Dehydrochlorination of 2-chloroethanol, 2-chloro-1-propanol, 1-chloro-2-propanol, 2-chloro-2-methyl-1-propanol and 1-chloro-2-methyl-2-propanol

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Dedicated to Professor Ferenc Fülöp on the occasion of his 60th birthday

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Abstract

The reactions between a few 1,2-chlorohydrins and sodium hydroxide have been studied and shown to involve a two-step nucleophilic elimination of hydrogen chloride. The data are given for the slow rate-determining step of 2-chloroethanol **1**, 2-chloro-1-propanol **2**, 1-chloro-2-propanol **3**, 2-chloro-2-methyl-1-propanol **4** and 1-chloro-2-methyl-2-propanol **5**. Compounds **4** and **5** gave 2-methyl-1,2-propanediol as the final product instead of oxiranes given by compounds **1–3**. In contrast to some earlier reports the mere water reaction was shown to be almost negligible. In constant ionic strength the base concentration had no effect on the rates whereas at different base concentrations (0.050–0.250 mol dm^{-3}) alone the rate of alkaline dehydrochlorination of **1** clearly decreased (10^3k_2, dm^3 mol^{-1} s^{-1}: 10.0–8.7, respectively). The rate of **2** at constant base concentration (0.010 mol dm^{-3}) and at different ionic strengths (dm^3 mol^{-1}: 0.010–0.500) decreased also (10^3k_2, dm^3 mol^{-1} s^{-1}: 76–65, respectively) indicating that the decrease is mainly due to the change in the ionic strength also in the former case.

Keywords: 1,2-Chlorohydrins, reactions in alkali, kinetics, mechanisms

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Introduction

Alkaline dehydrochlorination of 1,3-chlorohydrins is relatively well documented[1] whereas much less information is available on that of 1,2-chlorohydrins.[2–6] Most of the reports deal with the preparation of hydrogen chloride[7] or different oxiranes.[8,9] The best report is that of Ballinger and Long[10] on the dehydrochlorination of 2-chloroethanol **1** which also summarizes some early studies. They proved that the reaction between **1** and sodium hydroxide is a specific hydroxide ion catalysis *via* a two-step mechanism including the prior equilibrium and the slow rate-determining step:

$$\begin{aligned} &ClCH_2CH_2OH + HO^- \rightleftharpoons ClCH_2CH_2O^- + H_2O && \text{(fast)} \\ &ClCH_2CH_2O^- \xrightarrow{k_2} \text{Oxirane} + Cl^- && \text{(slow)} \end{aligned} \qquad (\mathbf{1})$$

However, some contradictory arguments have been presented about the water catalysis in context of the alkaline dehydrohalogenation of 1,2-halohydrins.[11–13] This is why we decided to study the alkaline dehydrochlorination of 2-chloroethanol **1**, 2-chloro-1-propanol **2**, 1-chloro-2-propanol **3**, 1-chloro-2-methyl-2-propanol **4** and 2-chloro-2-methyl-1-propanol **5** as well as their neutral water reactions in some detail.

Table 1. Pseudo first-order (k_1') and second-order (k_2) rate constants for the alkaline dehydrochlorination of 2-chloroethanol **1** at 35 °C, 2-chloro-1-propanol **2** at 25 °C and 1-chloro-2-propanol **3** at 10 °C at different base concentrations in a constant ionic strength (at 0.100 mol dm^{-3} adjusted with $NaNO_3$)

Compound	[OH$^-$]/mol dm^{-3}	10^3k_1'/s^{-1}	10^3k_2/dm^{3}mol^{-1}s^{-1}
1	0.010	0.346±0.033	34.6±0.3
1	0.040	1.26±0.02	31.4±0.4
1	0.060	1.92±0.03	31.9±0.5
1	0.080	2.47±0.03	30.9±0.4
1	0.100	3.13±0.03	31.3±0.3
			Av. 32.0±0.7
2	0.010	0.616±0.007	61.6±0.8
2	0.020	2.58±0.04	64.4±1.0
2	0.060	3.89±0.06	64.8±1.0
2	0.080	4.82±0.05	60.2±0.7
2	0.100	6.10±0.07	61.0±0.7
			Av. 62.4±0.9
3	0.010	0.374±0.003	37.4±0.3
3	0.040	1.58±0.02	39.5±0.6
3	0.060	2.38±0.03	39.6±0.5
3	0.080	3.15±0.02	39.3±0.3
3	0.100	3.98±0.03	39.8±0.3
			Av. 39.2±0.4

Results and Discussion

Based on the first-order rate constants of the alkaline dehydrochlorination of **1–3** it can be concluded that the dehydrochlorination caused by water reported earlier[11] is in fact practically negligible. The studies of Radulescu and Muresanu[12] on the neutral hydrolysis of 2-chloroethanol **1** pointed out that at the temperatures used in our study the dehydrochlorination caused by water is insignificant as shown also by our study on the neutral reaction. The second-order rate constants reported in literature for the latter are not significant in comparison with the rate constants for the alkaline dehydrohalogenation.[13–17] This is also true for **4** and **5** as shown for **4**. Our measurements carried out within the base concentration 0.010–0.100 mol dm^{-3} at a constant ionic strength (0.100 mol dm^{-3} adjusted by $NaNO_3$, Table 1) do not support a conclusion that the second-order rate constant increases along with decreasing base concentration[18–21] supposing that the ionic strength is kept constant; obviously this observation was due to a small specific salt effect. Instead the hydroxide-ion concentration exhibits a primary salt effect in larger than 0.100 mol dm^{-3} concentrations (Table 2). The same observation has been made by Ballinger and Long.[10]

Table 2. Pseudo first-order (k_1') and second-order rate constants (k_2) for **1** at different NaOH concentrations and in the constant (0.250 mol dm^{-3}) ionic strength at 25 °C

[OH$^-$], mol dm^{-3}	$10^3 k_1'$, s^{-1}	$10^3 k_2$, dm^{3}mol^{-1}s^{-1}
0.050	0.500±0.005	10.0±0.1 (9.9)[a]
0.100	0.994±0.001	9.94±0.01 (9.3)[a]
0.150	1.37±0.02	9.14±0.10 (9.0)[a]
0.200	1.77±0.03	8.84±0.13
0.250	2.16±0.03	8.66±0.10 (8.8)[a]

[a] The values of Ballinger and Long[10] in parentheses.

The rate constants for the alkaline dehydrochlorination of **1–3** are shown in Table 3 at 35, 25 and 10 °C, respectively. In the table k_1' is the pseudo first-order rate constant and k_2 the corresponding second-order rate constant. Also the average values of the latter are shown. Table 4 lists the recalculated average second-order rate constants for **4** and **5** at different temperatures. The Arrhenius parameters, A and E_a, together with the thermodynamic functions of activation, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ derived from the data in Tables 3 and 4 for **1–5** are collected in Table 5.

When inspecting the activation parameters of **1–3** shown in Table 5 it appears that ca 12 kJ mol^{-1} lower activation enthalpy explains the slowest dehydrochlorination rate of **1** (Table 3). Also the frequency factor of **1** is clearly higher than any of those for the other 1,2-chlorohydrins (**2–5**) studied. As to isomeric **2** and **3** both the enthalpy and entropy terms favor the clearly faster dehydrochlorination of the latter. Compounds **4** and **5** gave 2-methyl-1,2-propanediol as the predominant product whereas in the case of **1–3** the products were oxiranes.

Table 3. Pseudo first-order and second-order rate constants for the alkaline dehydrochlorination of 2-chloroethanol **1**, 2-chloro-1-propanol **2** and 1-chloro-2-propanol **3** at different temperatures

Compound	*t*, °C	$10^4 k_1´$, s^{-1}	$10^3 k$, dm^3 mol^{-1}s^{-1}
1[a]	15	1.65±0.03	2.75±0.04 (2.55[17a,b])
1[a]	25	6.16±0.04	10.3±0.06 (9.98[10], 10.0[17a], 10.0[17c], 10.6[17d])
1[b]	30		18.3±0.3 (18.1[5], 18.8[13])
1[a]	35	19.2±0.3	31.9±0.5
1[b]	35		32.6±0.6
1[b]	40		54.7±0.9
1[a]	45	67.7±0.5	112.9±0.8
1[b]	45		101±3
1[b]	50		164±3

[a] [OH$^-$] = 0.060 (mol dm^{-3}). [b] An average for different NaOH (from 0.012 to 0.047 mol dm^{-3}) and at 0.098 to 0.010 mol dm^{-3} substrate **1** concentrations.[11]

Compound	t, °C	$10^4 k_1´$, s^{-1}	$10^3 k_2$, dm^3 mol^{-1}s^{-1}
2[d]	10		12.5±0.1
2[c]	15	2.15±0.02	21.5±0.3
2[d]	15		21.5±0.3
2[d]	20		44.8±0.6
2[d]	25		81.4±1.0
2[c]	25	6.16±0.08	61.6±0.8 (72.6[10])
2[c]	35	19.4±0.3	194±3
2[c]	45	53.1±0.4	531±4

[c] [OH$^-$] = 0.010 mol dm^{-3}. [d] An average for different NaOH (from 0.010 to 0.045 mol dm^{-3}) and at 0.010 mol dm^{-3} substrate **2** concentrations.[11]

Compound	t, °C	$10^4 k_1$, s^{-1}	$10^3 k_2$, dm^3 mol^{-1}s^{-1}
3[e]	5	1.79±0.03	17.9±0.3
3[f]	5		20.4±0.1
3[e]	10	3.74±0.03	37.4±0.3
3[f]	10		37.9±0.7
3[f]	15		72.7±0.9
3[e]	15	6.06±0.06	60.6±0.6
3[f]	20		129±1.4 (130.8[33])
3[e]	25	20.9±0.3	209±2.5
3[e]	35	55.2±0.7	552±7

[e] [OH$^-$] = 0.010 mol dm^{-3}. [f] An average for different NaOH (from 0.010 to 0.045 mol dm^{-3}) and at 0.010 mol dm^{-3} substrate **3** concentrations.[11]

The dehydrohalogenation rates of **4** and **5** (at 10 °C, Table 4) are very close to each other as stated also earlier.[22] The structural difference between **4** and **5** is reflected in their activation enthalpies and entropies (Table 5) in such away that they largely compensate each other the enthalpy being much smaller and entropy very negative for **4** as compared to those of **5**.

The neutral reactions were tested for 2-chloroethanol **1** at 100 °C in 0.100 mol dm^{-3} $NaClO_4$ solution. Practically no neutral reaction occurred as reported also earlier.[12–17] The neutral reaction was also tested for 1-chloro-2-methyl-2-propanol **4** at 100 °C both in water ($10^5k = 3.2$ s^{-1}) and in 1–6 mol dm^{-3} HNO_3 solution (10^5k = 2.4–2.9 s^{-1}, respectively). These rates are practically negligible in comparison with the rates in NaOH solutions.

Table 4. The recalculated average second-order rate constants for the alkaline dehydrochlorination of 1-chloro-2-methyl-2-propanol **4**, and 2-chloro-2-methyl-1-propanol **5** at different temperatures[36]

Compound	t, °C	Av, 10^2k_2, dm^{3}mol^{-1}s^{-1}
4[a]	5	32.2±0.6
4[a]	7.5	41.7±0.7
4[a]	10	52.8±0.8
5[b]	5	33.9±1.6 (35.2±1.8)[c]
5[b]	7.5	45.1±1.7 (45.7±2.1)[c]
5[b]	10	59.7±1.3 (61.0±2.1)[c]

[a] 10^3[S] mol dm^{-3} 22.0–24.3 and $10^3[OH^-]$ 25.7–51.4 mol dm^{-3}. [b] 10^3[S] mol dm^{-3} 16.0–19.4 and $10^3[OH^-]$ 22.0–56.5 mol dm^{-3}. [c] The values for the 10.9:1.6 mixture of **4** and **5**.

Table 5. Activation parameters for the dehydrochlorination reactions of 2-chloro-1-ethanol (**1**), 2-chloro-1-propanol (**2**) and 1-chloro-2-propanol (**3**)

Compound[a]	**1**	**2**	**3**	**4**	**5**
A, dm^{3}mol^{-1}s^{-1}	24.7x10^{13}	1.6x10^{13}	3.3x10^{13}	1.8x10^{11}	3.6x10^{13}
$E_,$ /kJ mol^{-1}	93.6±2.0	82.1±1.7	81.2±2.0	62.6±0.4	74.7±0.3
R	-0.9995	-0.9996	–0.9990	–0.9996	–1.0000
$\Delta H^{\#}$, kJ mol^{-1}	91.1±2.1	79.5±1.7	78.8±2.2	63.0±1.2	72.3±0.4
$\Delta S^{\#}$, JK^{-1}mol^{-1}	22.3±6.9	–0.8±6.7	5.8±7.6	–46.6±4.2	6.6±0.7
$\Delta G^{\#}$, kJ mol^{-1}	84.4±0.1	79.8±0.1	77.1±0.1	76.9±2.4	70.3±0.6

[a] Porret[5] reports practically equal values of A, E_a, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ for **1**.

The effect of total ionic strength I on the second-order rate of **2** in alkaline dehydrochlorination was studied at a 0.010 mol dm^{-3} NaOH varying I from 0.010 to 0.500 mol dm^{-3} with $NaNO_3$. A slight decrease of the second order rate constant was observed (10^3k_2, dm^3 mol^{-1} s^{-1}: 76.1–65.0). The results are shown in Table 6.

Table 6. Pseudo first-order ($k_1´$) and second-order rate constants (k_2) for **2** at different ionic strengths in a constant NaOH concentration (0.010 mol dm^{-3}) at 25 °C. Equation for the linear dependence (log $k_2/k_2°$ vs $I^{½}$) shown under the table and the calculated k_2 values in parentheses

[$NaNO_3$], mol dm^{-3}	I, mol dm^{-3}	$10^3k_1´$, s^{-1}	10^3k_2, dm^3 mol^{-1} s^{-1}
0	0.010	7.61±0.06	76.1±0.6 (75.8)
0.010	0.020	7.49±0.06	74.9±0.6 (75.0)
0.040	0.050	7.34±0.06	73.4±0.6 (73.4)
0.190	0.200	6.85±0.06	68.5±0.6 (69.3)
0.490	0.500	6.50±0.03	65.0±0.3 (64.7)

$\log (k_2/k_2°) = (-0.113\pm0.006)(I)^{½} - (1.109\pm0.002)$.

When presenting the pseudo first-order rate constants as function of the hydroxide-ion (base) concentration

$$k_1´ = k_2[B] + I \qquad \textbf{(2)}$$

a straight line is obtained where the slope is equal to the second-order rate constant k_2 (dm^3 $mol^{-1}s^{-1}$) and i (s^{-1}) is the intercept which should be = 0 if OH^- is the only catalyst. Table 8 indicates that indeed i is practically zero in each case (**1–3)** and k_2 values remain, as expected, almost equal to the values in Table 2 shown in parentheses in Table 7.

Table 7. The second-order rate constants and the zero degree terms (i) calculated from equation (8) for 2-choroethanol **1**, 2-chloro-1-propanol **2** and 1-chloro-2-propanol **3**

Compound	t, °C	10^3k, $dm^3mol^{-1}s^{-1}$	10^{-3}i, s^{-1}	R
1	35	31.4±0.7 (32.6)	–0.01±0.04	0.9991
2	15	59.1±1.8 (61.6)	0.18±0.11	0.998
3	10	40.2±0.3 (37.9)	–0.05±0.02	0.9999

Conclusions

1,2-chlorohydrins react with NaOH(aq) predominantly with nucleophilic elimination of HCl. 2-chloroethanol **1**, 2-chloro-1-propanol **2** and 1-chloro-2-propanol **3** give oxiranes as the final products whereas in the case of 1-chloro-2-methyl-1-propanol **4** and 1-chloro-2-methyl-2-propanol the predominant final product was proved to be 2-methyl-1,2-propanediol besides a small amount of 2-methyl-1-propanal. The mere water reaction was shown to be almost negligible. In constant ionic strength the base concentration had no effect on the rates whereas at different base concentrations the rate of alkaline dehydrochlorination somewhat decreases. The rate at constant base concentration and at different ionic strengths decreased also indicating that the decrease is mainly due to the change in the ionic strength also in the former case.

Experimental Section

General. 2-Chloroethanol **1 (**>99%) and 1-chloro-2-propanol **2 (**97%) were commercial products from the British Drug Houses Ltd and Ega Chemie. 2-propionylchloride (purum) used for the preparation of 1-chloro-2-propanol **3** was from Fluga AG and $LiAlH_4$ (96%) from Ega Chemie.

2-Chloro-1-propanol 2 was prepared by reducing 2-propionylchloride with $LiAlH_4$-Et_2O mixture.[23] The boiling point was 51 °C at 2.5 kPa, yield 82%, n_D^{20} 1.4362 (lit.[24] b.p. 70.4 °C at 10 kPa, n_D^{25} 1.4365). ^{1}H NMR in CCl_4: C*H*$_3$ 1.47(d), –C*H*$_2$– 3.62(d), O*H* 4.07 (s) and –C*H*Cl– 4.25(m) ppm.
1-Chloro-2-propanol (**3**) was dried over anhydrous $MgSO_4$ and distilled (b.p. 309 K at 2.1 kPa), n_D^{20} 1.4366 (lit.[24] b.p. 323.6-323.8 K at 4.0 kPa, n_D^{30} 1.4352). ^{1}H NMR in CCl_4: C*H*$_3$ 1.25 (d), –C*H*OH– 3.95 (m), O*H* 3.70(s) and –C*H*$_2$Cl 3.45(d) ppm.
1-Chloro-2-methyl-2-propanol (**4**) was synthezised with the method of Burgin et al.[25] 45.3 g of methyl allyl chloride was hydrated at 5–10 °C in 80% H_2SO_4. The mixture was subsequently diluted by water to 10% in respect of sulfuric acid. Distillation gave 10.5 g (19.4%) of **4**. B.p. 63.5–64.9 °C/60 torr (lit. 71 °C/100 torr). ^{1}H NMR in $CDCl_3$: C*H*$_3$ 1.30, O*H* 2.83 and C*H*$_2$ 3.43 ppm.
2-Chloro-2-methyl-1-propanol (5) [^{1}H NMR in $CDCl_3$: C*H*$_3$ 1.56, O*H* 2.03 and –C*H*$_2$– 3.48 ppm] was prepared with the method of Petrov[26] which actually gave also some isomeric 1-chloro-2-methyl-2-propanol **4**. 2,2-Dimethyloxirane was treated with standard HCl at 5–10 °C and then diluted with fourfold amount of water and saturated with $(NH_4)_2SO_4$. The isomer mixture was extracted with ether and separated with distillation. The boiling points of **4** and **5** are so close to each other (132–3 and 128-9 °C, respectively) that their separation was not very successful. Because especially **5** tends to decompose at atmospheric distillation, it ought to be done in reduced pressure which further decreased their boiling point difference. The purest fraction of **5** still consisted 12.8 % of **4**.

Solutions. KCl (extra pure), KNO_3 (pro analysis), NaCl (pro analysis), $NaNO_3$ (cryst. extra pure), NaOH-ampoule (Titrisol), HNO_3 (pro analysis) and $NaClO_4{\cdot}H_2O$ (pro analysis) were commercial products from E. Merck AG. The ionic strength of the calibration solution was adjusted by 5 M $NaNO_3$ solution (ion analyzer) from Orion Research. Distilled water was used as the solvent and the solutions were prepared at 25 °C.

Calibration solutions. These were prepared from NaCl. The chloride ion concentration in these solutions varied from $9{\cdot}10^{-6}$ to $1{\cdot}10^{-2}$ mol dm^{-3}. At first 0.010 mol dm^{-3} NaCl solution was prepared by weighing 0.2923 g of the salt into 500 mL of distilled water. Other solutions were prepared by diluting this solution.

Dehydrochlorination solutions. NaOH-ampoule was used to prepare a 0.500 mol dm^{-3} solution. This was diluted to give the solutions having NaOH concentrations from 0.01 to 0.100 mol dm^{-3}. The ionic strength was adjusted with solid $NaNO_3$ to 0.100 mol dm^{-3} in solutions applied to study the catalytic effect of water. When studying the electrolyte effects the NaOH concentration was 0.010 mol dm^{-3} and the $NaNO_3$ concentrations varied from 0 to 0.490 mol dm^{-3}. For potentiometric measurements the $NaNO_3$ concentration was adjusted to 0.500 mol dm^{-3}. The alkaline dehydrochlorination was studied also at higher hydroxide ion concentrations (0.050–0.250 mol dm^{-3}) where the $NaNO_3$ concentration was adjusted to 0.250 mol dm^{-3}. The solution used to study neutral dehydrochlorination contained 0.100 mol dm^{-3} $NaClO_4xH_20$.

Kinetic measurements. The progress of alkaline dehydrochlorination of 1,2-chlorohydrines **1–3** was followed by measuring potentiometrically the concentration of the released chloride ions. The direct indication method, based on the measurement of the electromotive force, *E*, of the cell, was applied.

$$E = E°' + k \log a = E°' + k \log yc \qquad (\mathbf{3})$$

where $E°'$ [= $E°$(working electrode)– E(standard electrode)] is the apparent electromotive force of the cell, *y* is the activity coefficient, *c* the concentration of the sample and *k* is the Nernst constant:

$$k = (RT/zF)\ln 10 \qquad (\mathbf{4})$$

where *R* is the common gas constant (J K^{-1}mol^{-1}), *T* is absolute temperature (K), *z* is the charge number of the ion and *F* Faraday's constant.

The potentiometer used was Compensator E 388 Metrohm Herisau. The working electrode was a chloride-selective membrane electrode (94-17A9) from Orion and the standard electrode was a saturated calomel electrode (EA 404), which was equipped with a 3.0 mol dm^{-3} KNO_3 salt bridge solution to avoid diffusion. The chloride selective electrode was measuring the chloride ion concentration accurately until $5{\cdot}10^{-5}$ mol dm^{-3}. By measuring the electromotive force *E* for several chloride ion concentrations (Table 8) it was possible to create calibration curves where *E* was plotted according to equation (1) against log c/c° (c° = 1 mol dm^{-3}). These curves, the shape of which corresponded to those calibration curves reported in literature[28] and described by Orion for the ion selective membrane electrode, were used to estimate log c_i for the chloride ion concentrations at the measured electromotive forces E.

Table 8. For chloride-ion concentrations, c_i, at ionic strengths 0.100 (a) and 0.250 mol dm^{-3} (b) measured electromotive forces E_a and E_b, respectively

10^3c_i, mol dm^{-3}	$-\log c/c°$	E_a, mV	E_b, mV
10.000	2.000	102.7	-
5.000	2.301	120.0	130.3
2.500	2.602	141.2	146.0
1.000	3.000	164.0	166.7
0.625	3.204	176.0	178.0
0.500	3.301	180.2	184.1
0.400	3.398	-	188.8
0.3125	3.505	192.1	193.9
0.250	3.602	-	199.1
0.200	3.699	200.7	202.3
0.150	3.824	-	209.2
0.100	4.000	214.3	215.5
0.090	4.046	216.3	217.2
0.080	4.097	218.5	-
0.070	4.155	220.9	218.1
0.060	4.222	223.3	219.8
0.050	4.301	226.6	223.6
0.030	4.523	233.5	-
0.020	4.699	238.5	-
0.010	5.000	240.4	-
0.009	5.046	241.8	-

Alkaline dehydrochlorination reactions of 1–3. 100 mL of the reaction solution was pipetted with a 100 mL full pipet into a 100 ml Erlenmeyer bottle which was tightly closed by a cork and then thermostated at least for 30 minutes in a water bath with Lauda Thermostat. Thereafter 5.00 mm^3 of the chlorohydrine studied was added from a piston pipet with vigorous mixing and this was taken as the zero time for the reaction. However, 1-chloro-2-propanol **2** at 25 °C was thermostated in a methanol bath with a cryostate. Then 5.00 mL of the reaction mixture was pipetted with suitable intervals in test tubes which contained 1.1 mL HNO_3 solution the concentration of which was chosen in such a way that the final pH of the sample was 4.5. Altogether 18 samples were taken within two half-lives and the final samples after about 10 half-lives. For potentiometric measurements the sample was thermostated to 25 °C and the electromotive forces were measured as stated above. The chloride ion concentration c_i were obtained from the calibration curves based on the data in Table 8. The reaction products were not analyzed since several reports dealing with the dehydrohalogenation of 1,2-chlorohydrines have shown that they are oxiranes.[5,10,16,28-35]

Alkaline dehydrochlorination reactions of 4 and 5. Dehydrochlorination was followed by titrating the chlorine released in the reaction potentiometrically with a dilute $AgNO_3$ solution[34] which was prepared by dissolving 1.6987 g of $AgNO_3$ in 1 L of distilled water. The solution so obtained was kept in a dark bottle. The concentration of the $AgNO_3$ solution (ca 0.010 M) was determined by titrating standard NaCl samples. The standard NaCl solution was prepared by dissolving 9.35084 g of NaCl, dried first 2 h at 128 °C and kept over night in a desiccator, in 2.000 L of distilled water. Potentiometric titration was carried out using Ag- and Hg_2SO_4-electrodes. The sample volumes were adjusted to 16 mL by adding ethanol, acid (if the solution was still alkaline), and water. Potentiometric titrations occurred automatically and gave curves which enabled the evaluation of equivalent points at various times.

When studying the alkaline dehydrochlorination of **4** and **5** the substrate concentration of the reaction solution was ca 0.020 mol dm^{-3} and the NaOH concentration varied from 0.02 to 0.06 mol dm^{-3}. The reaction solutions were prepared by mixing known alkaline and substrate solution by pouring the former into the latter. These solution were kept in glass-stoppered glass bottles which were immersed in a thermostated water bath the temperature of which was controlled within 0.1 °C. The reaction rates were determined at three temperatures: 5, 7.5 and 10 °C (Table 6). At each temperature the rates were determined in 3-5 different base concentrations. The NaOH solutions were prepared by dissolving a weighed amount of solid NaOH in boiled distilled water. The solution concentration was determined with a known kaliumbipthalate solution using phenolliftalein as an indicator.

Calculation of the rate constants. The alkaline dehydrochlorination of 1,2-chlorohydrines is a specific second-order reaction catalyzed by the hydroxide ion (Equation 1).[10,28] It is first-order in relation of both the hydroxide ion and the chlorohydrin. The reaction happens in two steps where the first and fast pre-equilibrium is followed by a rate-determining step in which the chlorine is replaced by negatively charged oxygen. The reverse reaction is negligible.[29] The fast step follows the S_Ni-mechanism described for the intramolecular substitution reaction.[28] In fact the final main product in the case of compounds **4** and **5** was shown to be 2-methyl-1,2-propanediol.

Since the reaction follows the second-order kinetics, the rate can be obtained from the equation[35]

$$-d[A]/dt = k_2[A][B] \qquad \textbf{(5)}$$

where [A] is the chlorohydrine concentration, [B] the hydroxide-ion (base) concentration and k_2 the second-order rate constant. The ratio of the hydroxide ion (base) concentration and that of the chlorohydrine was ≥20. In other words we could use the Ostwald isolation method to derive the reaction rates[35] since [B] remains practically constant during the reactions, i.e. $[B] = [B_o]$. Accordingly

$$-d[A]/dt = k_2[B]_o[A] = k_1{'}[A] \qquad \textbf{(6)}$$

where k_1' is so-called pseudo first-order rate constant. Thus

$$k_2 = k_1'/[\mathrm{B}]_o \qquad (\mathbf{7})$$

The pseudo first-order rate constants were estimated from equation 8[36]

$$k_1' = (1/t)\ln\{[\mathrm{A}]_o/([\mathrm{A}]_o\text{-x}])\} = (1/t)\ln[(c_\infty - c_o)/(c_\infty - c_t)] \qquad (\mathbf{8})$$

where t is the reaction time, c_o the initial chloride ion concentration (mol dm^{-3}) at $t = 0$, c_∞ the chloride ion concentration at the end of the reaction and c_t the chloride ion concentration at time t. In each reaction the initial chloride ion concentration was equal to zero. Equation 6 gave then the second-order rate constants k_2.

The rate constants for **1–3** were also measured at 4 to 5 different temperatures (Table 3) to determine the activation parameters (Table 5) for their dehydrochlorination reactions from the equation

$$\ln (k_2/k_2^\circ) = \ln (A/A^\circ) - (E_a/\mathrm{R})(1/T) \qquad (\mathbf{9})$$

where A is the frequency factor (dm^{3}mol^{-1}s^{-1}), $A^\circ = k_2^\circ = 1$ dm^{3}mol^{-1}s^{-1} and E_a the activation energy (kJ mol^{-1}) from which the values of $\Delta H^\#$, $\Delta S^\#$ and $\Delta G^\#$ (Table 5) were obtained in the usual manner.

Also some earlier reports[11] from our department has dealt with the alkaline dehydrochlorination of **1–3**. In these reports the kinetic measurements were made titrimetrically. However, the reaction conditions did not fulfill the concentration ratio of the reagents required by a pseudo first-order reaction[35] since the base concentration was at most only four-fold compared to that of the substrate. The ionic strength was not kept constant either in the reactions carried out at different temperatures.

Therefore we recalculated the rate constants for these measurements[11] from equation[35]

$$k_2 = (1/t)[1/(\mathrm{a}-\mathrm{b})]\ln[\mathrm{b}(\mathrm{a}-\mathrm{x})/\mathrm{a}(\mathrm{b}-\mathrm{x})] \qquad (\mathbf{10})$$

where a is the initial concentration of **1–3** (mol dm^{-3}), b that of NaOH (mol dm^{-3}) and x the chloride ion concentration (mol dm^{-3}) at time t (s). The recalculated second order rate constants are given together with the present results in Table 2. This treatment also proved that in fact the neutral dehydrochlorination (water reaction) was insignificant in agreement with our test where we kept 10.0 mm^3 2-chloroethanol in 100 mL of boiling (t ~100 °C) 0.100 mol dm^{-3} $NaClO_4$ solution. 5 mL samples were withdrawn with a full pipet and cooled at 25 °C for potential measurements. The reaction was followed for an hour but did not proceed practically at all.

In an M.Sc. thesis[37] the alkaline dehydrochlorination of 1-chloro-2-methyl-2-propanol **4** and 2-chloro-2-methyl-1-propanol **5** was studied argentometrically. The second-order rate coefficients

(Table 4) were again recalculated from equation 10 since the reaction conditions applied did not obey the pseudo first-order kinetics because the NaOH concentration was at most only 2.6-fold as compared with the substrate concentration. Since **5** consisted 12.8 % of **4** the rate constants for the former were evaluated from equation

$$[A_1]_t = [A_1]_o(B_o - x_t)/B_o \exp\{[k_2]_1 t(B_o - A_o)\} \qquad (\mathbf{11})$$

where $[A_1]_t$ is the concentration of **4** at time t, $[A_1]_o$ its initial concentration, B_o is the initial NaOH concentration, A_o (= $[A_1]_o+[A_2]_o$) the initial concentration of the isomeric mixture, x_t is the chloride ion concentration formed at time t and $[k_2]_1$ the second order rate constant of **4**. Equation 12 gave then the chloride ion concentration , x_1, given by **4**

$$x_1 = [A_1]_o - [A_1]_t \qquad (\mathbf{12})$$

and then the chloride ion concentration, x_2, obtained from **5** was

$$x_2 = x_t - x_1 \qquad (\mathbf{13})$$

The calculations showed that the percentage proportion of x_2 corresponded within an error limit the initial contribution of **5** (87.2%). According to the literature the dehydrochlorination rates of **4** and **5** are very close to each other (cf Table 5).[22]

The effect of base concentration. The rate constants for **1**–**3** (Table 1) were also determined at different NaOH concentrations (0.01–0.100 mol dm^{-3}) keeping the ionic strength constant (0.100 mol dm^{-3}) with $NaNO_3$. For **1** the rate constants were also measured varying the NaOH concentration from 0.050 to 0.250 mol and keeping the ionic strength (0.250 mol dm^{-3}) constant with $NaNO_3$ (Table 2).

The effect of ionic strength (I). The effect of total I on the second-order rate coefficients of **2** in alkaline dehydrochlorination was studied at a 0.010 mol dm^{-3} NaOH varying the $NaNO_3$ concentration from 0 to 0.49 mol dm^{-3}. In other words the ionic strength was varied from 0.010 to 0.500 mol dm^{-3}. The results are listed in Table 6.

Neutral dehydrochlorination (water reaction). This was tested with 2-chloroethanol **1** at 100 °C in 0.100 mol dm^{-3} $NaClO_4$ solution. 10 mm^3 of **1** was placed with a plunger pipet in 100 mL of the reaction solution which was kept boiling with an electrical bath. Thirteen samples were withdrawn at intervals for an hour with a 5.00 mL full pipet and cooled immediately in an ice bath. Potential measurement were carried out at 25 °C. Practically no neutral reaction was observed. The same was true in the case of 1-chloro-2-methyl-2-propanol **4** which reacted only very slowly at 100 °C both in water ([S] = 0.021 mol dm^{-3}, $10^5 k = 3.2$ s^{-1}) and in 1–6 mol dm^{-3}

HNO_3 solution ([S] = 0.020–0.022 mol dm^{-3}, [HNO_3] 1–6 mol dm^{-3}, 10^5k = 2.4–2.9 s^{-1}, respectively).

Product analysis. The final reaction products of the alkaline dehydrochlorination of **4** and **5** were analyzed by GC-MS on a VG Analytical MM 7070E mass spectrometer coupled directly (splitless injection) to a DANI 3800 gas chromatograph with on-line 11-250 data system. GC separation was performed on a fused silica column (25 m x 0.25 mm i.d.) coated with SE-30. The products were tentatively identified by comparing their mass spectra with those reported in the literature or recorded on a model compound using a 25 m Carbowax 20 M column and programming the temperature from 45 to 80 °C with a speed of 6 °C/min. The EI mass spectra were taken at 70 eV on a VG Analytical MM 7070E instrument equipped with a VG 11-250 data system. The accelerating voltage was 6 kV, the temperature of the ion source was ~ 450 K and the ionization current 100μA.

1-Chloro-2-methyl-2-propanol **4** gave some 2-methyl-1-propanal but predominantly 2-methyl-1,2-propanediol [MS: $[M-CH_3]^+$ 75(12), 59(100), 57(21), 43(21), 41(19), 31(34), 29(15), 27(10)] which was identified by comparing its mass spectrum with that of the model compound. 2-Chloro-2-methyl-1-propanol **5** gave 2-methyl-1,2-propanediol together with a small amount of 2,2,5,5-tetramethyl-1,4-dioxane [MS at 70 eV: $M^{+\bullet}$ 144(1), $[M-H]^+$ 143(2), 101(100), 73(55), 71(12), 59(19), 56(40); 55(52), 43(33), 41(30)] and some 2-methyl-1-propanal (MS at 70 eV: $M^{+\bullet}$ 72(31), 43(100), 42(12), 41(57), 39(21), 29(28), 28(18), 27(63)] in contrast to an early report stating that it gives only the latter.[38]

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