

THE CHEMISTRY OF ETHYLENE OXIDE

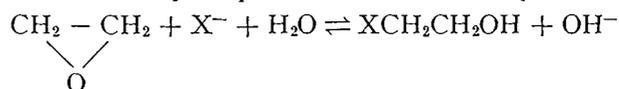
V. THE REACTION OF ETHYLENE OXIDE WITH HALIDE IONS IN NEUTRAL AND ACID SOLUTION¹

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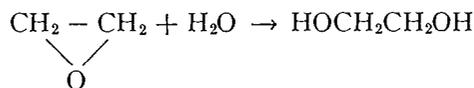
ABSTRACT

The rates of reaction of halide ions with ethylene oxide in neutral aqueous solution and the rate of hydrolysis of ethylene oxide in acid solution have been measured and the activation energies determined. From these data and from the ratio of glycol to chlorohydrin formed when ethylene oxide reacts with excess aqueous hydrogen halide, the rates of the acid-catalyzed addition of halide ions to ethylene oxide at 25°C. have been estimated.

In aqueous solution ethylene oxide reacts with halide ions to form halo-hydrins. These reactions were studied for a number of substituted oxides at 20°C. by Bronsted, Kilpatrick, and Kilpatrick (1) and shown to occur by both uncatalyzed and acid-catalyzed processes. The uncatalyzed reactions



were followed by measuring the rate of acid addition required to keep the solution neutral and were usually sufficiently rapid that the uncatalyzed hydrolysis of the oxide



did not seriously interfere with the measurements. In acid solution, however, the formation of glycol was an important side reaction and the accurate measurement of the rate of the acid-catalyzed addition of halide ions was therefore difficult. Bronsted *et al.* succeeded in making such measurements for the bromide-glycid system by measuring the rate of change in the conductivity of the solution, and established that the reaction was of the third order, dependent upon the oxide, hydrogen ion, and bromide ion concentrations. The method was laborious and was therefore applied only to the one reaction, but the authors did record some approximate rate constants for the acid-catalyzed addition of chloride and bromide ions to ethylene oxide.

In the course of work in these laboratories it became desirable to extend some of these data to ethylene oxide itself and accordingly, the uncatalyzed

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rates of halide ion addition were measured, using a slight modification of Bronsted's method. The rates were sufficiently slow to suggest that an estimate of the acid-catalyzed rates could be made by measuring the ratio of glycol to chlorohydrin formed from ethylene oxide in a large excess of acid. This ratio, as pointed out by Lichtenstein and Twigg (5) is expressed approximately by the equation

$$\frac{\text{Glycol}}{\text{Chlorohydrin}} = \frac{k_1}{k_2} (X^-)$$

where k_1 and k_2 are the rate constants for the acid-catalyzed formation of glycol and of halohydrin respectively and where (X^-) is the concentration of halide ion. The value of k_1 may be determined independently and therefore by using a large excess of halide ion to minimize concentration changes, the value of k_2 may be estimated from the glycol/halohydrin ratio, on the assumption that these are the only products formed.

EXPERIMENTAL

(a) The rates of the uncatalyzed addition of halide ions to ethylene oxide were determined as follows. A four-necked flask fitted with a mechanical stirrer, a 5 ml. burette and the external electrodes of a Beckman model G pH meter was held in a constant temperature bath regulated to 0.01°C. The burette was graduated in units of 0.01 cc. and was tipped with a small stainless steel hypodermic needle to permit the addition of very small drops of liquid. A solution of alkali metal halide was adjusted to pH 7.0 with the corresponding acid and a known volume introduced into the flask and allowed to come to bath temperature. A weighed ampoule of ethylene oxide was broken under the solution, the stirrer started, and acid was then added from the burette at such a rate that the pH of the solution was kept between 6 and 8. Measurements were made only in the first 5% of reaction and the concentration of acid was so adjusted that the increase in volume of the solution during the period of measurement was not over 2%. The chloride and bromide reactions were titrated with the corresponding acids and calculated as pseudo-first order reactions but, because of the instability of hydrogen iodide, the rate of iodide addition was followed with perchloric acid and calculated by second order methods. Sodium perchlorate was used as a neutral salt in the determination of salt effects.

(b) The rate of the acid-catalyzed hydrolysis of ethylene oxide was determined dilatometrically according to the method of Bronsted *et al.* and corrected for the uncatalyzed reaction by means of the data of Lichtenstein and Twigg (5).

(c) The ratio of glycol to chlorohydrin formed in the reaction of ethylene oxide with acid solutions of halide ions was determined by the following procedure. A weighed sample of ethylene oxide was broken into a hydrogen halide-sodium halide solution of known volume and concentration and allowed to react completely; the initial halide ion concentration of the solution was always at least 10 times that of the ethylene oxide but the hydrogen ion

concentration was varied from about 2 to 10 times that of the oxide. The reaction mixture was then analyzed for halohydrin by acid-base titration or for glycol by periodate oxidation, or both, using methods very similar to those previously described (3). The analyses were carefully tested on synthetic mixtures of acid, glycol, and halohydrin before use. No difficulty was experienced with chloride mixtures and bromides gave good results when procedures were standardized and blanks carefully determined. The determination of glycol in the iodide solutions by means of periodate, however, was only accomplished after first precipitating the excess iodide with silver nitrate and then rapidly removing the excess silver with sodium chloride; under these conditions, reproducible and apparently accurate analyses were obtained.

No appreciable amount of free iodine was liberated during the reaction of oxide with the iodide. Reactions with hydrofluoric acid were conducted in polystyrene containers.

The glycol/chlorohydrin ratios as determined by glycol analysis were in reasonable agreement with those obtained by acid-base titration at the lower halide concentrations but above about 0.5 molar discrepancies were observed (Fig. 7). The deviations may have been due to the formation of polymeric products such as diethylene glycol, etc. Altering the HX/NaX ratio did not appear to influence the deviation. Measurements were made at 25° and at 0° but the ratios were not sufficiently sensitive to temperature to permit an estimate of the activation energies. The data were plotted (Fig. 7) and the rate constants estimated from the smoothed curve.

RESULTS

The rates for the uncatalyzed addition of halide ions to ethylene oxide are shown in Figs. 1, 2, 3, and the activation energies for these reactions are shown in Fig. 4. In estimating the activation energies, rates were compared at a concentration of halide ions common to the three temperatures rather than at zero concentration to avoid extrapolation errors.

It is perhaps of interest to note that lithium chloride seems to give a positive salt effect whereas sodium chloride gives the usual negative salt effect in these reactions (Fig. 1). This difference may simply be due to the fact that the activity of lithium chloride increases while that of sodium chloride decreases in the concentration range of these experiments. It is however of interest to note that some recent experiments (to be published) in pyridine solution have led us to believe that lithium ions may indeed have some catalytic activity towards ethylene oxide reactions.

Figs. 5 and 6 show the rates, salt effects, and activation energy for the acid-catalyzed hydrolysis of ethylene oxide. The data appear to be in good agreement with those of Bronsted *et al.*

Fig. 7 shows the ratio of glycol to halohydrin obtained when ethylene oxide is allowed to react with acid solutions of halide ions. From the smoothed curves the acid-catalyzed rate constants were calculated and are shown in Table I; it is evident that the bromide and iodide constants show a consider-

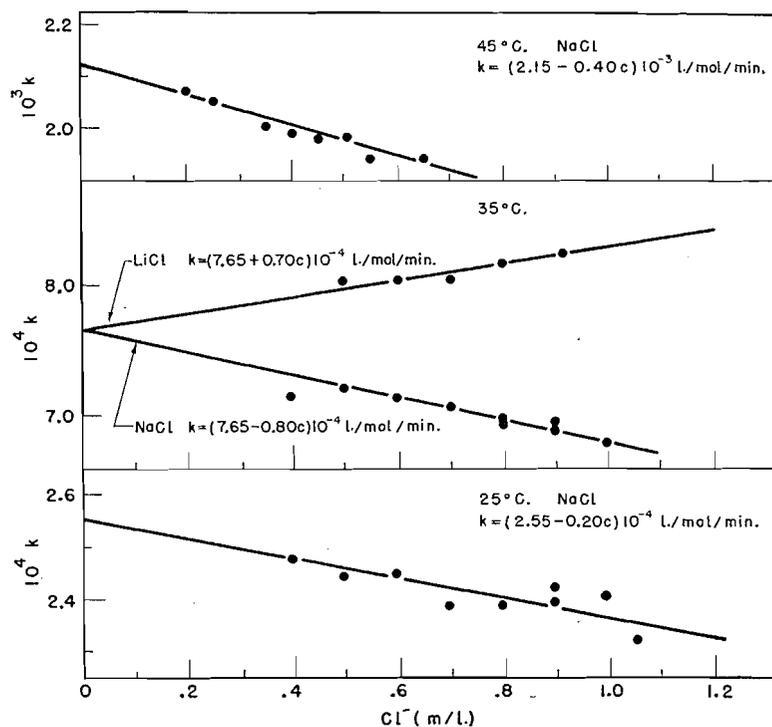


Fig. 1. Reaction of ethylene oxide with chloride ion in neutral solution.

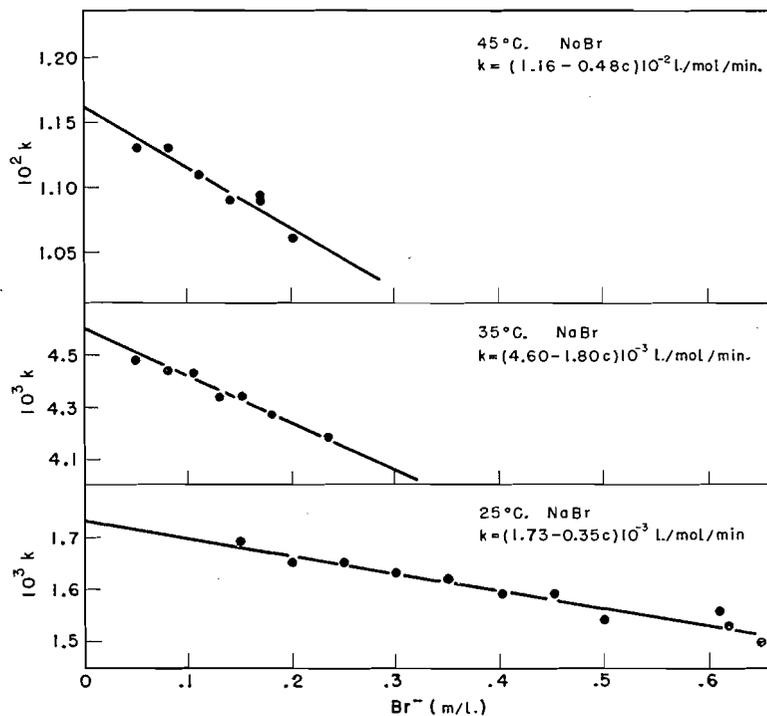


Fig. 2. Reaction of ethylene oxide with bromide ion in neutral solution.

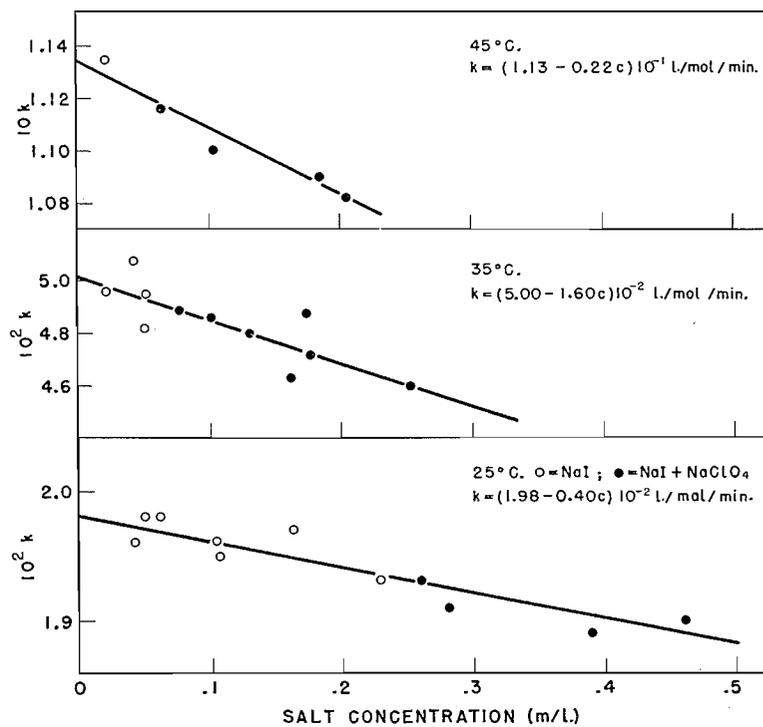


Fig. 3. Reaction of ethylene oxide with iodide ion in neutral solution.

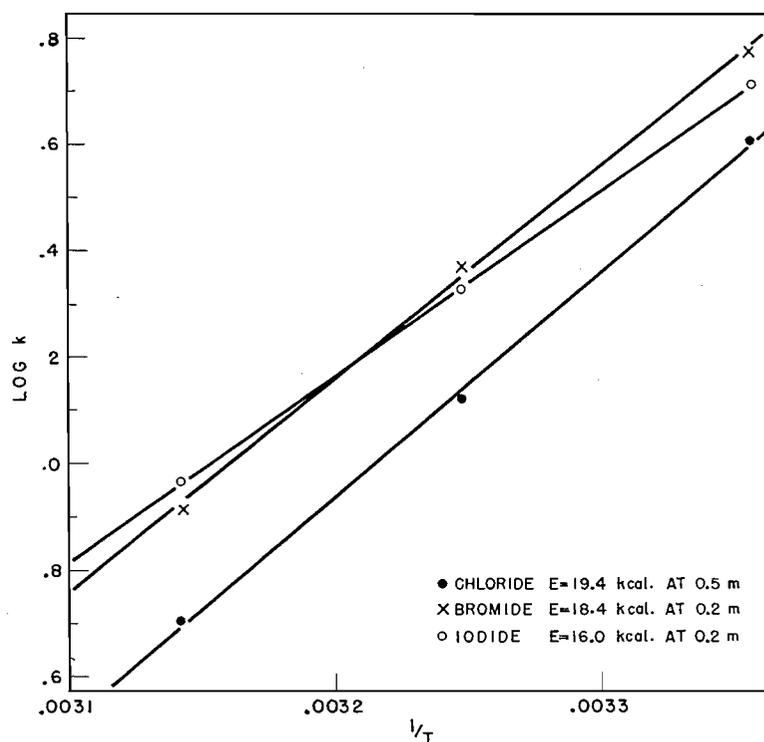


Fig. 4. Activation energies for the uncatalyzed addition of halide ions to ethylene oxide.

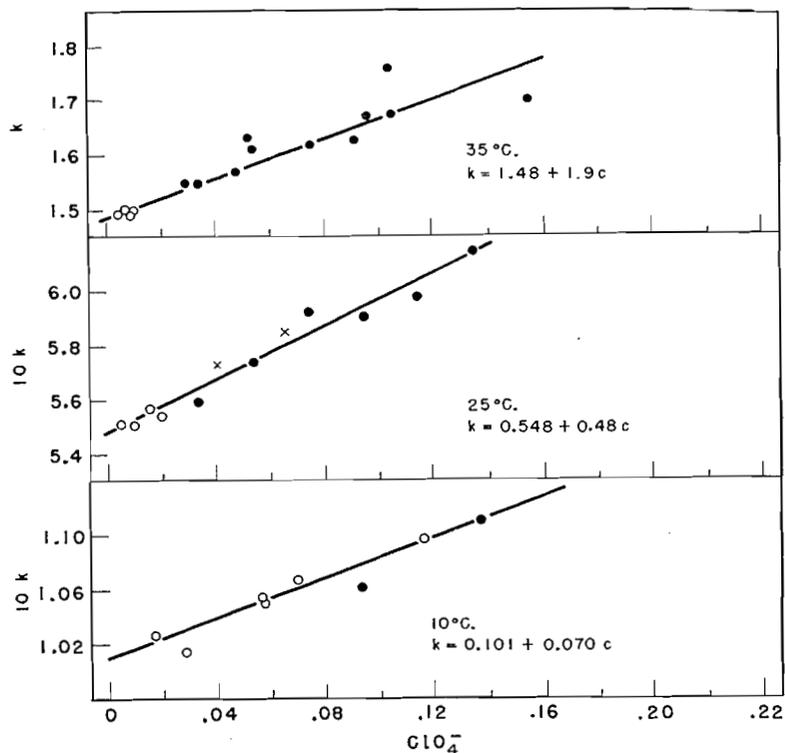


Fig. 5. The acid-catalyzed hydrolysis of ethylene oxide.
 ○ = $HClO_4$ alone; ● = $HClO_4 + NaClO_4$; × = $HClO_4 + LiClO_4$.

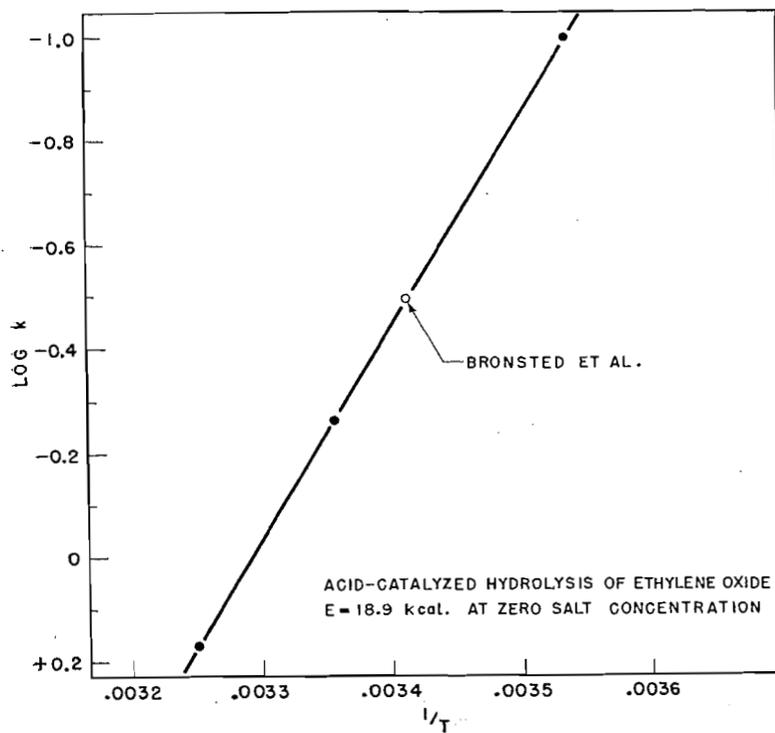


Fig. 6.

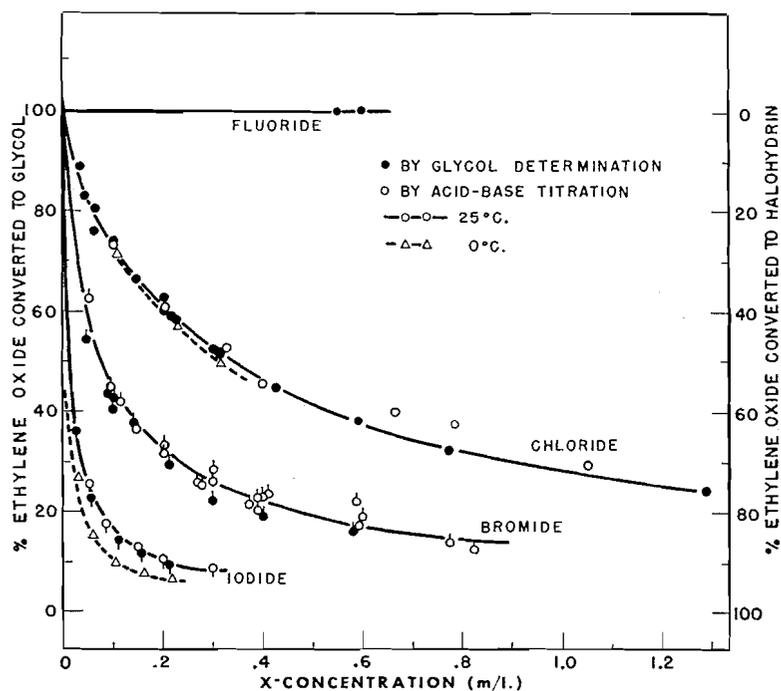


Fig. 7.

able drift towards lower rates as the concentration increases and the recorded average values must therefore be regarded as very approximate. The approximate values reported by Bronsted *et al.* are included for comparison.

The results of all these experiments, together with the corresponding data for a number of other reactions of ethylene oxide, are shown in Table II.

TABLE I

Halide ion concentration, moles per liter	k_{H^+} at 25° for the formation of:			
	Glycol (l.mol. ⁻¹ min. ⁻¹)	Chlorohydrin	Bromohydrin (l. ² mol. ⁻² min. ⁻¹)	Iodohydrin
.025	0.56			37
.050	0.57	2.5		34
.075	0.58	2.4	7.7	33
.10	0.60	2.3	7.5	32
.15	0.62	2.2	7.1	29
.20	0.64	2.1	6.8	30
.30	0.69	2.1	6.9	
.40	0.74	2.1	6.6	
.50	0.79	2.2		
Average		2.2	7.0	33
Bronsted <i>et al.</i>		2.2	8.7	

TABLE II

Reagent	Temp.	Uncatalyzed		Acid-catalyzed	
		k (l.mol. ⁻¹ min. ⁻¹)	Activation energy (kcal.)	k_{H^+} (l. ² mol. ⁻² min. ⁻¹)	Activation energy (kcal.)
I ⁻	25°	2.0×10^{-2}	16.0	33	
Br ⁻	"	1.7×10^{-3}	18.4	7.0	
Cl ⁻	"	2.5×10^{-4}	19.4	2.2	
F ⁻	"			Very small	
OH ^{-*}	"	6.7×10^{-3}	18.1		
H ₂ O**	"	7.3×10^{-7}	19.0*	.010	18.9
Most amines†	"	10^{-1} to 10^{-3}			
NH ₃ ††	"	8.2×10^{-3}	14.6		

* Lichtenstein and Twigg (5).

** The experimentally determined rate constants for the hydrolysis reactions have been divided by the concentration of water (55.5 moles per liter) in order to give them the same dimensions as the other constants.

† Eastham et al. (2).

†† Ferrero et al. (4).

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