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KINETIC STUDIES ON ETHYLENE OXIDES

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A. Introduction

The ethylene oxides form a group of compounds which is of great interest from the standpoint of both organic and physical chemistry. Their exceptional reactivity in solution already at ordinary temperature offers an inviting field for multifarious kinetic investigations. The "basicity" of these compounds in particular is a striking phenomenon, the mechanism of which does not seem as yet to have been fully understood.

In textbooks of organic chemistry the ethylene oxides are sometimes referred to as "pseudo bases." It is generally recognized that they cannot be classed as bases in the usual sense of this word owing to their lack of electric conductivity in pure aqueous solution. It also seems to be a general opinion that "basicity" of the substances is explicable from their tendency to unite with acids. The precipitation of insoluble metallic hydroxides, *e. g.*, ferric hydroxide, from solutions of the corresponding salts is then looked upon as due to reactions with the acid made free by "hydrolysis."

It will be shown in the present paper that this addition of acids exhibited by the ethylene oxides is kinetically only to a minor extent the reason for their apparent basicity. Regardless of this fact, however, it should be realized that the ability of a substance to add an acid is by no means a feature characteristic of bases. Bases are characterized by adding protons. Taking up the whole of an acid molecule is something quite different from the basic function; it depends upon the anion of the acid in an individual manner and need not have any relation to the strength of the acid added. For instance, the strongest of all electrically neutral acids, perchloric acid, does not react with ethylene oxides in the same way as do the hydrohalogenic acids, although in this group the addition velocity increases with the strength.

Hantzsch[1] was the first to study the reaction between ethylene oxides and acids from a physico-chemical standpoint. He found by conductivity measurements that hydrochloric acid is taken up by ethylene oxide with a considerable velocity, but the reaction came to a standstill long before all of the acid or oxide had disappeared. He did not give any explanation of the incompleteness of the reaction. However, at the same time Henry[2] showed that the oxides in the presence of acids take up water to form

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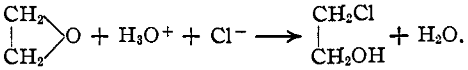
[1] Hantzsch and Hibbert, *Ber.*, **40**, 1514 (1907).

[2] Henry, *Compt. rend.*, **144**, 1404 (1907).

glycols. The part of the oxide reacting in this way is of course prevented from combining with the hydrochloric acid and this easily explains the result of Hantzsch.

The most obvious manner in which hydrochloric acid in dilute aqueous solution may react with ethylene oxide is kinetically as follows



$$(CH_2)_2O + H_3O^+ + Cl^- \longrightarrow CH_2Cl{-}CH_2OH + H_2O.$$

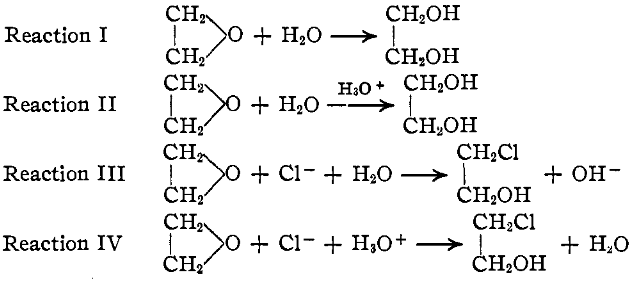
As it stands it presents a reaction between an electrically neutral molecule and two ions of opposite sign and accordingly from the theory of velocity of ionic reactions[3,4] the velocity should be given by

$$h = kc_{\mathrm{Ox}}{\cdot}c_{\mathrm{H_3O^+}}c_{\mathrm{Cl^-}}f_1^2 \tag{1}$$

the c's indicating the concentrations of the reacting molecules and f the activity coefficient of a univalent ion. A reaction like this might, therefore, be well suited for testing the theory of reaction velocity. In fact, the work described in the present paper was taken up with the primary purpose of providing such a test.

What happens in an aqueous solution of ethylene oxide in the presence of hydrochloric acid is, however, more complicated than the simple addition of the acid. It has already been mentioned that the oxide takes up water when acids are present. This is a hydrogen-ion catalysis. Furthermore, there is a "spontaneous" water addition. Finally, we have found that the oxide combines with the anion of the acid and water, a reaction which is independent of hydrogen-ion concentration. There may also be acid catalysis in the general sense of this term,[5] but this we have been unable to detect with certainty so far.

In other words, ethylene oxide in a solution of hydrochloric acid disappears by four different paths, as follows:



Reaction I $(CH_2)_2O + H_2O \longrightarrow CH_2OH{-}CH_2OH$

Reaction II $(CH_2)_2O + H_2O \xrightarrow{H_3O^+} CH_2OH{-}CH_2OH$

Reaction III $(CH_2)_2O + Cl^- + H_2O \longrightarrow CH_2Cl{-}CH_2OH + OH^-$

Reaction IV $(CH_2)_2O + Cl^- + H_3O^+ \longrightarrow CH_2Cl{-}CH_2OH + H_2O$

The reactions not only take place with the simple ethylene oxide, but are probably general for the whole group of oxides. In addition to the

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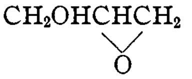
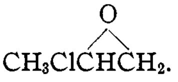
[3] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[4] Brönsted and Livingston, This Journal, **49**, 435 (1927).

[5] Brönsted, *Chem. Reviews*, **5**, 312 (1928).

simple oxide, we investigated glycid,  $CH_2OHCHCH_2$ and epichlorohydrin,  $CH_3ClCHCH_2$. Furthermore, hydrochloric acid can be replaced by a great number of other acids.

For the sake of simplicity the reactions will henceforth be referred to by the numbers assigned to them above.

B. Preparations

a. Ethylene Oxide.—Ethylene chlorohydrin, CH_2ClCH_2OH, was made from ethylene glycol by the method of Ladenburg.[6] A 25% solution of sodium hydroxide was admitted slowly from a dropping funnel onto ethylene chlorohydrin contained in a distilling flask in a water-bath at 50–60°. The side arm of the distilling flask was attached to a spiral condenser packed in an ice and salt freezing mixture and the tube of the condenser passed into a receiving bulb similarly cooled. The distillation of ethylene oxide proceeded slowly, taking four hours for an 80-g. portion of chlorohydrin; at the end of this time the temperature of the water-bath was raised to 80°. The contents of the receiving bulb were then redistilled directly into a storage tube packed in ice and salt in a Dewar flask. The greater part of the ethylene oxide passed over at 12–13°, as recorded by a thermometer, the bulb of which was immersed in the liquid oxide; this was the fraction used. The pure, dry oxide boils at 10.7° according to Maass and Boomer.[7] For our purpose, however, it was unnecessary to go through the tedious process of entirely removing the water.

b. Glycid.—α-Monochlorohydrin, $CH_2ClCHOHCH_2OH$, was made by passing hydrogen chloride into glycerin under the conditions of Smith's "Synthesis 2."[8] Nef's method[9] was used in the preparation of glycid from α-monochlorohydrin. After several fractionations of our product we obtained a quantity of glycid corresponding to 37% of the theoretical yield, free from any chlorine-containing impurity, boiling between 55 and 57° at 8–10 mm. pressure and of specific gravity 1.115^{20}_{4}. The specific gravities previously recorded are[9] 1.111^{22} and[10] 1.165°.

c. Epichlorohydrin.—For our experiments with epichlorohydrin we redistilled Kahlbaum's epichlorohydrin and took that fraction boiling between 116.5 and 117.5° at 765 mm.

C. Reactions I and II

It was found by Wurtz,[11] Nef[9] and Reboul[12] that the three oxides in question in the presence of water at 100° slowly transform into the corresponding glycols. Reaction I must then be very slow at ordinary temperature. In the case of oxides containing a tertiary carbon atom

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[6] Ladenburg, *Ber.*, **16**, 1407 (1883).

[7] Maass and Boomer, THIS JOURNAL, **44**, 1709 (1922).

[8] Smith, *Z. physik. Chem.*, **94**, 696 (1920).

[9] Nef, *Ann.*, **335**, 231 (1904).

[10] Beilstein, "Handbuch der organischen Chemie," 3d ed., Vol. I, p. 313. The specific gravity (20°/4°) is given in "International Critical Tables," Vol. I, p. 183, as 1.165; this seems to be an error.

[11] Wurtz, *Ann.*, **113**, 255 (1860).

[12] Reboul, *ibid.*, Suppl. I, 233 (1861).

the hydration proceeds much faster.[13] Our measurements of the rates are described below.

It has been mentioned that the addition of water to the oxides is accelerated by acids. It is, however, only recently that these reactions have been studied as examples of hydrogen-ion catalysis. After the present investigation was begun, Smith, Wode and Widhe[14] published measurements on the rates of addition of water to ethylene oxide and to epichlorohydrin at 25° in solutions of nitric acid and of perchloric acid of concentration 0.01 to 0.5 *M*. The reactions were followed by analytical methods and especially in the case of ethylene oxide the experimental errors were large. The authors state that, from their results, they are unable to judge whether the rate of reaction is proportional to the hydrogen-ion concentration or to the hydrogen-ion activity. From their results with nitric and perchloric acids, and from some results (as yet unpublished) with sulfuric acid, Smith, Wode and Widhe conclude that the nature of the anion of the catalyzing acid is unimportant.

1. Experimental Method

A dilatometric method was used in the present investigation for following Reactions I and II. From density data it was calculated that the hydration of ethylene oxides is accompanied by a considerable contraction. This was actually found to be the case also in solution, the contraction during reaction of 50 cc. of a solution originally 0.2 *M* in ethylene oxide being about 10 cm., measured in a capillary tube 1 mm. in diameter. Preliminary experiments showed that the conductivity of a solution 0.01 *M* in perchloric acid, or of a solution 0.01 *M* in perchloric acid and 0.1 *M* in sodium perchlorate, remained practically constant during the reaction; there was, therefore, no interference of Reactions III or IV. For this reason it was decided to use perchloric acid as catalyst. With the development of an accurate method of measurement it was thought that k_1, the constant of the "spontaneous" reaction (Reaction I), might be obtained by extrapolation of the velocity constants in dilute acid solution.

The apparatus is shown in Fig. 1. A is a vessel of 150-cc. capacity used as a mixing chamber and as conductivity cell; B and C are platinized electrodes; D is a tube through which carbon dioxide-free air may be admitted. The bulb E, of 50-cc. capacity, is the dilatometer. FG, the graduated portion of the capillary, is 0.0086 cm^2. in cross section and 20 cm. in length. It was found that the bore of the capillary was uniform to within 1% throughout the entire length and uniform to 0.5% throughout the upper half; the upper half was the region used. T, a glass chamber filled with mercury, is capped with a steel top through which moves the screw H acting as a plunger. With the screw H in its uppermost position mercury stands in the small reservoir K, and with the screw in its lowest position mercury extends to L and M in the tubes to the left

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[13] Eltekow, *Ber.*, **16**, 395 (1883).

[14] Smith, Wode and Widhe, *Z. physik. Chem.*, **130**, 154 (1927).

and right of the cock I. The upper part of the screw, H, and the connecting rod, R. are enclosed in a rubber tube. The apparatus was mounted and placed in an insulated glass thermostat at 20.00°; the maximum fluctuation in temperature observed in the thermostat during the course of the work was 0.005°.

The procedure was as follows: 150 cc. of a solution of ethylene oxide was placed in the cell A and allowed to come to the temperature of the bath. A given volume of the solution was removed with a pipet and the same volume of 0.1 *M* perchloric acid was added. Mixing was effected by bubbling air through the solution for a few minutes. On account of the electrodes it was not feasible to dry the apparatus between experiments and, after draining, a few drops of water always remained in the tubes connecting A and E. One-third of the solution was therefore allowed to flow over into E and was forced back into A by compressed air applied at O, before the dilatometer was finally filled. During the filling the mercury stood at N. Experience showed that if the solution was drawn up to G in the capillary, and the cock I closed, by alternately screwing down H (cock P open) and opening I, mercury could be brought to the position L and M, and the solution D to a convenient position near the top of the graduations on the capillary. Cock P was then closed. The mercury-sealed cock[15] J proved very satisfactory and only an occasional regreasing was necessary. The tightness of J was frequently tested by reading the position of the meniscus of a column of water confined in the apparatus at the beginning and at the end of a period of twelve hours. The process of mixing the solution and filling the dilatometer took approximately ten minutes. No trouble was experienced from the formation of air bubbles.

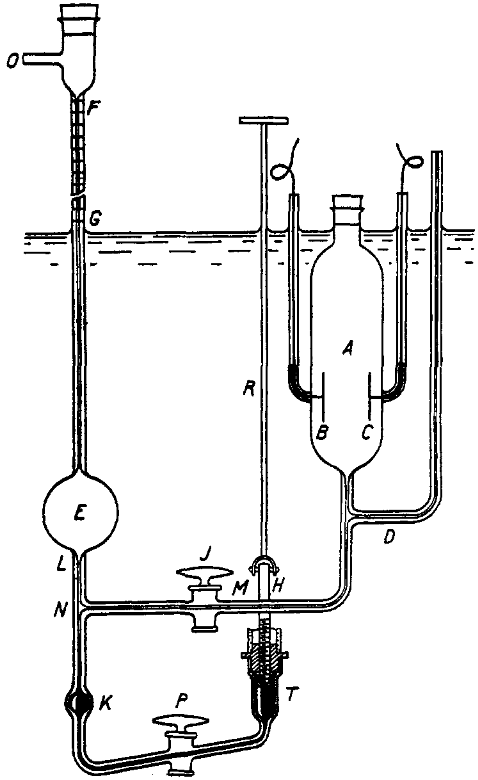

Fig. 1.

Readings were taken at convenient intervals over a period approximately twice the half time of the reaction, and later a second set of readings was taken at the same intervals. The time elapsing between the two sets of readings was always more than twice the period of half completion; as a rule it was twenty-four hours. The experiments were calculated by the method suggested by Guggenheim.[16]

For very slow reactions, as Reaction I in the case of ethylene oxide, the rate was determined by measuring the contraction in a sealed dilatometer. The dilatometer was a bulb of 50-cc. capacity, from the top of which extended a graduated capillary tube 0.6 mm. in diameter and 30 cm. long, and from the bottom a short thin-walled

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[15] Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927).

[16] Guggenheim, *Phil. Mag.*, 1, 538 (1926).

tube. Before filling the dilatometer the lower tube was drawn out each time in the flame. The dilatometer was filled by suction applied through the upper tube, and the lower tube was then sealed off at its narrowest point. If an air bubble formed in the solution during the process of filling or of sealing, it was expelled through the capillary by tilting and tapping while the dilatometer bulb was gently warmed. The solution was protected from the air by a glass cap fitting over the top of the capillary tube and dipping into a mercury-filled cup. The rate was calculated by Guggenheim's method, particularly convenient in the case of very slow monomolecular reactions such as this.

2. Results with Ethylene Oxide

Table I gives the data of a typical experiment to determine the velocity of Reaction II. The concentration of perchloric acid (*M* here and in the following means molarity, *i. e.*, moles per liter) recorded is the mean of the value calculated from dilution of a standard solution of perchloric acid and the value found by titration of 100 cc. of the residual solution against standard sodium hydroxide at the end of the experiment. The perchloric acid concentration given in all the experiments represents this mean. The difference between the two values was always small, and sometimes positive, sometimes negative. The resistance of the solution was measured at intervals during the course of the reaction. With perchloric acid and perchlorates there was usually an increase in resistance of about 0.5%; the

TABLE I

HYDRATION OF ETHYLENE OXIDE. A TYPICAL EXPERIMENT. $t = 20°$

Ethylene Oxide, 0.12 *M*. $HClO_4$, 0.007574 *M*. $0.4343k = 0.001070$

Time, min.	Dilatometer reading	Reading 24 hrs. later	Δv	Log Δv	Δv, calcd.	Deviation
0	18.48	12.40	6.08	0.784	6.08	0.00
15	18.27	12.395	5.875	.769	5.86	+0.015
30	18.05	12.39	5.66	.753	5.66	0.00
45	17.83	12.39	5.44	.736	5.44	0.00
60	17.62	12.38	5.24	.719	5.25	−0.01
75	17.43	12.375	5.055	.704	5.06	−0.005
90	17.25	12.37	4.88	.688	4.875	+0.005
105	17.07	12.365	4.705	.673	4.71	−0.005
120	16.89	12.36	4.53	.656	4.53	0.00
135	16.71	12.35	4.36	.640	4.37	−0.01
225	15.83	12.32	3.51	.545	3.51	0.00
240	15.70	12.315	3.385	.530	3.38	+0.005
255	15.58	12.31	3.27	.515	3.26	+0.01
270	15.47	12.305	3.165	.500	3.14	+0.025
285	15.34	12.30	3.04	.483	3.035	+0.005
300	15.22	12.30	2.92	.465	2.92	0.00
315	15.11	12.295	2.815	.450	2.82	−0.005
330	15.00	12.29	2.71	.433	2.71	0.00
345	14.90	12.29	2.61	.417	2.61	0.00
360	14.80	12.29	2.51	.400	2.525	−0.015
375	14.71	12.29	2.42	.384	2.43	−0.01
390	14.62	12.29	2.33	.367	2.34	−0.01

effect upon the resistance of the change in medium with the progress of the reaction will be discussed in a later section of the paper. The fourth column of the table gives Δv or the difference between the reading in the second column and the corresponding reading in the third column. When $\log \Delta v$ is plotted against the time, recorded in Col. 1, the slope of the best line drawn through the points is $-0.4343\ k$. The fifth column shows the values of Δv, of which the logarithms lie exactly on this line, and $\Delta v - \Delta v_{\text{calcd.}}$ gives the deviation of any point from the line.

Experiments were made in solutions of perchloric acid ranging in concentration from 0.003 to 0.02 *M*. The velocity constants are given in the sixth column of Table II, and in Fig. 2 they are shown plotted against the concentration of perchloric acid.

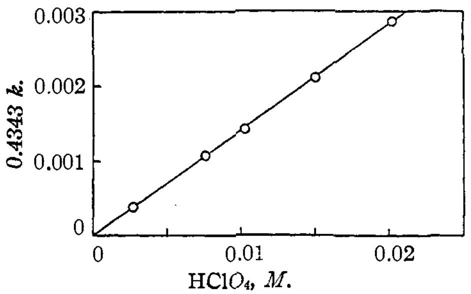


Fig. 2.—Effect of hydrogen ion upon the velocity of addition of water to ethylene oxide (Reaction II).

From Fig. 2 it is obvious that the observed velocity constants lie approximately on a straight line. It is evident, therefore, that the rate of reaction is proportional to the hydrogen-ion concentration. From the figure it is also evident that, without carrying out tediously long experiments in very dilute acid solution, it is futile to hope to detect, much less to measure, the spontaneous reaction (Reaction I) by extrapolation of the results in acid solution. It is also evident that the spontaneous reaction can have only a very slight effect upon the rates here measured.

In order to determine the spontaneous reaction the sealed dilatometer was employed, the measurement extending over a period of two months. The solution used was prepared from ethylene oxide and carbon dioxide-free water to which a drop of dilute sodium hydroxide solution was added; the resulting solution was 0.2 *M* in oxide and just alkaline to bromthymol

TABLE II

EFFECT OF HYDROGEN ION UPON THE RATE OF ADDITION OF WATER TO ETHYLENE OXIDE. SALT EFFECT. $t = 20°$. $0.434k_1 = 9.4 \times 10^{-6}$

Molarity, oxide	Molarity, $HClO_4$	Molarity, $NaClO_4$	ΔR, %	Total equiv. salt concn.	0.4343 k, obs.	0.4343 k_2
0.17	0.00272	0	−0.4	0.003	0.000385	0.138
.12	.007574	0	− .3	.008	.001070	.1401
.15	.01015	0	+0.2	.010	.001434	.1404
.17	.01496	0	0	.015	.002130	.1418
.11	.02017	0	+0.4	.020	.002868	.1417
.18	.01015	0.046	+ .6	.056	.001484	.1453
.20	.01014	.092	+ .7	.102	.001540	.1510
.18	.01493	.092	+ .5	.107	.002283	.1523

blue. The velocity constant, $0.434\ k_1$, was found to be 9.4×10^{-6}, corresponding to a half time of 23 days at 20°. The effect of any hydrogen-ion catalysis was negligible in our solution, which at the start was 1×10^{-8} molar in hydrogen ion. Experiments in sodium hydroxide solutions up to 0.1 *M* showed the effect of hydroxyl ion to be negligible also.

Knowing k_1 we can now determine exactly k_2, the constant of Reaction II for molar acid, at various salt concentrations.

The sixth column in Table II records the observed velocity constant, and the seventh shows this constant corrected for the spontaneous reaction and divided by the hydrogen-ion concentration, *i. e.*, $k_2 = (k - k_1)/(\text{molarity } HClO_4)$. The fourth column of Table II gives the percentage change in resistance during the reaction. In Fig. 3 $0.4343\ k_2$ is plotted against the total equivalent salt concentration, the salt effect of $NaClO_4$ and $HClO_4$ being taken as equal in the first approximation.

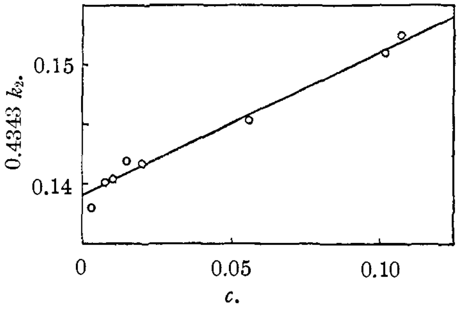


Fig. 3.—Salt effect upon Reaction II. Ethylene oxide. c = total salt concentration $= M_{HClO_4} + M_{NaClO_4}$.

The catalytic constant for ethylene oxide thus may be represented by the linear relationship

$$0.4343\ k_2 = 0.1391 + 0.120\ c$$

c being the salt concentration. The 9% increase in 0.1 *N* salt solution is a rather large primary salt effect.

3. Results with Glycid

Reaction I in the case of glycid was followed in a way similar to that described above for ethylene oxide. In Table III are collected the results of experiments in pure water and in various solutions.

TABLE III

THE "SPONTANEOUS" ADDITION OF WATER TO GLYCID. $t = 20°$

Composition of solution	$0.43\ k_1 \times 10^6$
Glycid, 0.1 *M*, CO_2-free water	6.8
Glycid, 0.1 *M*, CO_2-free water	6.9
Glycid, 0.1 *M*, Na_2HPO_4, 0.0025 *M*; KH_2PO_4, 0.0025 *M*	7.6
Glycid, 0.1 *M*, Na_2HPO_4, 0.0050 *M*; KH_2PO_4, 0.0050 *M*	7.0
Glycid, 0.1 *M*, Na_2HPO_4, 0.011 *M*; KH_2PO_4, 0.011 *M*	7.6
Glycid, 0.1 *M*, NaOH, 0.0001 *M*	8.6
	Average, 7.4×10^{-6}

The last experiment in Table III was measured over a period of two months and the data were plotted by Guggenheim's method; the reaction, however, was not unimolecular over its entire course, but after the time of half completion decreased in rate, the trend amounting to 20%. Experiments were also made in sodium acetate–acetic acid buffer solution, where the reaction was more rapid, and where the increase in rate was roughly proportional to the acetate concentration. The explanation was later discovered to be addition of acetate ion (Reaction III); this reaction will be discussed at some length for epichlorohydrin. From analogy with experiments on ethylene oxide and epichlorohydrin, it is probable that in the phosphate buffer solutions there was also addition.

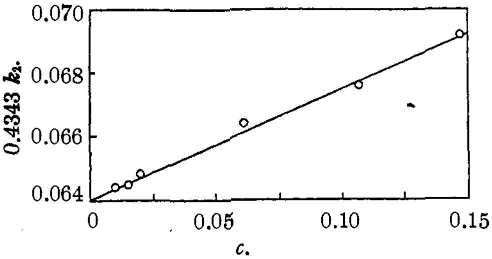


Fig. 4.—Salt effect upon Reaction II. Glycid, c = total salt concentration = M_{HClO_4} + M_{NaClO_4}.

In Table IV are given the results of the experiments in perchloric acid solution. The constant for molar acid, k_2, was obtained as before by subtracting k_1 from the observed velocity constant and dividing the difference by the acid concentration. The correction for the spontaneous reaction is very small as in the case of ethylene oxide. The values of 0.4343 k_2 given in Table IV are shown in Fig. 4 plotted against the total equivalent salt concentration. The salt effect is linear, amounting to 5% in 0.1 N salt solution, as is seen from the equation

$$0.434\ k_2 = 0.0640 + 0.035\ c$$

TABLE IV

EFFECT OF HYDROGEN ION UPON THE RATE OF ADDITION OF WATER TO GLYCID. SALT EFFECT. $t = 20°$. $0.434\ k_1 = 7.4 \times 10^{-6}$

Molarity, glycid	Molarity, $HClO_4$	Molarity, $NaClO_4$	ΔR, %	Total equiv. salt concn.	0.4343 k, obs.	0.4343 k_2
0.20	0.01013	0	+1.3	0.010	0.000660	0.0644
.17	.01493	0	+0.6	.015	.000970	.0645
.15	.02023	0	+ .3	.020	.001318	.0648
.14	.01495	0.046	+ .3	.061	.001000	.0664
.14	.01493	.092	+ .5	.107	.001016	.0676
.15	.01495	.132	+ .3	.147	.001042	.0692

Experiments were also carried out in solutions of nitric acid, of nitric acid and potassium nitrate, of benzenesulfonic acid, and of benzenesulfonic acid and sodium benzene sulfonate. The results of these experiments are given in Table V.

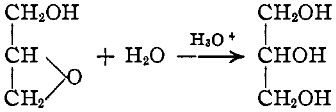
The first column shows the initial acid concentration as calculated from dilution of a standard solution, the second the acid concentration found upon titration of 100 cc. of the residual solution at the end of the experiment. In the first, second and fourth experiments there was undoubted

Table V

Experiments in Solutions of Nitric and of Benzene Sulfonic Acid. Glycid 0.1 *M*. $t = 20°$

	Molarity acid, initial	Molarity acid, final	Molarity salt	ΔR, %	$0.434\ k_{\text{obs.}}$	$0.434\ k_3$
HNO_3	0.01538	0.01483	0	+3.6	......	....
HNO_3	.01538	.01267	KNO_3, 0.094	+5.8	......	....
$C_6H_5SO_3H$	.01532	.01518	0	+0.3	0.000976	0.0640
$C_6H_5SO_3H$	.01532	.01419	$C_6H_5SO_3Na$, 0.100	+1.8	......	....

disappearance of glycid due to Reactions III and IV. Definite velocity constants are recorded for the third experiment only, that in benzenesulfonic acid, without salt. In the other cases it was difficult to draw a representative line through the points obtained by plotting log Δv against time as the later points lay well above the line through the earlier. The change in resistance during the experiments, recorded in the fourth column, also substantiate this difficulty. Without any addition of the ions of the acid to glycid during the reaction



in perchloric acid solution a slight change in the conductivity of the perchloric acid is expected because of the change in the medium occurring with disappearance of glycid and formation of glycerin. From measurements of the resistance of 0.01000 *M* perchloric acid in solutions 0.20 *M* in glycerin and in solutions 0.20 *M* in glycid, we concluded that an increase of 1% in the resistance is to be expected during the course of the reaction if the initial glycid concentration is 0.20 *M*. This is qualitatively confirmed by the experiments shown in Table IV.

The increases in resistance in the first, second and fourth experiments of Table V considerably exceed this medium effect.

All these observations tend to confirm the result of the direct titration that acid disappears by the addition Reactions III and IV, these reactions occurring to a greater extent with nitric than with benzene sulfonic acid.

Smith, Wode and Widhe[14] used nitric as well as perchloric acid in measuring Reaction II for ethylene oxide and for epichlorohydrin. They state that the nature of the anion of the catalyzing acid "seems to be of minor importance." Their method of following the reaction was not sufficiently accurate to enable them to detect the complications which we encountered. These complications should, of course, not be neglected when trying to apply the reaction here dealt with for determination of hydrogen-ion concentrations.

4. Results with Epichlorohydrin

The spontaneous addition of water to epichlorohydrin was measured in the same way as the addition of ethylene oxide. Daily readings were taken over a period of a month. The velocity constant, 0.434 k_1, was found to be 2.54 × 10^{-5}, which corresponds to a half time of eight days; Reaction I is therefore approximately three times as fast as in the cases of ethylene oxide and glycid. Two experiments were also carried out in sodium perchlorate solution to determine, if possible, the salt effect upon Reaction I. The results are summarized in Table VI, from which it is evident that there is no detectable salt effect in 0.1 M solution. The solution used in the first experiment was just alkaline to bromthymol blue; the solutions in the second and third experiments were at the change point of bromcresol purple. Hydrogen-ion catalysis was negligible in all experiments. After fourteen days a trace of chloride was detected in the residual portion of the solution used in the first experiment; this was probably due to the hydrolysis of the product of the reaction, $CH_2ClCHOHCH_2OH$, which hydrolyzes much more rapidly than does epichlorohydrin.[17] The reaction showed in no case deviation from unimolecularity.

TABLE VI

THE SPONTANEOUS ADDITION OF WATER TO EPICHLOROHYDRIN. t = 20°

Composition of solution	$0.434\ k_1 \times 10^{-5}$
0.10 M Epichlorohydrin in CO_2-free water	2.54
0.10 M Epichlorohydrin in 0.050 M $NaClO_4$	2.57
0.10 M Epichlorohydrin in 0.10 M $NaClO_4$	2.56

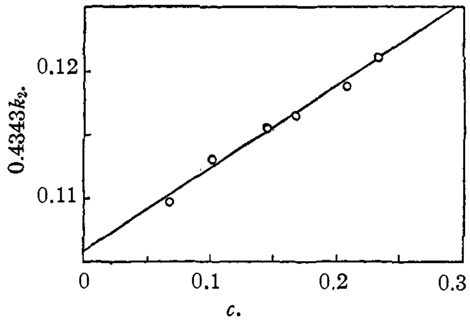


Fig. 5.—Salt effect upon reaction II. Epichlorohydrin, c = total salt concentration = $M_{HClO_4} + M_{NaClO_4}$.

The results of the experiments in perchloric acid solution are given in Table VII.

TABLE VII

EFFECT OF HYDROGEN ION UPON THE RATE OF ADDITION OF WATER TO EPICHLOROHYDRIN. SALT EFFECT. t = 20°. $0.434\ k_1 = 2.54.10^{-5}$

Molarity, epichlorohydrin	Molarity, $HClO_4$	Molarity, $NaClO_4$	ΔR, %	Total equiv. salt concn.	0.4343 k, obs.	$0.4343k_2$
0.12	0.0673	...	+0.4	0.067	0.000763	0.01097
.14	.1010	...	+ .7	.101	.001167	.01131
.14	.1010	0.042	+ .3	.143	.001192	.01156
.13	.1670	...	+ .5	.167	.001971	.01166
.14	.1009	.106	+ .3	.207	.001224	.01188
.14	.1010	.132	+ .5	.233	.001248	.01211

In Fig. 5, 0.4343 k_2 is plotted against the total equivalent salt concentration.

[17] Smith, *Z. physik. Chem.*, **92**, 724 (1918).

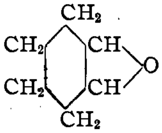
The relationship is evidently linear, k_2 being expressed by the equation

$$0.4343\ k_2 = 0.01059 + 0.0065\ c$$

In 0.1 N salt solution there is, therefore, a 6% salt effect.

5. Results with Cyclohexene Oxide

A few experiments were made with cyclohexene oxide.[18]

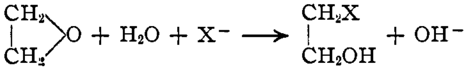


In the presence of perchloric acid this oxide added water very rapidly, the constant for molar acid being $k_2 = 50$.

The constant for the spontaneous reaction is probably small. Dilatometric measurements in acetate and phosphate buffers indicated that the reaction is complicated by Reaction III.

D. Reaction III

Reaction III consists stoichiometrically in an addition of acid to ethylene oxides just as does Reaction IV. Kinetically, however, it is quite different from an addition of acid, the kinetic scheme, as already mentioned, being



$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>O + H_2O + X^- \longrightarrow \begin{array}{l}CH_2X\\ |\\ CH_2OH\end{array} + OH^-$$

where X^- is the anion of the acid. The reaction is therefore independent of the hydrogen-ion concentration. X^- may represent chloride, bromide, iodide, thiocyanate, formate, benzoate, acetate or trimethylacetate ion. From numerous qualitative experiments it would appear that X^- can also represent other anions, the one exception found being perchlorate.

Smith[19] mentions this reaction in the case of chloride ion and glycid in connection with the preparation of β-monochlorohydrin; however, he makes no distinction between this reaction and the direct addition of hydrochloric acid (Reaction IV), which gives the same products as the above reaction in acid solution. As far as we are aware, Reaction III has in the past always been confused with Reaction IV, the direct addition of acid.[20]

Nevertheless, it is Reaction III, not Reaction IV which imparts to the ethylene oxides their conspicuous apparent basicity. These properties are shown not only in the case of "hydrolyzing" chlorides, where the addition of "free acid" may be made responsible for the precipitation of metal hydroxide.[21] They are exhibited in a no less conspicuous manner, for in-

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[18] "Organic Syntheses," Vol. V, John Wiley and Son, New York, **1925**.

[19] Smith, *Z. physik. Chem.*, **94**, 727 (1920).

[20] *Cf.* Bodfors, *Sammlung chemischer und chemisch-technischer Vorträge*, **26**, 194 (1922).

[21] *Cf.* Walker, *Ber.*, **34**, 4117 (1901).

stance, in a solution of potassium chloride. Adding to a 0.1 *M* potassium chloride solution phenolphthalein and a little epichlorohydrin or glycid, one very soon finds the solution pink, the color rapidly deepening to indicate a strongly basic reaction. After titrating the hydroxide formed, the reaction proceeds further.

It is easy to show that the reaction here described is much too rapid to be explained kinetically as an addition of hydrochloric acid. Since the addition of hydrochloric acid is roughly proportional to the concentrations, $c_{H_3O^+}$ and c_{Cl^-}, of the two ions, the reaction should be a million times slower in 0.1 KCl than in 0.1 HCl, if it was kinetically a direct addition of acid. This is very far from being the case. The rate in the salt solution is only fifty times slower than it is in the acid solution. An investigation also showed that the reaction in salt solution was independent of the hydrogen-ion concentration over a considerable range, in conformity with the kinetic scheme of Reaction III.

In order to follow Reaction III it must be isolated from Reactions II and IV. If the hydrogen-ion concentration is kept sufficiently low, Reactions II and IV become negligible and Reaction III may then be studied, account being taken of Reaction I. In addition, the solution must not become too alkaline, for then the reverse reaction may come in. The hydrogen-ion concentration must be kept within the limits 1×10^{-4} and $1 \times 10^{-8.5}$ *M*. In the study of the addition of the anions of weak acids this is a relatively simple matter, but in the case of the anions of the strong acids it is necessary to make and regulate an artificial buffer solution. On the other hand, the determination of the extent of the reaction is easier in the case of strong acids than in the case of weak.

1. Strong Acids

a. Experimental Method.—When an ethylene oxide disappears by Reaction III, for instance, in a potassium chloride solution, an equivalent amount of potassium hydroxide is set free. In order to study this reaction and to have it proceed undisturbed by other influences, the *P*H of the solution should be kept within the limits given above (4 to 8.5) and should also be kept constant as far as possible. The double purpose of measuring the speed titrimetrically and keeping the *P*H constant can be sufficiently fulfilled by running continuously into the reacting mixture from a microburet such amounts of strong acid that the solution, to which an indicator is added, always matches in color a constant reference buffer solution containing the same indicator. The reaction then proceeds at the *P*H characteristic of the indicator and color chosen, which can be varied from one experiment to another. Its extent is directly recorded by the readings on the buret.

The condition necessary for the application of this principle is, first, that a very small amount of acid should give a sufficient change in the color of the solution in which the corresponding potassium salt is present. For this reason the method is applicable only to salts of strong acids.

In order to avoid too much volume change of the reacting solution, the acid added should be rather concentrated. Since one drop of such a solution would change the *P*H far outside the permissible limits, the acid is added from the buret through a very fine capillary ending below the surface of the solution. With continuous stirring by air the color then remained practically uniform throughout the solution.

The details of the experimental procedure were as follows. Two cylindrical vessels of 100-cc. capacity and with capillary tubes sealed to their lower ends were mounted vertically in the thermostat and a white porcelain plate was arranged behind them. A buffer solution with a few drops of indicator was placed in one vessel and the solution of the salt to be studied was placed in the other vessel with an equal amount of indicator. Carbon dioxide-free air was bubbled through the solution and when the solution had come to the temperature of the bath, the oxide was added and the initial time was taken. Meanwhile, a special microburet had been filled with 0.5 *M* perchloric acid. The tip of the buret was 10 cm. in length and of very narrow bore (approximately 0.12 mm.). The graduated portion of the buret was 20 cm. in length and held 1 cc. of acid. As soon as the oxide was added the tip of the buret, extending through a rubber stopper, was set in the solution, the buret was clamped in place and connected to a device by which the pressure above the acid in the buret could be slightly changed so that the flow of perchloric acid from the buret was just sufficient to keep the solution at the desired hydrogen-ion concentration, as shown by a comparison of the color of the reacting solution with the color of the blank. At convenient times buret readings were taken and the time was recorded. The apparatus was arranged in duplicate and two experiments were carried out at the same time.

b. Calculations.—The velocity constants of each experiment were calculated by the velocity equation

$$-\frac{\mathrm{d}c_{\mathrm{Ox.}}}{\mathrm{d}t} = kc_{\mathrm{Ox.}}c_{\mathrm{X^-}}$$

where X^- is the anion of the salt solution employed. On integration it gives

$$kt = \frac{1}{0.4343(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

a being the initial concentration of the oxide, *b* that of the salt and *x* the concentration of both which has disappeared at the time *t*. Log $(a - x)/(b - x)$ was plotted against the time in minutes and the best line was drawn through the points. The line has an intercept at the initial time of log a/b. The slope of the line divided by $0.4343\ (a - b)$ gives the velocity constant. As it is not convenient to reproduce these plots, the numerical values are given in Col. 5 of Table VIII, which shows the data of a typical experiment.

In calculating the values of *x* in this table, the effect of the solution being diluted by the strong acid added has not been taken into account. There

TABLE VIII

ADDITION OF IODIDE ION TO GLYCID. A TYPICAL EXPERIMENT. $t = 20°$
Glycid molarity $= a = 0.0825$. KI molarity $= b = 0.0600$

Time, minutes	Buret reading, Cm.	Cm. × 523 × 10^{-6} = x, molarity of acid added	$\log \frac{a-x}{b-x}$	k_3
0	1.01	......	0.13830	....
10	2.46	0.000758	.13982	0.0156
12	2.79	.000931	.14016	.0159
14	3.08	.001082	.14048	.0159
16	3.37	.001234	.14079	.0159
18	3.69	.001402	.14114	.0161
20	3.94	.001532	.14139	.0159
24	4.51	.001831	.14201	.0158
28	5.04	.002108	.14261	.0158
32	5.62	.002411	.14323	.0157
35	6.19	.002709	.14386	.0163
40	6.83	.003044	.14457	.0161
44	7.33	.003305	.14517	.0160
49	7.98	.003651	.14591	.0159
53	8.50	.003917	.14650	.0158
55	8.77	.004058	.14681	.0159
57	9.03	.004194	.14712	.0158
59	9.30	.004336	.14743	.0158
63	9.80	.004593	.14802	.0158
68	10.40	.004911	.14873	.0157
77	11.50	.005486	.15005	.0156
80	11.87	.005680	.15051	.0156
82	12.10	.005800	.15079	.0156
85	12.50	.006009	.15128	.0156
89	13.00	.006271	.15192	.0156
93	13.45	.006506	.15247	.0156
97	13.91	.006747	.15305	.0155
100	14.29	.006945	.15354	.0156
107	15.10	.007369	.15458	.0155
112	15.67	.007667	.15531	.0157
117	16.27	.007980	.15610	.0155
122	16.75	.008232	.15673	.0154
127	17.33	.008535	.15752	.0154
132	17.90	.008833	.15827	.0154
137	18.41	.009100	.15897	.0154
142	18.90	.009357	.15966	.0154
147	19.45	.009644	.16041	.0154

is also a small correction to be introduced from the disappearance of the oxide by Reaction I. The slight trend shown by the values of k in the fifth column may be explained in that way. Corrections have been introduced for these effects in Table IX and the following tables.

c. **Results with Glycid.**—The results of a number of experiments with glycid and iodide are summarized in Table IX. The first six experiments show the effect of the acidity. The acidity seems to have no

TABLE IX

ADDITION OF IODIDE ION TO GLYCID. $t = 20°$

Expt.	Glycid, molarity	KI, molarity	Hydrogen ion, molarity	$NaClO_4$, molarity	k_1
1	0.0819	0.0980	6×10^{-5}	...	0.0190[a]
2	.0819	.0980	5×10^{-6}	...	.0161
3	.0819	.0980	6×10^{-7}	...	.0158
4	.0819	.0980	1×10^{-7}	...	.0161
5	.0819	.0980	6×10^{-9}	...	.0157
6	.0819	.0980	6×10^{-10}	...	.0140[a]
7	.0825	.0200	1×10^{-7}	...	.0161
8	.0825	.0400	1×10^{-7}	...	.0157
9	.0825	.0600	1×10^{-7}	...	.0157
10	.0825	.0800	1×10^{-7}	...	.0158
11	.0810	.0200	5×10^{-6}	...	.0161
12	.0810	.0400	5×10^{-6}	...	.0162
13	.0810	.0600	5×10^{-6}	...	.0159
14	.0918	.0200	1×10^{-7}	...	.0163
15	.0918	.0200	1×10^{-7}	0.176	.0158
16	.1197	.0400	1×10^{-7}	...	.0159
17	.1197	.0400	1×10^{-7}	0.176	.0153

[a] Approximate constants.

influence upon the velocity constant, k_1 within the considerable range of $c_{H_3O^+}$ from 5×10^{-6} to 6×10^{-9}. At higher hydrogen-ion concentration, $c_{H_3O^+} = 6 \times 10^{-5}$, however, the velocity increases, due to Reaction IV, the direct addition of hydrogen iodide. It is here no longer possible to obtain a good velocity constant, because the adjustment of the P_H by means of the color of the indicator is not accurate enough when the hydrogen ion enters into the reaction to a considerable extent. At a hydrogen-ion concentration of 6×10^{-10} M the calculated values of k decrease as the reaction proceeds; the reaction is probably no longer going to completion. This effect, however, was not investigated further.

Experiments 7–13 were carried out to study the effect of the concentration of the iodide. The rate is very nearly proportional to this concentration. As indicated by the results of these experiments and Expts. 14–17 in which sodium perchlorate was added, there seems to be a small negative salt effect.

The addition of bromide and of chloride is much slower than that of iodide and in the case of the chloride it is necessary to work at higher salt concentrations. As was found with the iodide the reaction is independent of the hydrogen-ion concentration and a negative salt effect is indicated. The results are summarized in Tables X and XI.

It was also found that thiocyanate adds to glycid at a rate comparable to that of iodide.

As is shown in Table XII, the rate was no longer found to be independent of the hydrogen-ion concentration at a hydrogen-ion concentration of

TABLE X

ADDITION OF BROMIDE ION TO GLYCID. $t = 20°$

Expt.	Glycid, molarity	KBr, molarity	Hydrogen ion, molarity	$k_3 \times 10^5$	
1	0.0857	0.0990	2×10^{-4}	215[a]	
2	.0842	.0990	6×10^{-5}	133[a]	
3	.0911	.0990	6×10^{-7}	98.6	100.7
4	.0886	.0990	5×10^{-6}	102.9	
5	.0911	.0990	1×10^{-7}	99.9	
6	.0905	.1000	1×10^{-7}	101.3	
7	.0886	.0990	6×10^{-9}	92.2[a]	
8	.0857	.0990	6×10^{-10}	90.0[a]	
9	.0842	.0990	1×10^{-7}	97.2	
10	.0905	.2000	1×10^{-7}	92.0	

[a] Approximate constants.

TABLE XI

ADDITION OF CHLORIDE ION TO GLYCID. $t = 20°$

Expt.	Glycid, molarity	KCl, molarity	Hydrogen ion, molarity	$k_3 \times 10^6$
1	0.2700	0.1000	1×10^{-7}	149
2	.2469	.2000	1×10^{-7}	142
3	.2117	.5000	1×10^{-7}	139
4	.2325	.8000	5×10^{-6}	130
5	.2330	.8000	1×10^{-7}	126

TABLE XII

ADDITION OF THIOCYANATE TO GLYCID. $t = 20°$

Expt.	Glycid, molarity	KCNS, molarity	Hydrogen ion, molarity	$k_3 \times 10^5$
1	0.08081	0.2000	4×10^{-4}	840[a]
2	.08273	.2000	6×10^{-5}	782
3	.08456	.2000	6×10^{-7}	744
4	.08273	.2000	6×10^{-7}	746
5	.08273	.2000	1×10^{-7}	792
6	.08456	.2000	6×10^{-9}	795
7	.08273	.2000	6×10^{-10}	785
8	.08176	.2000	6×10^{-9}	758
9	.08081	.2000	1×10^{-7}	744
10	.1670	.1000	1×10^{-7}	781

[a] Approximate constants.

4×10^{-4} *M*. Thiocyanic acid, therefore, adds to glycid as do the halogen acids.

The salt effect $(1/k_0)(dk/dc)$ in the experiments with chloride, bromide and iodide is on an average -0.30 (k_0 is the velocity constant at zero salt concentration). Taking this to be true also for the thiocyanate, we find that the constants of the four reactions can be represented by

$$k_{\mathrm{Cl}^-} = 150 \times (1 - 0.30c) \times 10^{-6}$$
$$k_{\mathrm{Br}^-} = 103 \times (1 - 0.30c) \times 10^{-5}$$
$$k_{\mathrm{Th}^-} = 79 \times (1 - 0.30c) \times 10^{-4}$$
$$k_{\mathrm{I}^-} = 162 \times (1 - 0.30c) \times 10^{-4}$$

d. **Results with Epichlorohydrin.**—The results with epichlorohydrin are quite parallel to those with glycid. The rate of addition is independent of the hydrogen-ion concentration over a considerable range and is proportional to the concentration of the reacting ion. In all cases the reaction is approximately four times as fast as the corresponding reaction with glycid. In studying the addition of iodide to epichlorohydrin, owing to the speed of this reaction, we were able to work at iodide concentrations less than 0.01 *M* and to follow the reaction practically to completion. In order to avoid the various corrections being greatly magnified with the extent of the reaction, we used, however, only the first part of the reaction, where these corrections are small. The results are given in Table XIII. In the fifth experiment of Table XIII the epichlorohydrin concentration was low and the iodide concentration high, so that the major part of the correction was for the spontaneous reaction.

TABLE XIII

ADDITION OF IODIDE ION TO EPICHLOROHYDRIN. $t = 20°$

Expt.	Epichlorohydrin, molarity	KI, molarity	Hydrogen ion, molarity	$k_1 \times 10^4$
1	0.2466	0.0100	5×10^{-6}	595
2	.2378	.00665	5×10^{-6}	610
3	.2970	.00810	5×10^{-6}	620
4	.2480	.00669	1×10^{-7}	587
5	.0119	.2100	1×10^{-7}	584
6	.0813	.02169	1×10^{-7}	604
7	.0813	.02500	1×10^{-7}	609
8	.0650	.02500	1×10^{-7}	584
9	.0650	.02255	1×10^{-7}	581

The experiments on the addition of bromide, chloride and thiocyanate ion to epichlorohydrin are summarized in Tables XIV, XV and XVI. In Tables XIV and XV, where experiments at widely varying salt concentrations are recorded, the figures show the presence of a negative salt effect as in the case of glycid, but somewhat smaller (0.2 instead of 0.3). If the same salt effect is assumed to exist in all four salt solutions, which

TABLE XIV

ADDITION OF BROMIDE ION TO EPICHLOROHYDRIN. $t = 20°$

Expt.	Epichlorohydrin, molarity	KBr, molarity	Hydrogen ion, molarity	$k_1 \times 10^5$
1	0.0836	0.1000	1×10^{-7}	359
2	.0836	.1000	6×10^{-7}	361
3	.0660	.2000	1×10^{-7}	345
4	.0660	.2000	6×10^{-7}	356
5	.0688	.5000	1×10^{-7}	338
6	.0688	.5000	1×10^{-7}	335
7	.1060	1.000	1×10^{-7}	282

TABLE XV

ADDITION OF CHLORIDE ION TO EPICHLOROHYDRIN. $t = 20°$

Expt.	Epichlorohydrin, molarity	KCl, molarity	Hydrogen ion, molarity	$k_3 \times 10^6$
1	0.0672	0.2000	1×10^{-7}	677
2	.0672	.2000	1×10^{-7}	667
3	.0868	.3000	1×10^{-7}	675
4	.0868	.4000	1×10^{-7}	633
5	.0776	.4000	1×10^{-7}	662
6	.0776	.5000	1×10^{-7}	650
7	.0867	.6000	1×10^{-7}	619
8	.1130	.8000	1×10^{-7}	569

TABLE XVI

ADDITION OF THIOCYANATE ION TO EPICHLOROHYDRIN. $t = 20°$

Expt.	Epichlorohydrin, molarity	KCNS, molarity	Hydrogen ion, molarity	$k_3 \times 10^4$
1	0.0979	0.02000	1×10^{-7}	370
2	.0898	.04000	1×10^{-7}	368
3	.0228	.1000	1×10^{-7}	371

is of course only approximately true, the constants can be given by the following equations

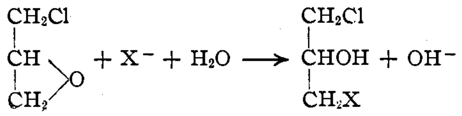
$$
\begin{aligned}
k_{\mathrm{Cl}^-} &= 69 \times (1 - 0.2c) \times 10^{-5} \\
k_{\mathrm{Br}^-} &= 37 \times (1 - 0.2c) \times 10^{-4} \\
k_{\mathrm{Th}^-} &= 38 \times (1 - 0.2c) \times 10^{-3} \\
k_{\mathrm{I}^-} &= 60 \times (1 - 0.2c) \times 10^{-3}
\end{aligned}
$$

Ethylene oxide is so volatile that it is impossible to obtain quantitative results using this method of following the reaction; qualitative experiments, however, indicate that the rates are approximately the same as with glycid.

2. Weak Acids

In a mixture of acetic acid and acetate ions and in similar buffers the weak acid is added to epichlorohydrin by Reaction III. As the reaction proceeds, the P_H of the buffer varies only slightly in the first part of the reaction. The device of artificially maintaining a certain value of the hydrogen-ion concentration, as in the case of strong acids just described, was therefore not necessary. For the same reason, however, also the method used there for following the reaction was inapplicable.

The rate of addition of the anion was determined by titration of the acid from time to time in samples of the reacting solution. Since addition of the anion results in the formation of the hydroxyl ion and consequent neutralization of the acid of the buffer



$$OH^- + HX \longrightarrow H_2O + X^-$$

the concentration of the anion remains constant. The epichlorohydrin in such a buffer solution disappears by two paths, by Reaction I, the spontaneous, and by Reaction III above. Since the duration of an experiment here was much longer than in the case of strong acids, Reaction I becomes predominant and must be eliminated in order to calculate the constant of Reaction III.

Representing by a the initial concentration of epichlorohydrin, by x the concentration of monochlorohydrin formed at time t and by y the concentration of addition compound formed by Reaction III, one has

$$\frac{dx}{dt} = k_1(a - x - y) \tag{1}$$

$$\frac{dy}{dt} = k'(a - x - y) \tag{2}$$

where k_1 is known ($0.434\ k_1 = 2.54 \times 10^{-5}$, *cf.* p. 438) and $k' = k_3c$, c being the concentration of the anion. In order to find k' one divides Equation 1 by Equation 2 and integrates

$$\frac{x}{y} = \frac{k_1}{k'} \text{ or } x + y = y \times \frac{k_1 + k'}{k'}$$

Substituting this value for $x + y$ in (2) and integrating, one has

$$\ln \frac{a}{a - \dfrac{k_1 + k'}{k'}y} = (k_1 + k')t \tag{3}$$

by which k' is determined, since y equals the concentration of acid which has disappeared, which has been found by the titration. In order to solve for k', we chose a number of arbitrary values of k', plotted the value of the ln of Equation 3 against k', and $t\ (k_1 + k')$ against k', the intersection of the curve representing the logarithmic expression and the line representing $(k_1 + k')\ t$ gave the value of k' satisfying Equation 3. In estimating the acetic acid, enough standard sodium hydroxide solution, 0.02 M, was added to neutralize nine-tenths of the acid; carbon dioxide-free air was bubbled through the solution for twenty minutes and the solution was then titrated to the appearance of the pink color of phenolphthalein. Table XVII shows a typical experiment.

The fourth column contains the arbitrarily chosen values of k', the fifth the corresponding values of the logarithmic expression, and the sixth the corresponding values of $t\ (k_1 + k')$. The seventh column gives the value of k' at the intersection of the curve and the line obtained when $2.30 \log \dfrac{a}{a - y(k_1 + k')/k'}$ and $(k_1 + k')\ t$, respectively, are plotted against k'. The velocity constant, k_3, is obtained by dividing k' by the acetate-ion concentration. Experiments were carried out with acetic, formic, benzoic and trimethylacetic acids. The results of all of the experiments are collected in Table XVIII.

TABLE XVII

ADDITION OF ACETATE ION TO EPICHLOROHYDRIN. $t = 20°$. A TYPICAL EXPERIMENT
NaAc, 0.100 *M*. Initial Concn. of Epichlorohydrin, 0.1000 *M*

Time, minutes	Concn. HAc, molarity	y	$k' \times 10^5$ assumed	$2.30 \times \log \dfrac{a}{a - \dfrac{k_1 + k'}{k'} y}$	$t(k_1 + k')$	$k' \times 10^5$ selected
..	0.02028	.....	....	....	....	..
1140	.01642	0.00386	3.00, 3.50, 3.60, 4.00	0.121, 0.109, 0.106, 0.100	0.101, 0.107, 0.108, 0.112	3.56
2685	.01148	.00880	3.30, 3.50, 3.70, 4.00	0.280, 0.268, 0.257, 0.243	0.245, 0.251 0.256, 0.264	3.71
4000	.00793	.01235	3.40, 3.70, 4.00	0.409, 0.383, 0.365	0.370, 0.382 0.394	3.71
5450	.00460	.01568	3.40, 3.70, 4.00	0.555, 0.518, 0.488	0.504, 0.520, 0.536	3.68
6890	.00179	.01849	3.40, 3.70, 4.00	0.698, 0.648, 0.607	0.637, 0.657, 0.678	3.66
					Average,	3.66

TABLE XVIII

ADDITION OF THE ANIONS OF CARBOXYLIC ACIDS TO EPICHLOROHYDRIN. $t = 20°$

Acid	Dissoc. const.	Initial concn. of acid, molarity	Concn. of Na salt, molarity	$k \times 10^5$	$k_3 \times 10^4$
Formic	2.1×10^{-4}	0.0203	0.200	5.57	2.79
		.0103	.200	5.83	2.91
		.0103	.100	2.88	2.88
				Average,	2.86
Benzoic	0.6×10^{-4}	.0141	.149	4.59	3.08
		.0193	.149	4.59	3.08
		.0096	.099	3.02	3.05
				Average,	3.07
Acetic	0.18×10^{-4}	.0203	.100	3.66	3.66
		.0104	.100	3.70	3.70
		.0202	.050	1.86	3.72
		.0100	.050	1.82	3.64
		.0200	.020	7.35	3.68
		.0100	.020	7.55	3.78
				Average,	3.70
Trimethylacetic	0.10×10^{-4}	.0146	.050	2.50	5.00
		.0179	.025	1.26	5.04
		.0150	.025	1.25	5.00
				Average,	5.01

The experiments in formate-formic acid buffer solution are within themselves less accurate than the rest. It was found to be impossible to titrate the formic acid using phenolphthalein as indicator; in the slightly alkaline solution formic acid was regenerated and no end-point could be obtained. The method finally adopted was to add enough sodium hydroxide solution to neutralize nine-tenths of the formic acid, air for fifteen minutes and to remove carbon dioxide and titrate rapidly to the change-point of bromthymol blue.

From Table XVIII it is evident that the rate of reaction is proportional to the anion concentration and independent of the concentration of the acid and of the hydrogen ion over the range studied. In other words, it is actually Reaction III which is responsible for the addition of weak acid. It is also evident that any salt effect amounts to less than 2% in 0.1 *N* solution.

E. Reaction IV

As mentioned already in the Introduction, the primary purpose of the present work was to study Reaction IV, the direct addition of strong acid to ethylene oxides, from the stand-point of the modern theory of the velocity of ionic reactons.

Only little is known of the kinetics of this addition reaction. Bodfors[20] states that the reaction is probably more rapid with hydrobromic than with hydrochloric acid. With hydriodic acid a simultaneous reduction of the oxide is known to occur.

The addition of hydrochloric acid to epichlorohydrin has recently been found by Smith, Wode and Widhe[14] to be a reaction of the third order. These authors followed the reaction by an analytical method; they worked at comparatively high acid concentrations (0.07–0.13 *M*), they did not recognize the presence of Reactions I and III, and from their results the salt effect upon Reaction IV cannot be determined.

A number of preliminary experiments were carried out in order to determine under what conditions Reaction IV might best be studied. In these experiments the reaction was followed by measurement of the diminution in the conductivity of the solution with addition of acid, the oxide being always present in great excess. An approximate velocity constant was calculated from the equation

$$-\frac{\mathrm{d}c_{\mathrm{Acid}}}{\mathrm{d}t} = kc_{\mathrm{Oxide}}c^2_{\mathrm{Acid}}$$

or

$$\frac{\mathrm{d}\left(\frac{1}{c_{\mathrm{Acid}}}\right)}{\mathrm{d}t} = kc_{\mathrm{Oxide}}$$

by plotting the reciprocal of the acid concentration against time and dividing the slope of the best line through the early points by the oxide concentration. The results of these preliminary experiments are given in Table XIX.

It appears from these figures that the addition of hydrobromic acid is four or five times as rapid as the addition of hydrochloric acid in both the ethylene oxide and epichlorohydrin reaction and also that the reaction with ethylene oxide is about four times as rapid as the reaction with

TABLE XIX

PRELIMINARY EXPERIMENTS ON REACTION IV

Oxide	Init. concn., molarity	Acid	Init. concn., molarity	Temp., °C.	*k*
Ethylene oxide	0.12	HBr	0.010	25	8.7
Ethylene oxide	.14	HCl	.010	25	2.2
Ethylene oxide	0.13– .27	HBr	.010	18	4.2[a]
Glycid	.14	HBr	.010	20	3.3
Epichlorohydrin	.15	HBr	.010	20	1.3
Epichlorohydrin	.15	HCl	.010	20	0.27

[a] The average of the values from four experiments.

epichlorohydrin. For the accurate measurements we decided upon the hydrobromic acid–glycid reaction as probably the most suitable.

1. Description of Experimental Part

The disappearance of hydrobromic acid in the glycid solution was measured by the conductivity of the solution in the conductivity cell shown in Fig. 1. The relation between conductivity and concentration of pure aqueous hydrobromic acid solutions was first determined in the same cell. From this relationship the concentration in the solutions in which the addition took place was calculated on two assumptions; first, that the medium effect of glycid upon the conductivity of hydrobromic acid was the same as the medium effect upon the conductivity of perchloric acid, for which an increase of 1.2% in resistance was found to correspond to a concentration of 0.10 *M* glycid; and, second, that the medium effect of the glycid, glycerin and bromohydrin present in the solution after the start was the same as the initial medium effect of the glycid. This is certainly not exactly true but may be taken as a sufficient approximation.

The cell constant was obtained by measurement of the conductivity of a *N*/50 potassium chloride solution; the value of Kohlrausch, Holborn and Diesselhorst,[22] was applied for the specific conductivity of *N*/50 potassium chloride solution at 20°.

The acid used was made from Kahlbaum's 25% hydrobromic acid, which was distilled in an all-glass apparatus; the second half of the distillate was redistilled and the middle portion of the second distillate (passing over under a pressure of 764 mm. and containing 47.8% of hydrogen bromide) was taken for the experiments. Solutions ranging from 0.06 to 0.001 *M* were measured. Excepting the original solution, 0.06173 *M*, each solution of hydrobromic acid was prepared at room temperature by dilution to one liter of 500 cc. of the preceding solution. No solvent correction was made; it may be mentioned, however, that the specific con-

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[22] Landolt, Börnstein, Roth, Scheel, "Physikalisch-chemische Tabellen," 5th ed., Vol. II, p. 1098.

ductivity of the water used was 2.4 × 10^{-6} reciprocal ohms. The molecular conductivities are given in Table XX and are shown in Fig. 6 plotted against the square roots of the hydrobromic acid concentration.

TABLE XX

MOLECULAR CONDUCTIVITY OF HYDROBROMIC ACID. $t = 20°$

HBr, molarity	Molecular conductivity	HBr, molarity	Molecular conductivity
0.06173	366.8	0.003858	386.4
.03087	374.2	.001929	388.9
.01543	379.6	.000965	389.9
.007717	383.4		

The experimental procedure for determining the rate of addition was the following. A glycid solution was placed in Cell A and allowed to come to the temperature of the thermostat, after which a certain volume was removed with a pipet and an equal volume of hydrobromic acid solution was added. Carbon dioxide-free air was bubbled through the solution in order to mix it and readings of the resistance of the solution were then made at convenient intervals.

The values of the molal conductivity shown in Table XX were plotted against the logarithm of the corresponding resistances. By referring the logarithm of the resistance of the reacting solution corrected for the medium effect, to this graph, the corrected molal conductivity was obtained and from this again the concentration of the hydrobromic acid in the reacting solution was calculated.

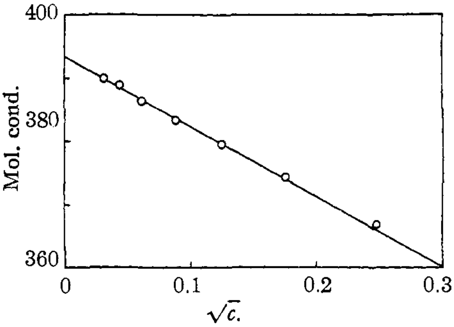

Fig. 6.—Molal conductivity of hydrobromic acid, c = molality of HBr.

2. Calculations

As already pointed out, in an aqueous solution of hydrobromic acid and glycid four reactions occur. Letting x be the concentration of glycid and y the concentration of hydrobromic acid in moles per liter, we may express the kinetic equations of these reactions as follows:

(Reaction I) Glycid + $H_2O \longrightarrow$ Glycerin

$$-\left(\frac{dx}{dt}\right)_1 = k_1x \tag{1}$$

(Reaction II) Glycid + $H_2O \xrightarrow{H_3O^+}$ Glycerin

$$-\left(\frac{dx}{dt}\right)_2 = k_2xy = (k_2' + k_2''y)xy \tag{2}$$

(Reaction III) Glycid + Br^- + H_2O ⟶ Bromohydrin + OH^-

$$-\left(\frac{dx}{dt}\right)_3 = k_3xy; \quad -\left(\frac{dy}{dt}\right)_3 = k_3xy \qquad (3,\ a \text{ and } b)$$

(Reaction IV) Glycid + Br^- + H_3O^+ ⟶ Bromohydrin + H_2O

$$-\left(\frac{dx}{dt}\right)_4 = -\left(\frac{dy}{dt}\right)_4 = k_4xy^2f^2 \qquad (4,\ a \text{ and } b)$$

In setting up these equations the salt effect upon Reaction I and III, which are insignificant, have been neglected. In Reaction II the salt effect has been taken care of by the member $k_2''y$. The equation developed for Reaction IV is identical with Equation 1 on p. 429 and is the relation to be tested; f indicates the activity coefficient of a univalent ion, for which the equation[23]

$$-\log f = 0.5\sqrt{c} - 0.5\,c \qquad (5)$$

is supposed to hold.

According to the theoretical Equation 4, the direct addition of hydrobromic acid to glycid is no simple third order reaction. Calculating the reaction constant, k_4f^2, under the presupposition of a simple third-order reaction, we shall expect it to increase steadily during an experiment due to the increase in f as the reaction proceeds.

The constants k_1, k_2', k_2'' and k_3 are all known from the preceding sections, namely, $k_1 = 2.30 \times 7.4 \times 10^{-6}$; $k_2' = 2.30 \times 0.0640$; $k_2'' = 2.30 \times 0.035$; $k_3 = 0.00100$. The problem is to decide whether the experiments can be satisfied by a constant value of k_4 and to find its value.

The rate of disappearance of glycid from Equation 1 to 4 is

$$-\frac{dx}{dt} = k_1x + k_2'xy + k_2''xy^2 + k_3xy + k_4xy^2f^2$$

and the rate of disappearance of acid

$$-\frac{dy}{dt} = k_3xy + k_4xy^2f^2$$

We wish to integrate these equations in such a way that from an observed relationship between y and t we are in a position to determine the unknown quantity, k_4. This problem can be solved in a way which has been pointed out by Mr. B. Jessen. We are much indebted to him for this assistance and also for his carrying out a great part of the rather lengthy numerical calculations.

Let

$$k_1 + k_2'y + k_2''y^2 = g \qquad (6)$$

a known function of y, and

$$k_3y + k_4y^2f^2 = h \qquad (7)$$

an unknown function of y. The differential equations then become

$$-\frac{dx}{dt} = (g + h)x \qquad (8)$$

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[23] *Cf.* Brönsted, *Trans. Faraday Soc.*, **23**, 416 (1927).

and

$$-\frac{\mathrm{d}y}{\mathrm{d}t} = hx \tag{9}$$

Subtracting, we have

$$-\frac{\mathrm{d}(x-y)}{\mathrm{d}t} = gx$$

and letting $x - y = X$

$$-\frac{\mathrm{d}X}{\mathrm{d}t} = gX + gy$$

Since g and gy are known functions of t, the above equation in X is linear and of the first degree in X and $\mathrm{d}X/\mathrm{d}t$ can be integrated; the integrated form is

$$X = \frac{1}{S}\left[X_0 - \int_0^t gyS\mathrm{d}t\right] \tag{10}$$

where S is given by

$$\ln S = \int_0^t g\mathrm{d}t$$

We now have x or $X + y$ as a function of t, and from the slope of the curve obtained by plotting y against t, the value of the function h may be found at any time. From Equation 2 we have

$$k_4f^2 = \frac{h - k_3y}{y^2} \tag{11}$$

the value of which is now determined by inserting for y and h their proper values. The constancy of k_4 thus determined will furnish a test of the correctness of the equation used for describing Reaction IV.

From Table XXI, in which the results of a typical experiment are given, the procedure of the calculations appears clearly.

TABLE XXI

THE ADDITION OF HYDROBROMIC ACID TO GLYCID. $t = 20°$

Time, minutes	$y \times 10^5$	$-\frac{\mathrm{d}y}{\mathrm{d}t} \times 10^6$	$g \times 10^6$	S	x	k_4f^2	$\log k_4 + 2 \log f$
0	991	...	148	1.00	0.1456	..	...
10	945	4.23	141	1.02	.1432	3.20	0.505
20	902	3.84	137	1.03	.1406	3.24	.511
30	866	3.49	129	1.04	.1385	3.24	.511
40	832	3.16	124	1.06	.1364	3.23	.509
50	802	2.88	120	1.07	.1345	3.24	.510
60	774	2.65	116	1.08	.1326	3.20	.505
70	749	2.45	112	1.09	.1308	3.21	.506
80	725	2.27	109	1.11	.1292	3.21	.506
90	702	2.12	105	1.12	.1275	3.24	.510
100	682	1.99	102	1.13	.1261	3.18	.503
110	662	1.86	99.2	1.14	.1246	3.26	.513
120	645	1.76	96.6	1.15	.1232	3.28	.516
130	627	1.66	94.0	1.16	.1219	3.31	.520
140	611	1.57	91.6	1.17	.1206	3.33	.522
150	595	1.49	89.3	1.18	.1194	3.36	.526

TABLE XXI (*Concluded*)

Time, minutes	$y \times 10^5$	$-\frac{dy}{dt} \times 10^6$	$g \times 10^5$	S	x	k_4f^2	$\log k_4 + 2 \log f$
160	581	1.41	87.2	1.20	0.1181	3.37	0.528
170	567	1.34	85.1	1.21	.1171	3.38	.530
180	554	1.27	83.2	1.22	.1158	3.38	.530
200	530	1.15	79.6	1.24	.1138	3.42	.534
220	508	1.04	76.5	1.26	.1118	3.41	.533
240	488	0.945	73.5	1.27	.1100	3.40	.532
260	470	.860	70.9	1.29	.1082	3.38	.530
280	454	.799	68.4	1.31	.1065	3.43	.535
300	438	.725	66.2	1.33	.1050	3.37	.528
320	424	.671	64.1	1.35	.1034	3.37	.528
340	411	.621	62.2	1.36	.1020	3.36	.526
360	399	.584	60.4	1.38	.1006	3.38	.530
380	388	.543	58.8	1.40	.0994	3.37	.528
400	377	.512	57.2	1.41	.0981	3.41	.533
1320	181	.0923	28.3	2.02	.0670	3.65	.562
1380	175	.0852	27.4	2.05	.0658	3.65	.562
1440	170	.0790	26.7	2.09	.0647	3.64	.561
1500	165	.0736	26.0	2.12	.0637	3.64	.561
1560	161	.0688	25.4	2.15	.0627	3.61	.558
1620	157	.0647	24.8	2.18	.0617	3.61	.558
1680	154	.0610	24.3	2.22	.0608	3.61	.558
1740	150	.0582	23.8	2.25	.0598	3.66	.564

The initial values of glycid and hydrobromic acid (x_0 and y_0) were 0.1456 and 0.00991, respectively. The values of the concentration of hydrobromic acid (Col. 2) at the time, t (Col. 1), are smoothed values taken from a graph in which y, determined by the conductivity method as described (p. 451), was plotted against t. The fourth column contains the function g or $k_1 + k_2'y + k_2''y^2$ calculated from the values of the constants given above. The fifth contains S, *i. e.*, the antilogarithm of the integral $0.4343 \int_0^t gdt$ obtained by graphic integration. The sixth column contains the glycid concentration x, which is equal to

$$\frac{1}{S}\left[X_0 - \int_0^t gySdt\right] + y$$

Here again the integral was evaluated graphically. The seventh column records k_4f^2, the classical velocity constant, calculated by Equation 11; the eighth, its logarithm.

3. Results

In Fig. 7 the velocity constant k_4f^2 from Table XXI is plotted against hydrobromic acid concentration and in Fig. 8 the logarithm of the same velocity constant is plotted against the square root of the acid concentration. From the first plot the increasing change in the constant with decreasing acid concentration predicted by the theory appears. The second plot gives a simple quantitative picture of this change. Since the activity coefficient f is given by Equation 5, the limiting slope for small concentrations in the plot, Fig. 8, should be

$$\frac{d \log (k_4f^2)}{d\sqrt{c}} = -1$$

The straight line in Fig. 8 is drawn with this slope, to which the measurements are seen actually to conform very well.

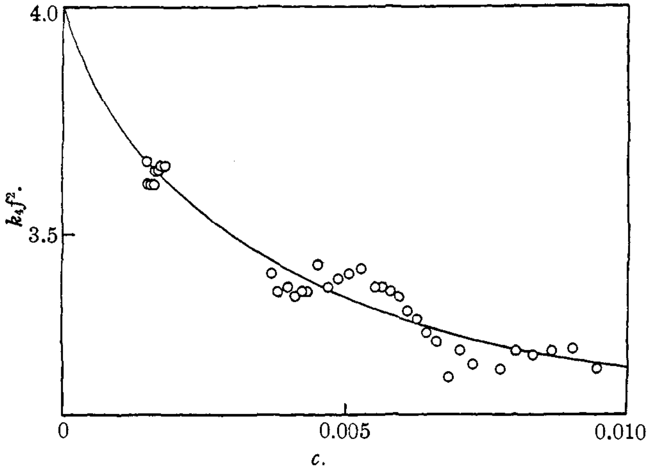


Fig. 7.—Addition of HBr to glycid. Reaction IV, c = HBr concentration.

In addition to the one experiment here described, five other experiments were performed in which the initial glycid concentration ranged from 0.045 to 0.15 M, and the initial hydrobromic acid concentration from 0.0067 to 0.041 M. The series of velocity constants k_4f^2 obtained for all the experi-

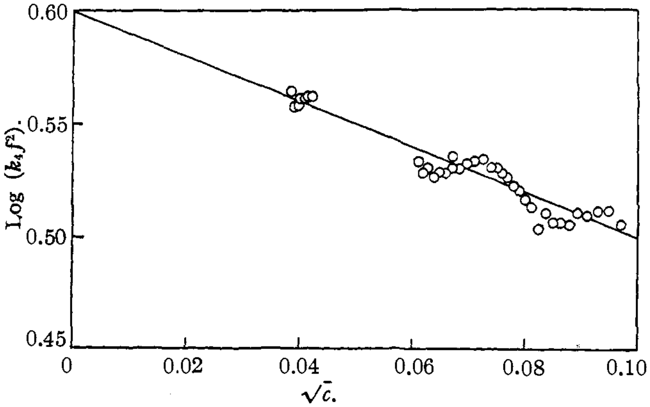


Fig. 8.—Addition of HBr to glycid. Reaction IV, c = HBr concentration.

ments in quite the same way as above were plotted against the hydrobromic acid concentrations, as is done for a single experiment in Fig. 7, and through the band of points a representative curve was drawn. In Table XXII are shown the velocity constants taken from this curve and corresponding to specified hydrobromic acid concentrations.

TABLE XXII

THE VELOCITY OF REACTION IV

Glycid + Hydrobromic Acid ⟶ Bromohydrin

HBr concn., molarity	Obs. velocity constant (k_4f^2)	log k_4 + 2 log f	HBr concn., molarity	Obs. velocity constant (k_4f^2)	log k_4 + 2 log
0.00100	3.72	0.571	0.0100	3.17	0.501
.00200	3.59	.555	.0125	3.10	.491
.00300	3.47	.540	.0150	3.04	.483
.00400	3.41	.533	.0175	2.99	.476
.00500	3.35	.525	.0200	2.95	.470
.00600	3.30	.519	.0250	2.87	.458
.00700	3.27	.515	.0300	2.81	.499
.00800	3.23	.509	.0350	2.75	.439
.00900	3.20	.505	.0400	2.69	.430

The logarithms of the velocity constants, k_4f^2, given in the third column of Table XXII are plotted in Fig. 9 against the square roots of the acid concentrations. The dotted line in the graph indicates the theoretical limiting slope. The full curve is drawn to satisfy the equation

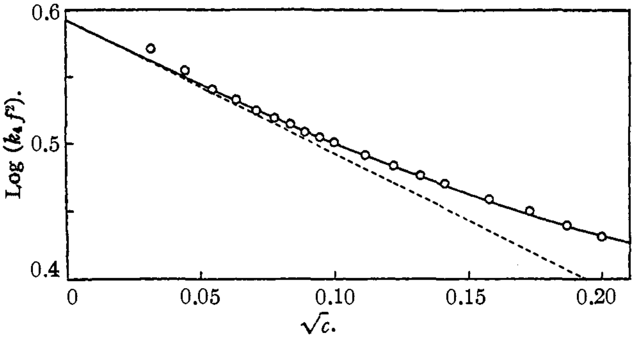


Fig. 9.—Addition of HBr to glycid. Reaction IV, c = HBr concentration.

$$\log (k_4f^2) = 0.592 + \sqrt{c} + c$$

which takes into account the deviations from the limiting slope at higher acid concentrations.

Except for the two points in the most dilute region, where the experimental error is greatest, the experimental points are obviously located very closely on this curve. This means that the experimental points satisfy the two equations $\log k_4 = 0.592$ and $2 \log f = \sqrt{c} + c$, the latter of which is identical with Equation 5. In other words, since f is known to follow Equation 5, the experiments have shown k_4 to be a constant independent of the acid concentration.

In spite of the interference of three other processes, it has thus been possible to show that the direct addition of a strong acid to glycid follows the requirement of the modern theory of velocity of ionic reactions.

F. Discussion

From the results stated in the previous sections it is evident that the "basicity" of ethylene oxides is a property which is exhibited in solutions of these substances only under certain conditions and is not at all inherent in the oxide molecules as in the case of true bases. The oxide molecules are unable—at least to an extent detectable in the ordinary experiment—to exert the basic function which consists in the simple addition of protons. If the oxide molecule takes up a proton it invariably at the same time adds also an anion, and if no suitable anion is available it remains unchanged.

The simultaneous addition of a proton and an anion amounts to the addition of a hydrogen compound. If this hydrogen compound is an acid, for instance, hydrochloric acid, the reaction makes the acidity of the solution decrease and the oxide seems to be basic. The tendency to add an acid may be so strong that the reaction proceeds rapidly even in an aqueous solution which is already "neutral" or "basic" (for instance in potassium iodide). The hydrogen compound in question, however, need not be of acid character. The ethylene oxides, for instance, add basic hydrogen compounds, and the occurrence of this reaction in water solution may cause an increase in acidity. The conclusion on the basis of such phenomena that ethylene oxide is an acid would be justified to the same extent as the conclusion of its being a base on the basis of its adding hydrogen chloride.

The truth, of course, is this, that the ethylene oxides do not possess the character of bases. Applying to them the term of "pseudo-bases" would not even be an adequate description of their nature. Their apparent basicity (and acidity) simply originate in their tendency to combine directly with, and thus to remove from the solution, a multitude of substances, whereby, according to the nature of the substance removed and formed, the acidity of the solution may increase or decrease. Since the reactions by which acids are taken up are the more numerous and conspicuous, the idea generally adopted of a special basicity of these oxides becomes intelligible.

As to the kinetic mechanism by which the basicity in a solution is produced, it has been shown above that two Reactions (III and IV) are effective. While Reaction IV, or the direct addition of acids, takes place in the case of the halide acids, Reaction III seems to occur more generally for both weak and strong acids. Perchloric acid is the only one for which no indication of addition has been found either by Reaction III or IV. It is Reaction III which is essentially responsible for the phenomenon of "basicity" observed in solutions of ethylene oxides under ordinary conditions.

The study of the different reactions in which the ethylene oxides take part has also contributed to the verification of the general theory of reaction velocity.[3,4] For Reaction II, which takes place between the oxide molecule and the hydrogen ion, this theory requires a linear salt effect which has actually been found (Tables II, IV and VII) in the hydrogen-ion catalysis of all three oxides investigated. It is in conformity with this theory that the concentration of the hydrogen ion in these reactions is the factor by which the reaction is mainly controlled. Essentially the same laws hold good in the case of Reaction III. Reaction IV, on the other hand, is a reaction between ions of opposite sign, and should theoretically be characterized by a negative exponential salt effect. As shown above (Section E, 3) this is actually found and the salt effect demonstrated corresponds closely to the requirements of the theory.

In order to compare the velocities of the various reactions, the constants are collected in tables below. Table XXIII contains the unimolecular constants for Reactions I and II for the three oxides investigated.

TABLE XXIII

$t = 20°$

	k_1 (Spont. react.)	k_2 (Hydrogen-ion catal.)
Ethylene oxide	2.16×10^{-5}	$0.320 + 0.28c$
Glycid	1.70×10^{-5}	$0.147 + 0.081c$
Epichlorohydrin	5.84×10^{-5}	$0.0244 + 0.0150c$

The constants seem to depend upon the substance in an individual manner. While in passing from ethylene oxide to glycid both constants decrease somewhat, there is a considerable increase in k_1 and a considerable decrease in k_2 passing from these oxides to epichlorohydrin. The ratios glycid/epichlorohydrin are

$$\left(\frac{k_{Gl}}{k_{Ep}}\right)_1 = 0.29 \qquad \left(\frac{k_{Gl}}{k_{Ep}}\right)_2 = 6.0$$

The constants for Reaction III are given in Table XXIV.

TABLE XXIV

k_3 AT ZERO SALT CONCENTRATION. $t = 20°$

Ion reacting	Glycid	Epichlorohydrin	$(k_{Gl}/k_{Ep})_0$
I^-	1.62×10^{-2}	6.0×10^{-2}	0.27
Th^-	7.9×10^{-3}	3.8×10^{-2}	.21
Br^-	1.03×10^{-3}	3.7×10^{-3}	.28
Cl^-	1.50×10^{-4}	6.9×10^{-4}	.22
Formate	....	2.8×10^{-4}	..
Benzoate	....	3.1×10^{-4}	..
Acetate	....	3.7×10^{-4}	..
Trimethylacetate	....	5.0×10^{-4}	..

In this table the anions—except for Th^-, the thiocyanate ion, the strength of which is unknown—are arranged according to basic strength. This factor, however, does not seem to control the reactions, since in the case of the halide ions the velocity increases with decreasing strength, while the converse is true for the anions of the four organic acids. In the cases of the very weak base Cl^- and the relatively strong trimethylacetate ion, the rates are practically the same. As shown by the last column in Table XXIV, the reaction is about 4 times faster with epichlorohydrin than with glycid. The ratio k_{Gl}/k_{Ep} is almost the same for Reactions III and I.

Reaction IV has been extensively studied only for glycid and hydrobromic acid. The preliminary results recorded in Table XIX, however, enable us to obtain an approximate comparison for a number of reactions. From the data in this table at 25 and 18°, the data for 20° have been calculated by the equation $d \log k/dT = 0.045$, which is shown to hold for ethylene oxide.

TABLE XXV

k_4 FOR HALOGENIC ACIDS AT ACID CONCN. 0.01 AND $t = 20°$

Ethylene oxide	HBr	5.2
Ethylene oxide	HCl	1.3
Glycid	HBr	3.3
Epichlorohydrin	HBr	1.3
Epichlorohydrin	HCl	0.27

As in Reaction III, glycid here also reacts somewhat more slowly than ethylene oxide, and epichlorohydrin again more slowly than glycid. For the ratio k_{Gl}/k_{Ep} we find

$$\left(\frac{k_{Gl}}{k_{Ep}}\right)_4 = 2.5$$

It is possible, therefore, to divide the four reactions here dealt with into two groups, one comprising Reactions I and III, in which epichlorohydrin reacts much faster than glycid, and another, comprising Reactions II and IV, in which the converse is true. Furthermore, comparing the constants of the four reactions for each oxide, the following simple relation is found to be approximately true

$$\frac{k_1}{k_2} = \frac{k_3}{k_4}$$

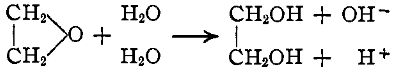
This is shown by the figures in Table XXVI, where the logarithms of the available ratios are tabulated.

TABLE XXVI

LOGARITHMS OF RATIOS

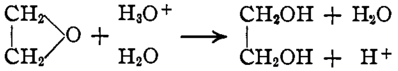
Oxide	Log k_1/k_2	Log k_3/k_4 (Cl)	Log k_3/k_4 (Br)
Glycid	$\bar{4}.1$	...	$\bar{4}.5$
Epichlorohydrin	$\bar{3}.4$	$\bar{3}.4$	$\bar{3}.6$

An explanation of this simple relationship is afforded by the assumption of the following mechanism underlying the reactions. If in Reaction I the water molecule taken up by the oxide originates from two molecules of water, the one providing a proton and the other an hydroxyl ion



(I)

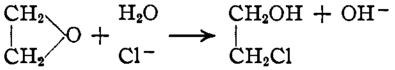
Reaction II may be described in an analogous way by simply exchanging the first water molecule which provides the proton by a hydrogen ion:



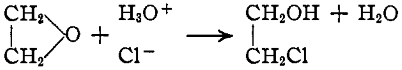
(II)

Since the H_3O^+ ion is much more acid than H_2O, the proton is more easily provided by the former, while the addition of OH^- is not affected by the presence of OH_3^+. Reaction II therefore proceeds much more rapidly than Reaction I.

If now in (I) and (II) the second water molecule is exchanged for an anion, for instance, Cl^-, Reactions III and IV appear



(III)



(IV)

and as in these reactions IV is obtained from III by again exchanging H_2O by H_3O^+, Reaction III is seen to be related to IV in just the same way as I to II. The simple relationship demonstrated by the figures in Table XXVI seems, therefore, to be well justified by the mechanism suggested.

The kinetic similarity found within the two groups of reactions here dealt with also justifies the point of view previously emphasized that catalytic reactions (Reaction II) and ordinary uncatalyzed reactions are intrinsically not different in nature.

Further insight into the reactions of the ethylene oxides may be obtainable by examining their kinetic properties in more alkaline solutions and from the stand-point of the extended theory of acid and basic catalysis. This problem is the subject of further studies in this Laboratory.

The authors are indebted to Rask-Örsted-Fondet, Copenhagen, for a grant which has made this investigation possible.

Summary

1. The ethylene oxides react in aqueous solutions in four different ways. They unite spontaneously with water to form glycols (Reaction I). The same reactions proceed, catalyzed by hydrogen ions H_3O^+ (Reaction II). They react with anions and water taking up acid (Reac-

tion III); and finally add acids directly (Reaction IV). It has been possible to separate and study separately all these reactions, using as material ethylene oxide, glycid and epichlorohydrin.

2. The hydration of ethylene oxides (Reactions I and II) is accompanied by a considerable contraction and can be followed dilatometrically. Reactions III and IV can be followed titrimetrically. A special titrimetric procedure in artificially controlled buffers was devised for following the addition of anions of strong acids (Reaction III). Reaction IV was followed by conductivity measurements.

3. The ethylene oxides exhibit apparently basic properties in certain solutions. They are, however, not bases or pseudo-bases. Their "basicity" is due to their taking up acids, which may occur through Reactions III or IV. Under ordinary conditions Reaction IV is predominant in causing basicity. The oxides may, however, also add bases and this causes acidity.

4. The hydrogen-ion catalysis (Reaction II) is determined by the concentration of the hydrogen ion. There is a considerable positive primary salt effect, which in accordance with the general theory of velocity is linear in character. Reaction III proceeds proportionally to the anion concentration and shows a slight negative primary salt effect. The velocity constant increases in the order Cl^-, Br^-, CSN^-, I^-, and in the order formate, benzoate, acetate, trimethylacetate ion.

5. The direct addition of strong acid was specially studied with glycid and hydrobromic acid. The reaction—in which two ions of opposite sign take part—was shown to follow the theoretical equation for such reactions, exhibiting an exponential negative salt effect of the predicted magnitude.

6. The constants k_1, k_2, k_3 and k_4 for Reactions I–IV satisfy approximately the equation $k_1/k_2 = k_3/k_4$. A plausible reaction mechanism has been suggested, which explains this relation.

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