tography for the isomer distribution. Determination C: In this experiment the same quantities were employed, the bromine was added dropwise to the solution. The analytical sample was obtained as described.

Gas Chromatographic Analysis.—Several attempts were made to achieve a resolution of the *o*- and *p*- isomers. It was found that liquid phases of tricresyl phosphate and Ucon polar showed considerable promise; Apiezon and various silicone fluids were unsatisfactory. For convenience, Ucon polar was selected for further work. The conditions adopted for analysis were a 7-m. column packed with Ucon polar (30%) on 30–60 mesh firebrick operated at 160° with a flow of 100 ml. of He min.^{-1} measured at the outlet. Under these conditions the retention times were *p*-bromoanisole 128 min., *o*-bromoanisole 137 min. Resolution was not complete, but the degree of separation was more than satisfactory for this analysis. The integrated areas were employed to calculate the percentage area. A small correction factor, 0.84, was necessary to convert the observed % area to mole % *ortho*. The results are summarized in Table III.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

The Acid-catalyzed Ring Opening of Epichlorohydrin

BY HAROLD KWART AND A. L. GOODMAN[1]

RECEIVED AUGUST 28, 1959

The A-1 solvolysis mechanism for ring opening of epichlorohydrin, suggested by Long and Pritchard[2] on the basis of the observed h_0 dependence of the rate, has been re-examined here by means of other kinetic criteria.[7] The results obtained here, as well as other considerations, would appear to indicate that the earlier mechanism requires some modification.

The acid-catalyzed ring opening reactions of epoxides and trimethylene oxides have been extensively investigated by Long and Pritchard and their co-workers.[2] These authors have presented various lines of evidence that appear to permit a clear choice between the A-1 and A-2 modes among the possibilities for ring opening mechanisms discussed by Ingold.[3] Thus, by the use of the isotopic oxygen tracer, isobutylene and propylene oxide have been shown[2a] to observe predominantly the A-1 (carbonium ion) mechanism. The same conclusion was reached with regard to the mechanism of acid-catalyzed ring opening of ethylene and trimethylene oxides on the basis of similarity in the activation parameters to the case of isobutylene oxide[2c] and the observation of a linear, approximately unit slope, h_0 correlation when applying the Zucker–Hammett hypothesis.[4] Other criteria such as the magnitude of the k_D/k_H ratio also gave results which appear to agree with these conclusions.[2d,e]

These workers also reached the decision[2b] that epihalohydrins and glycidols underwent acid-catalyzed ring opening by a clear A-1 mechanism when they demonstrated a linear plot of log k_1^+ *vs.* $-H_0$ with a slope of 0.87. This suggestion by Long and Pritchard has been accepted as a basis for interpreting the acid-catalyzed ring opening of oxides with other polar substituents; *e.g.*, glycidic esters.[5] Some doubt, however, arises as to the validity of this mechanistic deduction based solely on the application of the familiar Zucker–Hammett hypothesis,[4] in view of several demonstrations[6] of contradictions therein.

In these laboratories we have recently illustrated how a more reliable criterion[7] of the carbonium ion mechanism may be established by an examination of the rate dependence on both solvent composition and acidity. We are reporting here the application of this criterion to review the mechanism of epichlorohydrin solvolysis in a range of acidic water–ethanol solutions.

Experimental

All reagents used were Eastman Kodak Co, white label grade. **Epichlorohydrin** was distilled through a helix-packed column at atmospheric pressure prior to use; only the fraction boiling between 116–117° was utilized in the rate studies. ***p*-Nitroaniline** was recrystallized from absolute ethanol just before use in the colorimetric measurements and the **nitrobenzene** was used only immediately after distillation under vacuum through a 10″ Vigreux column.

The rate measurements were carried out by means of a dilatometric technique and the rates computed from Guggenheim plots in exactly the fashion described by Pritchard and Long.[2b] However, though the dilatometer we actually used was of somewhat different construction, the results so obtained could be roughly checked aginst the data previously reported[2b,8] on the reaction in pure water. All measurements were taken at 30.02 ± 0.01°. The acidic aqueous ethanol solutions were composed by weighing into a 200-ml. volumetric flask the required amount of absolute ethanol which had previously been purified and dried over magnesium in the manner described by Vogel.[9] The calculated amount of sulfuric acid was then added carefully and the flask made up to the mark with distilled water. The acidic aqueous ethanol solutions prepared in this manner were brought to the reaction temperature in one compartment of the dilatometer while a second compartment containing the calculated amount of epichlorohydrin reagent was being thermostated. Means were available in the design of the dilatometer for rapidly uniting the contents of the two compartments and then rapidly filling the capillary section

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[1] Part of the work being reported here has been taken from the honors paper submitted by A. L. Goodman in partial fulfillment of the requirements for the degree of Bachelor of Science with Distinction in Chemistry at the University of Delaware, June, 1959.

[2] (a) F. A. Long and J. G. Pritchard, THIS JOURNAL, **78**, 2663 (1956); (b) J. G. Pritchard and F. A. Long, *ibid.*, **78**, 2667 (1956); (c) F. A. Long, J. G. Pritchard and F. E. Stafford, *ibid.*, **79**, 2362 (1957); (d) J. G. Pritchard and F. A. Long, *ibid.*, **78**, 6008 (1956); (e) **80**, 4162 (1958).

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 341 ff.

[4] L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2791 (1939).

[5] J. A. Durden, Jr., H. Am. Stansbury, Jr., and W. H. Catlette, *ibid.*, **81**, 1943 (1959).

[6] "Annual Review of Physical Chemistry," Section by N. Deno, H, Eyring, Editor, Palo Alto, Calif., 1958, p. 303 ff. However, see M, Paul and F. A. Long, *Chem. Revs.*, **57**, 935 (1957), and F. A. Long, *Proc. Chem. Soc.*, 220 (1957), for further discussion of these points.

[7] H. Kwart and L. B. Weisfield, THIS JOURNAL, **80**, 4670 (1958).

[8] A full description of the design and the range of application of this instrument will be discussed in a forthcoming publication from these laboratories.

[9] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1956, p. 166.

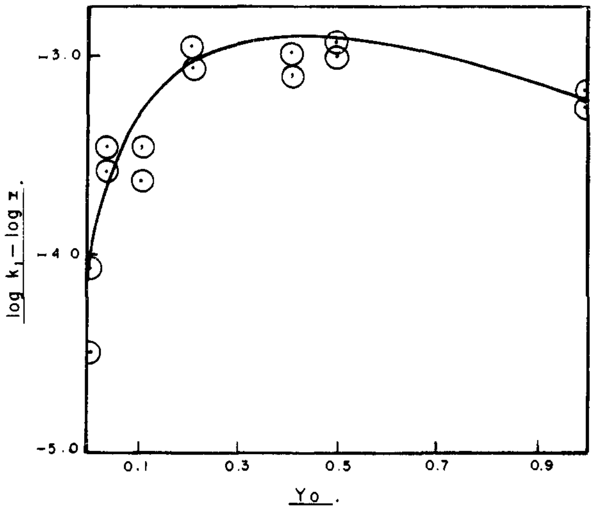


Fig. 1.—Acidity function plot for catalyzed solvolysis.

(therefrom) just prior to observation of the meniscus level with a cathetometer about 2 yards distant from the bath.

The indicator measurements were made by first weighing the required amount of purified, absolute ethanol into a 50-ml. volumetric flask, adding 0.5 ml. of a 4.0 × 10^{-3} M solution of the indicator followed by the calculated weight of sulfuric acid before diluting to the mark with distilled water. All solutions were checked by titration with standard base. The colorimetric determinations[10] were carried out on a Process and Instruments RS-3 recording spectrophotometer[11] and the conjugate acid to base ratio, I, was computed from the relationship

$$I = \frac{C_{BH^+}}{C_B} = \frac{\epsilon_N - \epsilon_A}{\epsilon_A - \epsilon_S}$$

where the symbols have their usual significance.[7,10]

Results and Discussion

The earlier exposition[7] has confirmed that the Gutbezahl–Grunwald[12] empirical measure of hydrogen ion activity in various ethanol–water solvent compositions may be employed as a kinetic criterion. If the reaction has an A-1 mechanism it will follow the equation

$$\log k_1 - \log I = MY_0 + C$$

where M and C are constants and Y_0 is a function only of solvent composition and a plot of the total term on the left side of the equation *versus* a range of Y_0 values should be a good straight line.

As can be seen in the accompanying graph which is a plot of the data computed and listed in Table IIC, the line for epichlorohydrin solvolysis is more nearly parabolic. This curve is similar to that obtained for the acid-catalyzed solvolysis of phenyl acetate,[7] a reaction of known A-2 character. This result would imply, therefore, that a solvent molecule or other nucleophile is involved in the ring opening activation step along with the conjugate acid of the epichlorohydrin.

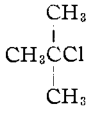
TABLE I

DATA FOR COMPUTATION OF I-VALUES[a]

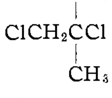
Wt. % ethanol	*p*-Nitroaniline Normality	*p*-Nitroaniline Opt. density	Nitrobenzene Normality	Nitrobenzene Opt. density
0.00	0.000	0.444	1.383	0.004
	1.361	.032	1.544	.004
	1.542	.027	1.656	.002
	1.637	.018	1.815	.004
	1.802	.018	1.967	.002
	1.829	.016		
15.80	0.000	0.438	All optical density values here were essentially zero over the range of acidities listed	
	1.363	.071		
	1.531	.076		
	1.649	.077		
	1.811	.041		
	1.941	.036		
30.35	0.000	0.557	1.331	0.009
	1.213	.191	1.440	.011
	1.364	.170	1.464	.011
	1.535	.165	1.596	.013
	1.621	.152	1.613	.019
	1.733	.139		
45.57	0.000	0.403	1.349	0.007
	1.314	.272	1.473	.000
	1.528	.237	1.508	.000
	1.632	.233	1.600	.000
	1.704	.208	1.707	.004
	1.938	.184		
60.52	0.000	0.543	1.150	0.000
	1.233	.339	1.358	.001
	1.386	.303	1.534	.003
	1.464	.301	1.620	.000
	1.710	.255	1.618	.003
	1.736	.246		
75.53	0.000	0.538	All optical density values here were essentially zero over the range of acidities	
	1.314	.319		
	1.473	.301		
	1.646	.260		
	1.750	.242		
	1.915	.215		
100.00	0.000	0.515	1.012	0.006
	1.068	.076	1.183	.005
	1.187	.066	1.332	.004
	1.269	.066	1.467	.003
	1.354	.058	1.523	.001
	1.510	.056		

[a] All colorimetric measurements were made at 385 mμ. The normalities listed are those determined by titration of the sulfuric acid solutions with standard NaOH solution.

It is perhaps not surprising that substitution of halogen on the methyl group in propylene oxide should have the effect of enhancing the A-2 nature of the reaction. Cases of a mechanistic transition of this character accompanying such a structural change are widely recorded. As a typical example, when the tertiary halogen atoms of I and II are hydrolyzed under conditions favoring the "carbonium ion" reaction, the rate of hydrolysis of I is about 4000 times that of II.[12] Clearly, the halogen



$(CH_3)_3CCl$ I



$ClCH_2C(CH_3)_2Cl$ II

substitution has acted powerfully to suppress ionization at the neighboring carbon center; inferentially, by reducing the carbonium ion stability.

The fact that III is by far the predominant product of acid-catalyzed alcoholysis of epichlorohy-

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(10) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1982 (1948).

(11) This instrument possesses a highly accurate density scale and a photomultiplier detector arrangement of high sensitivity; Process and Instruments Co., 15 Stone Ave., Brooklyn 33, N. Y.

(12) H. C. Brown, M. S. Kharasch and T. H. Chao, THIS JOURNAL, **62**, 3438 (1940).

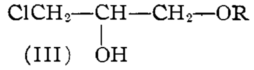
TABLE II

DATA COMPUTED FOR ACIDITY FUNCTION PLOT

Ethanol (wt. %)	H_2SO_4 (eq./l.)	10^3k_1	$-\log k_1$	ϵ_N[a]	ϵ_A[a]	ϵ_S[a]	I	$\log I$	$-Y_0$[13]	$\log k_1 - \log I$
0.00	1.43	1.41	2.851	11,100	740	87.4	15.87	1.201	0.00	−4.052
	1.93	1.53	2.815	11,100	310	87.4	48.47	1.685	.00	−4.500
15.80	1.40	1.09	2.962	10,950	2100	0.0	4.21	0.624	.04	−3.586
	1.63	1.81	2.742	10,950	1700	0.0	5.44	.736	.04	−3.478
30.35	1.58	1.07	2.971	13,900	3700	470.0	3.16	.500	.11	−3.471
	1.92	1.18	2.928	13,900	2800	670.0	5.21	.717	.11	−3.645
45.57	1.46	0.68	3.167	10,075	6200	58.3	0.631	− .200	.21	−2.967
	1.89	.96	3.018	10,075	4720	58.3	1.15	.061	.21	−3.079
60.52	1.26	.60	3.222	13,600	8300	58.3	0.643	− .192	.33	−3.030
	1.87	1.08	2.967	13,600	5650	58.3	1.42	.152	.33	−3.119
75.53	1.20	0.61	3.215	13,450	8450	0.0	0.592	− .288	.50	−2.987
	1.57	1.04	2.983	13,450	6900	0.0	0.949	− .033	.50	−2.950
100.00	1.12	3.41	2.466	11,000	1800	138.0	5.60	.748	1.00	−3.214
	1.51	4.71	2.327	11,000	1300	48.0	7.83	.894	1.00	−3.221

[a] Values obtained through interpolation of optical density measurements.

drin[14] may also be taken to support the A-2 mech-

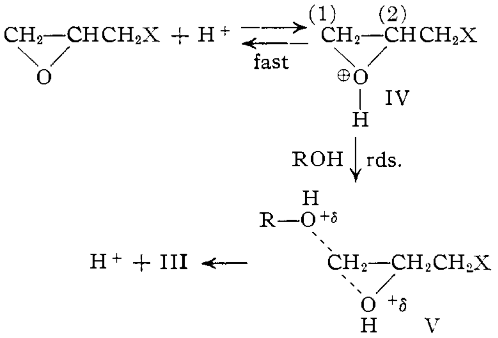


$$ClCH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}OR$$

(III)

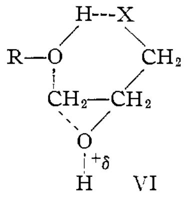
anism where the product-forming step and rate-determining step are identical. In the idealized case we would surely have expected bond making to occur less readily at C_2 if the nucleophilic involvement of the solvent molecule[15] were very large and constituted the dominant driving force of the reaction of the conjugate acid of the epichlorohydrin IV. This expectation is based on data[16] which indicate that the polar chlorine atom reduces the susceptibility of the β-carbon (C_2) to nucleophilic attack by about a factor of seven. In other words product III should predominate in both the A-2 and A-1 mechanisms of acid-catalyzed ring opening.

Ordinarily, we might have expected some favor for formation of a C_2 substitution product in view of the possibilities for anchimeric assistance by neighboring chlorine,[17] analogous to the formation of an intermediate chloronium ion in the reactions of 3-chloro-2-butanol with thionyl chloride[18] and in the reaction of stilbene dichloride with silver acetate.[19] Therefore, in view of the composition of the product and in view of the multiplicity of possible bond breaking modes at C_2 in the conjugate acid IV that do not occur, it may be assumed that solvent bonding at the primary carbon (C_1) in the transition states must be considerable. The following representation of the course of reaction consequently seems most consistent with the existing evidence. It must be admitted, also, that V



transition state

may only be a simplification of the actual (N)[15] character of the transition state. For instance, it is possible that the difference in rate observed when X is changed from Cl to Br or OH may be due to some assistance for the approaching ROH by hydrogen bonding to X in the cyclic transition state VI.



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(13) B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 565 (1953).

(14) (a) A. Fairbourre, G. P. Gibson and D. W. Stephens, *J. Chem. Soc.*, 1965 (1932); (b) S. Winstein and L. Goodman, THIS JOURNAL, **76**, 4368 (1954).

(15) S. Winstein, D. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951), present a full discussion of the various kinds of solvent interaction with substrate in the reaction transition state. We have in mind for the idealized case referred to above, the (N) classification used by these authors.

(16) J. Hine and W. H. Brader, Jr., *ibid.*, **75**, 3964 (1953).

(17) See ref. 14 for a full exposition of this and related questions.

(18) H. J. Lucas and C. W. Gould, Jr., THIS JOURNAL, **63**, 2541 (1941).

(19) S. Winstein and D. Seymour, *ibid.*, **68**, 119 (1946).