169. *The Mechanism of Epoxide Reactions. Part V.*[1] *The Reaction of* 1,2-*Epoxypropane with Chloride Ion in Water under Neutral and Acidic Conditions.*

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The reaction between 1,2-epoxypropane and chloride ion in 9 : 1 v/v water–dioxan has been followed by continuous titration with acid and rate constants (corrected for the competing hydrolysis) have been determined at three temperatures and four pH values. The proportions of 1-chloropropan-2-ol and 2-chloropropan-1-ol in the products, determined by gas chromatography, have been combined with the kinetic results to give rate constants and Arrhenius parameters for attack at the normal and at the abnormal position for both the acid-catalysed and the non-catalysed reactions. All four reactions are kinetically of the second-order (at constant pH), and bimolecular mechanisms are proposed, with transition states in which bond breaking has progressed further than bond making.

ACID-CATALYSIS in the ring-opening of epoxides is well established,[2] and kinetic investigations have been carried out for the reactions of various epoxides with water,[3] chloride ion,[4,5] bromide ion,[4,5] iodide ion,[5,6] nitrate ion,[7] and pyridine.[8] However, very few of these studies included an analysis of the products and, for the reactions of unsymmetrical epoxides, therefore, the observed rate constants represent the sum of the rate constants for normal attack (attack at the less substituted position) and for abnormal attack (attack at the more substituted position). Other workers have measured the proportions of normal and abnormal products [2] and have shown that the proportion of abnormal product is increased when the reactions are carried out under acidic conditions, but these measurements were not coupled with kinetic studies and it is not clear whether an increased proportion of abnormal product corresponds to an increased rate of abnormal attack or a decreased rate of normal attack or both.

We therefore decided to measure both the rate and the proportion of isomeric products for the acid-catalysed reaction of an unsymmetrical epoxide and, in view of our earlier work,[1,9,10] we chose the reaction between 1,2-epoxyethylbenzene and benzylamine. Browne and Lutz [11] claim to have shown that this reaction, in the absence of solvent, is at least three times faster in the presence of benzylammonium chloride. However, we have studied the reaction in ethanol, using the techniques previously employed,[1] and have failed to detect any acceleration whatever by added benzylammonium chloride or perchlorate. This is perhaps not surprising in view of the weakness of the benzylammonium ion as an acid and it suggests that the acceleration observed by Browne and Lutz is a salt effect, the added benzylammonium chloride considerably increasing the dielectric constant of the medium (a mixture of 1,2-epoxyethylbenzene and benzylamine, and relatively non-polar).

Accordingly, we decided to change to a reagent that is compatible with strong acids and we chose chloride ion. At the same time, we changed to an epoxide of lower molecular

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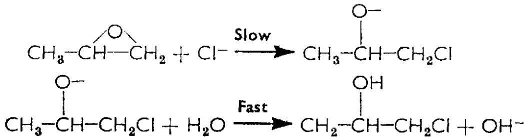
[1] Part IV, Laird and Parker, *J. Amer. Chem. Soc.*, 1961, **83**, 4277.
[2] Parker and Isaacs, *Chem. Rev.*, 1959, **59**, 737.
[3] Pritchard and Long, *J. Amer. Chem. Soc.*, 1956, **78**, 2667.
[4] Brönsted, Kilpatrick, and Kilpatrick, *J. Amer. Chem. Soc.*, 1929, **51**, 428.
[5] Eastham and Latremouille, *Canad. J. Chem.*, 1952, **30**, 169.
[6] Swain, *J. Amer. Chem. Soc.*, 1952, **74**, 4108.
[7] Petty and Nichols, *J. Amer. Chem. Soc.*, 1954, **76**, 4385.
[8] Eastham, *J.*, 1952, 1936; Eastham and Darwent, *Canad. J. Chem.*, 1951, **29**, 585.
[9] Isaacs and Parker, *J.*, 1960, 3497.
[10] Addy, Laird, and Parker, *J.*, 1961, 1708.
[11] Browne and Lutz, *J. Org. Chem.*, 1952, **17**, 1187.

weight than 1,2-epoxyethylbenzene, in the hope that the products, being thereby more volatile, would be susceptible to analysis by gas chromatography. This proved to be the case and the present paper records the results of a kinetic and orientational study of the reaction of 1,2-epoxypropane with chloride ion in water at three temperatures and four pH values.

The attack of a chloride ion in water at the normal position of 1,2-epoxypropane can be represented as follows:



If the hydroxide ions were allowed to accumulate, they would interfere with the reaction, either by reversing it or by reacting directly with epoxide to give glycol. Such accumulation is prevented by the continuous addition of perchloric acid to maintain a constant pH and the rate of addition is a measure of the rate of reaction. This rate has been corrected for the simultaneous hydrolysis of the epoxide by determination of formed glycol by periodate titration. The products, isolated by extraction with ether, have been analysed by gas chromatography on a column of diglycerol (bis-2,3-dihydroxypropyl ether) on Celite.

EXPERIMENTAL

Materials.—1,2-*Epoxypropane*. Commercial material (from British Drug Houses, Ltd.) was fractionated through a 60 × 1·5 cm. column packed with Fenske helices, and the middle fraction, b. p. 35°/760 mm., was collected. Gas chromatography on a column of diglycerol on Celite showed only one peak.

Sodium chloride. "AnalaR" sodium chloride was dried for 2 hr. at 120° before use.

0·1N-*Sodium arsenite*. Dried "AnalaR" sodium arsenite (4·946 g.) and sodium hydroxide (4 g.) were dissolved in water, and the solution was neutralised with dilute hydrochloric acid to phenolphthalein and diluted to 1 l.

Periodic acid solution. An approximately 2% solution, prepared by dilution of commercial 50% solution (from British Drug Houses, Ltd.), was standardised by addition of sodium hydrogen carbonate and an excess of sodium arsenite solution and back-titration with iodine solution to "Thyodene" indicator.

Buffer solutions and indicators. Buffer solutions were prepared by mixing appropriate quantities of 0·1M-citric acid and 0·2M-disodium hydrogen phosphate solutions to give solutions of pH 7·0, 4·5, 3·8, and 3·6. At these pH values the indicators Bromothymol Blue, "B.D.H. 4·5 indicator," screened Methyl Orange, and Bromophenol Blue, respectively, were found to give sharp colour changes.

Dioxan. "AnalaR" dioxan was used without further purification.

Rate Measurements.—Stock solutions of 1,2-epoxypropane in dioxan and of sodium chloride in water were prepared at thermostat temperature and the reaction was started by the addition of 25 ml. of epoxide solution to 225 ml. of sodium chloride solution and a few drops of indicator solution contained in a three-necked 250 ml. flask. The solution was continuously stirred by a sealed stirrer, and perchloric acid was added from a micro-burette at such a rate as to maintain the colour of the solution the same as that of a buffer solution containing indicator in an adjacent flask in the glass-sided thermostat. It was found to be necessary for the tip of the burette to dip below the surface of the solution, to avoid polymerisation of the 1,2-epoxypropane in the suspended drop of concentrated acid.

The volume of acid added was noted at frequent intervals. The total volume added never exceeded 2% of the volume of the reaction solution and no correction was made for this small dilution.

In order to measure the amount of glycol formation, we carried out duplicate runs under identical conditions and withdrew aliquot parts (5 ml.) at frequent intervals. Each aliquot part was added to 2% periodic acid solution (5 ml.), previously neutralised with a slight excess of solid sodium hydrogen carbonate, and the mixture was diluted to 20 ml. and set aside for

15 min. 0·1N-Sodium arsenite (20 ml.) was added, followed by 20% potassium iodide solution (1 ml.), and the mixture was kept for a further 45 min. The excess of arsenite was then titrated with 0·1N-iodine to " Thyodene " indicator. Control experiments showed that 1,2-epoxypropane was not attacked by periodate under these conditions.

Analysis of Products.—After the completion of each kinetic run, the reaction solution was cooled by addition of ice and extracted with ether. The ethereal extract was dried ($MgSO_4$) and the ether removed at water-pump pressure at room temperature. The residue (which contained some dioxan and ether) was submitted to gas chromatography on a column of diglycerol (20%) on Celite. At a column temperature of 110° and a flow rate of 2 l./hr. of carrier gas (nitrogen), the two products give peaks which are quite separate. The method was calibrated against synthetic mixtures of the two pure isomers and it was found that the height of each peak multiplied by its distance from the origin was a continuous (nearly linear) function of the isomer composition. It was also shown that there was no differential extraction of the isomers from aqueous solution by ether.

Synthesis of Products.—1-*Chloropropan*-2-*ol*. Reduction of chloroacetone with lithium aluminium hydride [12] gave 1-chloropropan-2-ol, b. p. 43°/24 mm. (lit.,[12] 50·7°/30 mm.).

2-*Chloropropan*-1-*ol*. α-Chloropropionyl chloride, prepared from α-chloropropionic acid and benzoyl chloride,[13] was reduced with lithium aluminium hydride [14] to 2-chloropropan-1-ol, b. p. 47°/21 mm. (lit.,[14] 70—70·5°/75 mm.).

RESULTS

Because of simultaneous hydrolysis to form glycol, the reaction of 1,2-epoxypropane with chloride ion does not obey a simple second-order rate law, but can be represented by the equation

$$\mathrm{d}x/\mathrm{d}t = k_2(a - x)(e - x - y), \qquad (1)$$

where a and e are the initial concentrations of chloride ion and epoxide, respectively, and x and y are the concentrations of total chlorohydrin and of glycol, respectively, at time t. Since one mole of hydroxide is formed for every mole of total chlorohydrin produced, the amount of perchloric acid added at time t is a direct measure of x. The concentration y is measured by the periodate titration. For each run a plot of x against t was drawn and values of the slope, $\mathrm{d}x/\mathrm{d}t$, were measured at several values of x. Substitution of these values of $\mathrm{d}x/\mathrm{d}t$, together with the values of a, e, x, and y, into equation (1) then allows the rate constant, k_2, to be calculated. The results of a typical run are shown in Table 1. The greater number of values of x than of y is necessary for the construction of a smooth x–t curve. Since the hydrolysis is a first-order reaction and the reaction with chloride ion second-order, the proportion of hydrolysis $[y/(x + y)]$ increases throughout the reaction. This proportion also increases slightly with temperature and markedly with acidity; at the beginning of the reaction it is about 13% at 20° and pH 7·0 and about 35% at 40° and pH 3·6.

TABLE 1.

0·4000M-1,2-Epoxypropane, 0·6000M-sodium chloride, 40°, pH 3·6.

Time (hr.)	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0	1·1	1·2	1·3
5·24M-$HClO_4$ added (ml.)	0·70	1·50	2·27	2·94	3·55	4·10	4·58	5·00	5·37	5·73	6·04	6·37	6·66
10^2x	1·47	3·14	4·76	6·16	7·44	8·59	9·60	10·48	11·26	12·00	12·66	13·35	13·96
10^2y		1·84		4·00		6·14		7·64		9·05		10·92	
$10^5\mathrm{d}x/\mathrm{d}t$		4·55		3·75		2·95		2·40		1·96		1·75	
10^4k_2		2·29		2·33		2·27		2·21		2·21		2·39	

Mean $k_2 = 2·28 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$.

The reaction at 40° and pH 3·8 was carried out at two different sets of initial concentrations;

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[12] Stewart and VanderWerf, *J. Amer. Chem. Soc.*, 1954, **76**, 1259.
[13] Brown, *J. Amer. Chem. Soc.*, 1938, **60**, 1325.
[14] Fickett, Garner, and Lucas, *J. Amer. Chem. Soc.*, 1951, **73**, 5063.

the ratio of products was not altered by the change in the ratio of initial concentrations (36·0% of abnormal product for $a = 0{\cdot}6$M and $e = 0{\cdot}4$M, 35·5% of abnormal product for $a = 0{\cdot}3$M and $e = 0{\cdot}4$M). It follows that the normal and the abnormal reaction are of the same kinetic order and, since the overall reaction obeys a second-order rate law, that they are both of second order. The observed rate constants, k_2, have therefore been divided in the ratio of the proportions of isomeric products to give the rate constants for normal attack, $k_{\rm N}$, and for abnormal attack $k_{\rm A}$, and the results are collected in Table 2.

Under acidic conditions the observed rates, both for the normal and for the abnormal reaction, represent the sum of the rates of the uncatalysed reaction (rate constant $k_{\rm W}$) and of the acid-catalysed reaction (rate constant $k_{\rm H}$), and equations (2) and (3) can be applied. Plots of $k_{\rm N}$ and of $k_{\rm A}$ against the concentration of hydrogen ion gave good straight lines and values

$$k_{\rm N} = k_{\rm WN} + k_{\rm HN}[{\rm H}^+] \qquad (2)$$

$$k_{\rm A} = k_{\rm WA} + k_{\rm HA}[{\rm H}^+] \qquad (3)$$

of $k_{\rm W}$ and $k_{\rm H}$ were obtained from the intercepts and slopes of these lines, respectively. All these values are collected in Table 3 and the values at 40°, together with the corresponding Arrhenius parameters and entropies of activation, are shown in Table 4.

TABLE 2.

Measured rate constants, proportions of normal and abnormal isomers, and rate constants for normal and abnormal attack (k_2, $k_{\rm N}$, and $k_{\rm A}$ in l. mole^{-1} sec.$^{-1}$).

Temp.	pH	10^6k_2	Normal product (%)	Abnormal product (%)	$10^6k_{\rm N}$	$10^6k_{\rm A}$
20·0°	7·0	2·59	91	9	2·36	0·23
	4·5	5·59	75	25	4·20	1·39
	3·8	19·6	68	32	13·3	6·3
	3·6	29·7	66	34	19·6	10·1
30·1	7·0	7·28	88	12	6·41	0·87
	4·5	16·2	73	27	11·8	4·4
	3·8	54·0	66	34	35·6	18·4
	3·6	82·0	65	35	53·3	28·7
40·0	7·0	21·4	86	14	18·4	3·0
	4·5	43·7	72	28	31·5	12·2
	3·8	151	64	36	97	54
	3·6	226	64	36	145	81

TABLE 3.

Rate constants for the normal and the abnormal, catalysed and uncatalysed reactions ($k_{\rm WN}$ and $k_{\rm WA}$ in l. mole^{-1} sec.$^{-1}$; $k_{\rm HN}$ and $k_{\rm HA}$ in l.^{2} mole^{-2} sec.$^{-1}$).

Temp.	$10^6k_{\rm WN}$	$10^6k_{\rm WA}$	$10^2k_{\rm HN}$	$10^2k_{\rm HA}$
20·0°	2·36	0·23	6·8	3·84
30·1	6·41	0·87	18·9	11·2
40·0	18·4	3·0	49·9	31·6

TABLE 4.

Rate constants at 40°, Arrhenius parameters and entropies of activation for the normal and the abnormal, catalysed and uncatalysed reactions ($k_{\rm W}$ and $A_{\rm W}$ in l. mole^{-1} sec.$^{-1}$; $k_{\rm H}$ and $A_{\rm H}$ in l.^{2} mole^{-2} sec.$^{-1}$; E in kcal. mole^{-1}; $\Delta S^‡$ in cal. mole^{-1} deg.$^{-1}$).

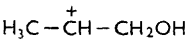
	Uncatalysed reaction				Catalysed reaction			
	$10^6k_{\rm W}$	E	$\log A_{\rm W}$	$\Delta S^‡$	$10^2k_{\rm H}$	E	$\log A_{\rm H}$	$\Delta S^‡$
Normal reaction	18·4	18·8	8·4	−22·2	49·9	18·3	12·5	−3·6
Abnormal reaction	3·0	23·5	10·9	−10·7	31·6	19·9	13·4	+0·9

Taking into account the errors involved in the rate measurements and the product analyses, we estimate that the rate constants in Tables 3 and 4 are accurate to ±5% or better, E to ±0·9 kcal. mole^{-1}, log A to ±0·6, and $\Delta S^‡$ to ±2·7 cal. mole^{-1} deg.$^{-1}$.

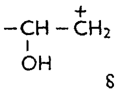
DISCUSSION

Reactions with Chloride Ion.—The results in Table 2 show that both isomeric products are formed under all the conditions used. At 40° the proportion of abnormal isomer increases from 14% at pH 7·0 to 36% at pH 3·6. This proportion must reach a limit of $k_{HA}/(k_{HN} + k_{HA})$ at high acidities (39% at 40°) and this was confirmed by an experiment carried out at pH 2, which gave a product containing 38·5% of abnormal isomer. Statements that epoxides react to give normal products under neutral conditions and abnormal products under acidic conditions are therefore very wide of the mark, at least as far as reaction with chloride ion is concerned.

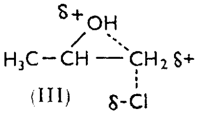
All the four reactions studied (normal and abnormal, catalysed and uncatalysed) obey second-order rate laws, and the ratio of products obtained from the reaction at 40° and pH 3·8 was unaffected by a change in the ratio of initial concentrations. In the latter case, as can be seen in Table 2, about 86% of the reaction takes place by the acid-catalysed route and, of this 86%, about a third produces abnormal product. In view of the substantial amounts of both normal and abnormal acid-catalysed reactions taking place, the insensitivity of the product composition to a change in the ratio of initial concentrations is clear proof that the normal and abnormal acid-catalysed reactions are of the same kinetic order, both with respect to chloride ion and with respect to epoxide. Because the overall reaction obeys a second-order rate law, these orders in chloride ion and in epoxide must each be unity. Unimolecular mechanisms for the normal and the abnormal acid-catalysed reactions, involving the rate-determining opening of the protonated epoxide to carbonium ions (I) or (II), are therefore ruled out and it is evident that these reactions involve bimolecular attack of chloride ion on the protonated epoxide, with transition states (III) and (IV) for the normal and the abnormal reaction, respectively. Unimolecular mechanisms are even less likely for the uncatalysed reactions (because the intermediate carbonium ions would carry both positive and negative charges) and these reactions must take place by a bimolecular attack of chloride ion on the epoxide itself, with transition states (V) and (VI) for the normal and the abnormal reaction, respectively.


$H_3C-\overset{+}{C}H-CH_2OH$

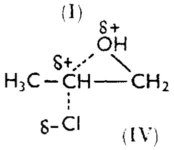
(I)


$H_3C-\underset{OH}{CH}-\overset{+}{C}H_2$

(II)



(III)



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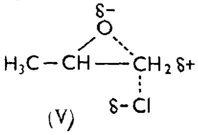
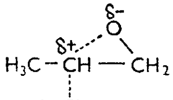


(V)

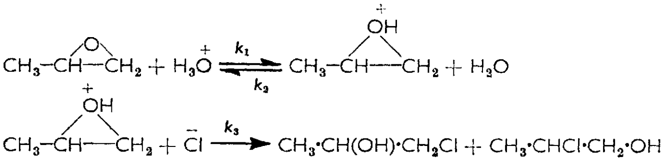


(VI)

The fact that acid-catalysis occurs at all implies that bond stretching is a factor of major importance in the formation of the transition states for the uncatalysed reactions (and, *a fortiori*, for the catalysed reactions). This is in line with the effects of substituents on rates of ring-opening of epoxides, such effects supporting mechanisms in which bond breaking has progressed further than bond making in the formation of the transition states.[1,2] If, as we believe, this is true of all four reactions, it follows that, in each of the four transition states, the two partial bonds are together less than a full single bond and therefore that the attacked carbon atom carries a fractional positive charge in each case. Such charges have been included in structures (III—VI) and are relative to any charges in the initial states.

In the uncatalysed reaction, the greater proportion of normal than of abnormal attack is almost certainly due to a primary steric effect caused by the presence of the methyl group, this effect being greater for abnormal attack. Such an interpretation is supported by the considerably higher energy of activation for abnormal attack (Table 4). If it is assumed that, as a result of this primary steric effect, the reagent has not approached so closely to the epoxide carbon atom in the abnormal transition state (*i.e.*, that the carbon–chlorine partial bond is longer in the abnormal transition state), the higher entropy of activation for the abnormal reaction is also explained, since a more loosely bound transition state would be expected to correspond to a higher entropy of activation.

The interpretation of the results for the acid-catalysed reactions is complicated by the fact that the rate constants k_H (Table 3) are really multiples of a rate constant and an equilibrium constant. These reactions involve an initial, rapidly attained equilibrium between epoxide and protonated epoxide, followed by a rate-determining attack of chloride ion on the protonated epoxide:


(4)

(5)

The measured rate constant k_H is therefore related to the equilibrium constant ($K = k_1/k_2$) by equations (6) and (7):

$$k_{HN} = Kk_{3N}; \qquad (6)$$

$$k_{HA} = Kk_{3A}. \qquad (7)$$

The same complication, of course, applies to the values of log A for the catalysed reactions (Table 4) and, therefore, to the entropies of activation. However, the ratio of measured rate constants, k_{HN}/k_{HA}, is equal to the ratio of the rate constants for the rate-determining step, k_{3N}/k_{3A}, and the fact that this ratio is smaller than that of the rate constants for the uncatalysed reaction, k_{WN}/k_{WA}, shows that the abnormal position is relatively more reactive in the protonated epoxide than in the epoxide itself. In particular, the protonated epoxide is less selective (as between normal and abnormal attack) than the epoxide itself, as would be expected of a more reactive species. The greater acceleration of the abnormal than of the normal reaction by acid-catalysis is also in agreement with the above postulate that the carbon–chlorine partial bond is longer in the abnormal transition state, since this implies that bond breaking is relatively more important in the formation of the abnormal transition state (and it is bond breaking that would be mainly affected by acid-catalysis).

The much smaller difference in energies of activation between normal and abnormal attack for the catalysed reactions (1·6 kcal. mole^{-1}) than for the uncatalysed reactions (4·7 kcal. mole^{-1}) suggests that the transition states for the former (III and IV) are more similar to each other than are the transition states for the latter (V and VI). This is supported by the smaller value of log A_{HN} — log A_{HA} (0·9) than of log A_{WN} — log A_{WA} (2·5) [since the quantity, log A_{HN} — log A_{HA}, is equal to the difference of log A values for the reactions of equation (5)].

Thus, the evidence from rate constants, energies of activation, and entropies of activation combines to suggest very similar mechanisms for the rate-determining steps of the normal and the abnormal catalysed reaction and it seems likely that these mechanisms involve transition states (III and IV) with long carbon–chlorine partial bonds (and, therefore, long carbon–oxygen partial bonds), *i.e.*, what are often termed " borderline " S_N2 mechanisms. We believe that the uncatalysed reactions also take place by borderline S_N2 mechanisms, but with transition states somewhat further from the S_N1 extreme (*i.e.*, with rather shorter partial bonds).

The higher absolute values of the entropies of activation for the catalysed than for the uncatalysed reactions are undoubtedly largely due to the fact that the rate-determining steps of the catalysed reactions [equation (5)] involve reaction between oppositely charged ions, with destruction of charge in the transition state and consequent decrease of solvation; solvent molecules are freed in the formation of the transition state and hence acquire additional degrees of freedom. Since the uncatalysed reactions are between a neutral molecule and an ion, the formation of the transition states involves only dispersal of charge and, therefore, a much smaller decrease of solvation. An unknown factor in the entropies of activation for the catalysed reactions is the entropy change in the equilibrium represented by equation (4), although it seems unlikely that this would be large.

Reactions with Water.—Although the reactions with water are not the primary concern of this work, it is possible to obtain values of the selectivity factor for reaction with chloride ion compared with reaction with water, k_{Cl}/k_{H_2O}, from the relation:

$$Y_{Cl}/Y_{H_2O} = k_{Cl}[Cl^-]/k_{H_2O}[H_2O], \qquad (8)$$

where Y_{Cl} and Y_{H_2O} are the yields of total chlorohydrin (normal plus abnormal) and of glycol, respectively, and k_{Cl} and k_{H_2O} are overall second-order rate constants for reaction with chloride ion and with water, respectively. At 40° and at the beginning of the reaction, the value k_{Cl}/k_{H_2O} is about 320 at pH 7·0 and about 140 at pH 3·6. These values were obtained by taking a value for the concentration of water of 48·8M. This is the concentration of total water and, if allowance were made for hydration of solutes, the concentration of free water would be less than 48·8M and the selectivity factors correspondingly lower. The values of the selectivity factor may be compared with the values k_{Cl}/k_{H_2O} of 3100 for triphenylmethyl chloride (in 15% water–85% acetone at —34°),[15] 180 for t-butyl chloride (in 95% water–5% ethanol at 25°),[15] and 3 for benzenediazonium ion (in water at 50°).[16] Since the last three reactions are known to take place by unimolecular mechanisms (and the selectivity factors refer to the fast, product-forming steps), whereas the present reactions (at least with chloride ion) are certainly bimolecular, it is clear that the magnitude of the selectivity factor is no guide to mechanism.

The decrease of the selectivity factor (increased proportion of glycol) with increase of acidity shows that, as would be expected, reaction with the weak nucleophile, water, is more susceptible to acid-catalysis than is reaction with chloride ion. The increase in the proportion of glycol as the reaction progresses (particularly noticeable at pH 3·6) is merely a consequence of the fact that the concentration of chloride ion decreases during the reaction while the concentration of water remains sensibly constant; it cannot distinguish between a unimolecular and a bimolecular reaction for either reaction.

Application of Swain and Scott's linear free-energy relation [17] to the selectivity factor at pH 7·0 gives a value of the substrate constant at 25° of 0·85 for 1,2-epoxypropane. Comparison of this value with those of 0·96 for glycidol and 1·00 for epichlorohydrin (also at 25°) [7,17] shows that electron-releasing groups attached to the epoxide ring lower the substrate constant and therefore increase the relative importance of bond breaking in the formation of the transition state. This is to be expected, since electron-releasing groups will stabilise the positive charges on transition-state structures (V) and (VI) and these charges would be greater the greater the relative importance of bond breaking.

We thank " Shell " Research Limited for a research studentship (to J. K. A.).

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