The Solvolysis of 1-Chloro-2-methylpropan-2-ol.

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The kinetics of solvolysis of 1-chloro-2-methylpropan-2-ol in water and aqueous ethanol have been examined. The results are consistent with the assumption that *iso*butyraldehyde is produced from previously formed 2-methylpropane-1 : 2-diol.

IN a kinetic investigation of the hydrolysis of ethylene halogenohydrins, Cowan, McCabe, and Warner (*J. Amer. Chem. Soc.*, 1950, **72**, 1194) found that only traces of acetaldehyde were produced, the main product being glycol. Various workers (*e.g.*, Groll and Kautter, U.S.P. 2,042,225; *Chem. Abs.*, 1936, **30**, 4872) have found *iso*butyraldehyde to be produced in good yield when 1-chloro-2-methylpropan-2-ol is refluxed with water. The latter aldehyde could have arisen by pinacolinic rearrangement of 2-methylpropane-1 : 2-diol previously formed in the reaction (cf. Hearne, Tamelle, and Converse, *Ind. Eng. Chem.*, 1941, **33**, 805). The kinetics of solvolysis of 1-chloro-2-methylpropan-2-ol are now reported.

EXPERIMENTAL

Materials.—(*a*) 1-Chloro-2-methylpropan-2-ol (*iso*butylene α-chlorohydrin), prepared by the method of Burgin, Hearne, and Rust (*Ind. Eng. Chem.*, 1941, **33**, 385), had b. p. 121°/680 mm.; they give b. p. 126·7°. After fractionation through a vacuum-jacketed column, 30 cm. long and 1·5 cm. in diameter, packed with $\frac{1}{16}$ in. Dixon rings and fitted with a Whitmore–Lux head, it had b. p. 64·8—65·0°/66 mm., $n_{\mathrm{D}}^{18\cdot5}$ 1·4400. Petrov (*J. Gen. Chem. U.S.S.R.*, 1945, **15**, 690; *Chem. Abs.*, 1946, **40**, 5698) reports b. p. 56·6—57·5°/50 mm., n_{D}^{20} 1·4392.

(*b*) 2-Methylpropane-1 : 2-diol, prepared from 1 : 2-epoxy-2-methylpropane by the action of dilute sulphuric acid (0·03N), had b. p. 93°/20 mm., n_{D}^{16} 1·4370 (Found : C, 52·8; H, 11·4. Calc. for $C_4H_{10}O_2$: C, 53·2; H, 11·2%). It gave the bisphenylurethane of m. p. 140° (Krasuskii and Movsum, *Chem. Abs.*, 1937, **31**, 1377). A trace of *iso*butyraldehyde (5%), identified as its 2 : 4-dinitrophenylhydrazone, m. p. 181°, was also obtained.

(*c*) The ethanol used was obtained by distillation of commercial absolute alcohol successively over 5% of concentrated sulphuric acid and sodium hydroxide pellets in the presence of silver oxide. It was dried by being refluxed over, and was distilled from, magnesium ethoxide. Head and tail fractions were rejected at each distillation. Aqueous ethanol mixtures, nominally "v%," were prepared by mixing v volumes of purified ethanol with $100 - v$ volumes of doubly distilled water at room temperature.

Products.—(*a*) 1-Chloro-2-methylpropan-2-ol (1·2 g.) was refluxed in water (25 ml.)for 29 hr. (temperature not measured). A solution of 2 : 4-dinitrophenylhydrazine (500 mg.) in concentrated sulphuric acid (1 ml.) was rapidly diluted with water (50 ml.) and added to the reaction mixture. The bulky yellow precipitate was collected after 24 hr., washed thoroughly with water, dried, and extracted with benzene; the residue on evaporation weighed 350 mg. The crude product had m. p. *ca.* 165° and, once recrystallised from aqueous alcohol, m. p. *ca.* 175°. Chromatography of a benzene solution on alumina gave a sharply defined initial fraction containing the bulk of the product which had m. p. 178—180° on recrystallisation from alcohol. A number of other yellow bands appeared on the column but the various small residues were not further examined. The product was therefore substantially *iso*butyraldehyde, traces of other carbonyl-containing substances being also present.

(*b*) 2-Methylpropane-1 : 2-diol and dilute hydrochloric acid readily gave *iso*butyraldehyde, identified as above.

Kinetic Measurements.—(i) Stock solutions of known concentration from which *a* (see below) was calculated were prepared from a quantity of the chlorohydrin weighed into a calibrated flask and made up to the mark with the required aqueous ethanol mixture. Pipetted portions (5 ml.) were sealed in Pyrex-glass bulbs which were placed in the thermostat and, after a measured time, the liberated acid was titrated with 0·01N-sodium hydroxide or -barium hydroxide with a methyl-red–bromocresol-green indicator (Bartlett and Swain, *J. Amer. Chem. Soc.*, 1949, **71**, 1407), no interference from atmospheric carbon dioxide being observed.

The thermostats were steady to 0·1°. First-order rate constants were calculated from the expression $k = (1/t) . \log_e[a/(a - x)]$, where a is the initial concentration of chlorohydrin and x is the decrease in its concentration (calculated from the titre) after time t. A typical run is shown in Table 1.

TABLE 1. *1-Cloro-2-methylpropan-2-ol in water at* 97·2°.

c_0, 3·49 × 10^{-2} mole/l.; a, 17·45 × 10^{-5} mole/bulb; NaOH, 0·0116N.

t (min.)	134	196	321	386	446	519	577	655	712	825	899	1002
Titre (ml.)	2·52	3·54	5·46	6·34	7·06	7·76	8·28	9·05	9·51	10·37	10·63	11·18
10^5k (sec.$^{-1}$)	2·27	2·28	2·37	2·38	2·37	2·33	2·32	2·35	2·37	2·37	2·32	2·28

Mean $k = 2·33 \times 10^{-5}$ sec.$^{-1}$.

TABLE 2. *Solvolysis of 1-chloro-2-methylpropan-2-ol in aqueous ethanol.*

EtOH (%)	Temp.	10^2c_0 (moles/l.)	10^5k (sec.$^{-1}$)	Temp.	10^2c_0 (moles/l.)	10^5k (sec.$^{-1}$)	E (kcal./mole)	$\log_{10} A$ (sec.$^{-1}$)
0	97·2°	3·49	2·33	85·5°	3·74	0·69	27·4 27·0	11·3
0	97·0	1·99	2·25	84·4	1·83	0·63	26·9 26·0	—
20	97·2	3·67	1·78	85·5	3·67	0·55	26·4	10·8
40	97·1	3·62	1·00	85·1	3·68	0·31	25·7	10·2
60	97·2	3·58	0·52	85·1	3·89	0·160	25·6	9·9
80	97·0	3·36	0·213	85·1	3·75	0·069	24·8	9·1

TABLE 3. *Yields of* iso*butyraldehyde and hydrochloric acid from 1-chloro-2-methylpropan-2-ol in water at* 97°.

Time (hr.)	7	9	27	62
C_4H_8O (mol.)	0·19	0·32	0·78	0·95
HCl (mol.) [a]	0·45	0·53	0·90	0·99
C_4H_8O/HCl	0·42	0·60	0·87	0·96

[a] Calc. from the rate equation.

TABLE 4. *Yields of* iso*butyraldehyde from 2-methylpropane-1 : 2-diol in* 0·24N-*hydrochloric acid at* 97°.

Time (min.)	16	31	123	1260
C_4H_8O (mol.)	0·16	0·23	0·56	0·99

k_1 of the order of 1·5 × 10^{-4} sec.$^{-1}$.

The data and results for the experiments made, together with the values of E and A derived from the Arrhenius equation, $k = Ae^{-E/RT}$, are collected in Table 2.

(ii) Portions (5 ml.) of a solution of the chlorohydrin (0·884 g.) in water (25 ml.) were sealed in glass bulbs and heated in a bath at 97° for the given times, the weights of crude *iso*butyraldehyde 2 : 4-dinitrophenylhydrazone then being determined as above. The results are shown in Table 3.

(iii) Portions (5 ml.) of a solution of 2-methylpropane-1 : 2-diol (0·802 g.) in 0·24N-hydrochloric acid (25 ml.) were treated as above. The yields of chromatographed *iso*butyraldehyde 2 : 4-dinitrophenylhydrazone are used in Table 4, to show that the rate of this reaction in 0·02N-acid would be about half that of the solvolysis of the chlorohydrin, proportionality of rate to acid concentration being assumed.

DISCUSSION

Course of the Solvolysis in Water.—The rate of production of acid during solvolysis of 1-chloro-2-methylpropan-2-ol follows simple first-order kinetics to at least 75% reaction, the rate constants being independent of initial concentration. *iso*Butyraldehyde is produced ultimately in 100% yield, but Table 3 shows that a reaction yielding this product takes place subsequently to the production of acid. Production of some *iso*butyraldehyde in a reaction simultaneous with that producing acid is not excluded, but the assumption of production of glycol as an intermediate in the solvolysis and its rearrangement as the subsequent reaction is feasible since, in the presence of 0·02N-hydrochloric acid, 2-methylpropane-1 : 2-diol would be converted into *iso*butyraldehyde at about half the rate of the solvolysis. Protonated oxide may be a precursor of the glycol which is rapidly produced in substantial yield with only a trace of *iso*butyraldehyde by the action of dilute acid on the oxide.

Effects of Solvent Composition.—The first-order rate, which is 5·5 times that of ethylene chlorohydrin in water (Table 5), decreases with increasing ethanol content of the medium, the reaction in water being about ten times as fast as that in " 80% " ethanol. The ratio of rates in " 60% " and " 80% " ethanol is 2·4, which is comparable with the values quoted for typical bimolecular solvolyses and very much smaller than those for typical unimolecular solvolyses (Dostrovsky and Hughes, *J.*, 1946, 166). Winstein and Grunwald (*J. Amer. Chem. Soc.*, 1948, **70**, 828) suggested that marked neighbouring-group participation would occur in solvolysis of a compound of the present type and that, in such a unimolecular solvolysis, " an internal variety of a bimolecular displacement," the rate would show less dependence on solvent composition than in unimolecular solvolyses not involving participation (S_N1). The present value differs only slightly from that for ethylene bromohydrin (2·2; calculated from the results of Cowan, McCabe, and Warner, *loc. cit.*) where participation is estimated to be small (Winstein and Grunwald, *loc. cit.*).

TABLE 5. *Aqueous solvolysis of halogenohydrins.*

	10^5k at 97° (sec.$^{-1}$)	E (kcal./mole)	$\log_{10} A$ (sec.$^{-1}$)
1-Chloro-2-methylpropan-2-ol	2·25	27·0	11·3
Ethylene chlorohydrin	0·40 [a]	26·4 [b]	10·2 [b]
Ethylene bromohydrin [c]	6·1	26·8	11·7

[a] Determined for comparison by Mr. I. K. Gregor. [b] Calc. from the rate measurements of Radulescu and Muresanu (*Bul. Soc. stiinte Cluj*, 1932, **7**, 129; *Chem. Abs.*, 1933, **27**, 2085). [c] Calc. from the rate measurements of Cowan, McCabe, and Warner (*loc. cit.*).

The values of E and A for the solvolysis appear to decrease steadily with increasing ethanol content of the medium but the magnitude of the effect cannot be assessed owing to experimental inaccuracies. The values in water are the most accurate and are comparable with those found for the aqueous solvolysis of other halogenohydrins (cf. Table 5).

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