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The Kinetics of the Hydrolysis of Trimethylene Oxide in Water, Deuterium Oxide and 40% Aqueous Dioxane[1]

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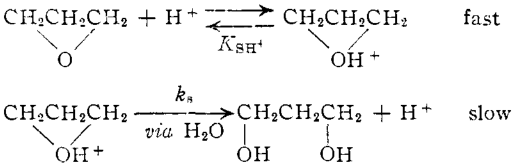
The rate-ratio for hydrolysis of trimethylene oxide in 1.5 *M* deuterosulfuric and sulfuric acids is $k^D/k^H = 2.2$. The rates of hydrolysis in solutions of from 0.4 to 3 *M* perchloric acid in both water and 40% aqueous dioxane are proportional to the h_0 acidity function in each solvent, the slopes of log k_1 *vs.* $-H_0$ plots being 1.00 and 0.80, respectively. These facts support an acid-catalyzed hydrolysis mechanism characterized by a preliminary equilibrium between trimethylene oxide and hydronium ion to form the conjugate acid followed by a rate-determining rearrangement of this species to give a highly reactive carbonium ion. Base-catalyzed and neutral hydrolysis reactions of trimethylene oxide are extremely slow.

Introduction

The hydrolysis of trimethylene oxide by aqueous acids to give propane-1,3-diol has been known for some time,[2] and it is usually assumed[3,4] that the reaction occurs by way of equilibrium formation of the conjugate acid of trimethylene oxide in a manner analogous to epoxide hydrolysis, as in equations 1 and 2. For aqueous solutions so dilute that activity coefficients are all equal to unity, equation 3 gives complete rate expressions for the above mechanism: k_s, k_1, k_{H^+} and K_{SH^+} are, respectively, the rate constant for the rate-determining step, the observed first-order rate coefficient, the second-order rate coefficient and the equilibrium constant for the dissociation of the conjugate acid of trimethylene oxide.



$$\underset{\diagdown\ \diagup\atop O}{CH_2CH_2CH_2} + H^+ \underset{K_{SH^+}}{\rightleftharpoons} \underset{\diagdown\ \diagup\atop OH^+}{CH_2CH_2CH_2} \qquad \text{fast} \qquad (1)$$

$$\underset{\diagdown\ \diagup\atop OH^+}{CH_2CH_2CH_2} \xrightarrow[\text{via } H_2O]{k_s} \underset{|\atop OH}{CH_2}CH_2\underset{|\atop OH}{CH_2} + H^+ \qquad \text{slow} \qquad (2)$$

$$-dC_{Oxide}/dt = k_1C_{Oxide} = k_{H^+}C_{H^+}C_{Oxide} = k_sK^{-1}_{SH^+}C_{H^+}C_{Oxide} \quad (3)$$

A well-known method for diagnosing reaction mechanisms which involve a preliminary equilibrium proton transfer consists in the determination of relative rates of reaction in deuterium oxide and in water, k^D/k^H. Values of this ratio of from 1.2 to 2.6 are found for various reactions with mechanisms similar to that in equations 1 and 2.[5-7] It has been shown previously that the values of k^D/k^H tend to fall in the higher range 1.9 to 2.6 for several acid-catalyzed reactions with a transition state to which the solvent molecules do not make a major contribution as a nucleophilic reagent. For these cases, the difference in k_s for the rate-determining reaction in deuterium oxide and water is presumably small, and the observed change in k_1 (and k_{H^+}) is due almost entirely to a change in K_{SH^+}.[8] In contrast, acid-catalyzed reactions having a transition state similar to that for hydrolysis of simple esters, in which a water molecule plays an active part as a nucleophilic reagent, are characterized by smaller k^D/k^H values, in the range 1.3 to 1.7. For these cases, K_{SH^+}/K_{SD^+} is still expected to be in the range 1.9 to 2.6[8] implying that the ratio of k_s values for the rate-determining step in deuterium oxide and water is considerably less than unity. These considerations suggest that the determination of a rate-ratio for reaction in deuterium oxide and water can give evidence on both steps 1 and 2 of the mechanism.

Another well-known criterion for mechanism classification is based on correlation of the acid-catalyzed reaction rate and the h_0 acidity function.[9] To establish such a correlation for trimethylene oxide, we have examined the kinetics of the hydrolysis in water and in 40% aqueous dioxane using widely varying concentrations of perchloric acid as catalyst. The availability of h_0 values for solutions

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[1] Work supported by a grant from the Atomic Energy Commission.

[2] L. Smith, G. Wode and T. Widhe, *Z. physik. Chem.*, **130**, 154 (1927).

[3] S. Searles, THIS JOURNAL, **73**, 4515 (1951).

[4] F. A. Long, J. G. Pritchard and F. E. Stafford, *ibid.*, **79**, 2362 (1957).

[5] R. P. Bell, "Acid–Base Catalysis," Oxford University Press, London, 1941.

[6] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[7] J. G. Pritchard and F. A. Long, THIS JOURNAL, **78**, 6008 (1956).

[8] The conjugate acids of trimethylene oxide, ethylene oxide, esters and related "oxygen bases" are normally very strong acids with pK_{SH^+} values in the range 0 to −14 since they are almost completely dissociated in dilute mineral acid solution. K_{SH^+}/K_{SD^+} ratios in the range 1.9 to 2.6 may be expected for these conjugate acids from the considerations below.

Equilibrium studies on phenols and carboxylic acids with pK_{SH^+} values in the range +12 to +2 give values of K_{SH^+}/K_{SD^+} in the range 4.3 to 2.7; see R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953, p. 154. The K_{SH^+}/K_{SD^+} ratios show a distinct trend toward lower values for lower pK_{SH^+}; and for a given small pK_{SH^+} region the K_{SH^+}/K_{SD^+} ratios are closely similar for the carboxylic acids and for the phenols although these two chemical types are rather different. An extrapolation of these data into the pK_{SH^+} range 0 to −14 leads to the expectation of K_{SH^+}/K_{SD^+} ratios in the range *ca.* 2.6 to 1.9. One example of direct experimental confirmation of this proposal is known to the authors. Thus, mesitaldehyde, a strong proton acceptor in *ca.* 70% sulfuric acid, has $pK_{SH^+} = -5.3$ and gives $K_{SH^+}/K_{SD^+} = 2.3$; see W. M. Schubert and H. Burkett, THIS JOURNAL, **78**, 66 (1956). These workers actually expressed their observed concentration ratios for mesitaldehyde and its conjugate acid in terms of a difference in the acidity function for the same stoichiometric concentrations of deuterosulfuric and sulfuric acids, thus

$$H_{0D_2SO_4} - H_{0H_2SO_4} = \log (C_S/C_{SD^+})/(C_S/C_{SH^+}) = ca.\ -0.36$$

However, from the definition of the acidity function, $H_0 = pK_{SH^+} + \log C_S/C_{SH^+}$, this difference may equally well be regarded as a change in pK_{SH^+}, so that for mesitaldehyde $K_{SH^+}/K_{SD^+} = \text{antilog } 0.36 = 2.3$. We prefer this latter interpretation since the H_0 function in deuterium oxide is most naturally defined as $H_0^D = pK_{SD^+} + \log C_S/C_{SD^+}$ so that for very dilute mineral acid solutions $H_0^D = -\log C_{D^+}$, just as for ordinary water. Accepting this definition, the H_0 scales in water and in deuterium oxide can only separate in more concentrated solutions of acid as a result of different behavior of the indicators in the stepwise procedure used to determine their pK values.[11] Since the ratio K_{SH^+}/K_{SD^+} for the Hammett-type indicators should vary only slightly for quite large changes in K_{SH^+}, the H_0 scales in water and deuterium oxide should be approximately the same at medium to high acidities.

[9] *Cf.* F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957).

in aqueous dioxane[10] allows the examination of the relationship of h_0 to the reaction rate for wide variations in the nature of the reaction medium. A comparison of the H_0 values for perchloric acid solutions in water and 40% aqueous dioxane is shown in Fig. 1. In particular, this figure shows that the H_0 function in 40% aqueous dioxane deviates much more sharply from log C_{H^+} than does H_0 in water.

We have also made a search for possible base-catalyzed and neutral "water" reactions of trimethylene oxide to make a more complete comparison with ethylene oxide which is known to show these reactions.[11]

Experimental

Materials.—For the preparation of trimethylene oxide commercial trimethylene glycol was purified by fractionation, giving an almost colorless product: b.p. 94-96° (5 mm.), n^{21}_{D} 1.4418. This material was converted by reaction with acetic anhydride and sulfur monochloride[12] to γ-chloropropyl acetate: b.p. 64.5-65° (14 mm.), n^{10}_{D} 1.4350. The 170 g. of γ-chloropropyl acetate was added dropwise to a stirred mixture of 365 g. of potassium hydroxide pellets plus 25 g. of water, at *ca.* 130°.[13] The volatile distillate was collected in a receiver, cooled in ice, and then fractionated, giving 17 g. of **trimethylene oxide**: b.p. 47.0-47.2°, n^{25}_{D} 1.3920. The infrared spectrum of the product was almost identical with that recorded elsewhere for trimethylene oxide,[14] but showed traces of water.

Solutions of **deuterosulfuric acid** were prepared by distilling sulfur trioxide into deuterium oxide (99.5%).[15] **Dioxane** was purified by the method of de la Mare, Ketley and Vernon[16] and had m.p. 11.5°; it was stored in the dark at *ca.* −5°. A stock solution of 40% aqueous dioxane was prepared by mixing 6 volumes of pure dioxane with 4 volumes of water and the acid solutions were prepared freshly from this for each dilatometric run. Measured amounts of 70% perchloric acid plus 0.45 ml. of pure dioxane per gram of 70% acid were made up to volume with the stock 40% aqueous dioxane solution.

Dilatometry.—Each acid solution was thoroughly degassed under vacuum at 30° and brought to 0° in the mixing chamber of a dilatometer of usual design.[7] *Ca.* 0.2 ml. of cooled trimethylene oxide was then added and mixed giving *ca.* a 0.3 *M* solution which was transferred by compressed air to the working chamber of the dilatometer. After several minutes, volume readings were taken *vs.* time; k_1 was determined graphically using the Guggenheim procedure. At the conclusion of each run the dilatometer and its contents were allowed to warm up to room temperature and a sample of the reaction mixture was titrated with standard alkali solution to determine the acid concentration. Some typical data are shown in Table I for a 1.533 *M* solution of sulfuric acid in water at 0°. Values of v and v' represent two series of dilatometer readings, in arbitrary units, at measured time intervals. $k_1 = 2.303(-G) = 2.36 \times 10^{-4}$ sec.$^{-1}$, where G is the slope of the plot of log $(v - v')$ *vs.* time. The results of Table III indicate that the degree of reproducibility of such experiments was within about 1%.

TABLE I

Time, sec.	0	300	600	900	1200	1500	1800	2100
v	0	5.2	10.3	14.8	19.1	23.2	27.0	30.2
v'	74.3	74.6	74.8	74.9	75.0	75.2	75.4	75.7

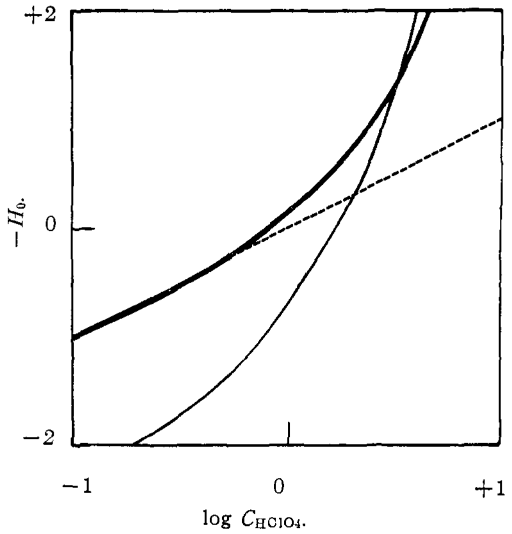

Fig. 1.—Comparison of H_0 for perchloric acid at 25° in water[19] and in 40% aqueous dioxane[10] with log $C_{\mathrm{HClO_4}}$. Heavy line = $H_0^{\mathrm{aq.}}$, light line = $H_0^{\mathrm{aq.-d.}}$; dashed line = log $C_{\mathrm{HClO_4}}$.

A dilatometric technique also was used to search for a base-catalyzed reaction. The rate of travel of the dilatometer meniscus $(-\mathrm{d}v_0/\mathrm{d}t)$ was observed over periods of about 10 days at 35° for solutions of trimethylene oxide in (a) dilute aqueous perchloric acid at *p*H 4, (b) a very dilute phosphate buffer at *p*H 7.5, (c) 0.5 *M* and (d) 5 *M* sodium hydroxide solutions. The observed values of $-\mathrm{d}v_0/\mathrm{d}t$ were *ca.* 2×10^{-6} cm./sec. for cases a and b, and *ca.* 3 and 5×10^{-6} cm./sec. for cases c and d. However, the rate of evaporation of water from the meniscus in blank runs was *ca.* 2×10^{-6} cm./sec., so that the experiments signify that there is probably no measurable neutral reaction with water and that only a very slow base-catalyzed reaction exists at 35°. In the acid-catalyzed reaction of similar concentrations of trimethylene oxide as were used in the above experiments, the meniscus travel for 100% reaction was *ca.* $(v_\infty - v_0) = 10$ cm. Hence assuming the initial-rate equation $-\mathrm{d}v_0/\mathrm{d}t = k_{\mathrm{OH}^-} C_{\mathrm{OH}^-} (v_\infty - v_0)$, the second-order rate coefficient for the base-catalyzed reaction may be estimated at *ca.* 10^{-7} l. mole^{-1} sec.$^{-1}$ for 35°. Some brief experiments using 0.5 *M* sodium hydroxide in sealed tubes showed the half-life of reaction of trimethylene oxide to be *ca.* 3×10^{5} sec. at 100°. Assuming an energy of activation of 20 kcal./mole the estimated value of k_{OH^-} for 35° is again in the order of 10^{-7} l. mole^{-1} sec.$^{-1}$. The matter was not pursued further.

Table II compares the rate coefficients for hydrolysis of trimethylene oxide with those for ethylene oxide; Table III compares rates of acid-catalyzed hydrolysis in the solvents H_2O and D_2O.

TABLE II

RATE COEFFICIENTS IN L. MOLE^{-1} SEC.$^{-1}$ FOR AQUEOUS HYDROLYSIS OF OXIDES AT 25°

Oxide	Acid-catalyzed $k_{\mathrm{H}^+} = k_1/C_{\mathrm{H}^+}$	Base-catalyzed $k_{\mathrm{OH}^-} = k_1/C_{\mathrm{OH}^-}$	Neutral $k_{\mathrm{H_2O}} = k_1/C_{\mathrm{H_2O}}$
Ethylene oxide[11,17,18]	9.86×10^{-3}	1.1×10^{-4}	1.0×10^{-8}
Trimethylene oxide[4]	1.57×10^{-3}	*ca.* 10^{-7}	Very, very small

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[10] C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt and C. A. Vernon, *J. Chem. Soc.*, 2327 (1957).

[11] *Cf.* F. A. Long and J. G. Pritchard, THIS JOURNAL, **78**, 2665 (1956).

[12] *Cf.* G. M. Bennett and F. Heathcoat, *J. Chem. Soc.*, 271 (1929).

[13] *Cf.* R. Lespieau, *Bull. soc. chim.*, **7**, 254 (1940); C. R. Noller, *Org. Syntheses*, **29**, 92 (1949); S. Searles, Jr., K. A. Pollart and F. Block, THIS JOURNAL, **79**, 952 (1957).

[14] G. M. Barrow and S. Searles, *ibid.*, **75**, 1175 (1953).

[15] The deuterium oxide was supplied by the Stuart Oxygen Co., by arrangement with the Atomic Energy Commission.

[16] P. B. D. de la Mare, A. D. Ketley and C. A. Vernon, *J. Chem. Soc.*, 1291 (1954).

[17] H. J. Lichtenstein and G. H. Twigg, *Trans. Faraday Soc.*, **44**, 905 (1948).

[18] A. M. Eastham and G. A. Latremouille, *Can. J. Research*, **30**, 169 (1952).

TABLE III

HYDROLYSIS OF TRIMETHYLENE OXIDE IN SOLUTIONS OF H_2SO_4 AND D_2SO_4 AT 0°

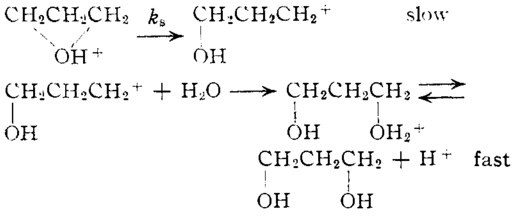
C_{SO_3} (M)	h_0 (in H_2O)[19]	$k_1 \times 10^4$ (sec.$^{-1}$) In H_2O	In D_2O
1.533		2.36	
1.540	3.55	2.37	
1.517			5.34
1.520	3.45		5.39

Discussion

Table III shows that the effect of replacing water by deuterium oxide as solvent in the acid-catalyzed hydrolysis of trimethylene oxide is an increase in reaction rate by a factor greater than 2. As noted below, in aqueous acid solutions more concentrated than *ca.* 1 *M*, the rate of trimethylene oxide hydrolysis is accurately proportional to h_0 (where $-H_0 = \log h_0$) rather than to C_{H^+}. Thus, in the general case, the relationships between the rate coefficient of equation 3 are given by

$$k_1 = k_{H^+}h_0 = k_s K_{SH^+}^{-1} h_0$$

It follows from the data of Table III that the first-order rate coefficient for a 1.52 *M* solution of sulfuric acid in ordinary water will be 2.37 × 10^{-4} × 3.4/3.5 sec.$^{-1}$. The ratio of first order coefficients in 1.52 *M* solutions of deuterosulfuric and sulfuric acids is then given by $k_1^D/k_1^H = (5.39/2.37)/(3.4/3.5) = 2.21 \pm$ *ca.* 0.1. This value is strong support for the proposed preliminary acid–base equilibrium of equation 1. Furthermore, the value lies in the upper part of the range 1.2 to 2.6 implying that k_0^D/k_0^H for the rate-determining step must be close to unity. From the introductory discussion this supports the proposal that the solvent does not enter significantly as a nucleophilic reagent in equation 2. We shall then consider it justifiable to divide equation 2 into what we will at first consider to be two separate steps, the first (2a) being in essence the rearrangement of an ion and the second (2b) the collapse of the ion by reaction with solvent



(2a)

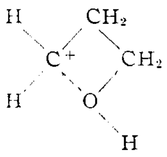
(2b)

Figure 2 shows the dependence of log k_1 for trimethylene oxide on the H_0 values of the reaction solutions. For both of the solvents the fit of the experimental points to straight lines is observed to be very good over the range of about two powers of ten in k_1 and H_0. The gradients of the lines for water and 40% aqueous dioxane are 1.00 and 0.80, respectively. A comparison of the widely differing $-H_0$ and log C_{H^+} functions for perchloric acid in both solvents (Fig. 1) with the results of Fig. 2 shows that log k_1 is in no way proportional to log C_{H^+} in the strongly acid media studied. Log k_1 is clearly closely proportional to $-H_0$.

The relationship between the experimental value of log k_1 and $-H_0$ is well known to be

$$\log k_1 = -H_0 + \log (f_S/f^*_{SH^+})/(f_B/f_{BH^+}) + \text{constant} \quad (4)$$

The symbol $f^*_{SH^+}$ represents the activity coefficient for the transition state in the acid-catalyzed hydrolysis and f_{BH^+} is the activity coefficient for the conjugate acid form of the Hammett indicator. All activity coefficients are referred to pure water as standard state ($f = 1$). The strict direct proportionality of log k_1 and $-H_0$ for aqueous perchloric acid requires that the activity coefficient term in equation 4 be very close to zero for this solvent. This can be so if $f_S/f^*_{SH^+} \backsimeq f_B/f_{BH^+}$ for the acid ranges studied, or if $f_S \backsimeq f_B$ and $f^*_{SH^+} \backsimeq f_{BH^+}$ separately. The latter equalities are probably true for aqueous solutions since it is known that the activity coefficients for neutral molecules of diverse types normally vary only slightly for quite large changes in concentration of mineral acids, including perchloric acid.[9,20] If $f_S \backsimeq f_B$, for the aqueous solutions it follows that $f^*_{SH^+} \backsimeq f_{BH^+}$ even though both $f^*_{SH^+}$ and f_{BH^+} must vary considerably with the large medium changes represented in Fig. 2. Following the Zucker–Hammett hypothesis,[21] such a result leads to the conclusion that the transition state for trimethylene oxide hydrolysis does not contain a water molecule, *i.e.*, that the transition state looks like structure I and not like structure II, allowing, of course, for solvation of an electrostatic nature for all species in solution.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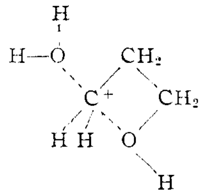
II

The proportionality of the hydrolysis rate for trimethylene oxide to h_0 for the 40% aqueous dioxane solvent system is very much like the behavior of sucrose in the same solvent and contrasts significantly with the behavior of ethyl acetate which shows a linear variation of log k_1 with log C_{H^+} in 40% aqueous dioxane for 0.6 to 1.7 *M* perchloric acid.[10] It is well accepted that the acid-catalyzed hydrolysis of ethyl acetate proceeds by an A-2 mechanism, *i.e.*, that water is strongly involved as a nucleophilic reagent. It is almost equally well accepted that sucrose hydrolyses by an A-1 mechanism in which water is not strongly involved.[9] The behavior of the above compounds in aqueous dioxane is thus consistent with the proposal that the transition state for the trimethylene oxide reaction is essentially independent of the nucleophilic activity of the solvent. We conclude that the results of the rate–h_0 studies in water and 40% aqueous dioxane are in agreement with the results of the study in deuterium oxide as solvent and provide additional evidence for the mechanism of equations 1, 2a and 2b for trimethylene oxide hydrolysis.

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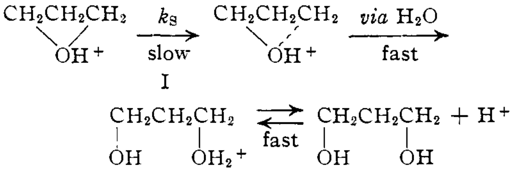
(19) Interpolated from the compilation of H_0 values for 25° by M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

(20) N. C. Deno and C. Perizzolo, THIS JOURNAL, **79**, 1345 (1957).

(21) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 275.

From two standpoints the agreement between the log k_1 *vs.* H_0 results for the solvents water and dioxane–water is not complete. One item is that the slope of the log k_1*vs.* $-H_0$ plot is substantially lower for the aqueous dioxane system, 0.8 as compared to 1.0. A decrease of this sort is not found for the sucrose hydrolysis[10] but is exhibited by the hydrolysis of paraformaldehyde in the solvent 75.6 mole % aqueous ethanol as compared to pure water.[22] A second point is that on an absolute H_0 basis the rate of the trimethylene oxide hydrolysis is about sixfold faster in the aqueous dioxane solvent relative to water (see Fig. 2). Very similar departures are shown by sucrose for this same pair of solvents and by paraformaldehyde for aqueous ethanol relative to water. These various results are evidence that the concept of H_0 acidity is less precise and less general for mixed solvents of low dielectric constant. However, they do not detract from the previous conclusions about the mechanism of the trimethylene oxide hydrolysis. On the contrary, one can argue that the similarity of behavior of this reaction in a mixed solvent to that of the sucrose and paraformaldehyde reactions constitutes good evidence for a similarity of mechanisms.

Nature of the Transition State.—The above results show that the acid-catalyzed hydrolysis of trimethylene oxide is very much like that of ethylene oxide, a fact anticipated from the knowledge that the entropies of activation for hydrolysis of the two compounds are very similar.[4] We may, therefore, discuss the acid-catalyzed hydrolysis of the two compounds under one head. For epoxide hydrolysis[4] it has already been suggested that it is unlikely that the reaction of the conjugate acid to give the final product proceeds in two separate steps (as in equations 2a and 2b) because of the extreme instability of primary, open carbonium ions. The collapse of the transition state by reaction with water molecules probably occurs immediately after the free energy maximum is attained in the opening of the oxide ring. Hence, the rate-determining step in oxide hydrolysis is best written as in equation 2c.



(2c)

Equations 1 and 2c together constitute a mechanism similar to the A-1 mechanism formulated by Day and Ingold[23] but a stable carbonium ion intermediate is excluded. Such a mechanism may be rationalized on the basis that in the strained oxide ring, given ionizing conditions, a carbon–oxygen bond does not have to stretch very far before a free energy maximum for the process of bond breaking is reached.[24] This follows from the greatly reduced carbon–oxygen–carbon bond angles in ethylene and trimethylene oxides, which are, respectively, 70 and 94°,[25] the normal angle in unstrained ethers being 111 ±4°.[26]

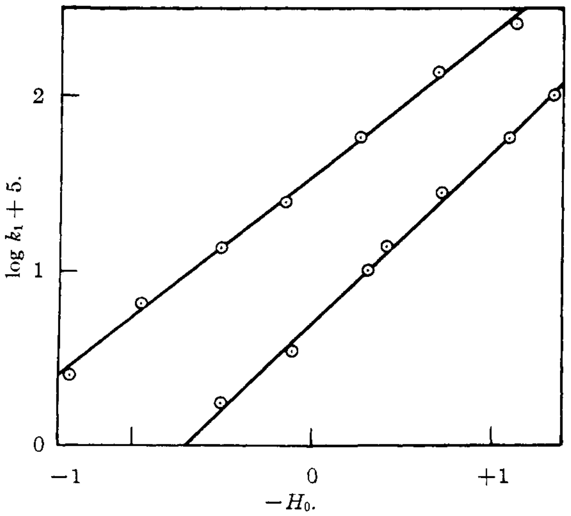


Fig. 2.—Log k_1 for perchloric acid-catalyzed hydrolysis of trimethylene oxide at 0° *vs.* H_0 in water[17] (lower plot) and *vs.* H_0 in 40% aqueous dioxane[10] (upper plot). All H_0 values are for 25° and are referred to infinite dilution in water as standard state.

From the relative degrees of strain in the two molecules, as indicated by the bond angles, it would be expected that trimethylene oxide would accommodate a proton more easily than ethylene oxide, particularly since the former has a larger electron availability in its larger carbon skeleton. Also, for the same reason the conjugate acid form of trimethylene oxide would be expected to be more stable with respect to bond-breaking than that of ethylene oxide. In fact, in aqueous acid solutions trimethylene oxide is almost certainly more basic than ethylene oxide,[3,27] and the energies of activation for the acid-catalyzed reactions, 20.7 kcal./mole for trimethylene oxide and 19.0 kcal./mole for ethylene oxide, are thus consistent with the conjugate acid of trimethylene oxide being considerably the more stable with respect to breaking of the ring.[4] This increased stability of the four-membered ring is also illustrated by the much slower rates of neutral and basic hydrolysis (Table II).

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[22] D. P. N. Satchell, *J. Chem. Soc.*, 3524 (1957).

[23] J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1942).

[24] S. Winstein, discussions, "George Fisher Baker Lectureship in Chemistry," Cornell University, Ithaca, N. Y., 1957.

[25] J. S. Allan and H. Hibbert, THIS JOURNAL, **56**, 1399 (1934).

[26] *Cf.* L. O. Brockway, *Rev. Modern Phys.*, **8**, 261 (1936).

[27] *Cf.* S. Searles and M. Tamres, THIS JOURNAL, **73**, 3704 (1951).