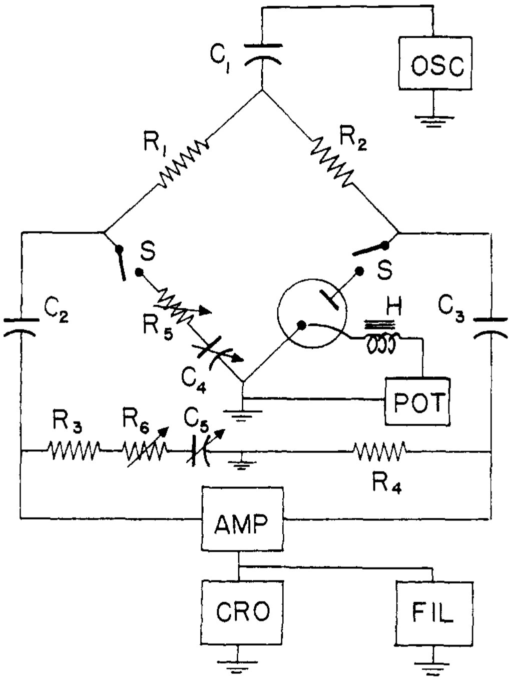

Fig. 7.—Bridge for differential capacity measurements.

The procedure was as follows: the voltage (peak voltage) applied to the bridge was set approximately at 5 mv. at 2000 c.p.s.; the earth compensation was first adjusted with R_6 and C_5 to achieve balance, switch S being open; the potential of the mercury drop was set with potentiometer POT, and S was closed; the bridge then was adjusted with R_5 and C_4. In general, results were precise within 0.1%.

Polarographic Measurements and Recording of Current-Time Curves.—Current-time curves were recorded by connecting a cathode-ray oscilloscope (Tektronix model 531 with preamplifier 53-54D) to a decade resistance box R in series with the cell. The ohmic drop in R did not exceed a few millivolts (Table I). Polarographic measurements followed conventional practice except for deaeration which was carried out by the procedure outlined in the previous section. Current-potential curves were recorded with a Sargent polarograph, Model XXI. The recorder of this instrument was replaced by a Brown recorder with fast response (1 sec. for full scale deflection).

Characteristics of capillary: for Fig. 4, m = 1.23 mg. sec.$^{-1}$, τ = 5.0 sec. (somewhat dependent on quinoline concentration) at −0.8 volt (*vs.* S.C.E.); for Fig. 6, m = 2.23 mg. sec.$^{-1}$ at −0.8 volt (*vs.* S.C.E.) for an uncorrected head of mercury of 81 cm.

Acknowledgment.—The investigation was begun with the support of the Humble Oil & Refining Company and was completed under the sponsorship of the Office of Naval Research. The generous help of these organizations is gladly acknowledged. Mr. Gleb Mamantov translated the Russian papers of reference 9 and discussed them in detail with us.

Added in proof.—Arrangements have been made with the Oak Ridge Institute of Nuclear Studies to carry out computer calculations for the complete isotherm for the plane electrode and the dropping mercury electrode.

Baton Rouge, Louisiana

[Contribution from the Department of Chemistry, Cornell University]

Entropies of Activation and Mechanism for the Acid-catalyzed Hydrolysis of Ethylene Oxide and its Derivatives[1]

By F. A. Long, J. G. Pritchard and Fred E. Stafford

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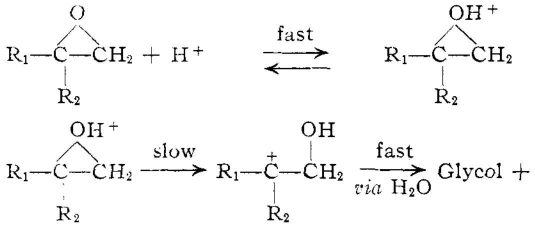
The rates of the acid-catalyzed hydrolysis of ethylene, propylene, isobutylene and trimethylene oxides have been measured at several temperatures and the energies and entropies of activation have been calculated. The close similarity in the entropy of activation values strongly suggests that all of the oxides hydrolyze by the same A-1 mechanism, which has been proposed previously for epoxides. A survey of entropies of activation for other acid-catalyzed hydrolysis reactions indicates that within similar classes of compounds the A-1 mechanism is generally associated with a much more positive entropy of activation than the A-2 mechanism.

Recent studies on the acid-catalyzed hydrolysis of epoxides have led to the conclusion that this reaction follows an A-1 mechanism in which the rate-determining step is the formation of a carbonium ion.[2-4] In the case of 1,1-disubstituted oxides, the evidence for the A-1 mechanism is sufficient to exclude all others. Thus: (a) the preliminary equilibrium step (1) is established[4] from rate studies in deuterium oxide; (b) the rate-determining spontaneous opening of the epoxide ring in step (2) is shown by the fact that the rates of reaction of several epoxides in strong aqueous solutions of perchloric acid show a good correlation[3] with the Hammett acidity function, h_0; (c) H_2O^{18} has been shown to enter the isobutylene oxide molecule in the tertiary position in accord with step (2)[2]; and (d) the reaction rate is significantly faster for epoxides having electron releasing substituent groups, R_1 and R_2, and slower for those with electron withdrawing groups. The same points of evidence have also been established for monosubstituted oxides (R_2 = H). However, for the symmetrical parent compound, ethylene oxide (R_1 = R_2 = H), only items (a) and (b) have been established since



(1)

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

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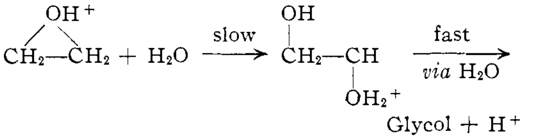
items (c) and (d) clearly have no application. Hence, the only significant evidence in favor of the formation of a primary carbonium ion during the acid-catalysed hydrolysis of ethylene oxide is the h_0 correlation.[3] (Actually, regarding (d), the rate for ethylene oxide does lie intermediate between the rates for monosubstituted oxides have electron withdrawing and electron releasing group substituents, respectively, as is *consistent* with a single mechanism.)

It is generally accepted that (other things being equal) the order of stability of carbonium ions of various structures is tertiary > secondary > primary, and very few examples of the latter are known. The presence of the hydroxyl group at the β-position with respect to the carbonium center in the primary ion derived from ethylene oxide, $CH_2OHCH_2^+$, should render it particularly unstable. Indeed, the existence of such an ion might well be doubted on this ground. It is therefore important to obtain additional evidence concerning the acid catalyzed hydrolysis of ethylene oxide to decide whether the A-1 mechanism, steps (1) and (2), or the alternative A-2 mechanism is operative. In the latter mechanisms, steps (1) and (3), no carbonium ion would be involved since the rate-determining step would be a simple nucleophilic attack of the solvent molecules on the conjugate acid of the oxide.



$$CH_2(O^+H)CH_2 + H_2O \xrightarrow{\text{slow}} CH_2(OH)\text{—}CH(OH_2^+) \xrightarrow[\textit{via } H_2O]{\text{fast}} \text{Glycol} + H^+ \quad (3)$$

The characteristic difference between the A-1 and the A-2 mechanisms is that the latter involves a specific water molecule in the transition state whereas the former does not. This difference should be reflected in a difference in the entropies of activation (ΔS^*) for the two mechanisms as discussed later. We have therefore measured ΔS^* values for the perchloric acid catalyzed hydrolysis of ethylene, propylene and isobutylene oxides in order to make a comparison for a primary, a secondary and a tertiary epoxide to see if any difference in mechanism is indicated. We have also determined a ΔS^* value for trimethylene oxide since, if it hydrolyzes by the A-1 mechanism,[5,6] this oxide should afford another example of a primary carbonium ion, $CH_2OH{\cdot}CH_2{\cdot}CH_2^+$, and should be of interest for comparison with the results for the epoxides.

Experimental

Rates were measured dilatometrically using the procedures previously described.[3] Chemicals were of reagent grade and all experiments were carried out in water-baths whose temperatures were controlled to ±0.01°. In the experiments with the very reactive isobutylene oxide, rate measurements were made at 0 and 25° using concentrations of perchloric acid varying between 10^{-2} and 10^{-5} molar, as determined with a standardized Beckman *p*H meter at the end of each dilatometric run. A value of k_{H^+} for $C_{H^+} = 10^{-3}$ molar at each temperature was then obtained by graphical interpolation. For each of the other three oxides, a single stock solution of aqueous perchloric acid was prepared, standardized at 25° and used for all the rate measurements, at temperatures ranging from *ca.* 0 to 40°. (Changes in acid concentrations caused by temperature changes were neglected.) The rate equation for these hydrolyses is $-dC_{\text{oxide}}/dt = k_1C_{\text{oxide}} = k_{H^+}C_{H^+}C_{\text{oxide}}$. First-order rate-coefficients (k_1) were calculated from the dilatometric data by the method of Guggenheim and were then converted to the second-order coefficients (k_{H^+}) recorded in Table I. The values of k_{H^+} shown are the mean values of at least four determinations for each oxide at each temperature. The results were reproducible to within ±2%.

TABLE I

MEAN VALUES OF SECOND-ORDER RATE COEFFICIENTS FOR PERCHLORIC ACID-CATALYZED HYDROLYSIS OF OXIDES

Oxide	Temp. (°C.)	C_{H^+} (*M*)	k_{H^+} (l. mole^{-1} sec.$^{-1}$)
Isobutylene	0.0	1.00×10^{-3}	3.80×10^{-1}
Isobutylene	25.0	1.00×10^{-3}	4.60
Propylene	1.0	1.97×10^{-2}	2.79×10^{-3}
Propylene	10.1	1.97×10^{-2}	8.46×10^{-3}
Propylene	30.0	1.97×10^{-2}	7.45×10^{-2}
Propylene	40.0	1.97×10^{-2}	1.99×10^{-1}
Ethylene	1.0	9.45×10^{-2}	5.79×10^{-4}
Ethylene	10.1	9.45×10^{-2}	1.84×10^{-3}
Ethylene	30.0	9.45×10^{-2}	1.69×10^{-2}
Ethylene	40.1	9.45×10^{-2}	4.36×10^{-2}
Trimethylene	1.0	7.02×10^{-1}	7.20×10^{-5}
Trimethylene	10.1	7.02×10^{-1}	2.42×10^{-4}
Trimethylene	30.0	7.02×10^{-1}	1.93×10^{-3}
Trimethylene	35.1	7.02×10^{-1}	4.72×10^{-3}
Trimethylene	40.1	7.02×10^{-1}	7.71×10^{-3}

Values of the Arrhenius energy of activation (*E*) were obtained in the usual fashion from the gradients of plots of log k_{H^+} *vs.* the reciprocal of the absolute temperature. In all cases, the data were well fitted by straight lines. Values of ΔS^* were calculated from the Eyring equation 4 where the logarithms are to the natural base "*e*" and the other symbols have their usual significance.

$$\ln k_{H^+} = \ln (ekT/h) + \Delta S^*/R - E/RT \qquad (4)$$

Our estimate is that the ΔS^* values are accurate to within ±1 e.u. except for isobutylene oxide where the accuracy may be two- or threefold less, since for this oxide rate measurements were recorded at only two temperatures. The values of ΔS^* recorded in both Tables II and III are for liter mole^{-1} sec.$^{-1}$ rate units.

Results and Discussion

In a discussion of the acid-catalyzed hydration of olefins Taft and co-workers[7,8] suggested that reaction by the A-1 mechanism should be characterized by a relatively more positive entropy of activation than reaction by the A-2 mechanism since the latter involves a relative increase of constraint on the reaction system in the transition state due to the orientation and reaction of a specific water molecule from the solvent. The work of Stimson[9] on the rates of acid-catalyzed hydrolysis of *t*-butyl esters is a good example of the application of this entropy criterion. Thus, the hydrolyses of *t*-butyl benzoate and *t*-butyl formate in acidified 60% acetone–water give ΔS^* values of +9.5 and −23.7 e.u., respectively, suggesting that the former hydrolysis proceeds by an A-1 mechanism and the latter by an A-2.

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

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TABLE II

VALUES OF ΔS^* AT 25° FOR SEVERAL A-1 AND A-2 ACID-CATALYZED HYDROLYSIS REACTIONS IN AQUEOUS SOLUTION

Substrate	Mechanism	ΔS^* (e.u.)
Ethyl orthoformate[10]	A-1[11]	+ 5.8
Sucrose[12]	A-1[11]	+ 7.9
Ethylal[13]	A-1[14]	+ 7.3
t-Butyl mesitoate[15]	A-1[15]	+ 9.
Methyl acetate[12]	A-2[16]	−21.3
Ethyl acetate[12]	A-2[16]	−23.0
γ-Valerolactone[17]	A-2[18]	−24.6
γ-Butyrolactone[17]	A-2[18]	−20.9

TABLE III

VALUES OF E AND ΔS^* AT 25° FOR ACID-CATALYZED HYDROLYSIS OF OXIDES

Oxide	$10^3 k_{H^+}$ at 25° (l. mole^{-1} sec.$^{-1}$)	E (kcal./mole)	ΔS^* (cal. mole^{-1} °C.$^{-1}$)
Isobutylene	4600	16.1	−4
Propylene	44.7	18.62	−4.3
Ethylene	9.86	18.99	−6.1
Trimethylene	1.57	20.73	−3.9

To find further examples of this ΔS^*-mechanism relationship, we have calculated ΔS^* values from available data for several acid-catalyzed reactions for which the mechanisms are quite well known. Table II shows that these ΔS^* values fall into two distinct groups separated by some 25 to 30 entropy units, corresponding to the two types of mechanism. The criterion that A-1 and A-2 reactions within the same class of compounds should be characterized by a difference in ΔS^* amounting to from 20 to 30 entropy units therefore appears to be quite general.

The results of the ΔS^* measurements for oxides are given in Table III which includes the appropriate rate and Arrhenius energy of activation data. It is evident that the large variations in hydrolysis rates for these oxides are almost entirely due to changes in the energy of activation and that the values of ΔS^* are almost constant. The observed values of E for the epoxides are in the order expected from a consideration of the stability of both the conjugate acids and the carbonium ions derived from the epoxides. Also, the less strained ring of trimethylene oxide would be expected to require a larger activation energy for opening than the epoxides.

The observed close similarity of the ΔS^* values in Table III provides strong evidence that the mechanism of reaction for all of the oxides is the same. By the argument of the previous paragraphs, the ΔS^* values for the primary oxides would be at least 20 entropy units lower than those for the substituted oxides if there were a change of mechanism from A-1 to A-2. This is clearly not the case. Therefore, since the A-1 mechanism is quite well established for the substituted oxides, we conclude that this same mechanism almost certainly holds for ethylene oxide and for trimethylene oxide.

While the ΔS^* values for the epoxides are closer to the absolute values for the A-1 rather than for the A-2 reactions of Table II, the fact that the values for epoxides are intermediate requires some comment. This may be due to a uniquely higher degree of solvation of the conjugate acids or the transition states in the case of the epoxides, or it may be that in A-1 hydrolyses the restriction of rotation about the breaking bond in the transition state for a cyclic structure leads to a more negative entropy change compared to linear structures. However, further study on this is required.

In view of the great instability of the carbonium ion derived from ethylene oxide, it is probable that the union of a water molecule from the solvation shell with a carbon atom of the epoxide ring, forming a covalent bond, occurs almost immediately after the conjugate acid has reached its free energy maximum in the breaking of one of the carbon-oxygen bonds in the ethylene oxide ring. Some realization of the relative stability of carbonium ions derived from the substituted epoxides of Table III may be obtained from the results of previous hydrolysis studies.[2] Thus, the glycol isolated from the A-1 hydrolysis of propylene oxide in water labeled with H_2O^{18} contained $CH_3{\cdot}CHO^{18}H{\cdot}CH_2OH$ and $CH_3{\cdot}CHOH{\cdot}CH_2O^{18}H$ molecules in a ratio close to 2:1. This result strongly suggests that the conjugate acid of propylene oxide yields the unstable ions $CH_3{\cdot}C^+H{\cdot}CH_2OH$ and $CH_3{\cdot}CHOH{\cdot}CH_2^+$ in this same ratio. Also, the A-1 hydrolysis of isobutylene oxide under similar conditions yielded a product labeled only in the tertiary position, $(CH_3)_2CO^{18}H{\cdot}CH_2OH$, showing that the tertiary ion is preferred in this structure to an extent excluding the primary.

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