THE REACTION BETWEEN ETHYLENE CHLORHYDRIN AND SODIUM HYDROXIDE

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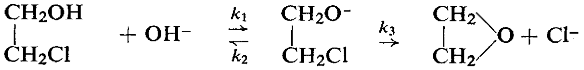
The reaction between ethylene chlorhydrin and sodium hydroxide has been investigated using kinetic measurements, u.v. absorption spectra, heat and electrical conductivity measurements. It has been shown that the reaction proceeds through an intermediate ion formed by the rapidly established equilibrium

$$CH_2ClCH_2OH + OH^- \rightleftharpoons CH_2Cl - CH_2O^- + H_2O;$$

the ion is unstable and decomposes slowly to ethylene oxide. From the variation in the apparent second order velocity constant, the equilibrium constant of the first reaction has been estimated.

The reaction between ethylene chlorhydrin and sodium hydroxide to form ethylene oxide has been studied by many previous investigators.[1-5] Porrett[5] showed that the reaction was second order but that the second-order constant was a function of the initial concentration of the reactants; he concluded that a simple bimolecular reaction did not account for the kinetics. A kinetic investigation, carried out at the same time as Porret, led us to believe that the formation of an intermediate



$$\begin{matrix}CH_2OH\\ |\\ CH_2Cl\end{matrix} + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \begin{matrix}CH_2O^-\\ |\\ CH_2Cl\end{matrix} \xrightarrow{k_3} \begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>O + Cl^-$$

accounts for the deviations from second-order kinetics. The formation of this intermediate has been suggested previously [4, 6-8] but there has been little direct evidence for the participation of the intermediate in the reaction, and it has been implicit in most previous work that the intermediate is formed only in very low concentration. It has now been found that the intermediate is formed in appreciable concentration as soon as the reactants are mixed; reactions 1 and 2 are rapid compared with reaction 3 which controls the production of ethylene oxide.

EXPERIMENTAL AND RESULTS

QUALITATIVE EVIDENCE FOR THE FORMATION OF THE INTERMEDIATE.—(*a*) *Heat measurements*.—Ethylene chlorhydrin and sodium hydroxide solutions were mixed in the Dewar flask calorimeter described below. A typical result of the change of temperature $\Delta\theta$ with time *t* is shown in fig. 1.

The solutions were mixed at the time corresponding to the point B. The temperature then rose by the amount BE. A small part of this temperature rise was due to the heat of dilution of the reactants which was estimated in separate experiments, and is represented in fig. 1 by BD. The temperature rise DE is due, we believe, to the exothermic formation of the intermediate ion. The reaction of the intermediate ion to give ethylene oxide is endothermic and accounts for the fall in temperature along EF. When sodium hydroxide was present in excess, heat was again evolved, as shown by FG. If ethylene chlorhydrin was present in excess, however, the temperature remained constant along FH. Kinetic measurements showed that the formation of ethylene oxide was completed by the time corresponding to the point F. The heat evolution along FG is due to the hydroxyl-ion-catalyzed reaction [9] of ethylene oxide to glycol.

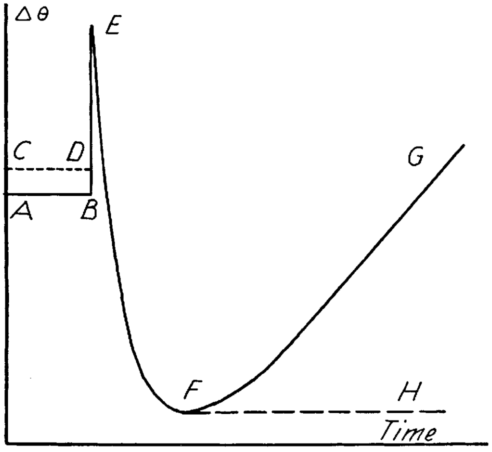


FIG. 1.—Graph of reaction temperature against time.

(*b*) *Spectroscopic evidence*.—Plate I shows the ultra-violet absorption spectrum of two 1-cm cells in tandem containing 2 M ethylene chlorhydrin solution and 2 M sodium hydroxide respectively together with the spectrum of a mixture of equal volumes of the reactants in a 2-cm cell taken at various times after mixing. It is clear that on mixing the reactants there was a marked increase in absorption which cannot be explained as being due to any of the stable reaction products (see Plate I). This absorption decreased with time as would be expected if it were due to the intermediate ion. Later the absorption increased again at about 85 % reaction. This new absorption was probably due to a side reaction producing traces of highly-absorbing substances, possibly condensation products of acetaldehyde.

(*c*) *Conductivity measurements*.—The conductivity of a mixture of chlorhydrin and soda decreases slowly with time owing to the replacement of the hydroxyl ion by the less mobile chloride ion. The conductivity of very dilute mixtures of chlorhydrin and soda, extrapolated to the instant of mixing, was, however, less than the conductivity of sodium

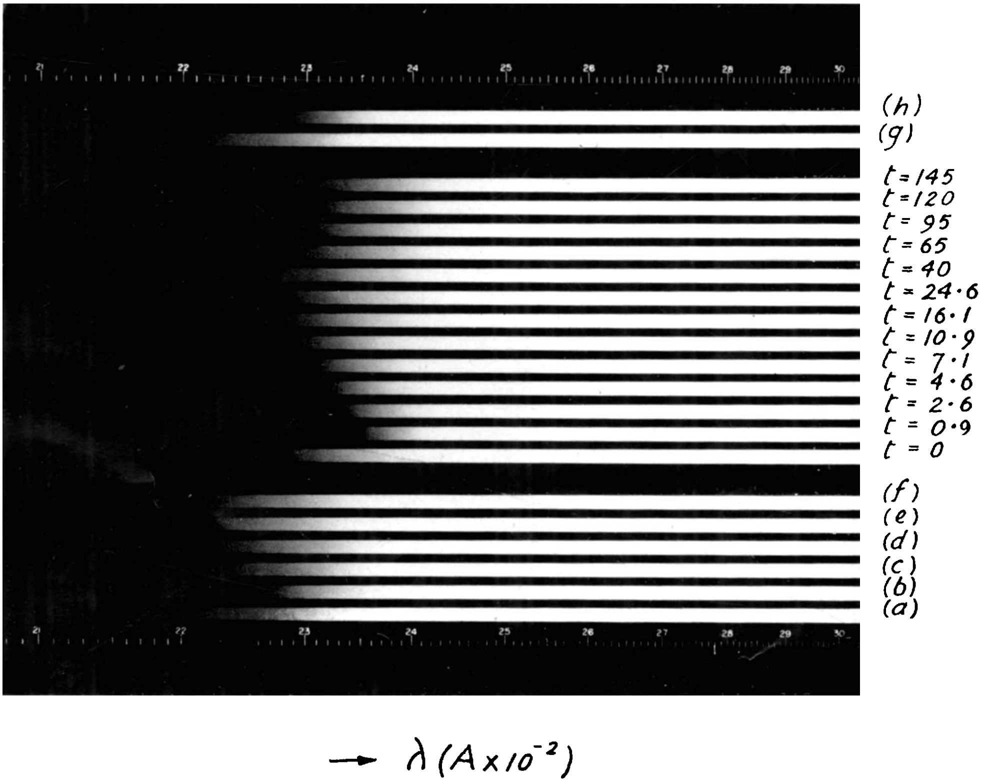


Plate I.—Plate, Ilford auto filter; source, hydrogen lamp; exposure, 15 sec; cell length, 2 cm. (*a*) distilled water, (*b*) 1·01 N NaOH, (*c*) 1·01 M $CH_2Cl—CH_2OH$, (*d*) 1·4 M $(CH_2)_2O$, (*e*) N NaCl, (*f*) M/10 $(CH_2OH)_2$, (*g*) distilled water, (*h*) N/10 Na_2CO_3. $t = 0$, 2·02 N NaOH (1 cm) + 2·02 M $CH_2Cl—CH_2OH$ (1 cm). Other indicated times, minutes after mixing 2·02 N NaOH + 2·02 M CH_2ClCH_2OH, timed to middle of exposure.

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hydroxide solution of the same strength as the mixture. Such a difference is due to the less mobile intermediate ion being rapidly formed on mixing the reactants. Typical results are shown in table 1. It was found difficult, however, to reproduce the mixing conditions with sufficient accuracy to obtain useful data.

TABLE 1

A concentration of chlorhydrin mole/l.	B concentration of soda mole/l.	cell resistance ($t = 0$) ohms
0·05	0·01	295
0	0·01	280
0·05	0·005	664
0	0·005	627
0·05	0·001	3210
0	0·001	2920

QUANTITATIVE MEASUREMENTS.—*Kinetics*.—At known times, samples were removed from a mixture of the reactants kept in stoppered flasks in a thermostat. Each sample was quickly added to enough dilute standard acid, calculated from preliminary experiments, to neutralize the alkali in the sample almost completely. The reaction was thus " frozen " without exposing the ethylene oxide to an excess of acid with which it would react. The titration was then completed to the end-point of phenolphthalein.

The ethylene chlorhydrin was refractionated (b.p. 127·5 to 128·0° C at 751 mm and n_D^{20} 1·4434). A.R. sodium hydroxide was used. All solutions were made with freshly-boiled distilled water and the chlorhydrin solutions were freshly made for each day's working. The concentration of the stock ethylene chlorhydrin solution was determined by hydrolysis with standard sodium hydroxide solution.

The second-order constant was obtained from the slope of the graph of the logarithm of the ratio of reactant concentrations against time, or in the case of equal initial concentrations, from the graph of the reciprocal of the reactant concentrations against time. At higher concentrations of reactant there was a significant deviation from a straight line, and in this case the value of the second-order constant was obtained by extrapolating to zero time. The product of reaction was shown to be ethylene oxide, the small amount of glycol found being exactly accounted for by the hydroxyl ion-catalyzed hydrolysis of the ethylene oxide.[9]

The results at 20° C of k_0, the apparent second-order constant, for the reaction between ethylene chlorhydrin and sodium hydroxide are tabulated below. Most of these are the mean of at least two determinations.

TABLE 2

A ethylene chlorhydrin (mole/l.)	B sodium hydroxide (mole/l.)	k_0 (l. mole^{-1} min^{-1})	k_0 (calc.) (l. mole^{-1} min^{-1})
0·02	0·02	0·34	0·32
0·05	0·05	0·32	0·32
0·05	0·10	0·31	0·31
0·05	0·20	0·30	0·30
0·25	0·25	0·28	0·28
0·50	0·25	0·27	0·26
0·25	0·50	0·25	0·26
0·50	0·50	0·26	0·25
0·50	0·75	0·25	0·24
0·50	1·00	0·23	0·22
1·00	0·50	0·24	0·22
1·10	0·50	0·23	0·22
1·00	1·00	0·22	0·21
1·10	1·00	0·25	0·20
1·90	0·50	0·21	0·19
0·50	2·00	0·22	0·19
1·00	2·00	0·22	0·18
1·10	2·00	0·23	0·17

HEAT MEASUREMENTS.—(*a*) *Dewar flask calorimeter.*—This apparatus consisted of a cylindrical wide-necked Dewar flask closed with a wooden lid carrying a thermistor, heating coil, reciprocating stirrer and a pipette with a short wide outlet tube dipping into a pool of mercury. 50 ml of one solution were placed in the pipette and 50 ml of the other in the body of the Dewar flask. The solutions were mixed by pulling the pipette away from the mercury pool. The calorimeter was kept immersed in a thermostat at 20° C. The thermistor was connected to a Wheatstone bridge and was balanced against a 4-dial resistance box. Temperature changes were measured by the off-balance current, the thermistor and circuit having been previously calibrated against an accurate thermometer. Temperature differences could be measured to about 0·01° C. The water equivalent of the apparatus (16·8 g) was determined by measuring the rise in temperature of 100 ml of water in the Dewar vessel when a known amount of electrical energy was passed through the heating coil.

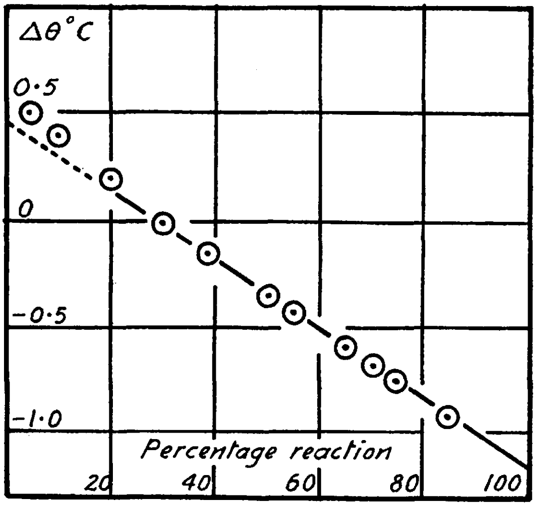

FIG. 2.—Graph of $\Delta\theta$ against percentage reaction.

The specific heat of 1 M ethylene chlorhydrin was found, in preliminary experiments, to be 1·02 cal/g. The specific heats of more dilute solutions were obtained by assuming a linear change with concentration. The specific heats of the sodium hydroxide solutions were taken from tables.[12] The heats of dilution of the reactants were obtained by separate experiments in which all conditions were kept constant except that water was substituted for one of the reactants.

Heat losses to and from the calorimeter were significant owing to the length of the experiments. In order to make them reproducible the apparatus was placed in a cellar and the air temperature kept constant at 20 ± 0·1° C. The cooling correction was determined, and applied to the results by graphical integration. In a typical experiment the correction amounted to 0·03° C in 1·2° C after 40 min.

A correction was also necessary for the exothermic production of glycol from ethylene oxide. The rate of production of ethylene oxide is

$$dc/dt = k_0(A - c - g)(B - c),$$

where c is the concentration of ethylene oxide at time t, and g is the concentration of glycol. Lichtenstein and Twigg[9] have shown that the rate of formation of glycol is

$$dg/dt = k_4c(B - c).$$

Combining and integrating these equations we obtain an expression relating g and c. The glycol concentration g was found by inserting the experimental values for c, k_4 and k_0.

By considering the case when the sodium hydroxide was in excess and taking the curve beyond the point F in fig. 1, the heat of formation of glycol from ethylene oxide and sodium hydroxide was found to be approximately 15 kcal/mole. Using this value the correction for the heat of formation of glycol could be calculated. This correction, in one experiment with excess soda, amounted to 0·3° C in a total of 0·8° C after

20 min. Usually it was much smaller, e.g. 0·01° C to 0·04° C in experiments with excess chlorhydrin.

The initial temperature peak was evaluated by extrapolating a graph of the corrected temperature against percentage reaction, which was obtained by separate experiments in the calorimeter using the above titration method. The temperature change due to dilution of the reactants was then subtracted from this temperature difference.

(*b*) *Apparatus for determining the initial temperature rise.*—Two glass vessels connected by a short length of glass tubing were placed in a thermostat bath. One vessel carried a stirrer and a thermistor. The solutions were mixed by blowing the contents of one vessel into the other by applying air-pressure through a coil immersed in the thermostat. Blank experiments showed that the transfer of liquid was quantitative and the mixing rapid. This apparatus was used to determine quickly the initial rise in temperature. It had the advantage that thermal equilibrium was reached in less than 30 min compared with several hours for the Dewar flask calorimeter. The corresponding disadvantage of the high heat loss through the glass walls was offset by the rapid response of the thermistor. The readings were extrapolated to zero time to obtain the initial heat rise.

The heat of neutralization of 0·1 N sodium hydroxide with 0·1 N hydrochloric acid was determined as a check in each apparatus. The values obtained were 13·8 kcal/mole for the Dewar flask calorimeter and 13·6 kcal/mole for the later apparatus. Fig. 2 shows a typical experimental plot for the Dewar flask calorimeter. The deviation from the straight line at the beginning of the reaction is due to the fact that the water equivalent of the apparatus is not reached instantaneously owing to the rapid response of the thermistor. The extrapolation shown by the dotted line in fig. 2 was therefore used. The results corrected for heats of dilution are shown in table 3. The last four experiments were made with the second apparatus.

TABLE 3

concentrations		
ethylene chlorhydrin mole/l. (A)	sodium hydroxide mole/l. (B)	initial heat rise cal/l.
0·98	0·98	1030
0·98	0·49	630
0·50	1·00	585
0·98	0·25	460
0·24	0·98	297
0·25	0·33	157
0·10	0·33	60
0·50	0·33	330
1·04	0·33	440

Values obtained for the overall heat of the reaction of ethylene chlorhydrin with soda to form ethylene oxide, measured with the Dewar flask calorimeter, are shown in table 4. The values were obtained by extrapolating curves such as that in fig. 2 to 100 % reaction. The average value of the heat absorbed per mole of ethylene oxide formed is 2·1 kcal.

TABLE 4

concentrations			
ethylene chlorhydrin mole/l. (A)	sodium hydroxide mole/l. (B)	heat absorbed kcal/l.	heat absorbed in producing 1 mole of ethylene oxide kcal
0·98	0·98	2·13	2·17
0·98	0·49	1·05	2·15
0·98	0·245	0·575	2·33
0·495	0·98	0·970	1·96
0·240	0·98	0·470	1·96

DISCUSSION

It is clear from table 2 that k_0 is a function of the initial concentration of reactants. This is to be expected if the intermediate ion is present in a significant amount.

With the reaction scheme shown above, let the initial concentrations of chlorhydrin, soda and intermediate be A, B and x_0 respectively. Assuming a stationary state for the intermediate ion, we have, if $\phi = (k_2 + k_3)/k_1$, that

$$AB - (A + B + \phi)x_0 + x_0^2 = 0. \qquad (1)$$

At low concentrations of reactants the term x_0^2 becomes small enough to be neglected, and since $k_3x_0 = k_0AB$, a graph of $1/k_0$ against $(A + B)$ should have a slope of $1/k_3$ and intercept ϕ/k_3 on the $1/k_0$ axis. The intercept was obtained fairly accurately as 3·05 mole l.$^{-1}$ min. From this value and the slope a rough value of $\phi \approx 3$ mole l.$^{-1}$ was calculated. These values were used to calculate the value of x_0^2 in eqn. (1). Using the value for ϕ/k_3, ϕ was calculated from each experimental k_0. The correction to ϕ for the x_0^2 term was only significant at the highest concentrations.

A graph of ϕ against $(A + B)$ is shown in fig. 3. There is some scatter due to the fact that the calculations are based on the difference between k_0 at each concentration and that at infinite dilution, but it is clear that ϕ changes only slowly over a fair range, increasing markedly when $(A + B)$ exceeds about 1 M. This increase is presumably due to salt effects and the changing medium at high chlorhydrin concentrations. A value of $\phi \approx 2·8$ mole l.$^{-1}$ is obtained from fig. 3 at low concentrations of reactants. Values of k_0 were calculated (table 2) on this theory using this value for ϕ and the value of 3·05 mole l.$^{-1}$ min for ϕ/k_3. Except at the highest concentrations, where salt effects come in, the calculated values agree well with the experimental ones.

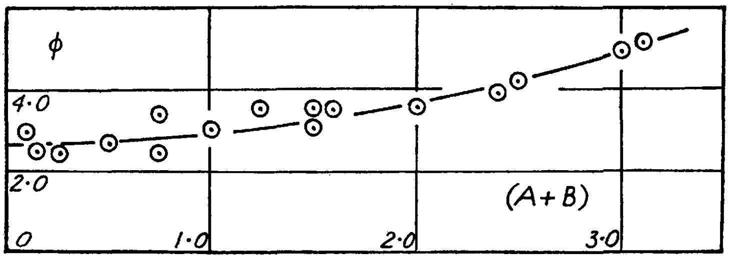

FIG. 3.—Graph of ϕ against $(A + B)$.

The variation of k_0 with concentration has been claimed by Winstrom and Warner [3] to be due to the presence of carbon dioxide. Their experiments were carried out at such low concentrations that the variation in k_0 due to the formation of the intermediate ion would be negligible. Moreover, their explanation of the effects of carbon dioxide is based on pilot-plant work which reported that glycol was formed by reaction of chlorhydrin and sodium carbonate.[10, 11] This was carried out before it was realized that there was a hydroxyl-ion catalyzed reaction of ethylene oxide to glycol. At 20° C we found no detectable reaction between chlorhydrin and sodium carbonate in 1 h.

The value found for ϕ shows that an appreciable amount of intermediate ion is formed; for instance, a solution initially 1 M in chlorhydrin and sodium hydroxide respectively contains 0·2 mole/l. of intermediate. The dissociation constant of ethylene chlorhydrin as an acid can be calculated from ϕ since $k_3 \ll k_2$, giving a value of 3×10^{-15}.

The results of the heat measurements were not sufficiently accurate to obtain a value of ϕ in an analogous manner to the kinetic results. Fig. 4 shows a plot of h, the initial heat evolved in cal/l. against x_0, the corresponding concentration of intermediate ion. The latter was calculated from eqn. (1) by using the value of ϕ (fig. 2) appropriate to the concentrations of reactants used. The fact that this plot is linear is substantial evidence for the correctness of the conclusions drawn from the kinetic scheme.

From the slope of this graph, the heat of formation of the intermediate is 5·4 kcal/mole. A value of 5·4 kcal/mole was also found by calculations based on curves as shown in fig. 2 by using the value of the percentage reaction when $\Delta\theta$ becomes zero instead of the initial peak.

Conclusion.—Although the formation of an intermediate ion in the reaction between ethylene chlorhydrin and sodium hydroxide has previously been assumed, it has always been taken that it was present at a low concentration. The evidence of four independent lines of approach has demonstrated clearly the existence of this intermediate, and enabled some of its physical properties to be assessed. The difficulty of more precise evaluation is that the amount of intermediate is obtained by the difference between expected second-order behaviour and the actual experimental values.

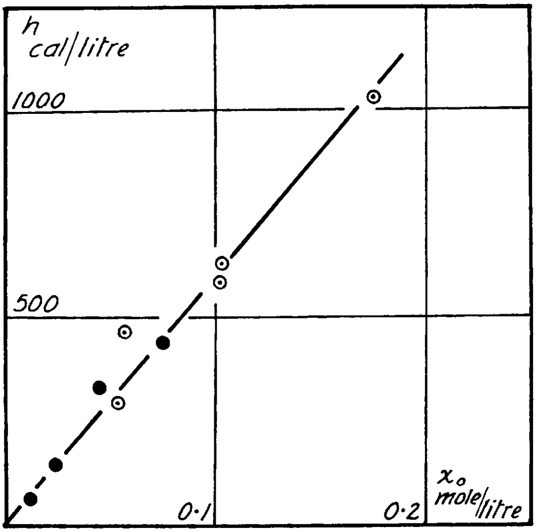

Fig. 4.—Graph of heat rise against concentration of intermediate calculated from kinetic results.

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