127. *The Steric Course of the Hydrolysis of α-Phenylethyl Chloride in Acetone containing Mercuric Chloride.*

By DENNIS R. READ and WILLIAM TAYLOR.

The rates of hydrolysis of α-phenylethyl chloride and bromide in acetone are much increased by mercuric chloride and bromide respectively.

From titrimetric measurements of the rate of hydrolysis of *l*-α-phenylethyl chloride in 95% aqueous acetone containing low concentrations of mercuric chloride, and from polarimetric measurements of the change of rotation during hydrolysis, it is inferred that substitution in the early stages occurs with retention of configuration. However, since the final product, α-phenylethyl alcohol, is very slightly inverted in configuration, later substitution must be inverted.

MERCURIC bromide accelerates the hydrolysis of alkyl bromides in acetone (Read and Taylor, J., 1939, 1872). It is now found that mercuric bromide and mercuric chloride accelerate the hydrolysis of the aralphyl halides α-phenylethyl bromide and chloride respectively (Table I).

TABLE I.

Second-order velocity coefficients (l. g.-mol.$^{-1}$ hr.$^{-1}$), measured titrimetrically, for the hydrolysis in acetone of α-phenylethyl halides in presence of mercuric halides, at 50°. The figures in parentheses are the ratios of the coefficients with and without mercuric halide, other conditions being identical.

[CHPhMeCl] = 0·2000 and added [HCl] ~ 0·05 throughout.

	[H$_2$O].			
[HgCl$_2$].	2·7778.		5·5556.	
0·0000	0·000195	(1·00)	0·000780	(1·00)
0·1000	0·140	(718)	0·380	(487)
0·2000	0·783	(4010)	0·671	(860)
0·3000	0·955	(4900)	—	

[CHPhMeBr] = 0·2000 and added [HBr] ~ 0·05 throughout.

	[H$_2$O].			
[HgBr$_2$].	2·7778.		5·5556.	
0·0000	0·00691	(1·00)	0·0158	(1·00)
0·0250	0·0721	(10·4)	0·104	(6·58)
0·0500	0·350	(50·6)	0·311	(19·7)
0·1000	0·926	(134)	—	

From our previous work (*loc. cit.*) it became of interest to examine the steric course of the hydrolysis of α-phenylethyl chloride in the presence of mercuric chloride. Bodendorf and Böhme (*Annalen*, 1935, **516**, 1) found that, in dry ethyl alcohol at 25° with [*d*-CHPhMeCl] = 0·366 and [$HgCl_2$] = 0·183, the solution originally having $\alpha_D^{25°}$ ($l = 2$) = + 3·68° had finally $\alpha_D^{25°}$ = − 1·35°, the only end-product being α-phenylethyl ethyl ether. Ward (J., 1927, 445) showed that in 80% aqueous ethyl alcohol at 28·6° with [*d*-CHPhMeCl] ~ 0·1000 and no mercuric chloride, the solution originally of $\alpha_{5780}^{28 \cdot 6°}$ ($l = 2$) = + 1·30° had finally $\alpha_{5780}^{28 \cdot 6°}$ = − 0·44°, the end-products being a mixture of α-phenylethyl alcohol and its ethyl ether. The first-order reaction rates, whether measured titrimetrically or polarimetrically, were the same. Hughes, Ingold, and Scott (J., 1937, 1201) discovered that at 70° the percentage of inversion of the substitution product obtained by the action of ethyl alcohol, 60% aqueous acetone, and 80% aqueous acetone on α-phenylethyl chloride decreased down the series of solvents, the product being almost entirely racemic in the last two instances. In 80% aqueous acetone Ward's result for the first-order velocity coefficient was paralleled, the titrimetrically-determined coefficient being $9 \cdot 04 \times 10^{-5}$ sec.$^{-1}$, whilst that obtained polarimetrically rose from 9·2 to $11 \cdot 5 \times 10^{-5}$ sec.$^{-1}$ during the run. In these experiments the reactions went to completion.

We have measured (*a*) the rate of racemisation of α-phenylethyl chloride in dry acetone (cf. Bodendorf and Böhme, *loc. cit.*), (*b*) its rate of change of rotatory power during hydrolysis in 95% aqueous acetone, and (*c*) its rate of hydrolysis (titrimetrically) in 95% aqueous acetone, all experiments being at 20° and with mercuric chloride present in solution. The product of hydrolysis was α-phenylethyl alcohol with a small proportion of styrene.

The first-order velocity coefficient for (*a*), *viz.*, $k_{(a)}$, was a constant during any one run (Table V) at all mercuric chloride concentrations, was independent of the concentration of organic chloride, and, within the limits of the rather large experimental error, was proportional to the square of the concentration of mercuric chloride for molar concentrations of the latter of 0·3 to 1·2 (Table II); *i.e.*, $r_{(a)} = k_{(a)}$ [RCl][$HgCl_2$]^2. Bodendorf and Böhme (*loc. cit.*) found that, for mercuric chloride concentrations of 0·037—0·37M, $r_{(a)} \propto [HgCl_2]^n$, where $n < 2$.

TABLE II.

First-order velocity coefficients (mins.$^{-1}$) for the racemisation of α-phenylethyl chloride in dry acetone containing mercuric chloride. Temperature 20°.

[CHPhMeCl] ...	0·18	0·18	0·18	0·18	0·18	0·18	0·18	0·18	0·18	0·12	0·06
[$HgCl_2$]	0·15	0·15	0·30	0·30	0·30	1·20	1·20	0·60	0·60	0·60	0·60
$k_{(a)} \times 10^4$	7·62	9·66	28·0	24·9	29·2	478	514	122	95·9	106	96·4

The first-order velocity coefficient for (*b*), *viz.*, $k_{(b)}$, was at first almost equal to that for (*a*), being generally very slightly greater. (We take this to mean that the water in the aqueous solvent has but little effect on the rate of racemisation.) The value of the coefficient rose steadily during any one run, the rise being bigger the smaller the initial mercuric chloride concentration (Table III). This rise was traced to the production of hydrogen chloride during the hydrolysis, because, by introducing hydrogen chloride of the appropriate concentration at the commencement of the reaction, the coefficient did not increase during the run and its value was relatively high (Table VI).

We have used the first-order coefficients for the velocity of hydrolysis as given by the titrimetric measurements (*c*) so as to be able to compare these coefficients with those of (*a*) and (*b*), and not because we favour a unimolecular mechanism. The coefficient $k_{(c)}$ was constant during that portion of molecular change of α-phenylethyl chloride equal to about one-tenth of the molar concentration of mercuric chloride introduced, but then in contrast with $k_{(b)}$ it fell rapidly (Table V). This fall is analogous to that which occurred with alkyl bromides (Read and Taylor, *loc. cit.*), where it was shown to be due to the generation of hydrogen bromide during the hydrolysis, probably owing to the removal of mercuric halide in complex-ion formation : $HBr + HgBr_2 \longrightarrow H^{\cdot} + HgBr_3{}'$. A similar explanation is assumed to explain the present data; *i.e.*, $HCl + HgCl_2 \longrightarrow H^{\cdot} + HgCl_3{}'$.

Possibly the most significant fact emerging from this investigation was that, although at the higher mercuric chloride concentrations the initial values of the velocity coefficients, $k_{(a)}$, $k_{(b)}$, and $k_{(c)}$, were almost identical, at the lower concentrations the earlier values of

$k_{(c)}$ were considerably higher than those of $k_{(a)}$ or $k_{(b)}$. From this it follows, first, that since hydrolysis is proceeding more quickly than racemisation it cannot occur subsequently to racemisation, and the mechanisms of the two processes must be distinct. Secondly, because α-phenylethyl chloride and alcohol of the same sign of rotation have the same configuration, because optically pure α-phenylethyl chloride and alcohol have $[\alpha]^{20^\circ}_{D} = 50{\cdot}6^\circ$ and $43{\cdot}4^\circ$ respectively (Hughes, Ingold, and Scott, *loc. cit.*), and because at these low mercuric chloride concentrations the early rate of hydrolysis is much higher than the early rate of change of rotation during hydrolysis, it is inferred that hydrolysis must at first occur with retention of configuration. However, the final product is very slightly inverted in configuration and therefore later on in the hydrolysis, *i.e.*, when $k_{(c)} < k_{(b)}$, substitution must occur with inversion.

TABLE III.

Initial and final values of the first-order velocity coefficients (mins.$^{-1}$) for (*b*) the change of rotation during hydrolysis and (*c*) the hydrolysis of α-phenylethyl chloride, in acetone containing mercuric chloride. Initial and final rotations and final acidity concentrations are also given.

$[H_2O] = 2{\cdot}7778$ throughout.

	$[CHPhMeCl] \sim 0{\cdot}18$.				$[CHPhMeCl] = 0{\cdot}1791$.		
$[HgCl_2]$.	Initial $k_{(b)}$ $\times 10^4$.	Final $k_{(b)}$ $\times 10^4$.	Initial α^{20}_{D}.	Final α^{20}_{D}.	Initial $k_{(c)}$ $\times 10^4$.	Final $k_{(c)}$ $\times 10^4$.	Final [HCl].
0·15	7·73	15·6	− 1·90°	+ 0·03°	35·3	small	0·1726
0·30	30·4	57·1	− 1·93	+ 0·08	51·3	9·8	0·1722
0·60	121	206	− 1·95	+ 0·12	120	59·9	0·1736
1·20	528	643	− 1·95	+ 0·22	542	230	0·1735

EXPERIMENTAL.

dl-α-*Phenylethyl alcohol.* This was prepared both from methylmagnesium iodide and benzaldehyde and from phenylmagnesium bromide and acetaldehyde; the products had b. p. 101—102°/17 mm. and 104—105°/16 mm., respectively, and the yields were 78% and 51%, calculated on the weight of the aldehyde used.

d- *and* l-α-*Phenylethyl alcohols.* The hydrogen phthalate of the *dl*-alcohol (Houssa and Kenyon, J., 1930, 2260), isolated by the method of Duveen and Kenyon (J., 1936, 621), was resolved by fractional crystallisation of the brucine salts from dry acetone (Downer and Kenyon, J., 1939, 1156), and the *d*- and the *l*-alcohol isolated by the usual methods.

dl-, d-, and l-α-*Phenylethyl chlorides.* These were obtained in good yield by the action of thionyl chloride on the corresponding alcohols (Hughes, Ingold, and Scott, *loc. cit.*); b. p. 82—83°/18 mm., 83—84°/19 mm. (Found : Cl, 25·2. Calc. : Cl, 25·2%).

dl-α-Phenylethyl bromide was prepared by treating the *dl*-alcohol in dry benzene with hydrogen bromide (Hughes, Ingold, and Scott, *loc. cit.*); b. p. 102—103°/17 mm. (Found : Br, 42·4. Calc. : Br, 43·2%).

TABLE IV.

$[CHPhMeBr] = 0{\cdot}2000$ and $[H_2O] = 2{\cdot}7778$ throughout.

$[HBr] = 0{\cdot}0490$, $[HgBr_2] = 0{\cdot}000$.

t.	[HBr].	*x*.	$k \times 10^3$.
2·20	0·0571	0·0081	6·78
6·35	0·0722	0·0232	6·99
20·10	0·1124	0·0634	6·91
22·61	0·1195	0·0705	7·01
25·01	0·1238	0·0748	6·85
43·3	0·1500	0·1010	(5·93)
49·2	0·1551	0·1061	(5·65)
67·2	0·1653	0·1163	(4·78)

$[HBr] = 0{\cdot}0481$, $[HgBr_2] = 0{\cdot}0500$.

t.	[HBr].	*x*.	$k \times 10^3$.
0·050	0·0574	0·0093	341
0·133	0·0729	0·0248	359
0·217	0·0869	0·0388	361
0·300	0·0971	0·0490	340
0·383	0·1016	0·0535	(295)
0·550	0·1059	0·0578	(226)
0·800	0·1093	0·0612	(166)
0·967	0·1109	0·0628	(142)

$[CHPhMeCl] = 0{\cdot}2000$ and $[H_2O] = 5{\cdot}5556$ throughout.

$[HCl] = 0{\cdot}0517$, $[HgCl_2] = 0{\cdot}0000$.

t.	[HCl].	*x*.	$k \times 10^3$.
3·45	0·0546	0·0029	0·773
20·2	0·0684	0·0167	0·775
44·5	0·0871	0·0354	0·789
68·4	0·1027	0·0510	0·778
92·0	0·1174	0·0657	0·784

$[HCl] = 0{\cdot}0550$, $[HgCl_2] = 0{\cdot}2000$.

t.	[HCl].	*x*.	$k \times 10^3$.
0·045	0·0864	0·0314	672
0·092	0·1119	0·0569	661
0·125	0·1301	0·0751	683
0·158	0·1443	0·0893	679
0·192	0·1552	0·1002	660
0·250	0·1645	0·1095	(578)
0·292	0·1724	0·1174	(552)
0·325	0·1740	0·1190	(507)

Mercuric chloride had m. p. 276°, and mercuric bromide m. p. 236°, and both gave neutral solutions in acetone. The acetone used in the kinetic experiments was purified by the method of Conant and Kirner (*J. Amer. Chem. Soc.*, 1924, **46**, 245).

Kinetic Experiments.—Hydrolysis of dl-*α-phenylethyl chloride and bromide at* 50° *in presence of added hydrogen and mercuric halides.* The procedure was as already described (J., 1939, 1875), bromophenol-blue being the indicator. For comparison with these previous results the second-order velocity coefficient was required and was calculated from

$$k = [2{\cdot}303/t(a - b)]\ .\ \log_{10} b(a - x)/a(b - x)$$

t being the time in hours, and *a* and *b* the concentrations (in g.-mols./l.) of water and organic halide respectively. A summary of the results is in Table I, and representative runs in Table IV. Even with added hydrogen halide of 0·05M concentration, this was insufficient to check the fall in the later values of the coefficient.

The hydrolysis and racemisation of α-phenylethyl chloride at 20° *in presence of added mercuric chloride but with no added hydrogen chloride.* The value of the rotatory power, $\alpha_{\mathrm{D}}^{20°}$ ($l = 2$), at zero time was obtained either by extrapolation or by measurement of a dry acetone solution containing only α-phenylethyl chloride and of the same concentration as was employed in the kinetic experiments. Mercuric chloride, especially at the higher concentrations and in dry acetone, caused the development of a yellow to brown colour which militated against accuracy in the later readings of some of the runs. The first-order velocity coefficients were calculated from the equations :

(*a*) for racemisation in dry acetone, $k_{(a)} = (2{\cdot}303/t)(\log_{10} \alpha_0 - \log_{10} \alpha_t)$,

(*b*) for change of rotation during hydrolysis,

$$k_{(b)} = (2{\cdot}303/t)[\log_{10} (\alpha_0 - \alpha_\infty)/\log_{10} (\alpha_t - \alpha_\infty)],$$

(*c*) for hydrolysis, $k_{(c)} = (2{\cdot}303/t)[\log_{10} a/(a - x)]$

t being the time in minutes and *a* the concentration (in g.-mols./l.) of α-phenylethyl chloride. The results have been summarised in Tables II and III. Representative individual runs are given in Table V.

TABLE V.

[HgCl$_2$] = 0·3000 throughout.

(*a*) [CHPhMeCl] ~ 0·18, [H$_2$O] = 0·0000.			(*b*) [CHPhMeCl] ~ 0·18, [H$_2$O] = 2·7778.			(*c*) [CHPhMeCl] = 0·1791, [H$_2$O] = 2·7778.		
t.	$\alpha_{\mathrm{D}}^{20°}$.	$k_{(a)} \times 10^4$.	*t*.	$\alpha_{\mathrm{D}}^{20°}$.	$k_{(b)} \times 10^4$.	*t*.	*x*.	$k_{(c)} \times 10^4$.
0	− 1·95°	—	0	− 1·93°*	—	6	0·0053	50 3
1·3	− 1·95	—	4·5	− 1·90	—	11	0·0103	53·8
3·0	− 1·95	—	6·5	− 1·89	—	16	0·0140	50·8
10·5	− 1·90	24·6	10	− 1·87	30·4	21	0·0185	52·0
17	− 1·84	34·1	18	− 1·82	31·2	26	0·0218	50·0
28	− 1·80	28·5	29	− 1·71	40·0	31	0·0261	50·8
73·5	− 1·55	31·2	70	− 1·39	44·7	61	0·0345	35·1
138	− 1·28	30·5	120	− 1·05	48·0	121	0·0464	24·8
232	− 0·98	29·8	173	− 0·73	52·6	200	0·0663	23·1
270	− 0·65	29·7	249	− 0·42	55·9	303	0·0778	18·8
			396	− 0·13	57·1	1339	0·1310	9·8
			1820	+ 0·08	—	7099	0·1734	—
			2940	+ 0·08	—	12,958	0·1734	—

* By extrapolation.

[HgCl$_2$] = 1·200 throughout.

(*a*) [CHPhMeCl] ~ 0·18, [H$_2$O] = 0·0000.			(*b*) [CHPhMeCl] ~ 0·18, [H$_2$O] = 2·7778.			(*c*) [CHPhMeCl] = 0·1791, [H$_2$O] = 2·7778.		
t.	$\alpha_{\mathrm{D}}^{20°}$.	$k_{(\alpha)} \times 10^4$.	*t*.	$\alpha_{\mathrm{D}}^{20°}$.	$k_{(b)} \times 10^4$.	*t*.	*x*.	$k_{(c)} \times 10^4$.
0	− 1·90°†	—	0	− 1·95°	—	7	0·0540	513
10	− 1·16	494	7	− 1·21	528	10·5	0·0788	553
13	− 1·01	504	9	− 1·02	513	13	0·0920	555
15·5	− 0·88	497	11	− 0·91	505	15·5	0·1028	569
19·3	− 0·70	518	14·5	− 0·73	537	18	0·1091	522
25	− 0·54	503	18·5	− 0·45	610	22	0·1129	453
29	− 0·45	497	24	− 0·25	618	31	0·1310	424
33·5	− 0·30	551	30	− 0·08	644	45	0·1439	361
43	− 0·24	481	38	+ 0·04	643	73	0·1608	313
45	− 0·14	580	58	+ 0·17	—	121	0·1680	230
60	0·00	—	80	+ 0·23	—	1319	0·1729	—
			240	+ 0·22	—	5672	0·1723	—

† By control experiment.

In connection with the titrimetric experiments mercuric chloride was itself found to suffer hydrolysis in 95% aqueous acetone at 20°, but the rate of such hydrolysis was so low as not to affect the early and constant values of $k_{(c)}$. The following figures show this when compared with those in Table V :

[CHPhMeCl] = 0·0000, $[HgCl_2]$ = 0·3000, $[H_2O]$ = 2·7778. Temp. 30°.

t (mins.)	51	112	190	275	355	1330	7088
[HCl]	0·0029	0·0161	0·0240	0·0240	0·0233	0·0250	0·0264

The effect of added hydrogen chloride on the rate of change of rotation during hydrolysis. The effect of added hydrogen chloride in increasing and rendering constant the first-order velocity coefficient for the change of rotation during hydrolysis is illustrated in Table VI.

TABLE VI.

[CHPhMeCl] ~ 0·18, $[H_2O]$ = 2·7778, $[HgCl_2]$ = 0·3000, [HCl] = 0·14.

t (mins.).	$\alpha_D^{20°}$.	$k_{(b)} \times 10^4$.	*t* (mins.).	$\alpha_D^{20°}$.	$k_{(b)} \times 10^4$.
0	− 2·05°†	—	135	1·05°	49·6
15	− 1·90	50·7	173	0·87	49·6
18	− 1·85	55·8	249	0·58	50·7
29	− 1·73	58·6	7260	0·00	—
56	− 1·55	50·0	8940	0·00	—
70	− 1·40	54·7			

† By control experiment.

Examination of Reaction Products.—*dl*-α-Phenylethyl chloride (14 g., 0·5 mol.), mercuric chloride (32·6 g., 0·6 mol.), and water (20 g., 5·6 mols.) were dissolved in acetone, and the solution (200 ml.) left at 20° for 48 hours. The liquid was filtered three times through anhydrous potassium carbonate, the acetone removed by distillation, and benzene added with the intention of extracting the reaction products—both mercuric chloride and water being almost insoluble in this solvent. However, no precipitation occurred, and the liquid was dried over anhydrous potassium carbonate. From this was obtained a liquid of b. p. 92·5—99°/18 mm. (6·5 g.). By the method of J., 1937, 347, this was found to contain 6·0% of styrene. The liquid (1·00 g.) also gave a phenylurethane (1·90 g.), m. p. 90° unchanged on admixture with the phenylurethane of authentic *dl*-α-phenylethyl alcohol.

One of us (W. T.) thanks the Leverhulme Trustees for a Fellowship.

THE POLYTECHNIC, REGENT STREET, LONDON, W. 1. [*Received, February* 14*th*, 1940.]