Organic and Biological Chemistry

The Influence of Solvent on the Oxidation of Thioxane by Hydrogen Peroxide and by *t*-Butyl Hydroperoxide[1]

Mary A. P. Dankleff,[2] Ruggero Curci,[3] John O. Edwards, and Hae-Yung Pyun

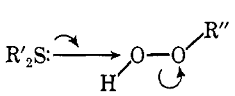
Contribution from the Metcalf Chemical Laboratories of Brown University, Providence, Rhode Island 02912. *Received July 17, 1967*

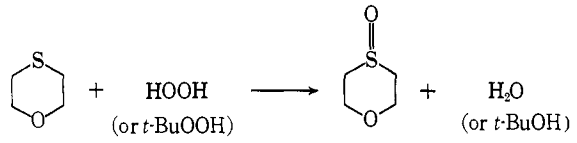
Abstract: The kinetics of the oxidation of thioxane (1-thia-4-oxacyclohexane) by hydrogen peroxide in several solvents (H_2O, D_2O, ethylene glycol, MeOH, *i*-PrOH, *t*-BuOH, acetic acid, dioxane, and N-methylacetamide) have been investigated. Some mixed solvent systems have been studied, as has the influence of solvent on the mechanistically related oxidation of thioxane by *t*-butyl hydroperoxide. The results are discussed in terms of solvent participation in the activated complex.

It is known[4-6] that organic sulfides can be readily oxidized to the corresponding sulfoxides by peroxyacids, hydroperoxides, and hydrogen peroxide in a variety of solvents. A large amount of data are available on various kinetic features such as rate law, acid catalysis, substituent, and steric effects, etc.; these have been covered in recent reviews.[7,8] Comparatively few studies, however, have been reported upon the effect of solvents for the oxidation of organic sulfides by peroxy compounds. Overberger and Cummins[9] reported a decrease in the oxidation rate of a sulfide by H_2O_2 with change from protic to aprotic solvent. Bateman and Hargrave[10] reported a change in rate and in kinetic order with a solvent change from alcohols (second order) to benzene (third order) for the oxidation of cyclohexyl methyl sulfide by *t*-BuOOH or by cyclohexenyl hydroperoxide. The rate increased with increasing protic character of the solvent or hydroperoxide, and the reaction was characterized by relatively low activation energy and high negative activation entropy values in alcohols. These authors did not evaluate $\Delta S^{\ddagger}$ values for the oxidation in benzene and cyclohexane; in these solvents, the oxidation exhibited product (sulfoxide) inhibition of rate and a free-radical competitive path involving the solvent. Both sets of investigators suggested a specific solvent effect which involves a transition state in which charge separation is avoided by means of proton transfers.

Modena and Todesco[11] studied the solvent effect on the oxidation rates of sulfides by peroxybenzoic acid ($C_6H_5CO{-}OOH$) in a variety of solvents, and concluded that the rates are not related to the dielectric constant of the solvent but rather appear to reflect specific interactions between the solvent and the reaction center.

It is believed[4,7,8] that the oxidation of organic sulfides provides an example of an SN2 displacement at peroxide oxygen by a neutral nucleophile. Since the rates of typical SN2 reactions between dipolar molecules do not seem to be appreciably influenced by a change from protic to aprotic solvents of the same polarity,[12] we planned: (a) to study the effect of solvent on nucleophilic diplacement on peroxidic oxygen involving the simple neutral reactants thioxane (1-thia-4-oxacyclohexane) and hydrogen peroxide (or *t*-butyl hydroperoxide) in aqueous, alcoholic, and aprotic media of varying polarity and acidity, and (b) to determine the reaction order, the activation thermodynamic parameters, the effect of salts and mixtures of aprotic–protic solvents on the rate. Thioxane was chosen as substrate because of its large solubility in all the solvents considered and its good steric characteristics.





Results

The rates of oxidation of thioxane by hydrogen peroxide (HOOH) and *t*-butyl hydroperoxide (*t*-BuOOH) were followed by iodometric determination of disappearance of the peroxide, generally under conditions where sulfide was in seven- to tenfold excess over peroxide. The one-to-one stoichiometry of sulfide to per-

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(1) From the Ph.D. Thesis of Mary A. P. Dankleff, Brown University, 1963, and the M.Sc. Thesis of Hae-Yung Pyun, Brown University, 1964.

(2) National Science Foundation Cooperative Fellow, 1960–1962.

(3) Fellow of the Italian National Research Council (C.N.R.), 1966–1967.

(4) A. G. Davies, "Organic Peroxides," Butterworth & Co. (Publishers) Ltd., London, 1961, Chapter 9.

(5) D. Swern, *Chem. Rev.*, **45**, 1 (1949).

(6) D. Barnard, L. Bateman, and J. I. Cunneen in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p 229.

(7) J. O. Edwards in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 67.

(8) E. J. Behrman and J. O. Edwards, *Progr. Phys. Org. Chem.*, **4**, 93 (1967).

(9) C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4783, 4250 (1953).

(10) L. Bateman and K. R. Hargrave, *Proc. Roy. Soc.* (London), A224, 389, 399 (1954).

(11) G. Modena and P. E. Todesco, *Boll. Sci. Fac. Chim. Ind. Bologna*, 23, 31 (1965).

(12) A. J. Parker, *J. Chem. Soc.*, 1328 (1961).

Table I. Rate Constants and Activation Parameters for the Oxidation of Thioxane by Hydrogen Peroxide in Water and D_2O

Component added	Temp, °C	10^3k_2(obsd)[a]	E_a[b]	$\Delta H^{\ne}$[b]	$\Delta S^{\ne}$[b]
		A. Water			
None	0	0.320 ± 0.007			
None	25	2.58 ± 0.08	13.5	13.0	−27
None	34.2	5.32 ± 0.2			
Na_2SO_4, 1.03 *M*	25	2.60			
0.471 *M*[c]	25	2.77			
0.425 *M*	25	2.58			
$NaNO_3$, 3.02 *M*	25	2.73			
1.72 *M*	25	2.88			
0.900 *M*	25	2.62			
KNO_3, 0.396 *M*[c]	25	2.48			
$NaClO_4$, 1.20 *M*	25	2.73			
$Mg(ClO_4)_2$, 0.068 *M*[c]	25	2.53			
$HClO_4$, 0.507–0.0109 *M*	0	5.92 ± 0.06[d]			
$HClO_4$, 0.511–0.0002 *M*	25	34.8 ± 0.0[d]	11.5	10.9	−29
		B. D_2O			
None	9.7	0.450 ± 0.007			
None	25	1.54 ± 0.02	13.5	12.9	−28
$HClO_4$, 0.0315–0.0099 *M*	25	32.0 ± 0.9[d]			

[a] In l. mol^{-1} sec^{-1}, unless otherwise indicated. [b] E_a and $\Delta H^{\ne}$ are in kcal mol^{-1}; $\Delta S^{\ne}$ is in cal mol^{-1} deg^{-1}. [c] ~10^{-3} *M* EDTA disodium salt added to prevent trace metal catalysis. [d] Acid catalysis constant k_3 (in l.^{2} mol^{-2} sec^{-1}) determined by plotting k_2(obsd) *vs.* $HClO_4$ concentrations, over the range reported.

Table II. Rate Constants and Activation Parameters for the Oxidation of Thioxane by *t*-Butyl Hydroperoxide in Water and D_2O

Component added	Temp, °C	10^4k_2(obsd)[a]	E_a[b]	$\Delta H^{\ne}$[b]	$\Delta S^{\ne}$[b]
		A. Water			
None	25	1.35 ± 0.03	14.1	13.5	−27
None	45.9	6.42 ± 0.49			
$HClO_4$, 0.40–0.10 *M*[c]	25	19.1 ± 0.3[d]			
		B. D_2O			
None	25	0.960 ± 0.007			
$HClO_4$, 0.58–0.12 *M*[c]	25	20.3 ± 0.3[d]			

[a] In l. mol^{-1} sec^{-1}, unless otherwise indicated. [b] E_a and $\Delta H^{\ne}$ are in kcal/mol^{-1}; $\Delta S^{\ne}$ is in cal mol^{-1} deg^{-1}. [c] ~10^{-3} EDTA disodium salt added to prevent trace metal catalysis. [d] Acid catalysis constant k_3 (in l.^{2} mol^{-2} sec^{-1}) determined by plotting k_2(obsd) *vs.* $HClO_4$ concentrations, over the range reported.

oxide was observed for the oxidation in protic and aprotic solvents by the nearly quantitative isolation of the sulfoxide either as pure thioxane oxide or in the form of a nickel perchlorate complex (see Experimental Section): no appreciable decomposition of HOOH or *t*-BuOOH in the given solvents was observed for the extent of time of the longest kinetic runs.[13] In agreement with the data reported by other authors,[6,14,15] it was found that the oxidation rate of thioxane oxide to the corresponding sulfone in the given solvents is usually much slower than oxidation of the sulfide to sulfoxide. For example, in some scout runs in water the oxidation rate of thioxane oxide to the sulfone by HOOH was estimated about 5000-fold slower than the oxidation of sulfide to sulfoxide; moreover, the presence of an initial concentration of about 0.01 *M* thioxane oxide showed no effect on the rate of aqueous oxidation at 25°. Peroxide decomposition and further oxidation of sulfoxide, therefore, as competitive kinetic paths seem unimportant under our conditions.

In protic solvents the oxidation rate obeyed, generally, a second-order kinetic law.

$$\text{rate} = k_2[R'_2S][R''OOH] \qquad (1)$$

Pseudo-first-order rate constants were a linear function of the thioxane (R'_2S) concentration (in large excess) and independent of the concentration of the peroxide (R'' = H or *t*-Bu). Integrated pseudo-first-order plots were usually linear over two or more half-lives and—in the majority of cases—second-order rate constants from these plots agreed with k_2 values obtained from kinetic runs in second-order conditions.

Water and D_2O. Data for the oxidation rates of thioxane by HOOH in water and D_2O are collected in Table I; activation parameters were calculated as usual. We found no salt effect from the addition of five salts to water or from a variation of ionic strength from *ca.* 0.2 to 3; the rate constants varied slightly but agreed with the k_2 value at zero ionic strength within the experimental error. No trace metal catalysis of a kind sensitive to inhibition by 10^{-3} *M* EDTA[13,16] was apparent for the oxidation in water, solution of salts, $HClO_4$ solutions (Table I), or acetate buffer (Table III). No change in rate constant was observed with a change from boiled distilled water to conductivity water. The rate constant in neutral conditions for a 26-fold variation in HOOH and a 12-fold variation in sulfide (2.58 × 10^{-3} l. mol^{-1} sec^{-1}, at 25°) is comparable to the data obtained by Ross,[17] in the

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[13] E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, **85**, 2263 (1963).

[14] G. Modena and L. Maioli, *Gazz. Chim. Ital.*, **87**, 1306 (1957).

[15] G. Modena and P. E. Todesco, *J. Chem. Soc.*, 4920 (1962).

[16] M. M. Crutchfield, Ph.D. Thesis, Brown University, 1960.

[17] S. D. Ross, *J. Am. Chem. Soc.*, **68**, 1484 (1946).

same conditions, for the HOOH oxidation of thiodiglycol (2.16×10^{-3} l. mol^{-1} sec^{-1}). Kinetic data for the oxidation of thioxane by *t*-BuOOH in water and D_2O are shown in Table II.

In the presence of perchloric acid the reaction is subject to acid catalysis[9,10,14] and follows the rate law

$$\text{rate} = k_2[\text{R}'_2\text{S}][\text{R}''\text{OOH}] + k_3[\text{R}'_2\text{S}][\text{R}''\text{OOH}][\text{HClO}_4] \quad (2)$$

At pH ≤ 3 the over-all rate constant was a linear function of the hydrogen ion concentration, and the acid catalysis constants were evaluated from the slope of the observed k_2 *vs.* [$HClO_4$], as shown in Figure 1. Values for k_3 are reported in Tables I and II. To ascertain if general acid catalysis was present, we ran some kinetic experiments in acetate buffer; the results are shown on Table III. The observed second-order constant remained practically constant up to 1 *M* acetic acid in the buffer and increased only 16% with an increase in AcOH to 3 *M*. The rate of attack by thioxane on HOOH in water, therefore, appears to be a function of the pH rather than of molecular acid. A similar trend and comparable values of activation parameters were reported[18] for the oxidation of thiodiglycol by *t*-BuOOH in water. *The oxidation rate, however, is sensitive to the generally increasing acidity of the medium;* indeed, increases in AcOH concentration to 5 and 8 *M* produced increases in the observed constants, respectively, of 28 and 70% relative to the observed rate constants for the aqueous reaction at the same pH (see Table III).

Data for the solvent isotope effects for neutral and acid-catalyzed oxidation of thioxane by HOOH and *t*-BuOOH at 25° are summarized in Table IV.

Table III. Rate of Oxidation of Thioxane by H_2O_2 Aqueous NaOAc–HOAc Buffer Solutions at 25°

[Sulfide]$_0$[g]	[H_2O_2]$_0$[g]	[HOAc][g]	pH	10^3k_2 (obsd)[f]	% inc[d]	10^3 dif[e]
0.089	0.00495[b]	8.00	1.8	5.33	70	2.20
0.135	0.0124[b]	7.00	1.9	4.65	54	1.64
0.135	0.0124[b]	5.02	1.9	3.85	28	0.833
0.215	0.0263[c]	5.00	2.0	3.73	28	0.815
0.135	0.0156[c]	4.00	2.0	3.52	21	0.600
0.181	0.0299[a]	3.19	2.08	3.32	16	0.450
0.212	0.0300[a]	2.13	2.18	3.13	11	0.333
0.160	0.0299[a]	1.065	2.41	2.83	4	0.117
0.160	0.0299[a]	0.532	2.54	2.65	−1	−0.050
0.181	0.0299[a]	0.213	2.71	2.68	0.6	0.0333

[a] Kokatnur and Jelling analytical method; EDTA was present in $\sim 10^{-3}$ *M* concentration in all kinetic runs. [b] Kolthoff analytical method; EDTA present. [c] Kolthoff analytical method; EDTA absent. [d] Per cent increase in rate over the rate calculated for the given [H^+]: $k_{obsd} = k_2 + k_3[H^+]$; $10^3k_{obsd} = 2.58 + 34.8[H^+]$. [e] 10^3 dif = (obsd)k_{HOAc} − (obsd)k_{HClO_4} at a given pH. [f] Observed k_2 is in l. mol^{-1} sec^{-1}. [g] In mol l.$^{-1}$.

Acetic Acid. The oxidation rate of thioxane by HOOH was studied under second-order and pseudo-first-order conditions in acetic acid containing zero to 1.57 *M* KOAc. To account for the equilibrium

$$\text{HOOH} + \text{AcOH} \rightleftarrows \text{H}_2\text{O} + \text{AcOOH} \quad (3)$$

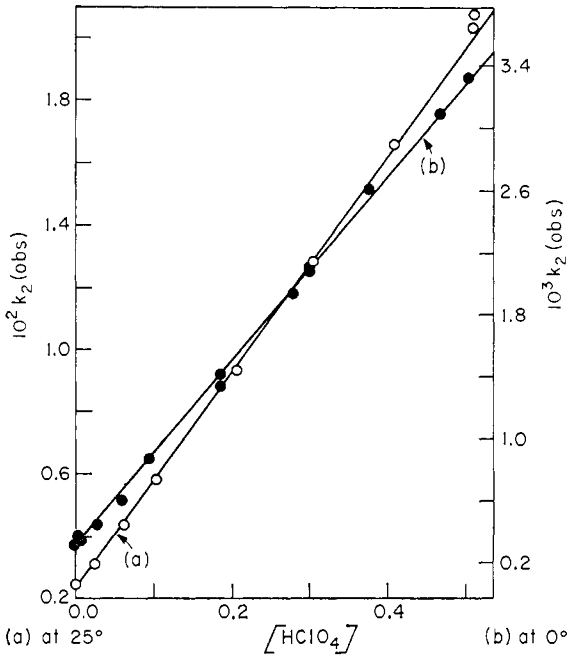

Figure 1. Determination of the acid catalysis constant for the oxidation of thioxane by HOOH in water, at 25° and 0°.

which is established on the addition of neat 97% H_2O_2 to glacial acetic acid, in each kinetic run the concentration of total peroxide was determined by the Kokatnur and Jelling iodometric method,[19] whereas the HOOH concentration was determined by a cerimetric method[20] (see Experimental Section). As reported in Table V, the contribution to total peroxide by peroxyacetic acid (AcOOH, with Ac = CH_3CO–) ranged from 0 to 7%, being less than 5% for more than half of the kinetic runs. The reaction rates were determined by following the disappearance of total peroxide; however, both the ratios [R'_2S]$_0$/[HOOH]$_0$ *and* [HOOH]$_0$/[AcOOH]$_0$ were ≥ 10. Since the AcOOH oxidation of thioxane should be *ca.* 40-fold faster[7] than the oxidation by H_2O_2 in acetic acid, and since our independent experiments[21] confirm that the formation of AcOOH is slow,[22] the peroxyacetic acid is likely to be removed very rapidly from the reaction solution, with no observable effect on the concentration of the sulfide and HOOH, *both in*

Table IV. Solvent Isotope Effect for the Oxidation of Thioxane by Hydrogen Peroxide and *t*-Butyl Hydroperoxide in Water at 25°

Hydroperoxide	Solvent	10^3k_2[a]	$k_2(H_2O)$/$k_2(D_2O)$	10^3k_3[a]	$k_3(H_2O)$/$k_3(D_2O)$
H_2O_2	H_2O	2.58		34.8	
			1.68		1.08
	D_2O	1.54		32.0	
t-BuOOH	H_2O	0.135		1.91	
			1.42		0.94
	D_2O	0.096		2.03	

[a] k_2 in l. mol^{-1} sec^{-1}; k_3 in l.^{2} mol^{-2} sec^{-1}.

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(18) J. O. Edwards and D. H. Fortnum, *J. Org. Chem.*, 27, 407 (1962).

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

(20) F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, 20, 1061 (1948).

(21) M. A. Dankleff, Ph.D. Thesis, Brown University, 1963.

(22) J. G. Wallace, "Hydrogen Peroxide in Organic Chemistry," E. I. du Pont de Nemours and Co., Electrochemicals Dept., Wilmington, Del., 1960, p 78.

Table V. Oxidation Rates of Thioxane by Hydrogen Peroxide in Acetic Acid at 25.0°

$[\text{Sulfide}]_0$, mol l.$^{-1}$	$[H_2O_2]_0$,[b] mol l.$^{-1}$	$10^3 \times$ [AcOOH],[a,b] mol l.$^{-1}$	% PA[c]	10^2k_2,[d] l. mol^{-1} sec^{-1}	[KOAc], mol l.$^{-1}$
0.218	0.0302	1.41	4.5	2.38	...
0.109	0.0151	0.70	4.5	2.48	...
0.043	0.0042	...	...	2.53	...
0.032	0.0120	1.17	8.9	2.42	...
0.104	0.0127	...	...	2.58	0.050
0.104	0.0115	0.80	6.5	2.43	0.100
0.106	0.0127	0.32	2.3	2.58	0.166
0.106	0.0139	0.15	1.1	1.93	0.495
0.104	0.0115	0.05	0.4	0.983	1.32
0.202	0.0368	3.00	7.5	0.796	1.50
0.101	0.0175	1.25	6.7	0.853	1.52
0.025	0.0109	0.20	1.8	0.771[e]	1.57

[a] Kokatnur and Jelling analytical method. [b] Analytical method using ceric sulfate to analyze for H_2O_2 in presence of peroxyacetic acid. [c] % PA = 100[AcOOH]/total peroxide. [d] Observed k_2 from pseudo-first-order plots, as $k_1/[\text{thioxane}]_0$. [e] From second-order plot.

large excess. In fact, good linear plots were obtained over 70–88% reaction in the majority of runs reported in Table V. In order to elucidate whether a preequilibrium of the kind

$$HOOH + AcOH \rightleftharpoons HOOH_2^+ + AcO^- \qquad (4)$$

had to be accounted for in the analysis of kinetic data, an investigation upon the effect of added KOAc on the rate was undertaken (see Table V). Since no significant decrease in the rate constant occurred for [KOAc] up to 0.18 *M*, it seems unlikely that the rate is affected by a mass law effect through preequilibrium 4, in agreement with what was shown by Bateman and Hargrave.[10] On the change in salt concentration from 0.18 *M* to 1.57 *M*, however, the observed rate constant decreased by a factor of 3 (Table V); this can be explained as the effect of high salt concentrations plus low dielectric constant of the solvent upon the activity coefficients of the reacting species.[23] The activation parameters were measured in acetic acid containing 1.57 *M* KOAc and are reported on Table VI.

Table VI. Rate Constants and Activation Parameters for the Oxidation of Thioxane by Hydrogen Peroxide in Protic and Aprotic Solvents

Solvent	ϵ[a]	Temp, °C	10^4k_2[b]	E_a[c]	$\Delta H^{\ddagger}$[c]	$\Delta S^{\ddagger}$[c]
Dioxane	2.209	25	0.0407[d]	16.3	15.7	−31
		45.9	0.0246			
AcOH	6.15	25	243			
AcOH (1.57 *M* KOAc)		25	77.1	11.1	10.5	−33[e]
AcOH (1.57 *M* KOAc)		5.7	21.7			
t-BuOH	10.9	25	0.0545	19.3	18.7	−22
		45.9	0.400			
i-PrOH	18.3	25	0.114	16.2	15.6	−29
		45.9	0.681			
MeOH	32.63	25	0.616	15.1	14.5	−29
		45.9	3.27			
Ethylene glycol	37.0	25	4.96	14.2	13.6	−28
		45.9	23.8			
D_2O	78.25	25	15.4	13.5	12.9	−28[f]
H_2O	78.54	25	25.8	13.5	13.0	−27[f]
N-Methylacetamide	178.9	25	0.0220	19.3	18.7	−22
		45.9	0.187			

[a] Dielectric constant values at 25° (A. A. Maryott and E. R. Smith, National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951), except for N-methylacetamide which is at 30° (C. P. Smythe, "Dielectric Behavior," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 87). [b] In l. mol^{-1} sec^{-1} unless otherwise noted. [c] E_a and $\Delta H^{\ddagger}$ values in kcal mol^{-1}; $\Delta S^{\ddagger}$ values in cal mol^{-1} deg^{-1}. [d] In l.^{2} mol^{-2} sec^{-1}, as rate law is different (third-order kinetics) in dioxane. [e] See Table V. [f] See Table I.

Other Protic Solvents. The HOOH oxidation of thioxane was studied in MeOH, *i*-PrOH, *t*-BuOH, ethylene glycol (EG), and N-methylacetamide (NMA) (see Table VI). For comparison, the oxidation rates of the same substrate by *t*-BuOOH were determined in MeOH and *i*-PrOH (Table VII). Each rate constant was obtained from several kinetic runs; the average deviation ranged from 1.5 to 8% in the majority of cases. In MeOH, *i*-PrOH, *t*-BuOH, and EG, the integrated pseudo-first-order plots were linear generally over 70% reaction; neither positive nor negative autocatalysis by the production of either water or sulfoxide, respectively, was observed. In EG, however, it was found that k_2(obsd) decreased *ca.* 28% when $[R'_2S]_0$ was increased from 0.138 to 1.93 *M;* since k_2 exhibited little deviation at thioxane concentrations ≤ 1.0 *M*, it would seem that the observed decrease in rate was produced by the decrease in the general protic character of the medium (see below). At variance with the other protic solvents, the oxidation in NMA exhibited acceleration of rate after 30–40% reaction; as will be discussed below, the acceleration would be expected here, since water, produced in the reaction, is much more acidic than N-methylacetamide. No significant salt effect seems to be present in these protic solvents, since addition of 0.10 *M* $LiNO_3$ to methanol caused an increase in rate of only 7%. Similarly,

Table VII. Rate Constants and Activation Parameters for the Oxidation of Thioxane by *t*-Butyl Hydroperoxide in Protic Solvents

Solvent	Temp, °C	10^5k_2, l. mol^{-1} sec^{-1}	E_a, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
Water	25	13.5	14.1	13.5	−27
MeOH	25	0.265	14.3	13.7	−34
	45.9	1.25			
i-PrOH	25	0.050	15.3	14.7	−34
	45.9	0.267			

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[23] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1958, p 138.

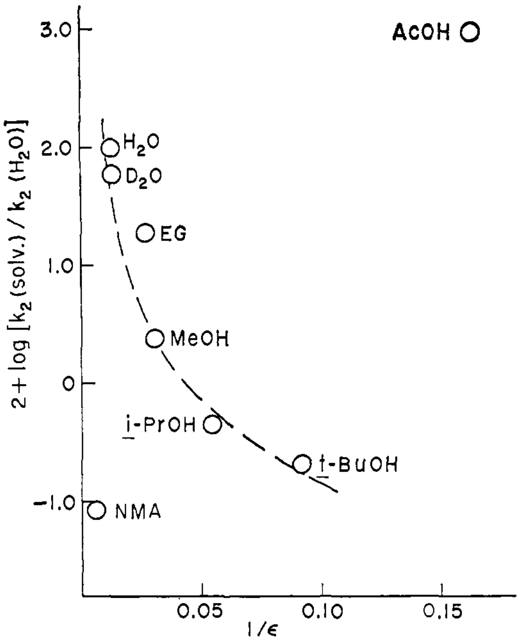

Figure 2. Variation of the relative rate of oxidation of thioxane by HOOH with $1/\epsilon$, in various solvents, at 25°.

Bateman and Hargrave[10] reported no significant salt effect for the oxidation of cyclohexyl methyl sulfide by cyclohexenyl hydroperoxide in methanol.

From the data in Table VI it is apparent that the rate is more sensitive to the protic character of the solvent than to the polarity as measured by dielectric constant ϵ or by Kosower's "*Z*" values.[24] The ϵ value for NMA is 16-fold greater than for *t*-BuOH, whereas the k_2(obsd) value for the reaction in *t*-BuOH is *ca.* 2.5-fold larger than in NMA; the dielectric constants for ethylene glycol and methanol are nearly the same, but the rate constant is 8-fold larger for the former than for the latter. In the plot of log relative rate *vs.* $1/\epsilon$ (see Figure 2), the data do not show any clear dependence of rate on ϵ (note especially NMA and AcOH). For alcohols and water, there is a systematic nonlinear decrease in k_2(obsd) for a decrease in the dielectric constant; *however, this trend is also the general trend of decreasing acidity of the protic solvents.*

Figure 3 (see also Table VIII) presents a plot of log $k_2(\text{solv})/k_2(H_2O)$ *vs.* the autoprotolysis constant (pK_H) values for each solvent;[25] a fairly good linear relationship is obtained, with the only exception of a small deviation for the data for AcOH, which would become more evident if a 1–1.8 unit larger pK_H value for this solvent[26,27] is accepted.[28]

Table VIII. Relative Rates for the Oxidation of Thioxane by Hydrogen Peroxide in Protic Solvents at 25°

Solvent	$\epsilon_{25°}$	Rel rate[b]	pK_H[c]
AcOH	6.15	941	12.6[d]
H_2O	78.54	100	14.0[e]
D_2O	78.25	59.7	14.7[f]
Ethylene glycol	37.0	19.2	(15.6)[g]
MeOH	32.63	2.39	16.7[e]
i-PrOH	18.3	0.442	20.8[e]
t-BuOH	10.9	0.211	(22.1)[g]
N-Methylacetamide	178.9[a]	0.0885	...

[a] Value at 30°. [b] As $100k_2(\text{solv})/k_2(H_2O)$. [c] Autoprotolysis constants in mol² l.⁻², at 25°. [d] From S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 10 (1956). [e] From K. Bowden, *Chem. Rev.*, **66**, 119 (1966). [f] From W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936). [g] Values in parentheses are rough estimates.

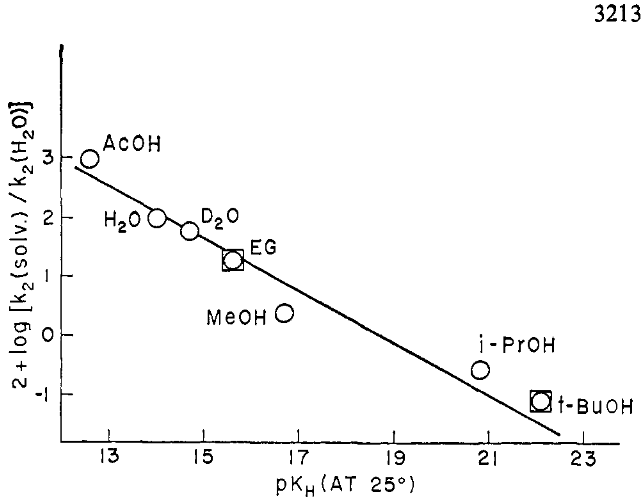

Figure 3. Variation of the relative rate of oxidation of thioxane by HOOH with the autoprotolysis constant of the solvent, at 25°.

Dioxane. Although the over-all reaction order was 2 in the protic solvents, a reaction order of 3 (1 in thioxane and 2 in HOOH) was observed in anhydrous dioxane. The third-order behavior of the oxidation is consistent with observations by Bateman and Hargrave[10] of third-order kinetics for the oxidation of cyclohexyl methyl sulfide by *t*-BuOOH or cyclohexenyl hydroperoxide in benzene and cyclohexane.

The reaction in dioxane exhibited no radical character of the type previously described,[10] since there was no change in rate when the experiments were carried on under N_2 or in the presence of 0.404 *M* nitrobenzene. In contrast to the retardation in the rate of sulfide oxidation by either the production or the addition of corresponding sulfoxide[10] in aprotic solvents, an increase of rate after 11–30% reaction was observed for either production or addition, at zero time, of small amounts of water (see below).[29] The orders in sulfide and HOOH in this solvent were evaluated from plots of log initial rate *vs.* log of sulfide or HOOH concentration (see Figure 4); kinetic data obtained from initial rates under pseudo-second-order conditions are shown in Table IX.

Dioxane–Protic Solvent Solutions. Kinetic data for the HOOH oxidation of thioxane were obtained in solvent mixtures generally containing 2.22 *M* protic solvent ROH (with R = H, Ac, Me, and *t*-Bu), in dioxane at 45.9°. The kinetics in 2.22 and 4.11 *M* aqueous dioxane were characterized by pseudo-first-

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(24) E. M. Kosower, *J. Am. Chem. Soc.*, 80, 3253, 3267 (1958).

(25) In making this plot, pK_H values were preferred over pK_a values in an attempt to account for the contribution by the dielectric constant of the solvent to the observed rate constant.

(26) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974, 10 (1956).

(27) I. M. Kolthoff and A. Willmann, *ibid.*, **56**, 1007 (1934).

(28) $pK_H^{25°}$ values for AcOH have been calculated from the specific conductivity of acetic acid, using Λ_0 for $AcOH_2^+$ which was estimated from the Λ_0 values of other electrolytes; according to R. J. L. Martin [*Australian J. Chem.*, **15**, 409 (1962)], these autoprotolysis constant values are likely to be only approximate.

(29) Both thioxane oxide and HOOH are likely to be sufficiently solvated by dioxane to prevent the formation of the H-bonded sulfoxide–hydroperoxide complex proposed by Bateman and Hargrave as the cause of their observed retardation of rate in benzene.

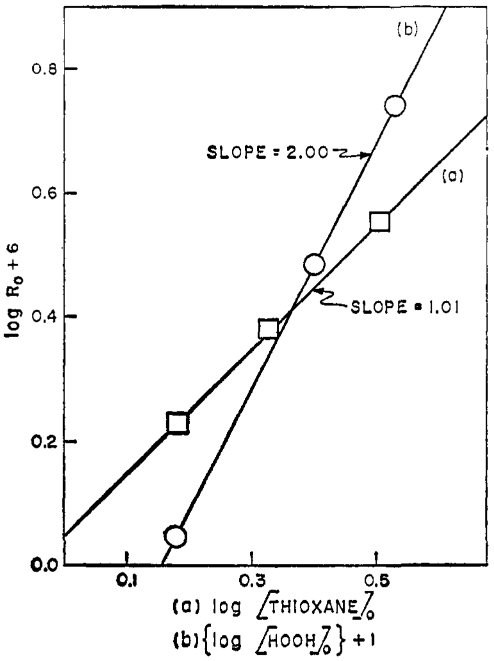


Figure 4. Determination of reaction order for thioxane and HOOH from initial rates in dioxane, at 45.9°: (a) log R_0 *vs.* log [thioxane]$_0$, at constant $[HOOH]_0 = 0.202$ *M;* (b) log R_0 *vs.* log $[HOOH]_0$ at constant $[\text{thioxane}]_0 = 2.13$ *M.*

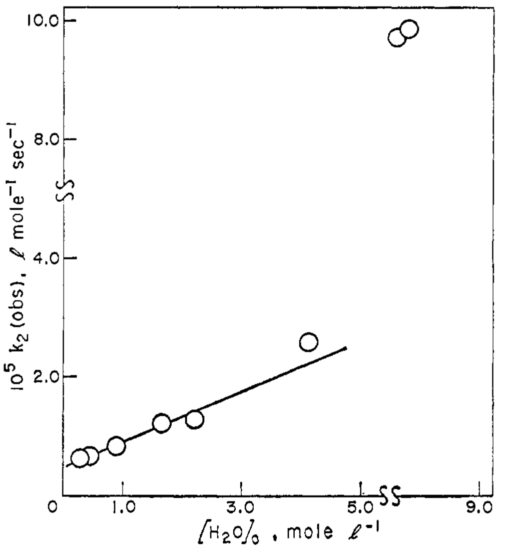


Figure 5. Effect of variation of $[H_2O]_0$ on the oxidation rate of thioxane by HOOH in aqueous dioxane, at 45.9°.

order plots which were linear over 70%; the k_2(obsd) values were obtained from $k_1(\text{obsd})/[R'_2S]_0$. A positive deviation (*i.e.*, faster rate), however, was observed in plots after 20–30% reaction when the ratio $[H_2O]_0/[HOOH]_0$ was ≤ 2. The data are reported in Table X. As shown in Figure 5, a linear increase along with a finite intercept in the k_2(obsd) values with $[H_2O]_0$ up to *ca.* 3 *M* was observed. The linear increase shown in Figure 5, the acceleration in rate observed in anhydrous dioxane, the finite intercept, the orders in protonic solvents, and the observed second-order dependence on [HOOH] in the absence of H_2O suggest a rate law of the kind

Table IX. Oxidation Rate of Thioxane by Hydrogen Peroxide in Dioxane

Temp, °C	$[\text{Sulfide}]_0$, mol l.$^{-1}$	$[H_2O_2]_0$, mol l.$^{-1}$	10^5k_3,[a] l.^{2} mol^{-2} sec^{-1}
25.0	2.00	0.193	0.415
	2.00	0.0965	0.407
	1.00	0.0965	0.423
	0.544	0.107	0.433
	1.01	0.123	0.440
	1.97	0.194	0.367
	2.02	0.245	0.362
			Av 0.407 ± 0.024
45.9	1.51	0.202	2.75
	2.12	0.202	2.78
	3.18	0.202	2.78
	2.14	0.118	2.83
	2.13	0.196	2.90[b]
	2.13	0.336	2.33
	1.06	0.109	2.33
	2.13	0.250	2.30
	1.78	0.281	2.33[c]
	2.13	0.150	2.32
	2.13	0.167	2.07
	2.14	0.294	2.10
	2.12	0.218	2.10
			Av 2.46 ± 0.26

[a] k_3 was calculated from initial rate data (11–30% reaction) by pseudo-second-order plots. [b] 0.404 *M* nitrobenzene was added. [c] Reaction was carried out under nitrogen.

Table X. Oxidation Rates of Thioxane by H_2O_2 in Aqueous Dioxane at 45.9°

$[\text{Sulfide}]_0$, mol l.$^{-1}$	$[HOOH]_0$, mol l.$^{-1}$	$[H_2O]_0$, mol l.$^{-1}$	10^5k_2(obsd), l. mol^{-1} sec^{-1}
1.96	0.236	0.266	0.633[a]
1.96	0.236	0.433	0.654[a]
1.96	0.236	0.886	0.833
2.13	0.244	1.65	1.23
2.12	0.196	2.22	1.28
2.12	0.212	4.11	2.60
1.96	0.236	8.02	9.73
2.14	0.244	8.25	10.3

[a] Acceleration with time was observed in integrated pseudo-first-order plots after first 20–30% reaction in experiments where $[H_2O]_0/[HOOH]_0 \leq 2$.

$$-d[H_2O_2]/dt = k_3^{HOH}[H_2O][R'_2S][HOOH] + k_3^{H_2O_2}[R'_2S][HOOH]^2 \quad (5)$$

For small percentages of reaction, this can be rearranged to the form

$$-d(\ln [H_2O_2])/dt = k_3^{HOH}[R'_2S][H_2O] + k_3^{H_2O_2}[R'_2S][HOOH] \quad (6)$$

and this gives the equation

$$k_2(\text{obsd}) = k_3^{HOH}[H_2O] + k_3^{H_2O_2}[HOOH] \quad (7)$$

Using the data of Table X, values of k_3^{HOH} and $k_3^{H_2O_2}$ were calculated.

The oxidation in 2.22 *M* AcOH–dioxane was characterized by high rates, pseudo-first-order plots linear to 80–92% reaction, and an over-all order of 2. In this mixture, the contribution by a term containing $[H_2O_2]^2$

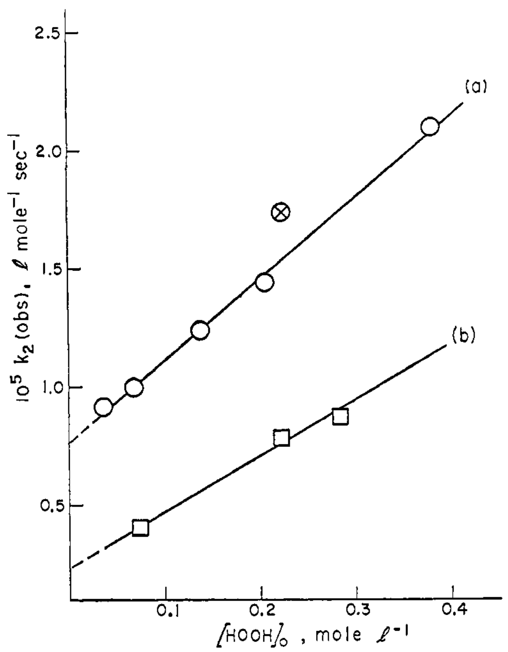


Figure 6. Effect of variation of $[HOOH]_0$ on the oxidation rate of thioxane by HOOH in alcoholic dioxane, at 45.9°: (a) in 2.22 *M* MeOH–dioxane; (b) in 2.22 *M* *t*-BuOH–dioxane.

is negligible, and the appropriate equation presumably is

$$k_2(\text{obsd}) = k_3^{\text{AcOH}}[\text{AcOH}] \tag{8}$$

For the oxidation in 2.22 *M* MeOH–dioxane and *t*-BuOH–dioxane, the pseudo-first-order plots showed acceleration after 15–35% reaction. Substituting into eq 7 H_2O with ROH and using rate data at various $[HOOH]_0$ (see Figure 6), values of k_3^{ROH} and $k_3^{H_2O_2}$ were calculated. The experimental data for the three mixed solvents are presented in Table XI, where $k_2^0 = k_3^{\text{ROH}}[\text{ROH}]$. All of the data are consistent with a general rate equation of the type

$$-d[H_2O_2]/dt = k_3^{\text{ROH}}[R'_2S][\text{HOOH}][\text{ROH}] + k_3^{H_2O_2}[R'_2S][\text{HOOH}]^2 \tag{9}$$

Rate constants for this equation are given in Table XI.

In Table XII, constants for the various rate terms are compared. It should be noted that the k_3^{ROH} values follow the order predicted on the basis of the acidity of ROH as measured by its pK_a value.[30–32] This order, AcOH > H_2O_2 > H_2O $\simeq$ MeOH > *t*-BuOH, is strikingly correlated with acidity (see Figure 7).

Discussion

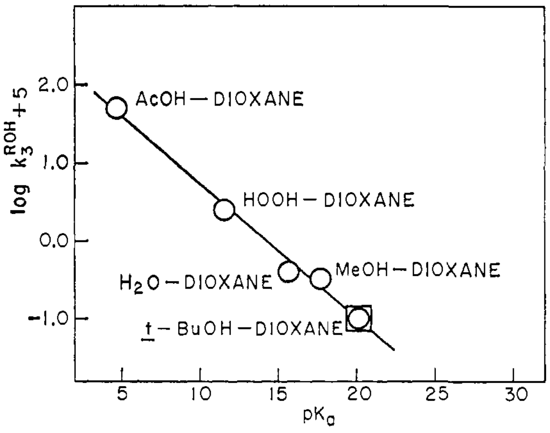
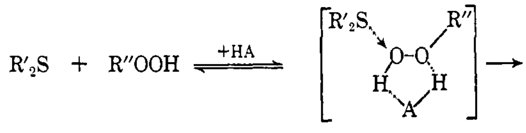


Figure 7. Variation of the "protic solvent catalysis constant" (k_3^{ROH}) with pK_a of the protic component of the solvent for the HOOH oxidation of thioxane in ROH–dioxane solvent mixtures, at 45.9°.

If the oxidation of thioxane by hydroperoxides was like typical SN2 reactions involving neutral reactants (*e.g.*, the Menschutkin reaction), the reaction would involve significant charge separation in the activated complex and, consequently, a sensitivity to ionic strength[12,33] and to solvent polarity.[24,33,34] From the results obtained here plus those reported earlier,[9,10] it is apparent that the kinetic data are better explained according to the following scheme.



(1)

$$\text{R''OH} + \text{R'}_2\text{SO} + \text{HA} \tag{10}$$

In this activated complex, appreciable charge separation is avoided by means of proton transfers, HA being an "acidic" molecule (acid, solvent, or even a second hydroperoxide molecule[10]); the proposed mechanism is supported by the evidence summarized below.

1. There was no significant salt effect in water (up to ionic strength 3) or in MeOH (0.10 *M* $LiNO_3$). In AcOH no decrease in rate was found on addition of the common ion AcO^- ($\leq$0.18 *M*). The absence of a mass law effect rules out, in this solvent, a prior equilibrium involving solvent protonation of the peroxide and it is consistent with a neutral proton shift *via* molecular acid in the activated complex.[10]

2. The rate reflects the solvent "acidity" better than its polarity (Figures 2 and 3). The curved plot of log (relative rate) *vs.* the reciprocal of dielectric constant for alcohols and water, the scatter for the rates in AcOH and NMA, and the rate enhancement on the change to more "acidic" solvents suggests that the oxidation of thioxane by hydroperoxides is primarily sensitive to the ability of a solvent to by-pass the formation of charge *via* proton transfers. A similar rate enhancement on change to a more protic solvent was observed by Ibne-Rasa and Edwards in the peroxyacetic acid oxidations of *p*-nitroaniline[35] and of nitrosobenzene.[36]

3. Solvent participation as a proton transfer agent in the activated complex is consistent with the observation of maximum activation energy for the oxidation in the least acidic of the protic solvents, *i.e.*, NMA (Table VI). The rationale for this specific interaction of solvent is based on the ability of protic solvents to

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(30) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(31) A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953).

(32) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952); see also K. Bowden, *Chem. Rev.*, **66**, 119 (1966).

(33) A. Streitwieser, *ibid.*, **56**, 571 (1956).

(34) M. Watanabe and R. M. Fuoss, *J. Am. Chem. Soc.*, **78**, 527 (1956).

(35) K. M. Ibne-Rasa and J. O. Edwards, *ibid.*, **84**, 763 (1962).

(36) K. M. Ibne-Rasa, C. G. Lauro, and J. O. Edwards, *ibid.*, **85**, 1165 (1963).

Table XI. Oxidation Rates of Thioxane by Hydrogen Peroxide in 2.22 *M* Protic Solvent–Dioxane Solutions at 45.9°

Solvent	$[\text{Sulfide}]_0$, mol l.$^{-1}$	$[\text{HOOH}]_0$, mol l.$^{-1}$	10^5k_2(obsd), l. mol^{-1} sec^{-1}	$10^6k_2^0$, l. mol^{-1} sec^{-1}
2.22 *M* AcOH–dioxane	2.13	0.280	105	...
	2.11	0.212	111	...
	1.27	0.140	111	...
			Av 109 ± 3	
2.22 *M* MeOH–dioxane	2.03	0.380[a]	2.10	7.80
	2.12	0.222	1.74	...
	2.03	0.206[a]	1.44	7.28
	2.12	0.138[a]	1.24	7.63
	1.27	0.068	0.997	7.58
	0.578	0.041	0.915	7.73
			Av 1.35	
				Av 7.60 ± 0.14
			$10^5k_3^{\text{H}_2\text{O}_2}$ =	3.46[b]
2.22 *M* *t*-BuOH–dioxane	2.13	0.283[a]	0.866	2.00
	2.12	0.222[a]	0.783	2.60
	2.11	0.074	0.408	2.33
	1.27	0.074	0.403	2.28
			Av 0.615 ± 0.210	
				Av 2.230 ± 0.17
			$10^5k_3^{\text{H}_2\text{O}_2}$ =	2.37[b]

[a] Values used to determine the order in hydrogen peroxide. [b] In l.^{2} mol^{-2} sec^{-1}.

Table XII. Rate Constants for the Oxidation of Thioxane by Hydrogen Peroxide in Dioxane and in 2.22 *M* Protic Solvent–Dioxane Solutions at 45.9°

	AcOH–dioxane	H_2O–dioxane	MeOH–dioxane	*t*-BuOH–dioxane	Dioxane
10^6k_2(obsd), l. mol^{-1} sec^{-1} [a]	109	1.28	1.35[b]	0.615[b]	...
$10^5k_3^{\text{H}_2\text{O}_2}$, l.^{2} mol^{-2} sec^{-1}	...	...	3.46[c]	2.37[c]	2.46[d]
$10^5k_3^{\text{ROH}}$, l.^{2} mol^{-2} sec^{-1}	49[e]	0.40[f]	0.34[e]	0.10[e]	...

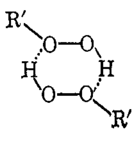
[a] All reported values were calculated as $k_1/[\text{R}'_2\text{S}]_0$ from pseudo-first-order integrated plots, with sulfide and protic solvent concentration in large excess. [b] k_2(obsd) average values (see Table XI). [c] $k_3^{\text{H}_2\text{O}_2}$ values were evaluated from the slope of the plot of k_2(obsd) *vs.* $[\text{HOOH}]_0$ (see Figure 6). [d] Third-order specific rate constant for the oxidation in anhydrous dioxane; value adopted in making the plot presented in Figure 7. [e] k_3^{ROH} is the protic solvent catalytic constant, evaluated as $k_2^0/[\text{ROH}]_0$. [f] Evaluated from the slope of the plot of k_2(obsd) *vs.* water concentration, at constant peroxide concentration, $\simeq$0.24 *M* (see Figure 5).

decrease the energy requirements of the displacement on peroxide oxygen by minimizing charge separation. Furthermore, the activation entropy became more negative by only *ca.* −4 cal mol^{-1} deg^{-1} on the change from the polar solvent water to the nonpolar solvent dioxane, *in which a second molecule of peroxide apparently plays the role of the protic solvent* in the proton shift.[10] Moreover, if significant charge separation was characteristic of the activated complex, one would expect the $\Delta S^{\ddagger}$ value to become more negative[37] by 10–20 cal mol^{-1} deg^{-1}; on the contrary relatively high, negative, and quite similar $\Delta S^{\ddagger}$ values were found for the oxidation in all solvents (Table VI).[8]

4. The oxidation rate of thioxane by HOOH in water, MeOH, and *i*-PrOH (Table VI) is 16- to 23-fold higher than the corresponding oxidation by *t*-BuOOH in the same solvents (Table VII). This order was expected for as the basicity of the leaving group increases, the oxidation rate by the corresponding peroxide should decrease.[7] Similarly, the third-order rate constant for the acid-catalyzed oxidation by HOOH in water is about 18-fold higher than the corresponding k_3 value for the oxidation by *t*-BuOOH. Evidently for both neutral and acid oxidations, an important factor in the activation free energy is the breaking of the peroxide link.

5. The solvent isotope effect (Table IV), $k_2(\text{H}_2\text{O})/k_2(\text{D}_2\text{O})$ = 1.68, for oxidation by H_2O_2, is consistent with the view that D_2O, being less acidic than H_2O, would participate in a proton shift less effectively as well as at a slower rate. A slightly smaller solvent isotope effect (1.42) for the oxidation by *t*-BuOOH was found.

6. Perhaps the most striking evidence in support of a cyclic activated complex is given by the apparent change in peroxide order from 1 to 1.6 to 2 (see Results) as the availability of acidity of protic solvent decreases. According to the eq 9, when a markedly protic solvent is present in significant concentration, only the first part of the general rate law is apparent. The partial order in hydroperoxide appears when a protic agent of similar acidic character to hydroperoxide is present as in alcoholic dioxane solutions. In the absence of any other protic material, the order in peroxide is two. Several authors[38–40] have reported spectral evidence, in a variety of aprotic solvents, that hydroperoxide molecules may exist in the cyclic hydrogen bonded dimer form **2**.



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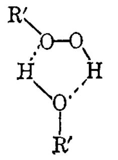

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[37] H. E. Cox, *J. Chem. Soc.*, 142 (1921).

[38] C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 48 (1965).

[39] R. West and R. H. Baney, *J. Phys. Chem.*, **64**, 822 (1960).

[40] H. E. De La Mare, *J. Org. Chem.*, **25**, 2114 (1960), and references therein.

It is likely that a protic solvent molecule can lead to the similar cyclic H-bonded species **3**; however, how many protic solvent molecules are contained in the solvation shell and how many of them are involved in proton transfers in the proposed transition state is, of course, hard to establish. Nevertheless it is significant that the protic solvent catalysis constants k_3^{ROH}, calculated from eq 9, fall in an order which correlates well with expectations. We have found no evidence for zero-order or multiple-order dependence on protic solvent, and we feel that our results firmly establish the reality of solvent participation in the activated complex in reactions of this type.

The observation of specific hydrogen ion catalysis in water (Tables I, II, and III) is in apparent contrast to the other evidence presented above and to the general acid catalysis which might have been expected. This peculiarity is probably connected to the particular efficiency of the highly hydrogen-bonded structure of the water solvent in performing the cyclic proton transfers; any other acidic molecule which is present in much smaller concentrations in this medium would be less effective. Also, the dependence on solvent is not inconsistent with general acid catalysis provided the substrate constant α in the Brønsted equation is small (*e.g.*, <0.2).

Since D_3O^+ in D_2O is a stronger acid than H_3O^+ in H_2O,[41] one would predict a solvent isotope effect $k_3(H_2O)/k_3(D_2O)$ appreciably less than one[42] for the specific acid catalyzed oxidation in view of the rapid preequilibrium

$$H_2O_2 + H_3O^+ \rightleftarrows H_3O_2^+ + H_2O$$

However, these isotope effects for oxidation by H_2O_2 and *t*-BuOOH are both near to unity (Table IV). Evidently the solvent isotope effects in these cases are complicated by several factors (including proton transfers) not easily separable.

On the basis of results presented here as well as in previous studies,[9,10,11,18,35,36] we conclude that specific solvent interactions provide a mechanistic path which avoids significant charge separation in the activated complexes for displacements on peroxide molecules by neutral nucleophiles and that the effectiveness of the protic solvents is correlated with their relative acidities.

Experimental Section

Materials and Solvents. Thioxane (1-thia-4-oxacyclohexane) (Aldrich) was dried over CaH_2 or Na_2SO_4 and fractionally distilled, bp 50–50.2° (21 mm), n^{25}D 1.5048 (lit.[43] n^{20}D 1.5081).

Thioxane oxide was obtained by oxidation with H_2O_2 (1:1 mole ratio) in acetone or 2-propanol;[44] after removal of solvent, drying over Na_2SO_4, and fractional distillation the pure sulfoxide was isolated in 81% yield, bp 125° (12 mm), mp 41–43° (lit. bp 147° (15 mm),[45] mp 44.5–45° [46]).[47]

Hydrogen peroxide (30%) was used in making aqueous solutions; 97% H_2O_2 (F.M.C. Corporation) was used for anhydrous organic solvents solutions. ***t*-Butyl hydroperoxide (70%)** (K & K Laboratories) was purified twice by fractional distillation, bp 39–39.5° (19.5 mm) (lit.[48] 38–38.5° (18 mm)); the sample used in kinetic experiments was found to contain 97.0% of active oxygen. **Inorganic salts**, reagent grade, were usually employed without further purification; $LiNO_3$, however, was recrystallized once from methanol and dried at 110° before use. **Ethylenediaminetetracetic acid (EDTA) disodium salt** was recrystallized from ethanol–water. **Distilled water, conductivity water, or 99.5% D_2O** (General Dynamics Corp.) were employed to make aqueous solutions. **Ethylene glycol, AcOH, *t*-BuOH, and MeOH** solvents, reagent grade, and ***i*-PrOH and dioxane** spectrograde solvents (Matheson) were used without further purification in many cases; the ir spectrum of dioxane, recorded before use, showed no peak for water and the iodometric blank for peroxide was negligible ($\leq 1\%$ of the smaller titer) or zero in any kinetic run. **N-Methylacetamide** (Eastman Kodak, "h.p.") solvent had mp 29–31° (lit.[49] mp 29.7°) and was also used without purification, n^{26}D 1.4307 (lit.[50] n^{26}D 1.4294).

Stoichiometry. The oxidation in a variety of solvents was shown to have a stoichiometry of 1 mol HOOH to 1 mol sulfide by the nearly quantitative isolation of the product sulfoxide as pure thioxane oxide or as the nickel perchlorate complex $[Ni(thioxane\ oxide)_6](ClO_4)_2$ (Table XIII); this complex was obtained practically in 100% yield in the stoichiometric determination experiments. The analytical data were obtained for four metal complexes of the sulfoxide; they have been reported in an independent study.[51]

Table XIII. Stoichiometry for the Oxidation of Thioxane by H_2O_2 in Aqueous and Organic Solvents

$[H_2O_2]$[c]	[Thioxane][c]	Solvent	Temp, °C	% yield[a]
0.4275	0.4275	H_2O	25	92.0
0.9775	0.9775	MeOH	45.9	90.5
2.12	2.14	*i*-PrOH	45.9	88.0
2.125	2.12	Dioxane–2.2 *M* H_2O	45.9	94.0
2.31	2.22	Dioxane	45.9	83.5
2.14	2.14	Acetone	56.5	81.0[b]

[a] The thioxane oxide was isolated as the nickel perchlorate complex. [b] In this one experiment, the sulfoxide itself was isolated in 94% yield crude product; 81% yield of pure sulfoxide was obtained after fractional distillation. [c] In mol l^{-1}.

Kinetics. Kinetic runs at 25.0 and 45.9° were carried out in a constant temperature bath (A. H. Thomas) with temperature control within ±0.05°. Temperatures constant within ±0.1° were maintained at 0.0, 5.7, and 9.7° in a dewar flask. Sulfide solutions for kinetic runs were made either by dilution of weighed samples of thioxane or by dilution of 3 to 20 ml of sulfide stock solution with solvent at the temperature of the experiment. At zero time an aliquot of peroxide standard solution was added with swirling to the reaction mixture and the total quickly brought to exact volume in the thermostat. Mixed solvents were made from weighted volumes of protic solvent which were then thermostated and diluted to volume with dioxane at given temperature. The reaction rates were determined by following the disappearance of the peroxide by iodometric titrations; for the oxidation of thioxane by HOOH the analytical method described by Kolthoff[52] was adopted in some runs, but most of the rate constants were determined by following the Kokatnur and Jelling[19] iodometric method. In the oxidation by *t*-BuOOH, the latter was determined according to the Wibaut[53] method or the Kokatnur and Jelling[19] method, both slightly modified.[54] In studies of acid catalysis in water, $HClO_4$ concentrations were calculated from dilution of standard solutions; appreciable

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(41) C. G. Swain and R. F. W. Bader, *Tetrahedron*, 10, 182, 200 (1960).

(42) F. A. Long and J. Bigeleisen, *Trans. Faraday Soc.*, **55**, 2077 (1959).

(43) H. T. Clarke, *J. Chem. Soc.*, 1806 (1912).

(44) A. Cerniani and G. Modena, *Gazz. Chim. Ital.*, **89**, 843 (1959).

(45) A. E. Cashmore, *J. Chem. Soc.*, 1739 (1923).

(46) Société des usines chimiques Rhône-Poulenc, French Patent 859,886, (Dec 31, 1940); *Chem. Abstr.*, 42, 3783*f* (1948).

(47) Since this sulfoxide is exceedingly hygroscopic, its samples were dried over barium oxide and handled in a drybox.

(48) N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 205 (1946).

(49) G. R. Leader and J. F. Gormky, *ibid.*, 73, 5731 (1951).

(50) G. F. D'Alelio and E. E. Reid, *ibid.*, **59**, 109 (1937).

(51) R. L. Carlin, J. Roitman, M. A. Dankleff, and J. O. Edwards, *Inorg. Chem.*, 1, 182 (1962).

(52) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p 282.

(53) J. Mitchell, Jr., and I. M. Kolthoff, "Organic Analysis," Vol. 4, Interscience, Publishers, Inc., New York, N. Y., 1960, p 14.

(54) H.-Y. Pyun, M.Sc. Thesis, Brown University, 1964.

air oxidation of I$^-$ in the Kokatnur, *et al.*, quench was inhibited by addition of *ca.* 1 g of KOAc. In acetic acid, the total peroxide concentration was determined by the Kokatnur, *et al.*, method, and the HOOH concentration by the technique reported by Greenspan and MacKellar[20] which uses ceric sulfate standard solution to titrate HOOH directly with ferroin indicator; the peroxyacetic acid concentration was then calculated by difference. The stock HOOH solutions in AcOH were made, standardized immediately, used in kinetic runs, and then restandardized to determine the concentration change of either HOOH or AcOOH; no detectable change occurred during the extent of the kinetic runs when KOAc was present. For the kinetic experiments in all solvents a blank was run on the reagents used in the quench for the same period of time as that occurring between the quenching and the titration of the first aliquot; the blank was negligible or zero for all reported data.

For each solvent used the extent of hydroperoxide decomposition was determined, in independent experiments, at the highest hydroperoxide concentration adopted for any given series of kinetic runs. Generally all runs were finished before any peroxide decomposition could be detected in the solvent, except for the case of N-methylacetamide; in this solvent, consequently, no run was extended over a time which would allow more than 1% peroxide autodecomposition.

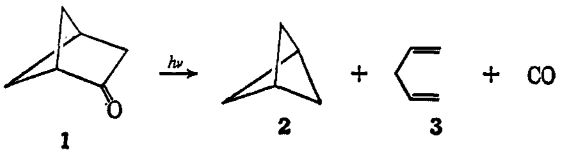
The Solution Photochemistry of Some Bicyclic Ketones[1]

Jerrold Meinwald[2] and Ralph A. Chapman[3]

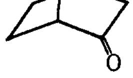
Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received December 15, 1967*

Abstract: Irradiation of pentane solutions of bicyclo[2.1.1]hexan-2-one (**1**), bicyclo[2.2.1]heptan-2-one (**4**), and camphor (**5**) leads to the formation of cycloolefinic aldehydes (**7, 17,** and **25**) which react further under continued irradiation. In the case of **7** and **17**, photocycloadditions of possible synthetic utility are observed, leading to the tricyclic oxetanes **10** and **18**. Analogous oxetane formation from campholenic aldehyde (**25**), followed by thermolysis, provides a new rationalization of earlier reports of an abnormal photoproduct derived from camphor. Under the experimental conditions chosen for the present work, however, this product was not detected. In diethyl ether, all three excited aldehydes (**7, 17,** and **25**) attack solvent to give α-hydroxy ethers, while in methanol partial conversion to dimethylacetals is observed.

We recently described an elementary, synthetic application of ketone photochemistry:[4] the *gas-phase* irradiation of bicyclo[2.1.1]hexan-2-one (**1**) to give bicyclo[1.1.1]pentane (**2**), along with 1,4-pentadiene (**3**).[5] We now wish to report on the *solution* photochemistry of **1**, and of the closely related bridged ketones norcamphor (**4**) and camphor (**5**).



1 **2** **3**



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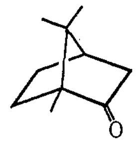

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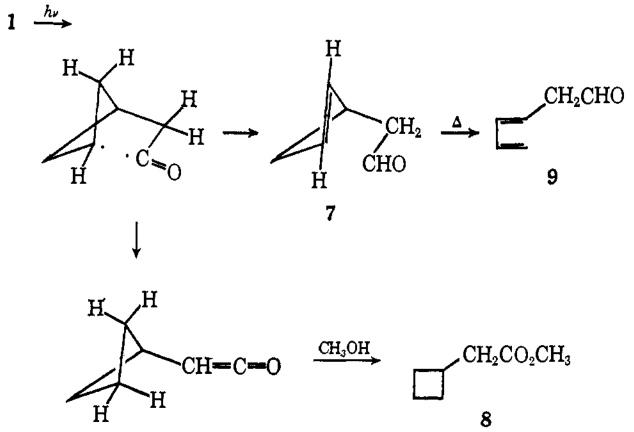
Bicyclo[2.1.1]hexan-2-one (1). In an exploratory experiment involving the irradiation of a dilute pentane solution of **1**, a product which appeared to be the isomeric unsaturated aldehyde **6** on the basis of infrared and nmr spectral evidence was isolated by preparative glpc. While one of the best known photochemical reactions of alicyclic ketones involves ring fission to give an acyl–alkyl diradical, followed by hydrogen atom transfer to give an unsaturated aldehyde (or ketene),[4,6] expectations for **1** based on this type of process, as outlined in Chart I, lead to **7** rather than to **6**. Since

6

Chart I



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[2] National Institutes of Health Special Postdoctoral Fellow, and Visiting Scholar at Stanford University, 1967–1968.

[3] Recipient of a National Research Council of Canada Scholarship, 1965–1967.

[4] For comprehensive reviews, see (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966; (c) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966; (d) D. O. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967.

[5] J. Meinwald, W. Szkrybalo, and D. R. Dimmel, *Tetrahedron Letters*, 731 (1967).

[6] For leading references, see J. Meinwald, R. A. Schneider, and A. F. Thomas, *J. Am. Chem. Soc.*, **89**, 70 (1967); G. Quinkert, *Angew. Chem.*, 77, 229 (1965).