15. *The Solvolysis of* 1-*Chloropropan*-2-*ol.*

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Solvolysis of 1-chloropropan-2-ol in water produces acid, acetone, and propane-1 : 2-diol simultaneously at comparable first-order specific rates. The glycol yields no carbonyl-containing products in moderately concentrated acid at 97°. Rates of solvolysis of ethylene chlorohydrin have also been determined.

Ethylene chlorohydrin on solvolysis yields only small amounts of acetaldehyde (*ca.* 1%) (Cowan, McCabe, and Warner, *J. Amer. Chem. Soc.*, 1950, **72**, 1194) whereas 1-chloro-2-methylpropan-2-ol gives eventually a quantitative yield of *iso*butyraldehyde by a reaction subsequent to that producing acid (Harvey, Riggs, and Stimson, *J.*, 1955, 3267). The kinetics and products of the solvolysis of 1-chloropropan-2-ol are now reported.

Rates of solvolysis in water of ethylene chlorohydrin have been determined by Radulescu and Muresanu (*Bul. Soc. stiinte Cluj*, 1932, **7**, 129; *Chem. Abs.*, 1933, **27**, 2085). Further measurements made with this compound (Table 1) agree very well with theirs.

Table 1. *Solvolysis of ethylene chlorohydrin and* 1-*chloropropan*-2-*ol.*

	Ethylene chlorohydrin			1-Chloropropan-2-ol		
Solvent (% v/v)	Temp.	10^2C_0 (mole/l.)	10^6k_1 (sec.$^{-1}$)	Temp.	10^2C_0 (mole/l.)	10^6k_1 (sec.$^{-1}$)
Water	124·9°	2·6	51·0	118·5°	2·72	28·8
	97·2	3·0	3·98	115·8	2·69	22·3
	83·2	2·8	0·95	97·2	2·63	3·23
	83·2	3·0	0·98	97·2	2·78	3·21
60%-EtOH	97·2	3·1	0·88	97·2	2·78	0·53
	97·2	3·4	0·92	—	—	—
80%-EtOH	97·2	3·1	0·38	97·2	2·75	0·16

Experimental

Materials.—1-Chloropropan-2-ol was made by the hydration of allyl chloride (Bancroft, *J. Amer. Chem. Soc.*, 1919, **41**, 426). The product (b. p. 43—46°/18 mm., n_D^{17} 1·4388) was fractionated through an 8″ × 1″ column packed with Fenske helices and fitted with a Whitmore–Lux head, a fraction having b. p. 40·8—41·0°/18 mm., n_D^{19} 1·4381, d_4^{20} 1·1123, being retained (Found : C, 37·8; H, 7·53. Calc. for C_3H_7OCl : C, 38·0; H, 7·46%).

Ethylene chlorohydrin (L. Light and Co.) was distilled; the fraction having b. p. 124°/680 mm. and n_D^{21} 1·4410 on being refractionated as above yielded a sample, b. p. 45·4—45·9°/26 mm., n_D^{21} 1·4411.

Products.—Samples of 1-chloropropan-2-ol (0·2 g.) in water (5 ml.) were heated at 97° in sealed tubes for measured times and cooled. The consumption of periodate during 2 hr. at room temperature in a borax–boric acid buffer was attributed to propane-1 : 2-diol, which was shown to react quantitatively under these conditions. Similar samples were treated with 2 : 4-dinitrophenylhydrazine solution. The resulting precipitate was filtered off, dried, and extracted with benzene. The extract was chromatographed on alumina, and the product (m. p. and mixed m. p. with acetone 2 : 4-dinitrophenylhydrazone 126°) weighed. No other yellow bands were observed on the column.

Samples of propane-1 : 2-diol (b. p. 91·3°/17 mm., n_D^{17} 1·4331; 0·2 g.) were heated at 97° for various times up to 160 hr. in hydrochloric acid of concentrations up to 2N. No carbonyl-containing product was detected with 2 : 4-dinitrophenylhydrazine.

Kinetics.—The solvents were purified, solutions made up, and the kinetics of acid production determined as described by Harvey, Riggs, and Stimson (*loc. cit.*). The specific rate constants for the production of glycol and acetone were calculated from $k_1 = (1/t) \log_e [x_\infty / (x_\infty - x_t)]$ where x_t is the amount of acetone or glycol produced after time t.

Discussion

In water at 97° 1-chloropropan-2-ol yields acid, acetone, and propane-1 : 2-diol simultaneously, the kinetics of production being of the first order in each case and the specific rate constants nearly equal, *viz.*, 10^6k_1 = 3·2, 2·6, and 3·5 sec.$^{-1}$, respectively. Since steady rate constants for acid production are obtained by calculation from the concentration of 1-chloropropan-2-ol (Table 2), 1·0 mol. of acid is liberated, whereas the ultimate yields of acetone and propane-1 : 2-diol are 0·42 and 0·48 mol., respectively, a total of 0·90 mol. The discrepancy may be due to accumulated errors in the methods of estimation or to the formation of other products; in particular, no propaldehyde was detected (cf. Krassuski, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 287). Further, propane-1 : 2-diol, unlike 2-methylpropane-1 : 2-diol, does not rearrange on prolonged heating with moderately concentrated acid. Wegscheider's test (Table 3) shows that acetone and propane-1 : 2-diol are produced in side reactions.

TABLE 2. *Rate of production of acid in the solvolysis of* 1-*chloropropan*-2-*ol.*

Solvent, water. Temp., 118·5°. Concn. of C_3H_7OCl, 13·65 × 10^{-5} mole/bulb. Concn. of $Ba(OH)_2$, 0·01025N.

Time (min.)	105	152	196	236	274	302	332	362	382	382
Titre (ml.)	2·23	3·12	3·86	4·45	5·04	5·39	5·69	6·15	6·36	6·42
10^5k_1 (sec.$^{-1}$)	2·90	2·93	2·92	2·88	2·90	2·85	2·82	2·85	2·83	2·87

Mean k_1 = 2·88 ± 0·04 × 10^{-5} sec.$^{-1}$.

TABLE 3. *Rates of formation of products in the solvolysis of* 1-*chloropropan*-2-*ol in water at* 97°.

Time (hr.)	15	46·5	99·5	189	426(∞)
Acetone (mol.)	0·059	0·15	0·26	0·34	0·42
10^6k_1 (sec.$^{-1}$)	2·8	2·5	2·8	2·5	—
Acetone/HCl (calc.)	0·37	0·36	0·38	0·38	—
Time (hr.)	48	108·5	171	498(∞)	—
Glycol (mol.)	0·22	0·38	0·41	0·48	—
10^6k_1 (sec.$^{-1}$)	3·6	3·9	3·1	—	—
Glycol/HCl (calc.)	0·51	0·53	0·48	—	—

The overall rate of disappearance of 1-chloropropan-2-ol, as measured by the acid produced, falls as ethanol replaces water in the solvent, and to a greater extent than in the solvolyses of ethylene chlorohydrin and 1-chloro-2-methylpropan-2-ol, being twenty times as great in water as in " 80% " ethanol at 97°, whereas the factor is 10 for the last two compounds; the ratios of rates in " 60% " and " 80% " ethanol are 3·3, 2·3, and 2·4 respectively.

The activation energy (29·6 kcal./mole) calculated from the Arrhenius equation is appreciably different from those for ethylene chlorohydrin and 1-chloro-2-methylpropan-2-ol (26·5 and 27·0 kcal./mole respectively), but the results do not show whether the present value can be assigned to a single rate-determining stage or whether it is a composite value for the side reactions. The values of $\log_{10}A$ are 12·1, 10·2, and 11·3 respectively.

The relative rates of solvolysis of ethylene chlorohydrin, 1-chloropropan-2-ol, and 1-chloro-2-methylpropan-2-ol in water at 97° are 1·0 : 0·81 : 5·5. Successive introduction of methyl groups into the β-position of ethylene chlorohydrin does not, therefore, cause progressive changes in the rates or kinetic parameters discussed above. Further, the nature and proportions of the products and the reaction paths by which they are produced differ considerably from case to case.

The microanalysis was carried out by Dr. W. Zimmermann, of C.S.I.R.O., Melbourne.

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