[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE POLYTECHNIC]

The Rate and Mechanism of Hydrolysis of Benzhydryl Chloride in Acetone

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Three current mechanisms which have been adopted to interpret the first-order reaction between an alkyl halide and a relatively high concentration of water, alcohol, or acetic acid are those of (a) Hughes and Ingold[1] who assume partially for secondary and completely for tertiary, a slow *unimolecular* ionization of the halide as the rate-determining stage followed by a rapid reaction of the organic cation with a solvent molecule; (b) Taylor,[2] and Olson and Halford,[3] who assume for alkyl halides generally a one-stage *bimolecular* reaction involving the simultaneous addition and dissociation of the reactants, according to the ideas of London,[4] Polanyi,[5] and Olson,[6] and (c) Hammett,[7] who assumes a *polymolecular* reaction, which depends essentially upon the affinity of alcohol or water molecules for halide ion, reaction taking place within something of the nature of a solvation complex.

Taylor[2c] showed that the reaction of *t*-butyl bromide with water of low concentrations in acetone at 50° was kinetically of the second order and that therefore the mechanism of hydrolysis could not be unimolecular but is presumably bimolecular. Olson and Halford,[3] at about the same time, showed that the hydrolysis and alcoholysis of *t*-butyl chloride in aqueous methanol are both second-order reactions, if the fugacities of the reactants (as measured by their vapor pressures) and not their concentrations are employed in calculating the rate constants. These results appear to remove the possibility of mechanism (a). There remain (b) and (c).

Mechanism (c) was based partially on Hammett and co-workers[7] finding that at 25° when benzhydryl chloride (or α-phenylethyl chloride) and small concentrations of water (or of ethyl alcohol) are both dissolved in acetone, the rate of reaction is very low, whereas at the same temperature in dry or wet ethyl alcoholic solution the rate of reaction is high. The purpose of the present investigation was to find whether or not this state of affairs obtains with benzhydryl chloride at 50°. In brief it does not, since there is a measurable rate of hydrolysis of benzhydryl chloride in acetone containing 1, 2, 5 or 10 g. of water per 100 cc. of solution at this temperature. (These solutions are referred to as containing 1, 2%, etc., of water.) Thus, to this extent, the basis of the polymolecular mechanism (c) is weakened. Positive evidence in support of mechanism (b) was sought along the lines of the previous work with *t*-butyl bromide.[2c] Since, when either 2 or 10% aqueous acetone was used, no *s*-tetraphenyldimethyl ether could be detected in the reaction products (compare Ward[8]) but only benzhydrol, the sole reaction between benzhydryl chloride and water which occurs under these conditions can be represented

$$\mathrm{Ph_2CHCl + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ph_2CHOH + HCl}$$

and is reversible. Figure 1 shows the dependence of the rate of hydrolysis upon the concentration of water even at the lowest water concentrations.

However, as with the hydrolysis of *t*-butyl bromide in acetone, a slow reaction persisted beyond the equilibrium position due again presumably to the formation of mesityl oxide and other acetone condensation products in the presence of hydrogen chloride. This caused the elimination of water and hence the continued hydrolysis of benzhydryl chloride. The slow increase in acidity thus produced was approximately directly proportional to time for a considerable time interval and thus the equilibrium position for any one system was determined by extrapolation of the straight-line portion of the curve back to the x-axis. From the equilibrium constants $K = k_1/k_2$ the equilibrium positions (n) were calculated,[2c] n being the equilibrium value of x. As in the case of *t*-butyl bromide there is close agreement between the calculated values of n and those observed for the forward reaction (Table I).

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(1) Gleave, Hughes and Ingold, *J. Chem. Soc.*, 236 (1935).

(2) Taylor, *ibid.*, (a) 344, (b) 992, (c) 1853, (d) 1962 (1937).

(3) Olson and Halford, THIS JOURNAL, **59**, 2644 (1937).

(4) London, *Z. Elektrochem.*, **35**, 552 (1929).

(5) Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932); Bergmann, Polanyi and Szabo, *ibid.*, **B20**, 161 (1933).

(6) Olson, *J. Chem. Phys.*, **1**, 418 (1933); Olson and Voge, THIS JOURNAL, **56**, 1690 (1934).

(7) Steigman and Hammett, *ibid.*, **59**, 2536 (1937); Farinacci and Hammett, *ibid.*, **59**, 2542 (1937).

(8) Ward, *J. Chem. Soc.*, 2285 (1927).

TABLE I

Showing the practical identity of observed and calculated values of n, the equilibrium position, it being assumed that both reactions are kinetically of the same order.

$[H_2O]$	$[Ph_2CHCl]$	2nd order k_1	2nd order k_2	K	n, obsd.	n, calcd.
0.5556	0.0974	0.00230	0.658	0.00350	0.0125	0.0127
1.1111	.1052	.00415	.556	.00746	.0270	.0255
2.7778	.1064	.0171	.127	.134	.0842	.0860
5.5556	.1170	.0636	.0186	3.42	.1140	.1157

The catalytic effect of water on the hydrolysis reaction, as shown by the increase in the values of the second-order coefficient k_1 with a rise in the water concentration, is ascribed[9] to the dissociating effect of water on itself in acetone solution *i. e.*

$$(\mathrm{H_2O})_n \underset{\mathrm{COMe_2}}{\overset{\mathrm{H_2O}}{\rightleftarrows}} n\mathrm{H_2O}$$

the associated form being assumed to be relatively unreactive, compared with the simple form, toward the alkyl halide. Constant values of k_1, therefore, could not be expected since these were calculated using ordinary water concentrations, owing to lack of information regarding the active mass of the simple form.

From the evidence presented, then, the view is taken that the hydrolysis of benzhydryl chloride in acetone is a second-order reaction and that the mechanism is bimolecular.

Experimental

Materials.—"AnalaR" *acetone*, refluxed for ten hours over potassium permanganate and calcium oxide, boiled at 56–56.5°. *Benzhydryl chloride*, prepared by the method of Farinacci and Hammett, had b. p. 190–191° (47 mm.) (Calcd.: Cl, 17.53. Found: Cl, 17.54). *Benzhydrol* (commercial) recrystallized from alcohol melted at 68°.

Rate Measurements.—These were made at 50°. The procedure was identical with that used for *t*-butyl bromide.[2c] As with this compound a dark color developed in the reaction liquids of lower water concentrations. The values of k for the forward reaction were calculated for an irreversible second-order reaction from $k_1 = [2.303/t(a - b)] \log_{10} b(a - x)/a(b - x)$, t being the time in hours, and a and b the concentrations (in g. moles/liter) of water and benzhydryl chloride, respectively. The value of k_1 employed in the calculation of the equilibrium constant $K = k_1/k_2$, where k_2 is the second-order rate constant for the reverse reaction, was that extrapolated at $t = 0$ from the plot of k_1 against t. Typical data for the forward reaction in 1 and 5% aqueous acetone are given in Table II.

TABLE II

TYPICAL KINETIC DATA OF THE FORWARD REACTION IN ACETONE AT 50°

1%			5%		
a = 0.5556	b = 0.0974		a = 2.7778	b = 0.1064	
t	x	k_1	t	x	k_1
22.4	0.0030	0.00251	1.65	0.0080	0.0170
70.5	.0072	.00197	3.0	.0140	.0169
100	.0095	.00187	5.35	.0224	.0159
146	.0118	.00161	8.43	.0320	.0154
237	.0170	.00148	11.53	.0420	.0158
334	.0210	.00133	23.5	.0660	.0150
450	.0228	.00102	29.5	.0740	.0147
671	.0250	.00082	48	.0830	..
837	.0266	..	218	.0842	..
1006	.0280	..			

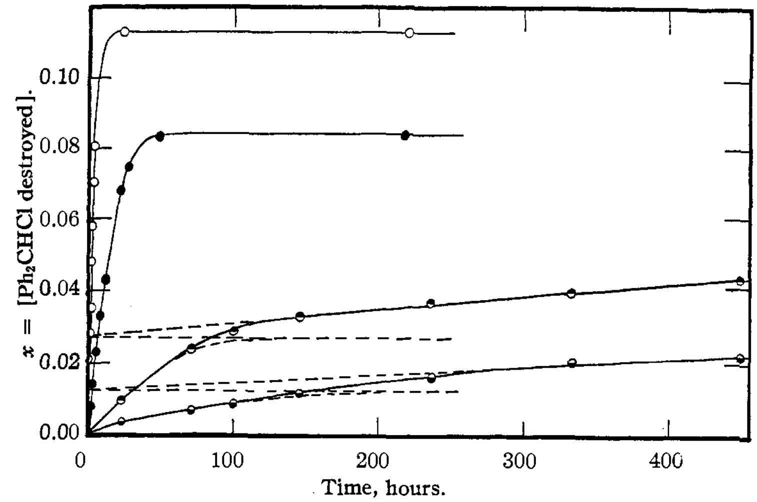

Fig. 1.—Effect of water on the rate of hydrolysis of benzhydryl chloride in acetone. Water "Percentages": ⊖, 1; ◓, 2; ●, 5; ○, 10.

The determination of the second-order rate coefficients of the reverse reaction in acetone, containing initially the same concentrations of water as for the forward reaction, was complicated by the rapid removal of hydrogen chloride by the acetone. These constants were therefore calculated from the equation

$$[\text{HCl removed by } \mathrm{Ph_2CHOH}]/t = k_2[\mathrm{Ph_2CHOH}][\mathrm{HCl}]$$

t being the time in hours, and all concentrations being in g. moles/liter, the two latter being mean concentrations for any one time interval. The amount of water formed by the condensation of acetone under the influence of hydrogen chloride

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[9] Taylor, *J. Chem. Soc.*, 840 (1938).

was so great as not only greatly to retard the formation of benzhydryl chloride in all except the initial stages, but ultimately even to cause the slow hydrolysis of that already formed, as shown by the rapid decrease in acidity giving place to a slow increase and this in spite of the continuous and simultaneous removal of hydrogen chloride by the acetone. Hence the equilibrium positions could not be observed for this reverse reaction. Typical data for the reverse reaction in 1 and 5% aqueous acetone are shown in Table III.

TABLE III

TYPICAL KINETIC DATA OF THE REVERSE REACTION IN ACETONE AT 50°

In column C is shown the rate of removal of hydrogen chloride by 1 and 5% aqueous acetone containing no benzhydrol.

	[HCl]	C [HCl]	[HCl removed by Ph_2CHOH]	k_2
1%				
$[Ph_2CHOH] = 0.0929$, $[HCl] = 0.1090$, $[H_2O] = 0.5556$				
0	0.1090	0.1090	0.0000	.
0.11	.0860	.0870	.0010	.
0.65	.0816	.0850	.0034	0.685
2.8	.0716	.0840	.0124	.601
3.38	.0682	.0835	.0153	.648
3.8	.0660	.0830	.0170	.697
19.5	.0510	.0780	.0270	..
68.5	.0354	.0635	.0281	..
125	.0340	.0550	.0210	..
332	.0374	..	..	..
5%				
$[Ph_2CHOH] = 0.0929$, $[HCl] = 0.1160$, $[H_2O] = 2.7778$				
0	0.1160	0.1160	0.0000	..
1.43	.1105	.1125	.0020	0.140
18.3	.0940	.1120	.0180	.114
67	.0920	.1100	.0180	..
163	.0930	.1080	.0150	..
331	.0936	..	..	..

Examination of Reaction Products.—These were examined in 2 and 10% aqueous acetone. Benzhydryl chloride (2.2 g.) in aqueous acetone (100 cc.) was kept at 50° for two hundred and forty and twenty-four hours, respectively; excess anhydrous sodium carbonate was added to remove water and acid. After filtering, and distilling the acetone, approximately 3 cc. of brown oil containing some crystalline solid was obtained; (1) the product had a faint odor of mesityl oxide but no 2,4-dinitrophenylhydrazone could be obtained from it; (2) that from 2% aqueous acetone contained considerable unchanged benzhydryl chloride (Found: Cl, 5.6) whereas that from 10% aqueous acetone contained negligible chlorine; (3) to 2 cc. of the product in each case was added ethyl alcohol (2 cc.) but there was no solid residue and hence no *s*-tetraphenyldimethyl ether had been formed.[8] Addition of water to the alcoholic solution gave benzhydrol only (m. p. and mixed m. p. with authentic specimen).

Summary

The hydrolysis of benzhydryl chloride and the action of hydrogen chloride on benzhydrol have been studied kinetically in acetone containing low concentrations of water. The hydrolysis reaction, under these conditions, yields benzhydrol and hydrogen chloride as the only reaction products. Assuming that both are second-order reactions, there is close agreement between the calculated equilibrium positions and those observed for the hydrolysis reaction, with different initial concentrations of water. This agreement indicates that the assumption is correct; and thus for both reactions a bimolecular mechanism is presumed.

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