glycol is produced by a base-catalyzed process. The data from both Tables I and II indicate that bromide ion traps this intermediate to give glycol at the expense of acetone, even accounting for the redox reaction as evidenced by **3** in Table I. Again, the effect of bromide ion on the yields of products has implications to the basic decomposition of β-bromohydroperoxides.[12] Namely, higher yields of glycol relative to carbonyl cleavage products are expected with β-bromohydroperoxides as compared to the chloro analogs. Since formaldehyde in base is potentially a reducing agent, similar trapping reactions were carried out with it. The yield of glycol is increased with a corresponding decrease in acetone with 1 *M* formaldehyde (Table II). Reductive trapping of the intermediate by formaldehyde is consistent with the data, but this needs to be subjected to further scrutiny which is done in the kinetics section. The intermediate which is consistent with the product studies is 3,3-dimethyl-1,2-dioxetane (**5**).[4] Reduction of the peroxidic bond by bromide or formaldehyde in base is proposed to give glycol, whereas unimolecular decomposition is suggested to give acetone and formaldehyde.



5

More direct evidence for **5** was obtained by slowly adding either chloro- or bromo-*tert*-butyl hydroperoxide to aqueous base at room temperature under reduced pressure. The distillate was collected in the receiver at −78° and then redistilled at room temperature. An nmr spectrum of the distillate in carbon tetrachloride showed the presence of acetone (δ 2.07 ppm), isobutylene oxide (($(CH_3)_2$ at δ 1.28 ppm, s, area = 6, and CH_2 at δ 2.42 ppm, s, area = 2) as well as **5** (($(CH_3)_2$ at δ 1.60 ppm, s, area = 6, and CH_2 at δ 4.90 ppm, s, area = 2). Using the methyl absorption areas, the following per cent composition was calculated: 21% **5**, 33% acetone, and 46% isobutylene oxide. Upon heating the solution, the absorptions for **5** disappeared and the acetone absorption increased in intensity. If the heating of **5** was carried out in a dark room, light emission could be observed visually. No further light emission was noted after the nmr signals for **5** disappeared. Light emission has been reported for other 1,2-dioxetanes that have been recently isolated.[14]

Certain 1,2-dioxetanes, formed from olefins and singlet oxygen under neutral conditions, are reported to give allylic hydroperoxides and solvolytic products.[15] The 1,2-dioxetane (**5**), which is generated in the basic decomposition of **1**, could lead to hydroperoxides **6** and **7** by analogy.[15] Upon glc analysis, the hydroperoxides will appear as the corresponding alcohols as does **1**.



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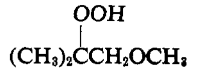

$$(CH_3)_2\overset{\displaystyle OOH}{\overset{|}{C}}CH_2OCH_3$$

7

No methallyl alcohol or 1-methoxy-2-methyl-2-propanol was observed by glc analysis.

Kinetics. The bulk of the kinetic data was obtained by iodometric titration of the hydroperoxide **1**.[16] To substantiate the kinetic method, three different methods were compared for uniformity (Table III).

Table III. Kinetic Control Studies in 60% Aqueous Methanol at 29.97°

[**1**], *M*	[NaOH], *M*	μ^a	10^3k_{obsd},[b] sec^{-1}	$10^3k_{obsd}'$,[c] l. mol^{-1} sec^{-1}	Method
0.178	0.00	0.500	*d*		Iodometric
0.0500	0.995	0.995	1.79		Iodometric
0.0500	0.995	0.995	1.81		Iodometric[e]
0.356	0.284	0.500		7.05	Iodometric
0.356	0.284	0.500		6.90	Acidometric
0.0100	1.58	1.58	2.19[f]		Iodometric
0.0100	1.58	1.58	2.10[g]		Glc

[a] Adjusted with sodium perchlorate. [b] Observed first-order rate coefficient. [c] Observed second-order rate coefficient. [d] No decrease in iodometric titer after 27.4 hr. [e] With 5.0×10^{-3} *M* 2,6-di-*tert*-butyl-*p*-cresol. [f] At 30.03°. [g] At 30.00°.

The first entry shows that the hydroperoxide is indeed stable under the reaction conditions in the absence of base. The second and third entries demonstrate that the rate is unchanged in the presence or absence of a radical trap and thus a radical chain mechanism is unimportant. This is consistent with the product studies in which no oxygen was observed. Oxygen is a characteristic product of a radical chain decomposition of a hydroperoxide.[17] The fourth and fifth entries show that the rate of disappearance of hydroperoxide equals, within experimental error, the rate of disappearance of base and thus should also equal the rate of appearance of chloride ion. Specific analysis for the hydroperoxide was made by glc, whereby reproducible amounts of the chlorohydrin were measured by com-

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(13) T. White and R. N. Haward, *J. Chem. Soc.*, 25 (1943).

(14) (a) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968); (b) E. H. White, J. Wiecko, and D. R. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969); (c) E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, **92**, 2167 (1970); (d) P. D. Bartlett and A. P. Schaap, *ibid.*, **92**, 3223 (1970); (e) S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970); (f) J.-J. Basselier and J-P. LeRoux, *C. R. Acad. Sci., Paris*, **270**, 1366 (1970).

(15) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969); we thank Professor Kearns for providing us with additional information prior to publication.

(16) W. H. Richardson, *ibid.*, **87**, 247 (1965).

(17) See, for example: (a) W. H. Richardson, *ibid.*, **87**, 1096 (1965); (b) W. H. Richardson and H. E. O'Neal in "Comprehensive Chemical Kinetics," Vol. 5, C. H. Bamford and C. F. H. Tipper, Ed., American Elsevier, New York, N. Y., 1971, in press.

parison to an internal standard. The agreement between the last two entries in Table III then shows that iodometric method does indeed measure the rate of disappearance of the hydroperoxide.

The order in chloro-*tert*-butyl hydroperoxide was studied at high base concentration (Table IV) and under these conditions, the reaction is first order in **1**. The effect of base concentration on the rate of decomposition of **1** is given in Table V, where a low concentration of **1** is maintained. By inspection of the data in Table V, it is evident that a linear relationship between sodium hydroxide initial concentration and k_{obsd} is not observed as is demanded by first-order dependence on the base.

Table IV. Order in Chloro-*tert*-butyl Hydroperoxide (**1**) in 60% Aqueous Methanol at 29.97° [a]

[**1**] × 10^2, *M*	$10^3 k_{obsd}$, sec^{-1}
1.00	1.71
2.00	1.79
4.00	1.79
7.50	1.78
10.0	1.76
	Av 1.76 ± 0.03

[a] [NaOH] = 0.995 *M*, μ = 0.995.

Table V. Effect of Base Concentration on the Rate of Chloro-*tert*-butyl Hydroperoxide (**1**) Decomposition in 60% Aqueous Methanol at 29.97° [a,b]

[NaOH], *M*	$10^3 k_{obsd}$, sec^{-1}
0.0997	0.590
0.199	1.03
0.515	1.53
0.792	1.63
0.995	1.67
1.78	1.68
1.79	1.71

[a] [**1**] = 0.0100 *M*. [b] The ionic strength is maintained constant at 1.80 with sodium perchlorate.

The formation and disappearance of the 1,2-dioxetane (**5**) may be treated by consecutive first-order methods[18] by eq 2, where $\tau_{max} = k_{obsd}t_{max}$, $\kappa = k_{f_{obsd}}/k_{obsd}$, and t_{max} is the time at maximum emission.

$$\tau_{max} = \frac{2.303 \log \kappa}{\kappa - 1} \qquad (2)$$

The data are given in Table VI as a function of base concentration and temperature. To substantiate that light emission results from the decomposition of the 1,2-dioxetane and not the hydroperoxide, a control measurement was made with 10^{-2} *M* *tert*-butyl hydroperoxide, 1.58 *M* sodium hydroxide, and 8 × 10^{-2} *M* fluorescein in 60% aqueous methanol at 30°. No light emission was observed under these conditions. Previously we had assumed that the decomposition of **5** was unimolecular;[4c] however, the data of Table VI show that the decomposition is in part base catalyzed. Plots of $k_{f_{obsd}}$ *vs.* [OH$^-$] were made according to eq 3 to

$$k_{f_{obsd}} = k_f + k_{fB}[\mathrm{OH}^-] \qquad (3)$$

give the unimolecular rate coefficient (k_f) for decomposition of **5** as the intercept and the base-catalyzed rate coefficient (k_{fB}) as the slope (Table VII). Activation parameters that result from the data in Table VII are: E_a = 19.1 ± 0.3 kcal/mol (r = 0.998), log A = 10.9, $\Delta H^{\ddagger}$ = 18.5 ± 0.3 kcal/mol, $\Delta S^{\ddagger}$ = −10.6 ± 1.2 eu for k_f and E_a = 16.3 ± 0.3 kcal/mol (r = 0.998), log A = 9.42, $\Delta H^{\ddagger}$ = 15.7 ± 0.3 kcal/mol, $\Delta S^{\ddagger}$ = −17.4 ± 1.1 eu for k_{fB}.

Table VI. Iodometric and Light Emission Data for the Basic Decomposition of Chloro-*tert*-butyl Hydroperoxide[a] in 60% Aqueous Methanol[b]

Temp, °C	[NaOH],[c] *M*	$10^3 k_{obsd}$,[d] sec^{-1}	t_{max}, sec	$10^3 k_{obsd}$, sec^{-1}
39.8	0.20	3.97	201	6.11
39.8	1.58	7.94	72.9	21.9
34.95	0.20	(2.52)[e]	325	3.75
34.90	1.58	4.17	122	14.1
30.00	0.20	1.36	561	2.28
30.03	1.58	2.19	208	9.00
25.20	0.20	(0.631)[e]	1015	1.45
25.23	1.58	1.15	366	5.35
20.30	0.20	(0.315)[e]	1800	0.895
20.32	1.58	0.575	600	3.66
15.68	0.20	(0.155)[e]	3270	0.536
15.68	1.58	0.295	1038	2.26
9.94	0.20	0.0614		
9.94	1.58	0.120		

[a] [**1**] = 1.00 × 10^{-2} *M*. [b] μ = 1.58, maintained with sodium perchlorate. In some instances 8.00 × 10^{-3} *M* fluorescein was added to increase the light intensity; however t_{max} values were unchanged with added fluorescein. [c] With 2 mol % EDTA. [d] The rate of decay of light emission after the maximum is reached closely approximates the iodometric rate of hydroperoxide disappearance. [e] Obtained from an activation plot of the 0.20 *M* sodium hydroxide data over a temperature range of 39.8–9.94°.

Table VII. Unimolecular and Base-Catalyzed Rate Coefficients for the Decomposition of 3,3-Dimethyl-1,2-dioxetane in 60% Aqueous Methanol[a]

Temp, °C	$10^3 k_f$, sec^{-1}	$10^3 k_{fB}$, l. mol^{-1} sec^{-1}
15.7	0.28	1.25
20.3	0.49	2.01
25.2	0.89	2.82
30.0	1.31	4.86
35.0	2.20	7.53
39.8	3.99	11.3

[a] μ = 1.58.

Since the products of the reaction were dependent upon bromide ion and formaldehyde, at high concentrations, it was of interest to determine whether or not the rate of 1,2-dioxetane decomposition showed such a dependence. The results are given in Table VIII along with comparative data without an added reactant and with chloride ion. The change in rate of 1,2-dioxetane decomposition is slight in the presence of 1 *M* chloride ion. Thus, chloride ion which is produced from decompositions of 10^{-2} *M* solutions of **1** will not complicate the kinetics. The iodometric rate coefficient (k_{obsd}) is also unchanged with added chloride ion (1.60 *M*) using 0.20 *M* base and maintaining constant ionic strength. At low concentrations of either bromide ion or formaldehyde, no change in $k_{f_{obsd}}$ is found. Thus, the formaldehyde which is produced in the basic decomposition of 10^{-2} *M* solutions of **1** will not influence the

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(18) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1961, p 166.

Table VIII. Effect of Chloride, Bromide, and Formaldehyde on the Rate of Decomposition of 3,3-Dimethyl-1,2-dioxetane in 60% Aqueous Methanol at 30.0° [a]

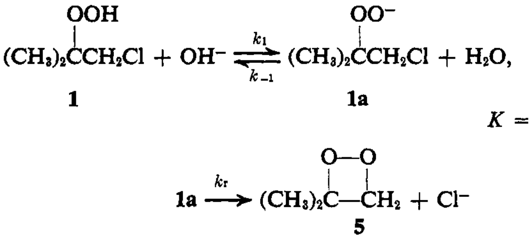
Added reactant, M	$t_{\max}$, sec	$10^3 k_{f_{obsd}}$, sec^{-1}	$10^3 k_{fd}$, l. mol^{-1} sec^{-1}	Relative[b] integrated intensity (I_n)
None	208	9.00	0	714
1.00 M NaCl	204	9.25	0.25	
0.0100 M NaBr	208	9.00		650
1.00 M NaBr	99.6	27.7	18.7	125
0.0100 M CH_2O	208	9.00		
1.00 M CH_2O	156	14.2	5.2	192

[a] With [**1**] = 1.00 × 10^{-2} M and [NaOH] = 1.58 M (containing 2 mol % EDTA). [b] For [NaOH] = 0.200 M, $\mu = 1.58$, $I_n = 8470$.

rate of 1,2-dioxetane (**5**) decomposition. In contrast, high concentrations of either bromide ion or formaldehyde do cause a significant increase in the rate of decomposition of **5**. The rate coefficient for the decomposition of **5** by these reactants (k_{fd}) may be calculated by using eq 3 with the added term k_{fd}[X], where X is the added reactant. Since the effect of base concentration on k_{fd} was not determined, it is possible that hydroxide concentration is included in k_{fd}.

Discussion

Formation of 5. Both product and kinetic studies suggest an ionic decomposition of **1** in the presence of base, which incorporates a 1,2-dioxetane intermediate. The primary products, acetone and formaldehyde, are conveniently explained by the mechanism shown in eq 4–6. For convenience the base is represented solely as hydroxide rather than a mixture of hydroxide and methoxide in the aqueous methanol solvent. The fact that the iodometric, acidometric, and glc rate constants are equal requires that step 5 be rate determining. It can be shown that the effect of base on the rate (Table V) and first-order dependence on **1** at high base concentration (Table IV) can be explained by this mechanism. With the steady-state approximation and the reasonable assumption that $k_{-1} \gg k_r$, eq 7 results where



$$(CH_3)_2\overset{\text{OOH}}{\overset{|}{C}}CH_2Cl + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CH_3)_2\overset{\text{OO}^-}{\overset{|}{C}}CH_2Cl + H_2O, \qquad K = k_1/k_{-1} \quad (4)$$

1 **1a**

$$\mathbf{1a} \xrightarrow{k_r} (CH_3)_2\overset{O\text{—}O}{C\text{—}CH_2} + Cl^- \quad (5)$$

5

$$\mathbf{5} \xrightarrow{k_f} CH_3COCH_3 + CH_2O \quad (6)$$

$$-d[ROOH]_T/dt = \frac{k_r K[ROOH]_T[OH^-]_T}{1 + K([ROOH]_T - [ROO^-]) + K[OH^-]_T} \quad (7)$$

$[OH^-]_T$ and $[ROOH]_T$ refer to the total concentrations of base and **1**, while $[ROO^-]$ is the concentration of the anion **1a**. From the derived rate law (eq 7), one obtains the observed rate coefficient k_{obsd} (eq 8). First-order dependence on **1** at high base concentration is predicted from eq 8. Under these conditions ($[ROOH]_T - [ROO^-]$) approaches zero and with $K[OH^-]_T \gg 1$, $k_{obsd} \simeq k_r$.

$$k_{obsd} = \frac{k_r K[OH^-]_T}{1 + K([ROOH]_T - [ROO^-]) + K[OH^-]_T} \quad (8)$$

The effect of base concentration on k_{obsd}, predicted from eq 8, can be approached in two ways. One approach is to evaluate K of eq 4 from the effect of base on k_{obsd} (Table V). This value of K may be compared to ionization constants for other hydroperoxides, which do not undergo decomposition in base. A second approach is to calculate k_r at various base concentrations from the data of Table V to determine if it is indeed constant. This is done in the following manner. The equilibrium constant K of eq 4 is expressed in stoichiometric concentrations and then rearranged to give eq 9. Rearrangement of eq 8 yields eq 10 to give two equations (9 and 10) and three unknowns: K, k_r, and

$$K[ROO^-]^2 - [ROO^-] \times (K[ROOH]_T + K[OH^-]_T + 1) + K[ROOH]_T[OH^-]_T = 0 \quad (9)$$

$$[ROO^-] = [OH^-]_T(1 - k_r/k_{obsd}) + [ROOH]_T + 1/K \quad (10)$$

$[ROO^-]$. An iterative computer program was used at this point with an initial value of k_r estimated from the approximation at high base that $k_{obsd} \cong k_r$ (*vide supra*). Thus, from Table V, $k_r \simeq k_{obsd} = 1.71 \times 10^{-3}$ sec^{-1} at $[OH^-]_T = 1.79$ M and now with data at low base concentration (0.0997 M, $k_{obsd} = 0.590 \times 10^{-3}$ sec^{-1}, Table V), a value of K may be obtained by simultaneous solution of eq 9 and 10. With this value of K, a new value of k_r at high base concentration (1.79 M) is obtained from eq 11, which results from eq 8 and the

$$k_r = \frac{k_{obsd}(1 + K[OH^-]_T}{K[OH^-]_T} \quad (11)$$

reasonable assumption that ($[ROOH]_T - [ROO^-]$) = 0 at high base concentration. The iteration is continued until constant values of k_r and K are obtained. With the value of K (5.98 M^{-1}), obtained from the low base concentration data, values of k_r are calculated from eq 11 at various base concentrations (Table IX). The reasonable constancy of k_r supports the proposed mechanism.

Table IX. Calculated Values of k_r in 60% Aqueous Methanol at 29.97° [a,b]

$[OH^-]_T$	$10^3 k_{obsd}$, sec^{-1}	$10^3 k_r$,[c] sec^{-1}
0.0997	0.590	1.87
0.199	1.03	1.90
0.515	1.47	1.95
0.792	1.63	1.97
0.995	1.67	1.95
1.78	1.68	1.84
1.79	1.71	1.87
		Av 1.91 ± 0.04

[a] $\mu = 1.80$. [b] [**1**] = 1.00 × 10^{-2} M. [c] Calculated with K = 5.98 M^{-1}, obtained from runs at $[OH^-]_T$ = 0.0997 and 1.79 M.

The pK_a of **1** can be estimated by a σ^* and an nmr LFE correlation to be 13.0 and 13.2, respectively, in 40% aqueous methanol at 25°.[19] Calculated values of

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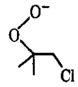
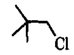
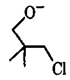
(19) W. H. Richardson and V. F. Hodge, *J. Org. Chem.*, **35**, 4012 (1970).

Table X. Observed and Calculated Rate Coefficients for the Basic Decomposition of **1** in 40% Aqueous Methanol[a]

Temp, °C	[NaOH],[b] M	10^3k_{obsd}, sec^{-1}	10^3k_r[c], sec^{-1}	K, M^{-1}
0.00	0.197	0.0122	0.0249	6.52
0.00	1.58	0.0227		
10.00	0.197	0.0604	0.134	5.76
10.00	1.58	0.121		
20.00	0.197	0.291	0.617	6.22
20.00	1.58	0.560		
29.97	0.197	1.18	2.35	5.24
29.97	1.58	2.10		

[a] [**1**] = 1.01×10^{-2} M, $\mu = 1.58$ adjusted with sodium perchlorate. [b] With 2 mol % EDTA. [c] $\Delta H^{\ddagger} = 24.4 \pm 0.2$ kcal/mol ($r = 1.000$), $\Delta S^{\ddagger} = 10.0 \pm 1.0$ eu.

Table XI. A Comparison of the Neighboring Group Effect of the Peroxide Anion

System	k at 30°, sec^{-1}	k_{rel}
	$2.35 \times 10^{-3\,a}$	2.35×10^4
 + $^-OC_2H_5$	$\sim 10^{-7\,b}$	$\equiv 1.00$
	$6.4 \times 10^{-5\,a,c}$	6.4×10^2

[a] For ring closure (k_r) in 40% aqueous methanol. [b] Estimated at 1 M $C_2H_5O^-$ in ethanol. [c] Calculated from data given in W. H. Richardson, C. M. Golino, R. H. Wachs, and M. B. Yelvington, *J. Org. Chem.*, **35**, 943 (1970).

K and k_r, along with the corresponding data in 40% aqueous methanol, are given in Table X. There may be a small trend to larger values of K as the temperature decreases, but this is not certain due to the inherent error in the iterative calculation (where the error is largest in K). The small temperature coefficient, in this temperature range, is typical of acid–base equilibria.[20] For this reason, an average value of K is used, which is 5.93. With this value of K, the pK_a of **1** is calculated as 13.2 from the standard relationship of $pK_a = pK_{auto} - pK_h$, where $K_h = 1/K$ and $pK_{auto} = 14.0$. The value of pK_{auto} was established previously for 40% aqueous methanol.[19] Considering the usual agreement between pK_a values, which are determined by different methods, and the approximate nature of the LFE correlations, we feel that the agreement is good.

The magnitude of the neighboring group effect is of particular interest. On the basis of the α effect[7,8] or the HSAB concept,[9] the peroxide anion may be a more reactive neighboring group than the corresponding oxide ion even though the latter ion is more basic than the peroxide anion. In general it is observed that nucleophiles, which contain an α atom with unshared electrons, are more reactive than predicted from their basicity and polarizability.[21,22] The first two entries in Table XI compare neighboring group participation by the peroxide anion (**1a**) with external displacement by ethoxide on neopentyl chloride. The comparison assumes that the steric effect of the solvated peroxide anion and methyl are similar, but no correction is made for polar effects which would favor the peroxide anion. The comparison is approximate, since data for neopentyl chloride are not available but an estimate can be made from the reaction of ethoxide with neopentyl bromide[23] and a survey of relative rates of SN2 reactions with chloride and bromide as leaving groups ($k_{Br}/k_{Cl} = 50$).[24] In order to compare relative rates of ring closure (k_r), the observed rate coefficient (k_{obsd}) for the 1,3-chlorohydrin (Table XI, entry three) is corrected for alcohol–oxide equilibrium with the aid of the ρ^* value (1.42) for alcohols.[25] The magnitude of the α effect in the $ND_I(^-OO\text{-}4)$ reaction ($2.35 \times 10^{-3}/6.4 \times 10^{-5} = 37$) is similar to that reported in the SN2 reaction of benzyl bromide with HOO^- and HO^- ions (35).[22]

Decomposition of V. Evidence from a number of sources indicates that light emission is associated with the unimolecular decomposition of the 1,2-dioxetane (**5**). In this study, the correspondence between light emission and disappearance of isolated **5**, as determined by nmr analysis, verifies this proposal. Similar findings have been reported recently for other isolated 1,2-dioxetanes.[14] Since the light emission produced in the unimolecular decomposition of 3,3,4-trimethyl-1,2-dioxetane approximates the fluorescence spectrum of the carbonyl products,[14a] the unimolecular decomposition of **5** can be given in more detail by eq 12 and 13

$$\mathbf{5} \xrightarrow{k_f} \underset{\mathbf{8}}{[(CH_3)_2CO \cdot CH_2O]^*} \qquad (12)$$

$$\mathbf{8} \xrightarrow{\text{fast}} (CH_3)_2CO + CH_2O + h\nu \qquad (13)$$

where **8** is the excited singlet state of one of the carbonyl products or an eximer. The reasonableness of the energetics of reactions 12 and 13 was discussed previously.[26,27] Recently it was proposed that oxo-1,2-dioxetanes, generated from ketenes and singlet oxygen *in situ*, form a complex with a fluorescer. Decomposition of the complex is then postulated to give the excited singlet state of the fluorescer, which subsequently emits light.[28] We find no evidence for this with **5** and fluorescein, since t_{max} and thus $k_{f_{obsd}}$ did not change in the presence or the absence of this fluorescer. The light emission reported here, from sources other than **5**, appears unlikely. For example, basic decomposition of the hydroxyhydroperoxide (**9**), which would result from direct displacement by hydroxide on **1**, could be considered as a source of light (eq 14). Two facts are incompatible with eq 14 being the source of light. First, competition of external SN2 attack by hydroxide with the neighboring group peroxide anion

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(20) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Wiley, New York, N. Y., 1962, p 14.

(21) W. P. Jencks and J. Carruiolo, *J. Amer. Chem. Soc.*, **82**, 1778 (1960).

(22) (a) R. G. Pearson and D. N. Edgington, *ibid.*, **84**, 4607 (1962); (b) J. Gerstein and W. P. Jencks, *ibid.*, **86**, 4655 (1964); (c) M. J. Gregory and T. C. Bruice, *ibid.*, **89**, 2327 (1967).

(23) I. Dostrovsky, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 173 (1946).

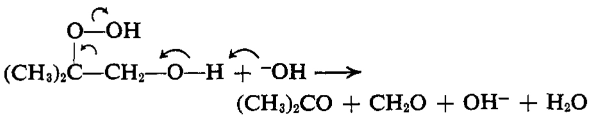
(24) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 30.

(25) P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **82**, 795 (1960).

(26) H. E. O'Neal and W. H. Richardson, *ibid.*, **92**, 6553 (1970).

(27) See also (a) F. McCapra, *Chem. Commun.*, 155 (1968); (b) D. R. Kearns and A. U. Khan, *Photochem. Photobiol.*, **10**, 193 (1969); (c) D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

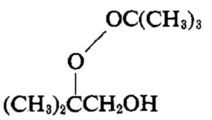
(28) L. J. Bollyky, *ibid.*, **92**, 3230 (1970).



$$(CH_3)_2\overset{\overset{\displaystyle O-OH}{|}}{C}-CH_2-O-H + {}^-OH \longrightarrow (CH_3)_2CO + CH_2O + OH^- + H_2O \quad (14)$$

9

reaction is poor (*cf.* Table XI) and 9 should not be produced in significant amounts. Second, no light emission is observed from the analogous basic decomposition of 10 in the presence of fluorescein.[29] Basic de-



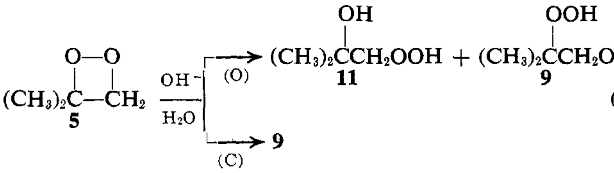
$$(CH_3)_2\overset{\overset{\displaystyle O-OC(CH_3)_3}{|}}{C}CH_2OH$$

10

composition of the hydroperoxide, exclusive of neighboring group reaction and thus the 1,2-dioxetane, can be eliminated as a source of light, since *tert*-butyl hydroperoxide with base and fluorescein gives no light emission.

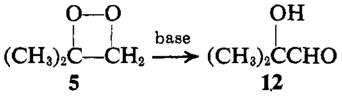
The activation parameters for unimolecular decomposition of 5 in aqueous methanol (E_a = 19.1 kcal/mol and log A = 10.9) are significantly lower than estimated in the gas phase (E_a = 22.9 kcal/mol and log A = 12.9).[26] Earlier[4c] it was pointed out that such a solvent effect is reasonable by analogy to the fragmentation of *tert*-butoxy radicals. The latter uncharged radical decomposes to give acetone and a methyl radical, and the activation energy is lowered by 8 kcal/mol in changing from an aprotic nonpolar solvent (carbon tetrachloride) to a protic solvent (acetic acid).[30] In the decomposition of 5, an uncharged molecule yields two carbonyl molecules and the activation energy is lowered by about 4 kcal/mol in changing from the gas phase to a polar protic solvent. The low log A value for the decomposition of 5 in aqueous methanol is also indicative of solvent association in the transition state.

Product and kinetic data indicate that base affects the decomposition of 5. With increasing base concentration, the yield of glycol (4) increases. Displacement by hydroxide on 5 at carbon or oxygen could be considered to explain these data (eq 15), where the resulting hydroxyhydroperoxides give glycol (4). This explanation seems unlikely for several reasons. As indicated above, 10 undergoes decomposition in base to *tert*-butyl alcohol, acetone, and formaldehyde at such a rate that the corresponding peroxides produced in eq 15 should not survive. If these peroxides did survive the reaction conditions, decomposition upon glc analysis could be considered as a source of glycol. However, this would require a finite iodometric titer resulting from peroxides 9 and 11 at the completion of reaction. This was not observed. Reduction of peroxides 9 and 11 by formaldehyde, which is produced in the unimolecular decomposition of 5, could be considered as a route to glycol. This also is unlikely, since *tert*-butyl hydroperoxide with formaldehyde and base under the reaction conditions showed no decrease in iodometric titer. By analogy to the basic elimination reaction of primary and secondary alkyl peroxides,[6] the most reasonable reaction of 5 with base is given by eq 16. A cross-Cannizarro reaction (eq 17) would explain the presence of glycol (4) and, in part, the low yield of formaldehyde. The hydroxy aldehyde 12 is reported to undergo the Cannizarro reaction as well as rapid polymerization.[31] The latter reaction of 12 may explain the poor product balance at high base to 1 concentration ratios, where increased yields of glycol are also found. The question arises as to whether or not eq 16 is light producing. Although this question cannot be answered precisely with the available data, it is clear from the I_n values of Table VIII that either reaction 16 is not light producing or that the efficiency of light emission is much less than for the unimolecular decomposition of 5.



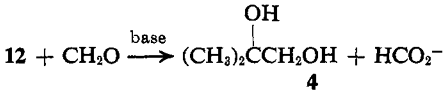
$$(CH_3)_2\overset{\overset{\displaystyle O-}{|}}{C}-\overset{\overset{\displaystyle O}{|}}{C}H_2 \xrightarrow[H_2O]{OH^-} \begin{cases} \xrightarrow{(O)} (CH_3)_2\overset{\overset{\displaystyle OH}{|}}{C}CH_2OOH + (CH_3)_2\overset{\overset{\displaystyle OOH}{|}}{C}CH_2OH \\ \xrightarrow{(C)} 9 \end{cases} \quad (15)$$

5   11   9



$$(CH_3)_2\overset{\overset{\displaystyle O-}{|}}{C}-\overset{\overset{\displaystyle O}{|}}{C}H_2 \xrightarrow{base} (CH_3)_2\overset{\overset{\displaystyle OH}{|}}{C}CHO \quad (16)$$

5   12

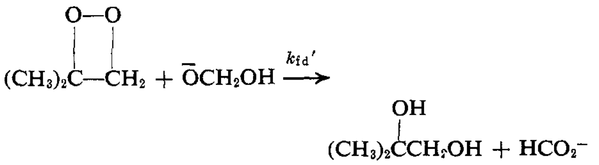


$$12 + CH_2O \xrightarrow{base} (CH_3)_2\overset{\overset{\displaystyle OH}{|}}{C}CH_2OH + HCO_2^- \quad (17)$$

4

At low concentrations of formaldehyde (10^{-2} M), on the order of initial concentration of 1, no direct reaction between formaldehyde and 5 occurs as seen from the invariance of t_{max} and thus $k_{f_{obsd}}$ (Table VIII). Glycol that is produced without added formaldehyde must result from the reaction sequence 16–17. The product studies (Table II) also support this conclusion, since the yield of acetone with 10^{-2} M added formaldehyde is unchanged but the yield of glycol is increased. At high formaldehyde concentrations (1 M), $k_{f_{obsd}}$ is increased (Table VIII) as well as the yield of glycol (Table II). Furthermore, the total amount of light emission, as measured by I_n, is decreased. Under these conditions direct reduction of 5 by formaldehyde is indicated. Hydride transfer according to eq 18 and 19[32] would reasonably explain the data. The rate coefficient k_{fd} given in Table VIII should be modified according to this mechanism to $k_{fd} = K_c k_{fd}'[OH^-]$, where $K_c k_{fd}' = 5.2 \times 10^{-3}/1.58 = 3.3 \times 10^{-3}$ l. mol^{-1} sec^{-1}.

$$CH_2O + OH^- \overset{K_c}{\rightleftharpoons} \bar{O}CH_2OH \quad (18)$$



$$(CH_3)_2\overset{\overset{\displaystyle O-}{|}}{C}-\overset{\overset{\displaystyle O}{|}}{C}H_2 + \bar{O}CH_2OH \xrightarrow{k_{fd}'} (CH_3)_2\overset{\overset{\displaystyle OH}{|}}{C}CH_2OH + HCO_2^- \quad (19)$$

Relative rates for displacement by bromide *vs.* chloride ion at carbon $(k^{Br}/k^{Cl})_C$ as compared to peroxy oxygen $(k^{Br}/k^{Cl})_O$ differ greatly. For $(k^{Br}/k^{Cl})_C$, values of 3.3 and 5.2 are observed for attack on a β-lactone and

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[29] (a) Details of the basic decomposition of 10 will be reported later; T. Heesen, unpublished results; (b) for the preparation of 10, see W. H. Richardson and R. S. Smith, *J. Org. Chem.*, 33, 3882 (1968).

[30] C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, 86, 3368 (1964).

[31] (a) R. Dworzak and J. Pierri, *Monatsh. Chem.*, 52, 141 (1929); (b) S. Danilov and E. V. Danilova, *Ber. Deut. Chem. Ges. B*, 67, 24 (1934).

[32] For a review of base-catalyzed hydride transfer from aldehydes, see J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, p 267.

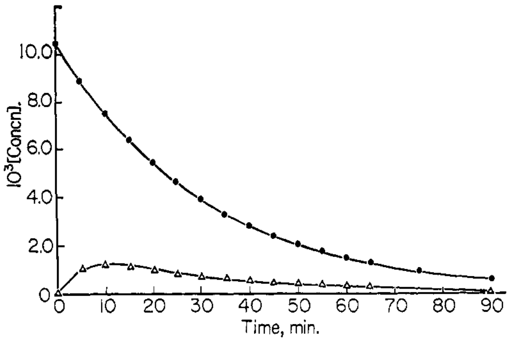

Figure 1. Numerical integration output with $[I]_0 = 1.04 \times 10^{-2}$ *M*, [NaOH] = 1.58 *M*, *K* = 6.22, $k_r = 6.17 \times 10^{-4}$ sec^{-1}, and $k_{f_{obsd}} = 3.66 \times 10^{-3}$ sec^{-1} at 20°: ●, $[ROOH]_T$; Δ, [V].

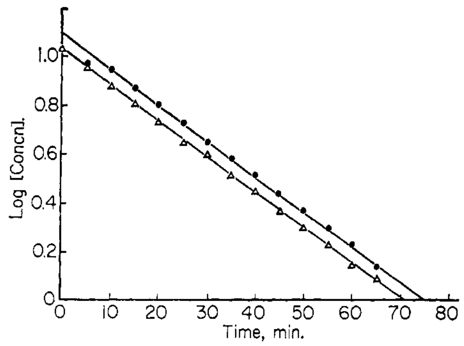

Figure 2. First-order plots for total hydroperoxide concentration ($[ROOH]_T$, Δ; $[ROOH]_T$ + [V], ●) at 20° from numerical integration data of Figure 1.

an epoxide, respectively.[33] The value of $(k^{Br}/k^{Cl})_O$ is 220 for displacement on hydrogen peroxide.[34] The slow rate of reaction of chloride, compared to bromide ion, with **5** precludes an accurate value for $k_{fd}{}^{Br}/k_{fd}{}^{Cl}$ (*cf.* Table VIII); however, a minimum value is 75. Since the latter minimum value is within a factor of 3 for attack at oxygen, compared to a factor of 1/14–23 for attack at carbon, halide displacement at oxygen appears more likely. This is consistent with the product data where bromide ion affects the reduction of **5** to give increased yields of glycol.

Although the iodimetric kinetic data agree with two other kinetic methods (Table III), interference by **5** might be questioned. Unfortunately the intensity of emission from **5** cannot be related to its concentration. However, numerical integration can be used to obtain the concentration of **5** as a function of time with the aid of *K*, k_r, and $k_{f_{obsd}}$. Using an IBM 1130 computer equipped with a Calcomp plotter, the total hydroperoxide concentration ($[ROOH]_T$) and the concentration of **5** were obtained for a typical run (Figure 1). The observed (600 sec, Table VI) and the calculated (600 sec, Figure 1) t_{max} values are in agreement. First-order plots of $[ROOH]_T$ and $[ROOH]_T$ plus [**5**] in Figure 2 show some curvature at the beginning of the reaction, but the first-order rate coefficients (5.56×10^{-4} and 5.60×10^{-4} sec^{-1}, respectively) are in good agreement with the experimental value for k_{obsd} (5.75×10^{-4} sec^{-1}, Table VI).

Experimental Section[35]

Materials. Formaldehyde solution (Matheson Coleman and Bell (M, C & B) reagent grade, 36–38% formaldehyde with 10–15% methanol preservative) was used directly. Methallyl alcohol was used as supplied (M, C & B) for glc analysis. Sodium perchlorate (Fisher Scientific Co., purified) was dried in a vacuum oven before use. The aqueous methanolic solvents were prepared as vol/vol per cent at 25° or by weight which corresponded to the volumes. Spectral grade (M, C & B) or purified methanol[36] was used along with doubly distilled water.

1-Chloro-2-methyl-2-propanol (2). The chlorohydrin (**2**) was prepared by a previously reported method[37] from methallyl chloride (M, C & B) in 66.4% yield: bp 56.5–57.0° (50 mm) (lit.[37] 126.7°); nmr $(CH_3)_2$ (1.28, s, 3), CH_2 (3.43, s, 2), and OH (3.16, s, 1).

Isobutene Oxide (3). The aqueous azeotropic mixture of **2** was treated with potassium hydroxide[38] to give **3** in 42% yield (based on methallyl chloride): bp 49.5–50.1° (lit.[38] 51°); nmr $(CH_3)_2$ (1.28, s, 6) and CH_2 (2.42, s, 2).

2-Methyl-1,2-propanediol (4). The epoxide (**3**) (3.6 g, 50 mmol) was added with stirring to 10 ml of 0.1 *M* perchloric acid at room temperature. After a 15-min stirring period, the solution was neutralized with 1 *M* sodium hydroxide solution. Water was distilled and then the glycol to give 2.0 g (44% yield) of **4**: bp 76° (10 mm) (lit.[39] 79° (10 mm)); nmr (in $CDCl_3$) $(CH_3)_2$ (1.20, s, 3), CH_2 (3.42, s, 1), and OH (3.3 (variable on dilution), s, 1).

1-Methoxy-2-methyl-2-propanol. The preparation was the same as that previously reported:[40] nmr $(CH_3)_2$ (1.13, s, 6), CH_3O (3.37, s, 3), CH_2 (3.14, s, 2), and OH (2.80, s, 1).

Chloro-*tert*-butyl Hydroperoxide (1). Sulfuric acid (95%, 950 g, 9.31 mol) was precooled to 10° and then added dropwise with stirring to 30% hydrogen peroxide (453 g, 4.00 mol) at 5–10°. To this solution, 108.5 g (1.00 mol) of **2**, dissolved in 730 ml of chloroform, was added dropwise with stirring at 15°. The resulting mixture was vigorously stirred at room temperature for 48 hr. The chloroform phase was separated, washed with water saturated with sodium sulfate, and dried over magnesium sulfate. The chloroform was removed under reduced pressure (bath temperature, 40°) and then **1** was distilled (48° (4.5 mm)) (lit.[41] 51–61° (2 mm)) after adding a small amount of 2,6-di-*tert*-butyl-*p*-cresol: yield 62 g (50%); nmr $(CH_3)_2$ (1.30, s, 6.2), CH_2 (3.50, s, 2.0), OOH (8.30, s, 0.89), and OOH (DMSO) (10.86, s). *Caution*: further distillation of the pot residue, at a later date, resulted in an explosion. The purity of **1** varied somewhat between preparations. In a typical preparation, the sample was 89% **1** by iodometric titration.[16] Analysis for bischloro-*tert*-butyl peroxide[42] (3%) and an unknown inert compound (3%) was carried out by glc with a 10 ft × 1/8 in. 15% Apiezon on Chromosorb G column at 150° using *tert*-amyl alcohol (Baker's reagent) as an internal standard. The unknown compound was isolated by preparative glc in order to calculate the percentage of it in the sample of **1**. The per cent chlorohydrin (**2**) in the sample of **1** was determined as the difference between the per cent **1** (iodometric analysis) and the sum of the percentages of bischloro-*tert*-butyl peroxide and the unknown compound. The basic decomposition of the sample of **1** gave the epoxide (**4**), which corresponded with the per cent chlorohydrin (**2**) in the sample.

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(35) Temperatures of kinetic measurements are corrected, but boiling points are uncorrected. The nmr spectra were measured in carbon tetrachloride solution, unless specified otherwise, with a Varian A-60 spectrometer. Tetramethylsilane is the internal standard and the data are reported on the δ scale in parts per million as (δ, coupling, area). Infrared spectra were determined with a Perkin-Elmer 337 or 621 grating spectrometer. Mass spectral analysis was obtained with a Hitachi RMU-6E spectrometer. Glc analyses were performed on a Varian Aerograph Hy-FI III, flame ionization instrument.

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Bromo-*tert*-butyl Hydroperoxide. The preparation was similar to that reported previously[12b] for other β-bromohydroperoxides. The crude hydroperoxide (86% pure by iodometric titration) was obtained in 62% yield. Distillation with a molecular still connected to a vacuum line at 10^{-3} mm (bath temperature, 40°) gave a clear colorless liquid (95% pure) (lit.[12a] bp 33° (0.05 mm)): nmr $(CH_3)_2$ (1.33, s, 6.3), CH_2 (3.50, s, 2.0), OOH (8.28, s, 0.91), and OOH in DMSO (11.04, s).

3,3-Dimethyl-1,2-dioxetane (5). To a distillation apparatus under 10 mm pressure, 0.1 g of bromo-*tert*-butyl hydroperoxide was added dropwise to 1 ml of saturated aqueous potassium hydroxide solution contained in the pot at room temperature. The receiver was cooled in a Dry Ice–isopropyl alcohol bath (−78°). The distillate was redistilled at 0° under reduced pressure with the receiver at −78°. Chloro-*tert*-butyl hydroperoxide was also used to prepare **5** by this method.

Product Studies. The reactions were carried out in sealed tubes with the internal standard (*tert*-amyl alcohol) and were allowed to proceed through at least ten half-lives before analysis. Analyses were obtained by glc using a 5 ft × 1/8 in. PAR-2 column at 120°. Calculation of yields was made by comparison with the glc record of a standard mixture which contained the products and the internal standard. Gas analyses were made by standard vacuum line techniques combined with mass spectral analysis.

Kinetic Methods. The base and the hydroperoxide solutions, in separate volumetric flasks, were thermally equilibrated and then mixed in a thermally equilibrated vessel under a nitrogen atmosphere. Aliquots were periodically withdrawn and analyzed iodometrically.[16] A similar procedure was used for the acidometric measurements, except that the aliquots were quenched by addition to standard acid and then titrated with standard base to the phenolphthalein end point. In the glc procedure, the aliquots were quenched with acid to a pH of 8. The relative amounts of **1** in the aliquots were determined by reference to an internal standard (*tert*-amyl alcohol). Various concentrations of a standard mixture of **1** with the internal standard gave reproducible amounts of **2**, by comparison to a standard mixture of **2** and the internal standard. The analyses were carried out on a 10 ft × 1/8 in. Apiezon column at 90°. The light emission studies were obtained with a Beckman DU, equipped with an RCA 1P28 phototube, thermospacers, and output to a recorder. For rapid reactions, the base solution was thermally equilibrated in the spectrometer and then a small amount of hydroperoxide solution was injected into the base solution and rapidly mixed. The kinetic data were normally processed with the aid of a least-squares computer program.

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The Exchange Route to Oxyphosphoranes[1]

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Abstract: It has been found that acyclic phosphoranes which contain at least two alkoxy groups often undergo exchange with 1,2- and 1,3-glycols to give oxyphosphoranes containing one or two rings. These materials undergo pseudorotation at room temperature. Pseudorotation is restricted to equatorial–apical switching in the five-membered ring compounds. The six-membered ring compounds are not so restricted. In some cases variable-temperature nmr measurements have given information on inhibition of pseudorotation. 1,4-Butanediol and 1,5-pentanediol react with pentaethoxyphosphorane and triphenyldiethoxyphosphorane, respectively, to give tetrahydrofuran and tetrahydropyran in very good yield. Attempts to exchange benzyl alcohol with pentaethoxyphosphorane led to decomposition. Similarly the reaction of tribenzyl phosphite with diethyl peroxide produced a very unstable phosphorane which decomposed almost as fast as it formed.

In earlier work it was shown that pentaethoxyphosphorane (**1**), undergoes an exchange reaction with *n*-propyl alcohol to give new phosphoranes containing *n*-propyloxy groups.[5] More recently Ramirez and coworkers have shown that the cyclic unsaturated oxyphosphoranes derived from 1,2-dicarbonyl compounds and trialkyl phosphites also undergo exchange of the alkoxy groups when they are allowed to react with alcohols. The unsaturated ring is preserved during these transformations.[6a] They have also shown that pentaphenoxyphosphorane exchanges with catechol to give five-membered ring containing phosphoranes.[6b,c] This report concerns itself with the exchange of a variety of alkoxy containing phosphoranes with glycols and alcohols. In general the phosphoranes were prepared by allowing the appropriate trisubstituted phosphorus compound to react with diethyl peroxide.[7] This method is perhaps the most general one for producing oxyphosphoranes; however, during their formation tetrasubstituted phosphorus compounds are usually formed. In this work such materials were generally present and they were only partially removed in a few cases by distillation. There is no reason for suspecting that these substances had any effect on the reactions under investigation. The presence of these substances and the general hydrolytic instability of the oxyphosphoranes

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