traction with sodium carbonate solution and water, drying, removal of the solvent, and distillation under reduced pressure: b. p. 79–80° at 16 mm.; Cl, found by Volhard titration 24.8, 25.2%, calculated 25.2%.

Optical measurements were made in a 10-cm. polariscope tube immersed in a thermostat at 25.00°. The polariscope was a Schmidt and Haensch instrument which could be read to 0.01°. Readings were taken to the nearest 0.1°. The source of illumination was a mercury arc lamp; the Hg green line (wave length 5461) was used.

The following experiments were performed: (1) 12.55 g. of α-phenylethyl chloride (α = +8.50°, obtained from a sample of alcohol with α = +9.7°) and 9.81 g. of anhydrous potassium acetate dissolved in anhydrous acetic acid to make a total volume of 500 cc. were kept at 50° for one week. The solution was decanted from the potassium chloride, the acetic acid was removed under reduced pressure, and the residue was poured into water, extracted with benzene, and dried over calcium chloride. After removal of the solvent, the product was distilled under reduced pressure. The portion which distilled below 101° at 15 mm. was rejected in addition to several cc. of the acetate ester. The remainder distilled at 104° at 17 mm. and showed no test for chloride. It showed the following analysis: C, 73.21%; H, 7.3%.[42] Calculated for phenylethyl acetate C, 73.2%; H, 7.3%. The specific rotation was −1.1°, being opposite in sign to the original alcohol, and considerably racemized.

(2) Fourteen grams of alkyl halide (α = +6.0°) and 19 g. of tetraethylammonium acetate dissolved in anhydrous acetone to make a volume of 500 cc. were kept for four days at 50°. The acetone was distilled off and the residue worked up as in (1). Seven and two-tenths grams of phenylethyl acetate boiling at 97° at 12 mm. was obtained with the analysis C, 73.5%; H, 7.6%.[42] It gave a slight test for chloride. The specific rotation was −4.7°, of the same sign as that obtained in (1) but much less racemized.

(3) A solution of 10 g. of alkyl chloride (α = +13.7°) dissolved in 300 cc. of anhydrous acetone, was allowed to stand for two months. Thereupon 15 g. of tetraethylammonium acetate was added, and the solution was allowed to stand at room temperature for several weeks. On working up as before 7 g. of phenylethyl acetate boiling at 105–107° at 17 mm. was obtained. The specific rotation was −11.5°. Clearly then the halide does not racemize spontaneously in acetone solution. It is most improbable therefore that it ionizes to form carbonium and chloride ions in this medium at an appreciable rate.

The extensive investigations of Hughes, Ingold and co-workers[45] on Reaction Kinetics and the Walden Inversion had not become available at the time when this article was submitted for publication. There is no essential contradiction between their conclusions, based upon different material, and our own.

Summary

The solvolytic reaction of α-phenylethyl chloride in anhydrous acetic acid at 50° has been shown to be essentially of the first order. The reaction of the same chloride with tetraethylammonium acetate in acetone at the same temperature has been shown to be of the second order. Both reactions produce a levo-rotatory phenylethyl acetate from dextro-rotatory chloride, racemization being greater in the first case. In the light of this and other data it is shown that the first order solvolytic reactions of alkyl halides in water, alcohol, and acetic acid are most probably of a polymolecular nature, involving several molecules of the solvent, and that the driving force derives largely from the energy of solvation of the halide ion.

(45) Hughes, Ingold, *et al.*, *J. Chem. Soc.*, 1196, 1201, 1208, 1236, 1243, 1252 (1937).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Polymolecular Solvolytic Reactions: Water Catalysis in the Alcoholysis of Benzhydryl Chloride[1]

BY NICHOLAS T. FARINACCI AND LOUIS P. HAMMETT

The first order reactions of solvolysis which alkyl halides undergo with solvents of the nature of water, alcohol or acetic acid[2] offer a reaction mechanism problem of the first importance. We have approached this by a method which starts from the observation of Norris and Morton[3] that the first order constant (independent of the acidity or alkalinity of the solution) for the formation of hydrogen chloride in a solution of benzhydryl chloride in ethyl alcohol is subject to a large increase upon the addition of water. As Fig. 1 shows, this increase is linear in the water concentration within the range of what may properly be called dilute solutions of water in alcohol. A

(1) Thesis submitted by Nicholas T. Farinacci in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) (a) Ward, *J. Chem. Soc.*, 445 (1927); (b) Ward, *ibid.*, 2285 (1927); (c) Hughes, Ingold and Shapiro, *ibid.*, 225 (1936); (d) Steigman and Hammett, THIS JOURNAL, **59**, 2536 (1937); (e) Nicolet and Stevens, *ibid.*, **50**, 135 (1928).

(3) Norris and Morton, *ibid.*, **50**, 1795 (1928).

similar effect of water has been observed in the likewise first order solvolysis of α-phenylethyl chloride in acetic acid,[2d] and in the alcoholysis of propyl and isopropyl bromides and iodides[2e] and the phenomenon is probably general. Such a state of affairs might arise from the superimposition of an independent reaction with water upon that with alcohol, the former producing benzhydrol, the latter its ethyl ether. Alternatively the water might act as a catalyst, the major product of the reaction remaining benzhydryl ethyl ether.
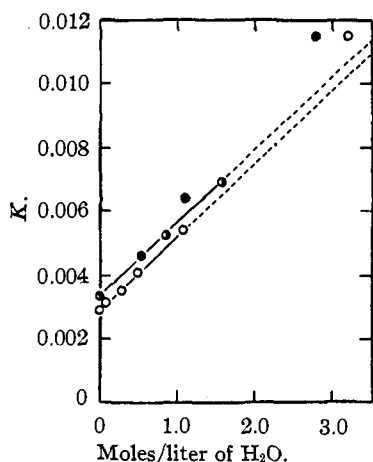
Fig. 1.—O, Norris and Morton; ●, Ward; ◑, Farinacci and Hammett.

We have solved this problem in favor of the catalysis by determining the composition of the reaction product. If there were two independent reactions we should have for the formation of the ether

$$dx_1/dt = k_1(a - x_1 - x_2) \qquad (1)$$

and for the formation of benzhydrol

$$dx_2/dt = k_2(a - x_1 - x_2)(c_w - x_2) \qquad (2)$$

where x_1 = moles/liter of benzhydryl ethyl ether formed
x_2 = moles/liter of benzhydrol formed, both at time t
a = initial moles/liter of benzhydryl chloride
c_w = initial moles/liter of water

From this

$$dx_1/dx_2 = \frac{k_1}{k_2(c_w - x_2)} \qquad (3)$$

$$x_1 = \frac{k_1}{k_2} \ln \frac{c_w}{c_w - x_2} \qquad (4)$$

and by expansion of the logarithm

$$\frac{x_1}{x_2} = \frac{k_1}{k_2 c_w}\left(1 + \frac{x_2}{2c_w} + \ldots\right) \qquad (5)$$

The constants k_1 and k_2 are known from rate measurements, the former being the rate constant in pure alcohol, while the total rate constant in the presence of water is given by $k_1 + k_2$.

The results of our experiments, summarized in Table I, show that the actual proportion of benz-

hydrol formed is only a small fraction of that predicted from equation (5). They show further that benzhydrol is not converted to the ethyl or to other products under the conditions of the experiments. Consequently the major effect of water at low concentrations is the catalytic one of increasing the rate of reaction with alcohol rather than the replacement of part of the reaction with alcohol by a reaction with water. This catalysis is of a most interesting type, being linear in the water concentration and of considerable magnitude at low concentrations.

TABLE I
COMPOSITION OF REACTION PRODUCT

Reaction mixture moles/l.		Rate constant	Mole % benzhydrol in product		
H_2O	Ph_2CHCl	$\times 10^5$	Found	Calcd.	eq. (5)
0.0	0.1000	343			0.0
.6004	.1090	474[a]	2.1	1.5	18.7
1.320	.1228	634[a]	11.9	11.7	52.8

[a] Interpolated.

Since several of the conceivable mechanisms for this type of reaction involve the formation of ionic intermediates[2c] or the appearance of an activated state in which there is a large separation of charges[4] the effect might be considered to be of the nature of a dielectric phenomenon. The sign of the effect is correct for this interpretation, further we find by interpolation from Graffunder and Heymann's[5] data on the dielectric constant of alcohol–water mixtures that our results lead to a value of -125 for the quantity d log k/d-$(1/D)$, which is an entirely reasonable one in terms of the treatment given by Stearn and Eyring[4] for such cases.

We have investigated, therefore, the effect of the addition of small amounts of other solvents upon the rate and found it completely inconsistent with this theory. Nitrobenzene which increases the dielectric constant of alcohol[5] lowers rather than raises the rate, and a general plot of log k against $1/D$ shows a picture of intersecting curves, one for each solvent added (Fig. 2).
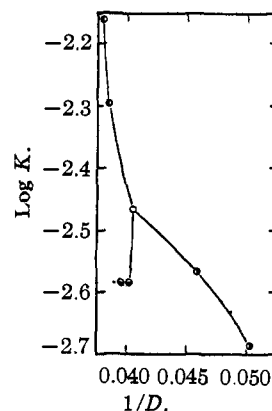

Fig. 2.—O, Pure alcohol; ◐, solutions of water; ◑, solutions of heptane; ◒, solutions of nitrobenzene.

(4) Stearn and Eyring, J. Chem. Phys., 5, 112 (1937).
(5) Graffunder and Heymann, Z. Physik, 72, 744 (1931).

Another most significant feature of the situation is the practically complete failure (see Table IV) of the halide to react with small concentrations of water or of alcohol when both are dissolved in the solvent acetone, whose dielectric constant is comparable with that of ethyl alcohol. These reactions do therefore deserve the name solvolytic in the sense that they are reactions with the solvent; they occur only when the halide is dissolved in a large excess of the hydroxylic substance with which it is to react, and they fade out when both reactants are dissolved in an inert solvent.

One could, of course, take refuge in the negation of a specific solvent effect, although the magnitude of the effect is surprisingly large considering the small variations in solvent composition. On the other hand, the results of the present research together with those obtained by Steigman and Hammett[2d] suggest most emphatically the hypothesis of a polymolecular course of the reaction. This implies a 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. Substitution of a water molecule for one of the alcohol molecules in this complex increases the rate, presumably because of a greater affinity of halide ion for water than for alcohol. So long as the process depends upon this one for one substitution the rate increase is linear; at higher water concentrations double or triple substitutions may be expected to occur, and the rate should and indeed does increase more rapidly. Meanwhile an alcohol molecule reacts with the carbon end of the carbon-halogen link, either simultaneously and with inversion of configuration,[6] or subsequently to the separation into a carbonium and a halide ion. There is a much smaller tendency for a water molecule to play the part of this alcohol molecule, consequently the proportion of benzhydrol remains small. Since the rate is given by

$$dx/dt = k[RCl][S]^n \qquad (7)$$

where S is the hydroxylic solvent, and n is greater than unity, transfer to an inert solvent decreases the rate more than in proportion to the decrease in the concentration of alcohol or water.

The present investigation has also demonstrated that the rate constant for the solvolytic reaction in alcohol is independent of the initial

concentration of alkyl halide; also that hydrogen chloride has an accelerating effect of a magnitude comparable to that produced by water. The latter fact has a probable bearing on the kinetic anomalies noted by Branch and Nixon[7] in the reaction of triphenylmethyl chloride in alcohol–ether mixtures. It has also shown that the reaction

$$(C_6H_5)_2CHOH + HCl \longrightarrow (C_6H_5)_2CHCl + H_2O \qquad (8)$$
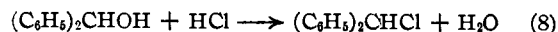
proceeds at a significant rate in acetone medium. Since the reverse reaction has a negligible rate under these conditions the reaction runs nearly to completion.

Experimental

Materials.—Solvents were dried and in some cases chemically purified, then distilled retaining a middle fraction. *Ethanol*, dried over calcium oxide, b. p. 78.3–78.4°, d^{25}_4 0.78506. *Acetone*, refluxed over potassium permanganate and calcium oxide for four hours, b. p. 56–56.5°. *Nitrobenzene*, dried over phosphorus pentoxide, b. p. 82–82.5° at 6 mm., color, pale yellow. *Heptane*, dried over sodium carbonate, b. p. 97.3–97.4°.

Benzhydrol was prepared from benzophenone[8] or the commercially available material was recrystallized from cold alcohol, m. p. 68°. *Benzhydryl ethyl ether.*—(a)[9] Fifty grams of benzhydrol, 100 cc. of ethyl alcohol and 15 cc. of concd. sulfuric acid were allowed to stand three days at room temperature. The solution was diluted with water, neutralized, extracted with benzene, and the ether was finally fractionally distilled. (b) Ten grams of benzhydrol and 3 cc. of concd. hydrochloric acid in 50 cc. of ethyl alcohol were refluxed for two hours and the product was worked up as in (a): b. p. 288° at 760 mm., 139.5–140° at 5 mm.; analysis by ethoxyl determination 99.3–99.5%; $n^{25}_{5876-He}$ 1.5676. *Benzhydryl chloride.*[2b,3,10]—Dry hydrogen chloride was passed into a solution of 75 g. of benzhydrol in 300 cc. of a 50–50 mixture of benzene and petroleum ether in the presence of anhydrous calcium chloride. After three hours the solvent was distilled off, and the residue fractionated: b. p. 146.5–147° at 6 mm.; analysis by Volhard method, 100.0%. *Symmetrical benzhydryl ether.*—Fourteen grams of benzhydrol was boiled with 150 cc. of 5 N hydrochloric acid, and the product was fractionally crystallized from cold alcohol to separate the product from unchanged benzhydrol,[2b] m. p. 110°. Distillations were made in all-glass apparatus using Vigreux or bulb stillheads, and purified materials were kept in glass stoppered bottles in desiccators over phosphorus pentoxide or calcium chloride.

Rate Measurements in Alcohol.—These were made at 25.00°. The rate of alcoholysis of benzhydryl chloride was followed by Norris and Morton[3] by a conductimetric method, which involves assumptions about the effect of

(6) This picture is closely related to the one suggested by Ogg and Polanyi, *Trans. Faraday Soc.*, **31**, 604 (1935).

(7) Branch and Nixon, THIS JOURNAL, **58**, 492 (1936).

(8) "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. VIII, 1928, p. 24.

(9) (a) Linnemann, *Ann.*, **133**, 17 (1865); (b) v. Kostanecki and Lampe, *Ber.*, **39**, 4019 (1906).

(10) (a) Böeseken, *Rec. trav. chim.*, **22**, 313 (1903); (b) Montagne, *ibid.*, **25**, 405 (1906).

various substances upon the conductivity, and by Ward[2b] and by Kny-Jones and Ward[11] by a direct titrimetric method. Appreciable differences exist between the results of the two methods, but there is every reason to believe that Ward's results, with which some measurements of our own are also in agreement, are correct. On the other hand, the relative accuracy of the Norris and Morton results should be amply sufficient to support the conclusion that the effect of water upon the rate is linear (see Fig. 1).

In our work 10-cc. samples of reaction mixture were run into ice-cold absolute alcohol, and titrated with sodium ethylate solution in absolute alcohol with phenolphthalein indicator. The total time from sampling to completed titration was two to three minutes. An appreciable indicator blank was required in those experiments in which nitrobenzene, acetone, or heptane was present. It is to be remembered that the solvolytic reaction is slowest in the absence of water, and that there is no difficulty due to local excess of titrating reagent since alkalies do not accelerate the reaction.[2b]

In agreement with Ward we find the reaction to follow first order kinetics with precision. Typical data are shown in Table II. This refers to the reaction of 0.09798 molar benzhydryl chloride in pure alcohol, the titer being given in cc. of 0.0484 M sodium ethylate. The last measurement represents 97.2% of complete reaction. Experiments in solutions containing hydrogen chloride show a downward drift in the constant of the order of 3 to 5%.

TABLE II
TYPICAL KINETIC DATA IN ALCOHOL, AT 25°

Time, min.	Titer	k
8	0.55	0.003440
18	1.23	.003480
33	2.17	.003437
48	3.07	.003445
64	3.97	.003411
92	5.47	.003424
268	12.11	.003402
1466	19.68	....
		Average 0.003434

Table III contains the results of measurements in alcoholic medium with various additions. As Fig. 1 shows those obtained in absolute alcohol and in the presence of small amounts of water are in satisfactory agreement with

TABLE III
RATE OF SOLVOLYSIS IN ALCOHOL AT 25°

Ph₂CHCl	Other solutes	$k \times 10^3$
0.0980	None	3.43
.0635	H₂O 0.860	5.22
.1041	H₂O 1.579	6.91
.0756	C₇H₁₆ 0.525	2.72
.0906	C₇H₁₆ 1.063	2.06
.1006	C₆H₅NO₂ 0.333	2.62
.1107	C₆H₅NO₂ 0.793	2.62
.2247	None	3.43
.4343	None	3.50
.0929	HCl 0.428	4.06
.0899	HCl 0.225	4.11

(Column headers row: Moles/liter over Ph₂CHCl / Other solutes)

those of Ward. The constants k are first order constants for time in minutes.

Data on dielectric constants of mixtures of alcohol with other solvents used in the preparation of Fig. 2 were taken from the papers of Graffunder and Heymann[5] and of Smyth and Stoops.[12]

Rate Measurements in Acetone Medium.—These were made similarly by dilution of the sample of reaction mixture with ice-cold absolute alcohol and titration. The results for the solvolysis are found in Table IV. Table V shows data for the reverse reaction, which clearly proceeds largely toward completion, with second order constants k decreasing with time.

TABLE IV
SOLVOLYSIS IN ACETONE SOLUTION AT 25°

Ph₂CHCl	C₂H₅OH	H₂O	Time, hrs.	% reaction	k
0.073	0.0	0.130	71.3	0	
.073	.068	.130	168	0	
.0858	.411	.50	240	0	
.0971	.0	.50	240	0	
.0858	1.091	.50	286	6.94	ca. 4 × 10⁻⁶
.0917	0.0	1.5	277	3.35	ca. 2 × 10⁻⁶

(Column group header: Moles/l. over Ph₂CHCl, C₂H₅OH, H₂O)

TABLE V
THE REVERSE REACTION IN ACETONE

Ph₂CHOH, 0.1088 m; HCl, 0.1018 m; H₂O, 0.38 m. Titer in cc. of 0.048 n sodium ethylate. Second order constants with t in hrs.

Time, hrs.	Titer	% reaction	k
0	21.02	0	
20.0	14.32	32.0	0.1143
70.3	9.77	53.5	.1454
97.3	8.43	60.0	.1354
192.5	5.85	72.0	.1117
311.8	4.62	78.0	.1047
412.3	4.05	80.73	.0830
480.6	3.80	82.0	.0766

Analysis of the Reaction Product.—This was accomplished in the main by determination of ethoxyl and of halogen. The ethoxyl determination was made by a refinement of the Zeisel method the details of which will be published elsewhere. Its precision is demonstrated by the results of the analysis of known materials: a sample of methyl phenylacetate (purified by R. L. Betts and found by him to have a purity of 99.8% by saponification) analyzed 99.8% by this method; a sample of vanillin analyzed 99.9%; our purified benzhydryl ethyl ether analyzed 99.3–99.5%. The average reproducibility was 0.3%.

For halogen determinations the material was allowed to react with 0.1 N silver nitrate in 90% alcohol, the solution was diluted with three volumes of normal aqueous nitric acid, and filtered, and the excess silver was titrated by the Volhard method.

In order to determine the composition of the product resulting from the solvolysis of benzhydryl chloride the reaction was allowed to proceed to probable completion, the solvent was distilled off at room temperature at 5 mm. pressure, and the residue was kept over calcium chloride in

(11) Kny-Jones and Ward, THIS JOURNAL, 57, 2394 (1935).

(12) Smyth and Stoops, ibid., 51, 3312 (1929).

a desiccator for twenty-four hours. That this procedure does not seriously alter the composition of the reaction product is demonstrated by the data in Table VI, which show the result of allowing solutions of benzhydrol, benzhydryl ethyl ether and hydrogen chloride of approximately the composition of our final reaction mixtures to stand for the time given after which the solvent was removed and the residue analyzed. The only change is a small conversion of the ether to the chloride.

Table VI
Test of Recovery Method

Moles/l.		Taken, %	Mole %	Time,	Found, mole %		Total recovery.
HCl	H₂O	ether	hydrol	hrs.	ether	chloride	%
0.100	0.0	81.9	18.1	4	81.0	1.4	100.1
.073	.33	82.1	17.9	53	80.8	1.4	99.5
.073	.33	82.1	17.9	166	81.4	0.5	100.0

The Composition of the Reaction Product.—Table VII contains the results of duplicate determinations of the composition at two different water concentrations. These data were used in the preparation of Table I. In view of the bare possibility of an inductive effect of benzhydryl chloride on the conversion of hydrol to ether, we have also run experiments, the results of which appear in Table VIII, in which benzhydryl chloride was solvolyzed in the presence of the hydrol. The calculated composition of the reaction product is based upon the assumption that the same amount of hydrol is formed from the chloride in the presence of benzhydrol as in its absence. The agreement of this value with the one actually found is excellent.

Table VII
Composition of Reaction Product

Moles/l.		Time,	Found, mole %		Hydrol
H₂O	Ph₂CHCl	hrs.	ether	chloride	(by dif.)
0.600	0.1090	53.5	97.2	0.7	2.1
.600	.1090	142.3	98.5	ca 0	1.5
1.320	.1228	50.0	87.8	0.3	11.9
1.320	.1228	142.5	88.3	ca 0	11.7

Table VIII
Effect of Benzhydrol

Moles/l.			Time,	Found, mole %		Calcd., mole %
H₂O	Ph₂CHCl	Ph₂CHOH	hrs.	ether	chloride	ether
1.345	0.0993	0.0516	52.0	59.4	2.3	59.4
1.345	.0993	.0516	150.8	59.5	2.4	59.4

A small proportion of some undetermined material of high index of refraction is, however, produced in the solvolysis. Our reaction products always had an index higher by about 0.25% than did synthetic mixtures of composition corresponding to the analysis (the refractive index–composition curve for hydrol–ether mixtures at 25° is linear). The material of high index is neither the symmetrical dibenzhydryl ether, benzophenone, nor benzhydryl chloride, all of which lower the index. In the effort to determine what it might be we have subjected 90.45 g. of chloride to solvolysis in 5 liters of alcohol containing 1.32 m water, and have determined benzhydrol directly by an acetylation method as well as benzhydryl ethyl ether and benzhydryl chloride. The acetylation method was carried out as follows: a sample containing approximately 0.2 g. of benzhydrol was refluxed with 20 cc. of redistilled acetic anhydride for four hours. The anhydride and acetic acid were removed by distillation at room temperature under 5 mm. pressure. The residue was refluxed with standard alcoholic sodium ethoxide for three hours and the excess titrated with hydrochloric acid with phenol red indicator. We have obtained the following results on pure benzhydrol and mixtures with its ethyl ether by this method: taken 0.200 g. benzhydrol, found 0.198; taken 0.202 g. benzhydrol, 0.685 g. benzhydryl ethyl ether, found 0.204 g. benzhydrol.

The product of our large scale reaction was found to contain 10.1% benzhydrol, 89.1% benzhydryl ethyl ether, and 0.1% benzhydryl chloride. Since these add to 99.3% the proportion of the highly refractive material is too small for profitable investigation.

Summary

We have determined the composition of the product resulting from the first order solvolysis of benzhydryl chloride in ethyl alcohol containing small amounts of water, and found the proportion of benzhydrol to be many times smaller than would be the case were a reaction of the chloride with water to form the hydrol simply superimposed upon the reaction with alcohol to form benzhydryl ethyl ether. The linear increase in rate produced by water is therefore chiefly catalytic. A study of the effect of small amounts of water, heptane and nitrobenzene upon the rate of solvolysis shows that it is not a function of the dielectric constant of the medium. The rate of reaction is reduced nearly to zero when both benzhydryl chloride and water or alcohol are present as solutes in a dilute solution in acetone. These results strongly support the hypothesis that the solvolytic reactions are polymolecular.