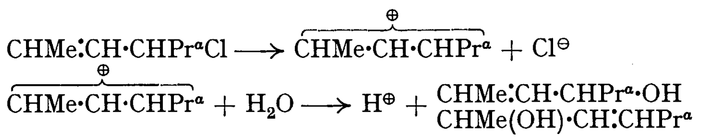
356. *The Mechanism of the Hydrolysis of αγ-Dimethylallyl Chloride.*

By C. L. Arcus and J. W. Smith.

The hydrolysis of αγ-dimethylallyl chloride in aqueous acetone has been followed by a conductometric method, and shown to follow a unimolecular law, in accord with the mechanism deduced from stereochemical observations. The apparent incompleteness of the reaction in the conductivity cell employed is attributed to adsorption of the αγ-dimethylallyl chloride on the platinum-blacked electrodes.

In a recent study of replacement reactions in allyl compounds (Arcus and Kenyon, J., 1938, 1912) it was found that the hydrolysis of (—)-Δ^{β}-δ-chloroheptene (γ-methyl-α-*n*-propylallyl chloride) is accompanied by great loss of optical purity and that a mixture of isomeric heptenols results. From these observations it was considered that the reaction proceeds by a unimolecular mechanism, in which the rate is controlled by the slow primary dissociation into a solvated carbonium kation:



$$\mathrm{CHMe{:}CH{\cdot}CHPr^{\alpha}Cl} \longrightarrow \overbrace{\mathrm{CHMe{\cdot}CH{\cdot}CHPr^{\alpha}}}^{\oplus} + \mathrm{Cl}^{\ominus}$$

$$\overbrace{\mathrm{CHMe{\cdot}CH{\cdot}CHPr^{\alpha}}}^{\oplus} + \mathrm{H_2O} \longrightarrow \mathrm{H}^{\oplus} + \begin{matrix}\mathrm{CHMe{:}CH{\cdot}CHPr^{\alpha}{\cdot}OH}\\ \mathrm{CHMe(OH){\cdot}CH{:}CHPr^{\alpha}}\end{matrix}$$

The hydrolysis of (—)-αγ-dimethylallyl chloride has a similar stereochemical result (Hills, Kenyon, and Phillips, J., 1936, 576) and a similar mechanism should apply.

The rate of hydrolysis of *dl*-αγ-dimethylallyl chloride in aqueous acetone (75% by vol.) at 0° has now been studied. This compound was selected in preference to Δ^{β}-δ-chloroheptene because its symmetrical substitution precludes the formation of an isomeride during its preparation from the corresponding alcohol. The velocity of the reaction proved too great to permit determination of the liberated hydrogen chloride by withdrawal of portions of the solution and titration with alkali or silver solutions. Accordingly, the conductivity of the solution during the process of hydrolysis was determined at suitable intervals, and the corresponding concentrations of hydrogen chloride were deduced by reference to the conductivities of known solutions of hydrogen chloride in the same solvent. (A similar method has been applied to the alcoholyses of substituted triphenylmethyl chlorides by Nixon and Branch, *J. Amer. Chem. Soc.*, 1936, **58**, 492.)

Experiment 1.

Wt. of αγ-dimethylallyl chloride, 0·350 g.

t (mins.).	[HCl].	$k \times 10^4$ (calc. from $t = 0$).	$k \times 10^4$ (calc. from $t = 33$ mins.).
5	0·0006	58·5	—
10	0·0012	59	—
15	0·00175	58·5	—
22	0·0025	58	—
33	0·00365	58	—
42	0·00452	58	57·5
53	0·00553	58	57·5
94	0·0088	58	58
108	0·00973	58	58
132	0·01115	58	57·5
155	0·01235	57·5	57·5
216	0·01482	57	57
262	0·01618	57	56·5
298	0·0170	56·5	56
325	0·0175	56	55·5
1 day	0·0209		

Final concn. of HCl by titration = 0·02105 = 93% of theoretical.

Experiment 2.

Wt. of αγ-dimethylallyl chloride, 0·341 g.

t (mins.).	[HCl].	$k \times 10^4$ (calc. from $t = 0$).	$k \times 10^4$ (calc. from $t = 32$ mins.).
4	0·00048	60	—
9	0·00108	61	—
15	0·00173	59·5	—
20	0·00226	59	—
32	0·00348	59	—
42	0·0044	58	56·5
52	0·0053	58	57·5
77	0·00733	58	58
116	0·00995	58	58
141	0·0113	57·5	57·5
174	0·01282	57·5	57
197	0·0137	57	57
253	0·01545	56·5	56·5
302	0·01655	56	55·5
328	0·0170	55·5	55
3 days	0·02028		

Final concn. of HCl by titration = 0·0205 = 93% of theoretical.

The hydrolysis of our sample of αγ-dimethylallyl chloride by the above solvent in glass vessels yielded 98% of the theoretical amount of hydrogen chloride, and the reverse reaction between αγ-dimethylallyl alcohol and hydrogen chloride could not be detected at the concentrations used. It was found, on the other hand, that the hydrolysis in the conductivity cell proceeded to the extent of only 93%. This difference is ascribed to adsorption of αγ-dimethylallyl chloride on the platinum-black coated electrodes. The final concentration of hydrogen chloride was employed for the calculation of the first-order velocity constants given in the table. Concentrations of hydrogen chloride are given as the normality at 0°.

It is evident that the reaction is substantially of the first order, in agreement with the unimolecular mechanism deduced from the stereochemical result.

EXPERIMENTAL.

dl-αγ-Dimethylallyl chloride was prepared by slow addition of a mixture of *dl*-αγ-dimethylallyl alcohol (25 g.) and pyridine (5 g.) to phosphorus trichloride (15 g.) cooled in ice–acetone. After standing at room temperature for 1·5 hours, the upper layer was decanted and redistilled. It had b. p. 68°/270 mm. [Found, by saponification with alcoholic potassium hydroxide : *M*, (i) 106·2, (ii) 106·2. Calc. : *M*, 104·6].

Acetone was purified *via* its sodium iodide compound (Shipsey and Werner, J., 1913, **103**, 1255), dried with calcium chloride, and redistilled. The solvent used was prepared by adding distilled water (1 vol.) to acetone (3 vols.) at 22°; it had no measurable conductivity; 75 c.c. of acetone and 25 c.c. of water, both at 22°, yielded 97·3 c.c. of solvent at 22° and 94·5 c.c. at 0°.

The conductivities of the solutions were measured with the apparatus described by Righellato and Davies (*Trans. Faraday Soc.*, 1933, **29**, 429), in which the bridge reading is directly proportional to conductivity. (This method permitted determination of minima to ± 1 unit, corresponding to ± 0·00002N-HCl.) The conductivity cell comprised a wide-mouthed glass bottle of about 250 c.c. capacity into which dipped a pair of parallel platinum disc electrodes mounted on a rigid glass framework passing through the stopper of the bottle. The electrodes, about 4 sq. cm. in area and 1 cm. apart, were coated with platinum black. A further tube passing through the stopper of the bottle, normally kept closed, served for the introduction and removal of solution.

The solvent (150 c.c.) and conductvity cell were cooled to 0° in a well-stirred bath of ice and water. About 100 c.c. of the solvent were decanted into the cell, and *dl*-αγ-dimethylallyl chloride was added rapidly from a weighing bottle fitted with a teat-pipette; the remainder of the solvent was added with agitation of the cell. Thereafter the conductivity of the solution was measured at suitable intervals, the apparatus being maintained at 0° throughout. Finally, the cell and its contents were kept overnight at room temperature, cooled to 0°, and the conductivity redetermined. Portions of the solution were then titrated with sodium hydroxide.

0·1158, 0·1178, and 0·0995 G. of *dl*-αγ-dimethylallyl chloride were added to 50 c.c. portions of the solvent, the hydrolyses were allowed to proceed at room temperature for 1, 3, and 3 days, respectively, in closed flasks, and the hydrogen chloride liberated was titrated with sodium hydroxide; the concentrations found were 97·4, 98·2, and 97·4% of the theoretical.

To test for the occurrence of a back-reaction, the conductivity at 0° of a solution of hydrogen chloride in the same solvent (0·0198N at 0°) was measured; *dl*-αγ-dimethylallyl alcohol (0·488 g.) was then added to 159 c.c. of the solution. The conductivity at 0° remained unaltered during 3 days.

For purposes of calibration, 150 c.c. of a solution of hydrogen chloride in the same solvent (0·0203N at 0°), measured at 0°, were placed in the cell, and the conductivity at 0° determined. Then 50 c.c. were withdrawn and replaced by 50 c.c. of solvent, measured at 0°, and the conductivity redetermined. This was repeated twice. The measurements were duplicated, the maximum difference between corresponding readings from the two experiments being 0·5%, and the bridge-readings plotted against concentrations of hydrogen chloride at 0°.

Thanks are expressed to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Ltd. for grants.

BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, September 28th,* 1939.]