[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rate and Mechanism in the Reactions of Benzyl Chloride with Water, Hydroxyl Ion and Acetate Ion[1]

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Because of the importance of solvolytic and displacement reactions and because of the relative scarcity of precision measurements on their rates, we have studied in detail some typical reactions of benzyl chloride.[2] The reactions investigated were the solvolysis[3]

$$C_6H_5CH_2Cl + H_2O \longrightarrow C_6H_5CH_2OH + HCl \qquad (A)$$

and the displacements by hydroxyl (B) and acetate (C) ions

$$C_6H_5CH_2Cl + OH^- \longrightarrow C_6H_5CH_2OH + Cl^- \qquad (B)$$

$$C_6H_5CH_2Cl + C_2H_3O_2^- \longrightarrow C_6H_5CH_2OOCCH_3 + Cl^- \qquad (C)$$

in a dioxane–water mixture, 60.72% dioxane by weight. The presence of dioxane served to make the reacting systems homogeneous without introducing additional reaction possibilities. All measurements were made at 50°.

Experimental

Apparatus.—Only calibrated weights and volumetric apparatus were used. The temperature of 50.000 ± 0.005° was fixed by a thermometer calibrated by the Bureau of Standards.

Materials.—Benzyl chloride (Mallinckrodt Analytical Reagent) was distilled *in vacuo*, the middle third being retained (b. p. 51–52° at approximately 4 mm.). It was kept in a glass-stoppered bottle in a desiccator containing phosphorus pentoxide. Benzyl chloride from three different containers gave identical rates of reaction after this treatment. Benzyl alcohol (Eastman Kodak Co. chlorine-free) was likewise fractionated *in vacuo*, the first and final thirds being rejected (b. p. 81.5–82.5° at approximately 4 mm.). Benzyl acetate (Eastman) was given the same treatment (b. p. 66–68° at approximately 4 mm.).

1,4-Dioxane (Carbide and Carbon Chem. Co.) was refined in 3–4 liter batches by a modification of the method of Kraus and Vingee.[4] Each batch was kept on a steam-bath in contact with solid sodium hydroxide until fresh additions of the latter caused no further resin formation. After filtration through paper it was refluxed over metallic sodium in an all-glass apparatus closed with a drying tube until no further discoloration of the surface of the sodium was apparent over a period of several hours. It was then distilled at atmospheric pressure, the first and final quarters being discarded. To each 1000 g. of this hygroscopic product, 327.4 g. of carbon dioxide-free distilled water was immediately added. Whatever reaction occurs between dioxane and oxygen[5] did not interfere in our experiments as evidenced by the agreement between results obtained in fresh samples of solvent and samples which had stood at 50° for eight days prior to use.

Primary standards for titration were Bureau of Standards acid potassium phthalate and A.C.S. grade sodium chloride which was reprecipitated, fused in a platinum crucible, pulverized in an agate mortar, and stored over phosphorus pentoxide. Within experimental error, this was found (by H. R. McCleary) to be 100.0% pure in an analysis with reprecipitated mercuric oxide standard. This sodium chloride was added directly in those runs made in presence of this salt. Sodium perchlorate solutions were prepared from A.C.S. 60% perchloric acid, 99.0%–99.5% neutralized with A.C.S. sodium hydroxide which was free of carbonate.[6] The sodium hydroxide solution was weighed into a known amount of C. P. acetic acid in preparing acetic acid–acetate buffers.

Standard solutions of mercuric nitrate, silver nitrate, potassium thiocyanate, hydrochloric acid and sodium hydroxide (carbonate-free) were all prepared from reagent grade stock. The C. P. nitrobenzene used in the Volhard titration was found by long standing with alcoholic silver nitrate to be free of chlorides.

Method.—The dioxane–water mixture described in the preceding section was of such composition that 100.00 cc. of it when added to 25.00 cc. of water, both at 25°, produced a mixture containing 60.72% dioxane by weight. The general procedure in starting experiments was to pipet water and the dioxane–water mixture together in a reaction bottle. In the case of reaction mixtures containing sodium acetate, hydroxide, or perchlorate, or perchloric or hydrochloric acids, these solutes were present in the above-mentioned 25.00 cc. When the mixture had reached temperature equilibrium in the thermostat, benzyl chloride was weighed in and the mixture thoroughly shaken. In the case that benzyl alcohol or sodium chloride was present, it was also added at this point. A comparatively rapid hydrolysis reaction on the first addition of benzyl chloride (occurring presumably at the interface) rendered the initial time reading invalid in the case of the water reaction. Accordingly in measurements in that reaction, no initial time reading was taken, benzyl chloride being added to the medium at room temperature and the sample mixed before setting in the thermostat.

At convenient intervals 10-cc. samples were withdrawn for analysis. The dried pipet, initially at room temperature, delivered highly reproducible weights of any given mixture if the filling was completed within a few seconds.

The water reaction was arrested by pipeting the samples into a water–dioxane mixture at room temperature. The

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[1] Dissertation submitted by George William Beste in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] Gomberg and Buchler, THIS JOURNAL, **42**, 2059 (1920).

[3] The nomenclature is consistent with that employed by Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[4] Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934).

[5] Hess and Frahm, *Ber.*, **71B**, 2627 (1938).

[6] Sörensen, *Biochem. Z.*, **21**, 168 (1909).

dioxane serves the dual purpose of reducing the extent of further reaction to a negligible level and of preventing the unreacted benzyl chloride from forming a separate phase with consequent interference with the end-point in the titration. A calculated excess of nitric acid was added and the sample titrated with 0.025 *N* mercuric nitrate using diphenyl carbazide indicator.[7] The procedure for analysis of samples from the reaction with hydroxyl ion differed from that just outlined only in this, that sufficient nitric acid was present in the dioxane–water mixture used to arrest the reaction so that at no time was that resulting mixture basic. An independent study has shown that the probable error in any one of these end-points is scarcely more than 0.02 cc. of 0.025 *N* mercuric nitrate. The progress of either of these reactions can be measured equally well by titrating the acid produced. In five experiments it was found that identical results within the precision noted are obtained from analyses for either product. This was equally true when perchlorate was present.

The mercuric nitrate titration cannot be used in the presence of acetates. Therefore, samples containing acetate were pipetted into a glass-stoppered bottle containing ice-cold, carbon dioxide-free water. After titration to a phenolphthalein end-point with 0.025 *N* sodium hydroxide, the sample was promptly acidified with nitric acid. A measured excess of silver nitrate was added together with a few cc. of nitrobenzene,[8] and the bottle stoppered and shaken vigorously. It was found that by using somewhat more nitrobenzene than recommended by Caldwell and Moyer in their modification of the Volhard method there was no measurable further reaction of benzyl chloride despite the menacing presence of excess silver nitrate and silver chloride.[9] Presumably the nitrobenzene not only isolated the silver chloride from contact with the solution but extracted at least some of the remaining benzyl chloride as well. This eliminates the necessity of an ether extraction of benzyl chloride prior to the addition of silver nitrate as practiced in this titration by Olivier.[10]

Twelve samples were analyzed in each run in the solvolytic reaction. These were drawn over a period of from five to fourteen days, the final reading being at a time equivalent to 40–80% reaction. From each run with hydroxyl ion, from 8–10 samples were analyzed over a period of from nine to forty-five hours representing from 40–90% reaction for the reactant present at lower concentration. Eleven samples from the runs with acetate ion were analyzed over a period of fifty to fifty-five hours during which the reactant present at lower concentration was from 45–70% consumed.

Rate Calculation.—In this section the following abbreviations will be used: a is initial concentration of benzyl chloride, b initial concentration of sodium hydroxide, c initial concentration of sodium acetate, x concentration of chloride ion at time t, t time in seconds. The benzyl group will be written Bz and the acetate group Ac.

Data for the solvolytic reaction (A) was found to fit the first-order equation $\ln a/(a - x) = kt$. While the slope of the rate curve proved sensitive to variations in initial concentrations of benzyl chloride as well as to additions of benzyl alcohol, water and various electrolytes, it was, in most cases, constant in any one experiment. In occasional runs a serious drift upward was observed in the plot. This was, however, never reproducible and was accordingly assigned to inadvertent loss of dioxane at some point early in the run. It follows from the available vapor pressure data[11] at 50° that this solvent mixture tends to become more concentrated in the water component.

When hydroxyl ion is added to the previous mixtures a second-order displacement of chloride ion by hydroxyl ion is superimposed on reaction (A). On the assumption that reaction (B) is second-order, the rate of decomposition of benzyl chloride is given by

$$\frac{-\mathrm{d}[\mathrm{BzCl}]}{\mathrm{d}t} = k_1[\mathrm{BzCl}] + k_2[\mathrm{BzCl}]\,[\mathrm{OH}^-] \qquad (1)$$

While this equation may be readily integrated, the result is too complicated to be useful. Therefore, a less elegant approach was substituted.[12] Equation (1) may also be written

$$\frac{-\mathrm{d}[\mathrm{BzCl}]}{\mathrm{d}t} = k[\mathrm{BzCl}]\,[\mathrm{OH}^-] \qquad (2)$$

where

$$k = k_2 + k_1/[\mathrm{OH}^-] \qquad (3)$$

The quantity k so defined is a function of time but its value at any time may be obtained by reading the slope of a plot of $\frac{2.303}{a - b} \log \frac{(a - x)}{(b - x)}$ against time. (It is apparent that since the acid formed by reaction (A) neutralizes hydroxide present in these systems, x will measure the decreases in concentration of both benzyl chloride and hydroxide.) It is necessary, then, only to substitute the value of k in equation (3) in order to evaluate k_2. Some uncertainty exists concerning the value of k_1 to be used. Those independently measured were of necessity obtained in absence of hydroxides. Yet perchlorates accelerate reaction (A) and chlorides slow it down, which suggests that the reaction is quite sensitive to foreign ions. The rate constant k_2 was therefore evaluated both on the assumption that hydroxyl ion exerts a salt effect quantitatively the same as perchlorate, and on the assumption that k_1 is not changed by the addition of

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[7] Roberts, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 365 (1936).

[8] Caldwell and Moyer, *ibid.*, **7**, 38 (1935).

[9] (a) Burke and Donnan, *J. Chem. Soc.*, **85**, 555 (1904); (b) Senter, *ibid.*, **97**, 346 (1910).

[10] Olivier, *Rec. trav. chim.*, **49**, 697 (1930).

[11] Makovetzkiĭ, *C. A.*, **3**, 1009 (1909).

[12] Eagle and Warner, THIS JOURNAL, **61**, 488 (1939).

hydroxides. Because of the possibility of specific salt effects some third value may be more accurate than either of these. Calculated on either assumption k_2 drifts upward. That the drift is real and does not arise from the method of calculating was confirmed by a number of experiments of the following sort. The initial rate in a run containing 0.04 M benzyl chloride, 0.08 M sodium hydroxide, 0.04 M benzyl alcohol, and 0.04 M sodium chloride was found to be in fair agreement with the rate at the half-time of benzyl chloride in a run starting with 0.08 M benzyl chloride and 0.12 M sodium hydroxide.

When the displacement of chloride ion by acetate ion (C) takes place in an acid buffer, the extent of chloride ion formation measures the progress of reaction (A) plus that of reaction (C). The constants in the complete rate equation

$$-\mathrm{d}[\mathrm{BzCl}]/\mathrm{d}t = k_1[\mathrm{BzCl}] + k_3[\mathrm{BzCl}]\,[\mathrm{Ac}^-] \quad (4)$$

were obtained in the same way as in the case of the hydroxyl ion reaction, namely, by the equation

$$\frac{-\mathrm{d}[\mathrm{BzCl}]}{\mathrm{d}t} = k''[\mathrm{BzCl}]\,[\mathrm{Ac}^-] \quad (5)$$

where

$$k'' = k_3 + k_1/[\mathrm{Ac}^-] \quad (6)$$

However, since the constants k_1 and k_3 differ by only one order of magnitude, a plot of $\frac{2.203}{a - c}\log\frac{(a - x)}{(c - x)}$ against time possesses considerable curvature at all points, with the result that an evaluation of k_3 is correspondingly less exact. It is noted that the change in chloride ion concentration is equal and opposite to the change in acetate ion concentration since the acid formed by reaction (A) removes a corresponding amount of acetate ion and the acetic acid formed thereby introduces no complication.

Since the product is different in reactions (A) and (C) it was possible to make an independent evaluation of k_1 for use in equation (6) by the formula

$$\mathrm{d}[\mathrm{HAc}]/\mathrm{d}t = k_1[\mathrm{BzCl}] + k_4[\mathrm{BzAc}] \quad (7)$$

The solvolysis rate, k_4, of benzyl acetate was measured independently. The concentration of benzyl acetate is known at any time as the difference $[\mathrm{Cl}^-] - \Delta[\mathrm{HAc}]$, where $\Delta[\mathrm{HAc}]$ denotes the difference between the concentration of acetic acid at a given time and the concentration of necessity initially present in the buffer. Consequently the value of k_1 might be evaluated from the slope of a plot of [HAc] against t. Because of the curvature, graphical determination of the slope is difficult for this plot and we have sought for a function which would be more nearly linear. It happens that the quantity $\Delta[\mathrm{HAc}]/[\mathrm{Cl}^-]$ is nearly linear in the early part of the reaction and we have defined a quantity Z independent of time which is equal to the estimated initial value of the quantity $\Delta[\mathrm{HAc}]/[\mathrm{Cl}^-]$. Regardless of the meaning of Z it follows from its constancy that

$$\frac{\mathrm{d}\ln(Z - \Delta[\mathrm{HAc}])}{\mathrm{d}t} = \frac{1}{Z - \Delta[\mathrm{HAc}]}\cdot\frac{\mathrm{d}(Z - \Delta[\mathrm{HAc}])}{\mathrm{d}t} \quad (8)$$

and

$$\frac{\mathrm{d}(Z - \Delta[\mathrm{HAc}])}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{HAc}]}{\mathrm{d}t} \quad (9)$$

By combining these expressions we obtain

$$\frac{\mathrm{d}\ln(Z - \Delta[\mathrm{HAc}])}{\mathrm{d}t} = -\frac{k_1[\mathrm{BzCl}] + k_4[\mathrm{BzAc}]}{Z - \Delta[\mathrm{HAc}]} \quad (10)$$

A plot of $\ln(Z - \Delta[\mathrm{HAc}])$ against t is nearly linear and its slope S can be determined with satisfactory precision. The rate constant, k_1, may then be computed from S and other known quantities by the expression

$$k_1 = -\left(S + k_4\frac{[\mathrm{BzAc}]}{Z - \Delta[\mathrm{HAc}]}\right)\left(\frac{Z - \Delta[\mathrm{HAc}]}{[\mathrm{BzCl}]}\right) \quad (11)$$

k_1 is sensitive to the changing medium; the values obtained drift upward. In using equation (6) it was, therefore, necessary to substitute a different value of k_1 for every value of k''.

The evaluation of k_3 requires the use of the solvolysis rate of benzyl acetate in 60.72% dioxane at 50°. This was measured in three different buffers covering the range of buffer composition employed in the experiments with benzyl chloride and sodium acetate. These reactions were followed by titration with standard sodium hydroxide solution. Due to the low reaction rate and the relatively short period over which the reaction was followed, the results exhibit no significant dependence on buffer composition within the narrow range studied. The specific rate was found to be $3.74 \pm 0.15 \times 10^{-8}$.

Error.—The probable error in the values of k_1 tabulated in Table IV, as estimated by least squares methods, varies from 0.8% at low concentrations of benzyl chloride to 0.1% at high concentrations, with a mean value of 0.35%. The estimation of k_2 (Table VI) involves the determination of the initial slope of a plot of the quantity $\frac{2.303}{a - b}\log\frac{a - x}{b - x}$ against time. A careful estimate of the probable error incurred is 1.1%, except where much sodium chloride was added, when it mounts to 1.7% because of the increased relative error in the determination of the extent of reaction. The estimation of k_1 in the presence of acetate ion (Table V) depends upon a similar graphical differentiation, whose probable error we estimate at 2% except in the last three runs tabulated in which for some unknown reason it rises to 8%. A similar analysis of the estimation of the value of k_3 from the same experiments leads to a probable error of 1.3% in most of the runs and of 3.5% in the last three tabulated.

Sample Data.—Because of the indirect method of obtaining the constants k_1 (in presence of acetate), k_2, and k_3, a skeleton record for experiments on each is given.

TABLE I

TYPICAL EXPERIMENTAL RECORD FOR k_2

Expt. 203: initial concn. BzCl = 0.08424; initial concn. NaOH = 0.04401; k_1 as read from Fig. 1 is 1.177×10^{-6}

t, sec.	Chloride titer[a]	$[Cl^-]$	k	$k - \frac{k_1}{b - x} = k_2$
0	0	0	0.0002338	0.0002071
4860	1.63	0.00398	.0002356	.0002062
7980	2.54	.00621	.0002381	.0002070
11520	3.53	.00863	.0002404	.0002072
15000	4.39	.01073	.0002422	.0002069
19440	5.43	.01323	.0002458	.0002075
22560	6.09	.01489	.0002486	.0002084
25800	6.73	.01645	.0002509	.0002082
28860	7.30	.01785	.0002554	.0002105

[a] In cc. of 0.02454 N $Hg(NO_3)_2$ per 10.04 cc.

Results

The results on the solvolytic reaction are presented in Table IV. Data from this table for experiments containing initially only benzyl chloride and solvent are plotted in Fig. 1. These specific rates do not change appreciably in any run up to at least 80% conversion of benzyl chloride.

In Table V appear the solvolysis constants determined in presence of sodium acetate. While it cannot be stated with certainty it is probable that these values, at least in some cases, drift up from the values listed as the reaction proceeds. Since the medium is being changed independently and simultaneously by the displacement reaction of acetate ion, a drift in these constants does not contradict the absence of a drift mentioned in the preceding paragraph. Since the acetate displacement constants were determined in the same experiments, values of k_3 are entered here also.

The constants for displacement by hydroxyl ion appear in Table VI, each calculated on each of the two assumptions previously described. These values exhibit a consistent upward drift with time. This drift is usually greatest for the constants which are initially lowest, corresponding to higher initial concentrations of either reactant.

TABLE II

TYPICAL EXPERIMENTAL RECORD FOR k_3 AND k_1 IN PRESENCE OF ACETATE

Expt. 318: Initial concn. BzCl = 0.10470; initial concn. NaAc = 0.20026

t, sec.	$[Cl^-]$	$\Delta[HAc]$	$S \times 10^5$	$k_1 \times 10^6$	$k'' \times 10^4$	$k_3 \times 10^4$
0	0	0	0.4176	0.918	0.2149	0.1691
4140	0.00175	0.00038	.4174	.918	.2149	.1687
10800	.00444	.00100	.4200	.924	.2156	.1685
16980	.00693	.00161	.4222	.927	.2156	.1677
22680	.00938	.00210	.4230	.931	.2162	.1675
31560	.01297	.00284	.4257	.941	.2184	.1682
37560	.01496	.00336	.4261	.938	.2209	.1703
78120	.02842	.00661	.4327	.942	.2251	.1703
94560	.03336	.00766	.4370	.954	.2273	.1702
119280	.03964	.00923	.4438	.958	.2309	.1713

TABLE III

TYPICAL EXPERIMENTAL RECORD FOR k_1 IN PRESENCE OF PERCHLORATE

Expt. 87: initial concn. BzCl = 0.10583; concn. $NaClO_4$ = 0.244. The least squares constants are: $1.370 \pm 0.005 \times 10^{-6}$ from the acid titer, $1.365 \pm 0.009 \times 10^{-6}$ from the chloride titer.

t, sec.[a]	[acid]	$[Cl^-]$	t, sec.	[acid]	$[Cl^-]$
40260	0.00682		383580	0.04365	
74520		0.01103	423600		0.04641
123540	.01730		468480	.05062	
150060		.02051	509520		.05334
217680	.02822		555900	.05710	
312540		.03695	592200		.05936

[a] As explained previously the zero time point is arbitrary.

Discussion

Salt and Medium Effects.—From a purely empirical point of view none of these reactions are of simple integral orders. Thus the specific rate

$$k_1 = -\frac{1}{[BzCl]}\frac{d[BzCl]}{dt}$$

of the solvolytic reaction (A) decreases with increasing concentration of benzyl chloride in the

TABLE IV

SPECIFIC RATE OF THE SOLVOLYSIS k_1 IN 60.72% DIOXANE AT 50°, TIME IN SECONDS

Initial concn. BzCl	Added substances, concn. in mole/l.		$k_1 \times 10^6$
0.01996			1.311
.02576			1.304
.03127			1.262
.04104			1.248
.05039			1.230
.05912	BzOH	0.05471	1.195
.05961	BzOH	.08170	1.183
.06114			1.217
.06646	$NaClO_4$	.0491	1.301
.07058	(solv. aged 1 wk.)		1.205
.07276	H_2O	.3386	1.251
.07413	H_2O	.6943	1.289
.07466	HCl	.04909	1.157
.07509	HCl	.04882	
	BzOH	.05109	1.108
.07531	$NaClO_4$	.0490	1.280
.07561			1.191
.07580	$HClO_4$	.0490	1.283
.07628	NaCl	.04888	1.138
.08709			1.168
.09306	BzOH	.02745	1.149
.09770			1.163
.09839			1.149
.10587	$NaClO_4$	.244	1.366
.11209			1.138
.11745	(solv. aged 1 wk.)		1.137
.12086	$NaClO_4$	.0487	1.200
.12091	$NaClO_4$	.0488	1.193
.12144			1.125
.12203	HCl	.04854	
	BzOH	.04888	1.077
.12241	$HClO_4$	.0487	1.212
.12464	HCl	.04879	1.090
.12516	NaCl	.04860	1.076
.13926			1.120
.14663			1.107
.15782			1.079
.16498			1.076
.17388			1.064
.18747			1.045
.20119			1.039
.22082			1.015

TABLE V

SPECIFIC RATES OF SOLVOLYSIS k_1 AND OF DISPLACEMENT BY ACETATE ION k_3 IN 60.72% DIOXANE AT 50°, TIME IN SECONDS

Initial concn. HAc = 0.01 *M;* exceptions noted

Initial concn. BzCl	Initial concn. NaAc	Added solutes, concn. in mole/l.		$k_1 \times 10^6$	$k_3 \times 10^5$
0.1032	0.1502			0.95	1.90
.2102	.1482			.83	1.63
.1031	.1501	NaCl	0.0499	1.00	1.93
.2099	.0988	NaCl	.0494	0.83	1.64
.2107	.0989			.92	1.86
.1565	.0996			.97	2.06
.1047	.2003			.92	1.68
.1613	.1989			.85	1.55
0.2095	0.0992	$NaClO_4$	0.0494	0.96	1.66
.1025	.1496	$NaClO_4$	.0507	.97	1.82
.1061	.1986	H_2O	.428	.93	1.75
.1040	.1970	H_2O	.974	1.00	1.79
.1021	.2004	Initial HAc	.05	0.86	1.68
.1044	.2010	Initial HAc	.03	.94	1.72

TABLE VI

SPECIFIC RATE OF DISPLACEMENT BY HYDROXYL ION k_2 IN 60.72% DIOXANE AT 50°, TIME IN SECONDS

Initial concn. BzCl	Initial concn. NaOH	Added solutes, concn. in mole/l.		$k_2 \times 10^4$	$k_2^{*a} \times 10^4$
0.0800	0.1274			1.554	1.542
.0842	.0440			2.068	2.049
.1297	.0438			1.894	1.875
.0842	.0418	NaCl	0.0827	1.644	1.624
.0852	.0431	H_2O	.413	1.992	1.969
.0853	.0428	H_2O	.870	2.048	2.026
.0800	.1270	H_2O	.418	1.601	1.588
.0798	.1260	H_2O	.834	1.642	1.632
.1681	.0430			1.782	1.765
.0819	.0414	$NaClO_4$	.0857	1.644	1.636
.0457	.1285			1.570	1.562
.0869	.1273	BzOH	.0404	1.580	1.566
.0828	.0433	BzOH	.0400	2.028	2.008
.0412	.0831			1.804	1.792
.1228	.0822			1.665	1.650
.0848	.0485	BzOH	.0415		
		NaCl	.0418	1.682	1.672
.1215	.0821	NaCl	.0814	1.330	1.310
.1242	.0853	$NaClO_4$	.0851	1.350	1.336
.0422	.0827	BzOH	.0404		
		NaCl	.0416	1.668	1.657
.1231	.0822	NaCl	.0414	1.415	1.398
.1264	.0852	$NaClO_4$	.0425	1.416	1.400

[a] k_2^* is computed on the assumption that NaOH and $NaClO_4$ exert identical salt effects on k_1. k_2 is computed with a value of k_1 read from Fig. 1 modified only by the known effects of adding BzOH, NaCl, $NaClO_4$, and H_2O.

way shown in Fig. 1, the total change in specific rate between a benzyl chloride concentration of 0.02 *M* and one of 0.20 *M* being 20.0%. That the reaction simulates so closely a true first order

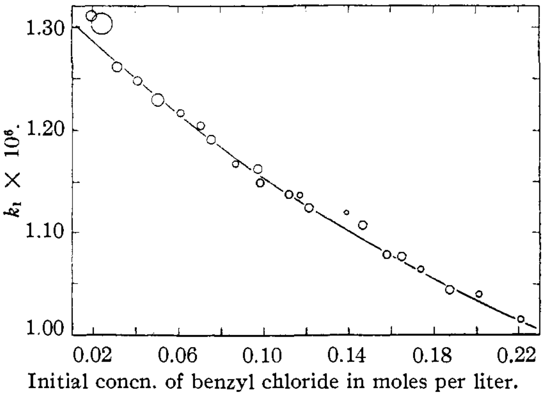

Fig. 1.

one is due to the retarding effect produced by both of the reaction products, benzyl alcohol and, to a greater extent, hydrochloric acid. As the reaction proceeds the increase in concentration of the reaction products therefore compensates for the decrease in concentration of benzyl chloride, which would otherwise increase the specific rate. Such a compensation has been observed in other studies of solvolytic reactions[13] for some of which the effect of solute concentration is opposite in sign to the one observed here.

The deviation from first order kinetics is, therefore, an effect of benzyl chloride upon specific rate which is comparable in magnitude to the effect of other solutes, or indeed to that of changing the proportions of dioxane and water in the solvent. Thus Table VII shows for a 0.075 M benzyl chloride solution the percentage changes in specific rate produced by the addition of the solutes named. Similar conclusions may be derived from Table IV for other concentrations of benzyl chloride. It will be noted that the effect of benzyl chloride is, however, at least three times as great as that of the other low polarity solutes, benzyl alcohol and dioxane.

TABLE VII

PERCENTAGE CHANGE IN SPECIFIC SOLVOLYSIS RATE OF 0.075 M BzCl CAUSED BY ADDITION OF INDICATED SOLUTES AT 0.05 M CONCENTRATION

Solute	% change in sp. rate	Solute	% change in sp. rate
BzCl	−5.9	NaCl	−4.3
BzOH	−1.7	NaAc	−8[a]
Dioxane	−0.6	$NaClO_4$	+7.6
HCl	−2.9	$HClO_4$	+8.0
HCl + BzOH	−7.0		

[a] Obtained by extrapolating data from Table V.

Similar but even larger effects are observed in the displacement reaction. Thus the specific rate

$$k_2 = -\frac{1}{[\mathrm{BzCl}]\,[\mathrm{OH}^-]}\,\frac{\mathrm{d}[\mathrm{BzCl}]}{\mathrm{d}t}$$

of the displacement by hydroxyl ion (B) decreases by 13.9% when the concentration of benzyl chloride is increased from 0.08 to 0.16 M, whereas the corresponding change for the solvolytic reaction is 9.1%. Further, the specific rate

$$k_3 = -\frac{1}{[\mathrm{BzCl}]\,[\mathrm{Ac}^-]}\,\frac{\mathrm{d}[\mathrm{BzCl}]}{\mathrm{d}t}$$

of the displacement by acetate ion (C) decreases by 12.8% when the benzyl chloride concentration increases from 0.1 to 0.2 the corresponding change for the solvolytic reaction being 10.3%. It follows that the deviation from proportionality between rate and concentration of benzyl chloride cannot be ascribed solely to a change in the activity coefficient of benzyl chloride.

Both displacement reactions exhibit a pronounced negative salt effect which has the same sign and approximately the same magnitude for chloride, perchlorate, hydroxyl and acetate ions as Table VIII shows. The addition of benzyl alcohol or an increase in the proportion of dioxane in the solvent also decreases the rate.

TABLE VIII

EFFECT OF ELECTROLYTES ON k_2 AND k_3

Electrolyte added at concn. of 0.08 N	% change in k_2	Electrolyte added at concn. of 0.05 N	% change in k_3
NaOH	−24.2	NaAc	−12.5
NaCl	−20.1	NaCl	−11.7
$NaClO_4$	−21.4	$NaClO_4$	−11.1

The salt effect in the displacement reactions and the effect of perchlorate, but not that of chloride, in the solvolytic reaction are in the direction to be expected on theoretical grounds. In the displacement reaction the transition state consists of a complex of benzyl chloride with hydroxyl or acetate ion in which approximately one-half of the negative charge resides on chlorine and the remainder on the displacing group,[14] whereas in the initial state this is concentrated on the hydroxyl or acetate ion. The tendency of this charge to become as widely distributed as possible is less the greater the density of charges in the surrounding medium, hence an increase in ionic strength decreases the rate. In the solvolysis the relatively non-polar benzyl chloride is converted to a partly ionized transition state, a process which should be favored by increasing charge density, and consequently by increasing ionic strength. The effects produced by changes in the medium other than by change in ionic strength do not seem to be amenable to theoretical treatment, in terms, for instance of the dielectric constant.

The Mechanism of the Solvolytic Reaction.—Both chlorides and acetates decrease the rate of the solvolytic reaction by considerable and comparable amounts (Table VII). The acetate case is particularly interesting. When benzyl chloride is reacting with acetate ion to form benzyl acetate, the rate of its simultaneous solvolysis to benzyl alcohol is decreased by as much as 20%. The

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(13) (a) Nixon and Branch, THIS JOURNAL, **58**, 492 (1936); (b) Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **A164**, 295 (1938).

(14) Evans and Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).

simplest interpretation is in terms of the ionic mechanism of the solvolytic reaction[15]

$$C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2^+ + Cl^-$$
$$C_6H_5CH_2^+ + H_2O \longrightarrow C_6H_5CH_2OH + H^+$$

The decrease in rate produced by the chloride and acetate ions is then attributed to an attack of these ions on the carbonium ion

$$C_6H_5CH_2^+ + Cl^- \longrightarrow C_6H_5CH_2Cl$$
$$C_6H_5CH_2^+ + CH_3COO^- \longrightarrow C_6H_5CH_2OOCCH_3$$

which either returns to the form of benzyl chloride or diverts to that of benzyl acetate some of the carbonium ion which would otherwise be converted to benzyl alcohol. The fact that the effects of chloride and acetate ions are so nearly the same is not a difficulty in view of the ample evidence that no parallelism exists between rate of reaction with carbon and the affinity for protons in the case of reactants so dissimilar in structure as are these ions.[16]

Because of the existence of two relatively improbable alternatives this mechanism cannot be taken to be unambiguously proven by the present data, but is merely given powerful support. The first alternative is that perchlorate reacts with benzyl chloride by a displacement reaction, and that the benzyl perchlorate is very rapidly hydrolyzed. Such a process would increase the total rate of formation of benzyl alcohol, and one might then conclude that chloride and acetate ions exert a salt effect, which, contrary to expectation, is negative, and which is masked in the case of perchlorate by the additional reaction. Certainly there is no measurable accumulation of benzyl perchlorate in the system, because the extent of reaction in the presence of perchlorate determined by acidimetric titration agrees exactly with that obtained by the titration of the chloride ion (Table III). The arguments against the hypothesis that benzyl perchlorate might be instantaneously hydrolyzed have been presented elsewhere.[17] The second alternative is that the salt effect in the solvolysis is a specific one, with perchlorate accelerating, while chloride and acetate retard, the reaction. This also is improbable.

Summary

The rates of the solvolytic or first-order reaction of benzyl chloride and of its second-order displacement reactions with hydroxyl and acetate ions have been measured in a 60.72% dioxane–39.28% water medium at 50°. The reactions exhibit pronounced salt and medium effects with relatively small changes in the nature of the medium, and the specific rates consequently vary with the initial concentrations of the reactants. Both chloride and acetate ions retard the solvolytic reaction, an effect which lends strong support to the hypothesis of an ionic intermediate in this reaction.

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[15] (a) Ward, *J. Chem. Soc.*, 445 (1927); (b) Gleave, Hughes, and Ingold, *ibid.*, 236 (1935); (c) Hughes and Ingold, *ibid.*, 244 (1935).

[16] Hammett, *op. cit.*, pp. 137, 302, 307.

[17] Roberts and Hammett, THIS JOURNAL, **59**, 1063 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Acidity Scale in Glacial Acetic Acid. I. Sulfuric Acid Solutions. $-6 < H_0 < 0$[1,2]

BY NORRIS F. HALL AND WILLARD F. SPENGEMAN[3]

The ready availability of acetic acid and its properties as a solvent medium make desirable a quantitative survey of the acidity of its solutions. The successful application of colorimetric methods by Hammett and his associates[4–7] to acidity measurements in mixed solvents and in formic acid suggested an extension to this solvent. It was also thought that such a study would provide a desirable re-interpretation of the earlier work of Conant, Hall, and their co-workers[8,9] carried out largely by potentiometric methods.

This paper presents a survey of the values of

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[1] Reported at the Kansas City meeting of the American Chemical Society, April, 1936.

[2] This work was supported in part by a grant from the Wisconn Alumni Research Foundation.

[3] Present address: care E. I. du Pont de Nemours & Co., 256 Vanderpool St., Newark, N. J.

[4] (a) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932); (b) **54**, 4239 (1932).

[5] (a) Hammett and Paul, *ibid.*, **56**, 827 (1934); (b) **56**, 830, (1934); (c) **58**, 2182 (1936).

[6] (a) Hammett, Dingwall and Flexser, *ibid.*, **56**, 2010 (1934); (b) **57**, 2103 (1935); (c) Flexser and Hammett, *ibid.*, **60**, 885 (1938).

[7] (a) Hammett, *Chem. Rev.*, **13**, 61 (1933); (b) **16**, 67 (1937); (c) "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 265 ff.

[8] (a) Hall, *Chem. Rev.*, **8**, 191–212 (1931); (b) THIS JOURNAL, **52**, 5115 (1930); (c) Hall and Voge, *ibid.*, **55**, 239 (1933).

[9] (a) Conant, "Equilibria and Rates of Some Organic Reactions," Columbia University Press, New York, N. Y., 1932; (b) Conant and Bramann, THIS JOURNAL, **50**, 2305 (1928); (c) Conant and Werner, *ibid.*, **52**, 4436–50 (1930); (d) Conant and Chow, *ibid.*, **55**, 3745, 3752 (1933).