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The Specific Rates of Solvolysis of *t*-Butyl Chloride in Aqueous Methanol, Aqueous Acetone and Aqueous Dioxane and of *t*-Butyl Bromide in Aqueous Acetone[1]

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The rates of solvolysis of *t*-butyl chloride have been measured at 24.80 and 30.00° in aqueous methanol solutions, at 5.12, 24.80 and 30.00° in aqueous dioxane solutions and at 24.80 and 30.00° in aqueous acetone solutions. The rates of solvolysis of *t*-butyl bromide have been measured at 5.12, 24.80 and 30.00°, in aqueous acetone solutions. Both conductance and titration methods were used for following the reactions.

The solvolysis of tertiary halides has been the subject of many investigations since the original paper by Hughes[2] twenty years ago. The mechanisms proposed for the solvolysis range from (a) the simple primary ionization to carbonium ions followed by various rapid bimolecular reactions to produce the products, to (b) several simultaneous primary bimolecular or higher order reactions to produce the products. One of the factors contributing to this lack of agreement must be the lack of a sufficiently extensive set of precise data. This article is the first in a series designed partially to remedy this situation.

Experimental

Preparation of Materials.—*t*-Butyl chloride, either the Eastman Kodak Co. product or that prepared in this Laboratory by the usual method[3] was distilled twice in a meter long column; the fraction boiling between 51.4 and 51.6° was used for the experiments. Weighed samples, permitted to solvolyze completely in approximately 50 volume per cent. aqueous methanol and then titrated with standard base, were always found to be more than 99% pure on the basis of the amount of acid produced. Rate measurements made with different preparations of *t*-butyl chloride agreed as well as duplicate measurements made with the same preparation.

t-Butyl bromide was prepared by the method described by Cooper and Hughes.[3a] Commercial methyl alcohol was distilled once in a meter long column; the fraction boiling between 64.7 and 64.9° was used. A Fischer reagent titration showed the water content to be 0.05 mole/l. or 0.2%. The density found with a Westphal balance was 0.7916 at 20°.

Commercial acetone was purified by the method of Conant and Kirner.[3b] The water content of different preparations varied somewhat; a single batch having 0.83% water was used for the runs followed by conductance.

Dioxane was purified by Fieser's method.[3c] The material distilling at 101° was retained. It had a density of 1.0338 at 20° and m.p. of 11.1 to 11.3°. The water content by a Fischer Reagent titration was 0.78%.

The aqueous solvents were prepared by weight. Thermostat temperatures, maintained to ±0.02°, were read from NBS calibrated thermometers.

Rate Measurements by the Conductance Method.—Conductances as such were not used since resistance, the measured quantity, can be converted directly to the concentration of acid, *i.e.*, HCl, a reaction product of the solvolysis of *t*-butyl chloride, or HBr, a product of the solvolysis of *t*-butyl bromide. A Jones–Josephs precision conductance bridge was used for the resistance measurements. Readings, taken periodically on a large known resistance, were found never to vary more than 0.5 ohm.

Resistance–acid concentration data for constructing calibration curves were obtained in a conductance cell to which was attached a reservoir in which the standard acid solutions used for calibration were prepared by successive quantitative dilutions. When the solvent was aqueous methanol the initial HCl solution to be diluted was prepared by passing HCl gas, generated from concentrated H_2SO_4 and NaCl and dried with $CaCl_2$, into the solvent. When the solvent was aqueous acetone or aqueous dioxane the initial HCl solution to be diluted was prepared by adding about 0.3 cc. of J. T. Baker Reagent Grade 12 *N* HCl per 100 cc. solvent. C.P. HBr gas was used for preparing the HBr solutions used for calibration. Acid solutions used for calibration were standardized by titration with standard base. Calibration curves were obtained for every temperature and solvent composition used.

For a rate run, time–resistance readings were made after the solvent and alkyl halide were mixed in the cell and had reached temperature equilibrium in a thermostat. These were converted to time–acid concentration data by reference to a calibration curve. The specific rate constant was obtained from the slope of a Guggenheim plot of these data. Although it was not needed for the Guggenheim treatment, the initial concentration of *t*-butyl halide in the aqueous methanol solvents was found by titrating the acid formed in complete solvolysis of samples taken from the reaction mixture. In the aqueous acetone and aqueous dioxane solvents, the reaction mixtures were made up with a certain initial concentration of alkyl halide (usually 0.14 *M*) and were not titrated for more precise values of concentration.

Rate Measurements by the Titration Method.—For the preparation of a rate run, a stock solution of the alkyl halide in the organic solvent was prepared and permitted to reach temperature equilibrium in a thermostat. Then, 10.0 ml. of this stock solution was transferred by pipet into a labeled, thin-walled, glass bulb containing 10.0 ml. of a solution of water and the organic solvent. The stem of the bulb was immediately capped with a policeman made from tygon or tygothene tubing, shaken and submerged in the thermostat. A series of 8 to 15 similarly filled bulbs constituted the samples for a run. When a fast reaction was being followed, a zero time (the time of placing the bulb in the thermostat) was recorded for each bulb in the run. For a very slow reaction, the same (average) zero time was recorded for every bulb.

The concentration of the alkyl halide stock solution was found by titration for acid of the completely solvolyzed samples; the recorded initial concentration of alkyl halide is one-half the concentration of the stock solution.

The solvolysis was followed by titrating the samples at various times for the acid produced. A sample bulb to be analyzed was removed from the bath, rinsed quickly with distilled water, broken in a 500-ml. glass stoppered erlenmeyer flask into approximately 250 ml. of ice-cold commercial methanol (or acetone) containing methyl red indicator (or lacmoid indicator), and titrated with standard base. The time of breaking a bulb was the recorded time of the sample.

Specific rate constants were obtained from the slopes of conventional first order plots of the data. The compositions of the solvents were calculated from the densities, compositions and volumes of the solutions mixed.

Results

Aqueous Methanol.—The individual rate runs for the solvolysis of *t*-butyl chloride in aqueous

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(1) This work was supported in part by the Office of Naval Research, United States Navy.

(2) E. D. Hughes, *J. Chem. Soc.*, 255 (1935).

(3) *Org. Syntheses*, **8**, 50 (1928).

(3a) K. A. Cooper and E. D. Hughes, *J. Chem. Soc.*, 1183 (1937).

(3b) J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 246 (1924).

(3c) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941.

methanol were found always to be first order. The specific rates obtained by the conductance method at 30.00° satisfy the empirical equation

$$10^3 k_{\text{hr.}^{-1}} = 4.95\,(e^{0.80 N_A} - 1) + 4.50\,(e^{9.88 N_W} - 1) \quad (1)$$

with an average deviation of ±1.2% in the experimental range of solvent compositions, *i.e.*, from $N_W = 0$ to $N_W = 0.5$ (where N_W is the mole fraction of water and N_A is the mole fraction of methyl alcohol).

At 24.80° the specific rates obtained by the conductance method satisfy the equation

$$10^3 k_{\text{hr.}^{-1}} = 2.21\,(e^{0.80 N_A} - 1) + 2.33\,(e^{9.88 N_W} - 1) \quad (2)$$

with an average deviation of ±0.8% in the same region of solvent composition. At higher water concentrations the specific rates increase more rapidly with N_W than the equation implies—an experimental value at $N_W = 0.600$ lies about 16% above that calculated by equation 2.

In general, the initial concentrations of reactant used were higher for runs followed by the titration method than for those followed by the conductance method. In pure methanol, the specific rate of solvolysis was found to decrease somewhat with increasing initial concentration of *t*-butyl chloride. Such an effect in solvolytic reactions has been observed by other workers.[4] However, in solvents containing water this effect was not detected. The specific rates obtained by the titration method at 30.00 and 24.80° conform to equations 1 and 2 for $N_W > 0$.

The data obtained by both methods at 24.80 and 30.00° are collected in Tables I and II. A single run at 5.12° in a solvent of $N_W = 0.600$ gave $k = 72.1 \times 10^{-3}$ hr.$^{-1}$.

TABLE I

THE SPECIFIC RATES OF SOLVOLYSIS OF *t*-BUTYL CHLORIDE AT 24.8° IN AQUEOUS METHANOL SOLUTIONS

N_W	Initial *t*-BuCl, moles/l.	10^3k (hr.$^{-1}$) Expt.	Calcd.	Dev., %
0.000^a	0.2648	2.41	2.71	−11.1
.000^a	.0509	2.64	2.71	− 2.6
.000	.025	2.67	2.71	− 1.5
.000	.022	2.74	2.71	+ 1.1
.0568	.014	4.40	4.24	+ 3.8
.065^a	.1490	4.60	4.59	+ 0.2
.065^a	.0975	4.59	4.59	0.0
.124^a	.1490	7.83	7.85	− 0.2
.240	.024	24.5	24.5	0.0
.240	.023	24.5	24.5	0.0
.348	.025	71.9	71.7	+ 0.3
.400	.024	118	120	− 1.7
.400	.024	120	120	0.0
.450	.029	198	198	0.0
.500	.024	327	324	+ 0.9
.500	.023	324	324	0.0
.600	.027	1007	873	+15.3
.600	.022	1018	873	+16.6
Av. (excluding titration values at N_W = 0.000 and conductance values at N_W = 0.600)				± 0.7%

[a] These values were obtained from rate runs followed by titration. Others were obtained by the conductance method.

TABLE II

THE SPECIFIC RATES OF SOLVOLYSIS OF *t*-BUTYL CHLORIDE AT 30.0° IN AQUEOUS METHANOL SOLUTIONS

N_W	Initial *t*-BuCl, moles/l.	10^3k (hr.$^{-1}$) Expt.	Calcd.	Dev., %
0.000^a	0.2648	5.11	6.07	−15.8
.000^a	.2030	5.29	6.07	−12.8
.000^a	.1790	5.24	6.07	−13.7
.000^a	.0509	5.59	6.07	− 7.9
.000	.025	6.15	6.07	+ 1.3
.000	.025	5.99	6.07	− 1.3
.0568	.014	8.96	8.96	0.0
.0650^a	.1104	9.55	9.56	− 0.1
.1102	.014	14.33	14.00	+ 2.4
.124^a	.1104	16.2	15.8	+ 2.5
.124^a	.0550	16.2	15.8	+ 2.5
.148^a	.0880	20.2	19.8	+ 2.0
.150	.027	19.7	20.1	− 2.0
.150^a	.0216	21.3	20.1	+ 6.0
.246^a	.0523	49.9	50.7	− 1.6
.249^a	.1013	54.4	52.2	+ 4.0
.250	.025	52.9	52.8	+ 0.2
.254^a	.1716	54.1	54.9	− 1.4
.254^a	.0878	53.0	54.9	− 3.5
.254^a	.0554	53.5	54.9	− 2.6
.350	.024	140	142	− 1.4
.370^a	.0542	169	173	− 2.3
.400	.024	230	233	− 1.3
.400	.024	234	233	+ 0.4
.450	.024	381	382	− 0.3
.500	.024	643	627	+ 2.6
Av. (excluding titration values at N_W = 0.000)				± 1.9%

[a] These values were obtained from rate runs followed by titration. Others were obtained by the conductance method.

The maximum error in any k for $0 < N_w \leq 0.5$ is 6% corresponding to an error in the apparent heat of activation (calculated between 24.80 and 30.00°) of 2 kcal. However, the data are sufficiently numerous that the error in the apparent heat of activation may be about 500 cal.

At $N_W = 0$, two different sets of titration data yield $\Delta H\ddagger = 26.0$ kcal. In this solvent, *i.e.*, pure methanol, the conductance data show the greatest divergence from the titration data. From conductance data the heat of activation at $N_W = 0$ is 28.0 ± 1 kcal. At $N_W = 0.5$, $\Delta H\ddagger$ is 22.5 to 23.0 kcal. The change in apparent free energy of activation between $N_W = 0$ and $N_W = 0.5$ at 24.80° is 2830 cal. Thus, the entire change in rate could be accounted for by a change in apparent heat of activation if we used the titration value at $N_W = 0$. The data do not exclude some change in apparent entropy of activation.

The apparent heat of activation at $N_W = 0.600$ calculated between 5.12 and 24.80° is 22,100 cal. This value is consistent with the trend in $\Delta H\ddagger$ with N_W which was found from values of k at 24.80 and 30.00°. Thus, there is no indication of a marked change in mode of reaction beyond $N_W = 0.5$ where the simple exponential dependence of k on N_W, equations 1 and 2, no longer holds, nor does the lower value necessarily reflect a change in apparent heat of activation with temperature.

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[4] For example, see G. W. Beste and L. P. Hammett, THIS JOURNAL, **62**, 2481 (1940), and references given there.

Aqueous Acetone. *t*-Butyl Bromide.—The logarithms of the specific rates of solvolysis of *t*-butyl bromide in aqueous acetone obtained from conductance data increase linearly with N_W in the region from $N_W = 0.170$ to $N_W = 0.606$, so that the equation

$$\log k = a + bN_W \qquad (3)$$

may be written. Specifically, least squares treatment of the data yield slopes, *i.e.*, values of b, of 5.513 at 30.00°, 5.561 at 24.80°, and 5.534 at 5.12°.

If values of b should be the same at different temperatures, the apparent heat of activation must be the same throughout this region of solvent composition. The change in b from 24.80 to 30.00° given above indicates that a decrease in apparent heat of activation of about 1600 cal. occurs from $N_W = 0.170$ to $N_W = 0.606$. On the other hand, at 5.12°, a temperature significantly different from the other two temperatures, the value of b is so near to b-values found at the higher temperatures that a change of no more than 230 cal. in the apparent heat of activation between $N_W = 0.170$ and $N_W = 0.606$ is indicated. Thus, the value of b found at 24.80° appears to be 0.5 to 1% high, and, indeed, omission of k at $N_W = 0.170$ (which appears to be out of line) from the least squares treatment of 24.80° data leads to a slightly lower slope, *i.e.*, 5.524. It seems clear that an increase in apparent entropy of activation accounts for 80% or more of the decrease in apparent free energy of activation from $N_W = 0.170$ to $N_W = 0.606$, which amounts to 3300 cal. at 24.80°.

Since the maximum difference between least squares slopes at the three temperatures is less than 0.5% and not experimentally significant, it is convenient to assign a single value for the slopes and to express the data by the equations

$$\log k = 5.524_2 N_W - 2.909_7 \text{ at } 30.00° \qquad (4)$$

$$\log k = 5.524_2 N_W - 3.172_2 \text{ at } 24.80° \qquad (5)$$

$$\log k = 5.524_2 N_W - 4.225_6 \text{ at } 5.12° \qquad (6)$$

Specific rate constants calculated from these equations are recorded along with the experimental values in Table III. It is seen that, within 1% of k the linearity of the logarithm of k with N_W holds in a region where k changes by a factor of 75 at 30.00°, a factor of 140 at 24.80°, and a factor of 12 at 5.12°. Data taken beyond $N_W = 0.606$ at 5.12° show that at higher water concentrations the logarithm of k increases more rapidly than linearly with N_W. (This is consistent with the behavior found for *t*-butyl chloride in aqueous methanol where k increases more rapidly beyond $N_W = 0.5$ than the simple exponential form implies.) Thus, equations 4, 5 and 6 describe surprisingly long segments of more complex curves. They are useful as empirical equations, and their particular form is convenient since the coefficient of N_W is directly proportional to the fractional change in k with N_W.

The average apparent heat of activation in the experimental region described by the equations is 20,800 cal. when calculated between 24.80 and 30.00° and 20,300 when calculated between 5.12 and 24.80°. The higher value could result from some systematic error. For example, an error of 0.1° in the difference between the two higher temperatures would cause an error of 400 cal. in the calculated heat of activation but such a temperature error is too large for NBS calibrated thermometers.

TABLE III

SPECIFIC RATES OF SOLVOLYSIS OF *t*-BUTYL BROMIDE IN AQUEOUS ACETONE SOLUTIONS[a]

Moles per liter, *t*-butyl bromide initially = 0.013

N_W	10^3k (hr.$^{-1}$) Expt.	10^3k (hr.$^{-1}$) Calcd.	Dev., %
	$t = 30.00°$		
0.170	10.9	10.7	+ 1.9
.218	19.4	19.7_1	− 1.6
.315	68.0	67.6_7	+ 0.5
.509	795	$798._2$	− 0.4
.509	795	$789._2$	− 0.4
		Av.	± 1.0%
	$t = 24.80°$		
0.170	5.5	5.84_7	− 5.9[b]
.218	10.7	10.8	− 0.9
.315	37.3	36.9_7	+ 0.9
.411	125	$125._4$	− 0.3
.509	437	$436._1$	+ 0.2
.509	438	$436._1$	+ 0.4
.606	1490	149_8	− 0.5
		Av.	± 0.6%
	$t = 5.12$		
0.411	11.0	11.0_9	− 0.8
.509	39.0	38.5_7	+ 1.1
.606	132	$132._5$	− 0.4
.704	531	$460._7$	+15.2[b]
.802	3020	160_3	+88.5[b]
		Av.	± 0.8%

[a] Conductance data only. [b] Excluded from average.

***t*-Butyl Chloride.**—For measurements of the specific rates of solvolysis of *t*-butyl chloride in aqueous acetone by the conductance method there was employed a smaller range of solvent composition than was used for the measurements on *t*-butyl bromide. However, at 24.80°, the solvent range was extended by the titration method, and the specific rates were found to obey equation 3 in the region from $N_W = 0.308$ to $N_W = 0.704$. Combination of titration data with conductance data yielded a b-value of 6.752 with an average deviation in k of ±2.5% through this region where k changes by a factor of about 450. Because of the strong dependence of k on solvent composition as well as the somewhat poorer precision among titration results at low N_W, combination of these data, obtained by different methods for different batches of acetone, obscures the internal consistency of the conductance data and the conclusions which may be drawn from them. Thus, only the conductance data are presented here. (The titration data will be presented in a later paper on salt effects.)

The conductance values of k in the region, $N_W = 0.509$ to $N_W = 0.704$, obey the equations

$$\log k = 6.694_0 N_W - 5.323_9 \text{ at } 30.00° \qquad (7)$$

$$\log k = 6.694_0 N_W - 5.609_6 \text{ at } 24.80° \qquad (8)$$

Specific rate constants calculated from these equations are recorded along with the experimental values in Table IV. The table shows that beyond $N_W = 0.704$ the rates increase more rapidly than the equations imply. (Deviations from the simple relationship became experimentally distinguishable in the *t*-butyl bromide case beyond $N_W = 0.606$.)

TABLE IV

SPECIFIC RATES OF SOLVOLYSIS OF *t*-BUTYL CHLORIDE IN AQUEOUS ACETONE SOLUTIONS[a]

N_W	Initial *t*-BuCl, moles/l.	10^3k (hr.$^{-1}$) Expt.	Calcd.	Dev., %
		$t = 30.00°$		
0.509	0.014	12.2	12.1_1	+ 0.8
.606	.014	53.6	54.0_4	− 0.8
.704	.014	245	$244._7$	+ 0.1
.802	.014	1457	1108	+31.4[b]
			Av.	± 0.5%
		$t = 24.80°$		
0.509	0.0692	6.26	6.27_5	− 0.2
.606	.0135	28.0	27.9_9	0.0
.704	.0149	127	$126._8$	+ 0.2
.802	.012	720	574	+25.3[b]
			Av.	± 0.1%

[a] Conductance data only. [b] Excluded from average.

Since the *b*-values are the same at both temperatures, the equations suggest that the increase in rate in this region of solvent composition arises entirely from an increase in apparent entropy of activation. Actually, although the slopes are experimentally indistinguishable, experimental errors are such that half of the increase in rate between $N_W = 0.509$ and $N_W = 0.704$ could be accounted for by a decrease in apparent heat of activation. However, by inference from the *t*-butyl bromide case it is probable that entropy changes are largely responsible for the rate changes in this region.

The average apparent heat of activation in the experimental region described by the equations is 22,700 cal. (The single value of heat of activation, 24,300 cal., calculated from the data at $N_W = 0.802$ is certainly high.)

Aqueous Dioxane.—Specific rates of solvolysis for *t*-butyl chloride in aqueous dioxane are recorded in Table V along with some apparent heats of activation calculated from them. At 30.00° the logarithm of *k* is not linear with N_W; it is concave upward. It seems probable that a long linear region exists at lower mole fractions since *t*-butyl nitrate[5] shows one. The region, $N_W = 0.560$ to $N_W = 0.881$, studied here, apparently corresponds to the region of upturn found in aqueous methanol and aqueous acetone at high water concentrations.

TABLE V

SPECIFIC RATES OF SOLVOLYSIS OF *t*-BUTYL CHLORIDE IN AQUEOUS DIOXANE SOLUTIONS[a]

N_W	Initial moles/liter t-BuCl	10^3k (hr.$^{-1}$) 30.00°	24.80°	5.12°	$\Delta H\ddagger$ 24.80-30.00°	$\Delta H\ddagger$ 5.12-24.0°
0.560	0.019	11.7	...	..	....	....
.656	.019	44.6	...	..	....	....
.705	.014	104.6	52.9	..	23,500	....
.705	.014	104.3	52.5	..	23,800	....
.754	.014	290	149.5	10.7	22,900	22,000
.803	.014	765	393	33.6	23,000	20,600
.803	.014	764	...	..	....	....
.803	.014	772	...	..	(23,300)	....
.881	.014	6290	...	..	....	....

[a] Conductance data only.

Rates were measured only from $N_W = 0.705$ to $N_W = 0.803$ at 24.80 and at 5.12° so that heats of activation could be calculated only in this range. The average value of $\Delta H\ddagger$ calculated between 24.8 and 30.00°, is 23.3 kcal. The decrease in apparent free energy of activation from $N_W = 0.705$ to $N_W = 0.803$, which amounts to only 1200 cal. at 24.80°, cannot be separated with certainty into heat and entropy terms.

Discussion

For both *t*-butyl chloride and *t*-butyl bromide the logarithms of the specific rates of solvolysis in aqueous acetone show a linear dependence on N_W over a range of solvent composition of 0.4 unit in N_W. A similar straight line relationship holds for *t*-butyl chloride in aqueous methanol over a shorter region of solvent composition, say 0.3 unit in N_W. Beyond the regions of linearity, three types of deviations from linearity are observed in these systems.

(i) In aqueous methanol, the slope of log *k* for *t*-butyl chloride *vs.* N_W becomes less than the slope of the linear segment as N_W approaches zero.[6]

(ii) The data of Taylor[7] and of Bateman, Cooper and Hughes,[8] indicate that for *t*-butyl bromide in aqueous acetone the slope of log *k* *vs.* N_W as N_W approaches zero becomes increasingly larger than the slope of the linear portion. These data cannot be analyzed quantitatively because they are complicated by reversibility of the solvolysis and in addition by the reaction of the acid with the solvent. Although our own investigation has not invaded the region of very low water concentrations, such a negative deviation must occur if the organic solvent is truly inert.

(iii) In all solvents investigated, positive deviations from linearity occur at high water concentrations.

Examination of the literature shows that linear dependences of log *k* of solvolysis on N_W over a considerable region of N_W are exhibited by such various systems as *t*-butyl nitrate[5] and methane sulfonyl chloride[9] in aqueous dioxane and triphenylsilyl fluoride[10] and benzyl tosylate[11] in aqueous acetone. In addition, one or both of the characteristic deviations described by ii and iii are usually found. (Although examples of iii are common,

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(5) G. R. Lucas and L. P. Hammett, THIS JOURNAL, **64**, 1928 (1942).

(6) This result is not in agreement with that inferred from previous data by Grunwald and Winstein, THIS JOURNAL, **70**, 846 (1948). In their plot of *Y*, which is a function defined to be linear with log *k* for *t*-butyl chloride, against N_W (Fig. 2, curve I), these authors have drawn a curve with a negative deviation from linearity at low water concentrations. The positive deviation which we find does not show up well on a small logarithmic plot, but the precision of the data assures us that it is real.

(7) W. Taylor, *J. Chem. Soc.*, 1853 (1937).

(8) L. C. Bateman, K. A. Cooper and E. D. Hughes, *ibid.*, 913 (1940).

(9) H. Böhme and W. Schürhoff, *Chem. Ber.*, **84**, 28 (1951).

(10) C. G. Swain, R. M. Esteve and R. H. Jones, THIS JOURNAL, **71**, 965 (1949).

(11) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

examples of ii are rare because of experimental difficulties. An especially good example of ii is found in the solvolysis of benzhydryl chloride in aqueous acetone at 50°. The reaction is measureably reversible at low water concentrations, but initial first-order specific rates calculated from the data[12,13] are found to fall off very rapidly as N_W approaches zero. It is interesting that, in this region of low water concentration where the percentage change in N_W is large, a plot of log (k/N_W) against N_W is found to be linear and to extend so far as $N_W = 0.505$[14].)

It is clear that the straight line segments of plots of log k *vs.* N_W in aqueous mixtures with acetone or dioxane are actually regions about points of inflection. Usually a point of inflection arises in a complex phenomenon where two or more physical factors combine to control the process. The linearity found in this work for *t*-butyl bromide and *t*-butyl chloride in aqueous acetone is deceptive in that it holds with such high precision over a wide range. We can look upon the solvent as playing a dual role: (1) as a reactant in which solvent molecules are used up, and (2) as a catalyst in which one or more solvent molecules must be oriented or combined in a specific manner in the transition state of a reaction path, but the molecules are not used up. The characteristic negative deviation ii shows that, relative to water, acetone must be a very poor catalyst for olefin formation as well as for water substitution. On the other hand, methanol, though a poorer catalyst than water, is comparable with water at low water and high methanol concentrations and gives rise to the positive deviation i, which eliminates the point of inflection. (Since isobutene is formed even in pure methanol, methanol must catalyze the elimination reaction in addition to introducing the substitution reaction in which methyl *t*-butyl ether is formed.) The methanol catalyzed path or set of paths has a higher heat of activation than the water-catalyzed path or set of paths so that the apparent heat of activation decreases with increasing N_W.

The two-term form of the empirical equations 1 and 2 seem to imply that the heats of activation for the two separate sets of paths are independent of N_W whereas the entropies of activation of the two sets depend strongly on N_W but in opposite directions so that the apparent entropy of activation changes little throughout this region. This dependence of heat and entropy effects on solvent composition is not a necessary consequence of the data but is an inference from the example of *t*-butyl bromide in aqueous acetone. One could argue that entropy effects should be smaller in aqueous methanol solutions where the two solvent components are more nearly alike than in aqueous acetone, and another empirical form could be chosen to represent the data. According to the viewpoint adopted, the form of equations 1 and 2 is an oversimplification since there must be at least one set of paths catalyzed by both methanol and water. Additional information on this system will be presented in later papers.

Grunwald and Winstein[15] have offered a correlation of solvolysis rates in which the logarithm of the specific rate for a given compound in a certain solvent when plotted against the logarithm of the specific rate for *t*-butyl chloride in the same solvent yields a single straight line for all solvents. The slope, *m*, of this straight line is considered to be a constant characteristic of the given compound relative to *t*-butyl chloride. The straight line of Grunwald and Winstein for *t*-butyl bromide can be expressed by

$$\log k^{\mathrm{BuBr}} = 0.917 \log k^{\mathrm{BuCl}} + 1.471 \qquad (9)$$

where the rate constants are in reciprocal hours. The rate data from which this equation was composed were taken in aqueous ethanol solutions over a range of solvent compositions, $N_W = 0$ to $N_W = 0.682$, through which the specific rate for *t*-butyl bromide changed by a factor of 660.

Since our data show that both log k^{BuBr} and log k^{BuCl} are linear with N_W through an overlapping region of N_W, *i.e.*, $N_W = 0.308$ to $N_W = 0.606$, these functions must be in a linear relationship with each other through this same region. Elimination of N_W from equations 5 and 8 yields the equation

$$\log k^{\mathrm{BuBr}} = 0.825 \log k^{\mathrm{BuCl}} + 1.457 \qquad (10)$$

That equations 9 and 10 cannot be the same within the limits of experimental error is illustrated by the observation that, whereas k^{BuCl} is about the same in pure ethanol as it is in aqueous acetone of $N_W = 0.32$, k^{BuBr} is about 80% greater in the latter solvent than it is in the former. Indeed, the slope of (9) is probably accurate to ±4% and the slope of (10) is probably accurate to ±1%. Thus, m (= 0.917) of the Grunwald–Winstein correlation is not characteristic of *t*-butyl bromide for all solvents.

For the log k^{BuBr}–log k^{BuCl} correlation to hold
each solvent system, curves 9 and 10 must
fo at the value of log k^{BuCl} corresponding to N_W
mee At $N_W = 0.987$ in aqueous acetone, Swain
= 1. [16] have estimated the specific rate of
and R of *t*-butyl chloride to be 92.5 hr.$^{-1}$ which
solvolysis point of intersection to fall at log k^{BuCl}
requires th extrapolated point of intersection is
> 1.97. Th $k^{\mathrm{BuCl}} = -0.15$ (or $k^{\mathrm{BuCl}} = 0.71$
actually at log the value obtained in aqueous
hr.$^{-1}$), which is 0.72 and in aqueous acetone at
ethanol at $N_W \simeq$ gh the point of intersection is
$N_W \simeq 0.80$. Altho ges in slopes, it cannot lie so
sensitive to small cha . Clearly, (9) or (10) or
far out as log k^{BuCl} = concentrations.
both must fail at high wat d to data in regions of

Both (9) and (10) are fit g k for both com-
solvent compositions where h N_W. Our data
pounds is linear or nearly so g k^{BuBr} begins to
indicate that in aqueous acetone slightly below
show the characteristic deviation s linear with
$N_W = 0.7$ whereas log k^{BuCl} rema obably be-
N_W through $N_W = 0.7$. Thus, (10) 7.
gins to fail in the neighborhood of N_W = olysis

A somewhat different correlation of

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(12) W. Taylor, This Journal, **60**, 2094 (1938).

(13) E. D. Hughes, C. K. Ingold, S. Masterman and B. J. McNulty, *J. Chem. Soc.*, 899 (1940).

(14) Data for higher mole fractions of water were taken from E. D. Hughes, C. K. Ingold and N. A. Taher, *ibid.*, 949 (1940); M. G. Church, E. D. Hughes and C. K. Ingold, *ibid.*, 966 (1940).

(15) E. Grunwald and S. Winstein, This Journal, **70**, 846

(16) C. G. Swain and S. D. Ross, *ibid*, **68**, 658 (1946).

rates has been proposed by Swain and Dittmer,[17] *i.e.*

$$\log (k^{A}/k_0^{A}) - \log (k^{A_0}/k_0^{A_0}) = a_A b \qquad (11)$$

where a is a constant characteristic of compound A and $a = 0$ for the arbitrarily chosen standard compound A_0, b is a constant characteristic of the solvent in which the specific rates are denoted by k and $b = 0$ for the arbitrarily chosen standard solvent, 80% aqueous ethanol, in which the specific rates are denoted by k_0. Writing one such equation for *t*-butyl chloride and another for *t*-butyl bromide we obtain by difference

$$\log (k^{BuCl}/k_0^{BuCl}) - \log (k^{BuBr}/k_0^{BuBr}) = b(a_{BuCl} - a_{BuBr}) \qquad (12)$$

The authors give a-values for *t*-butyl chloride and *t*-butyl bromide and b-values for 90% ($N_W = 0.311$) and 80% ($N_W = 0.505$) aqueous acetone which lie within the range of solvent composition that we have investigated for both compounds. Using the same k_0-values which Grunwald and Winstein used for 80% aqueous ethanol,[18] we obtain from our experimental data values for the left hand side of (12) equal to −0.495 and −0.247 for 90 and 80% aqueous acetone, respectively, to be compared with −0.05 and 0.00 as calculated from the Swain–Dittmer constants. Indeed, equation 11 cannot hold for both *t*-butyl chloride and *t*-butyl bromide when b is a constant for a given solvent since, as we have already noted above, k^{BuCl} (or k^{BuCl}/k_0^{BuCl}) is about the same in pure ethanol as it is in aqueous acetone of $N_W = 0.32$ whereas k^{BuBr} (or k^{BuBr}/k_0^{BuBr}) is about 80% greater in the latter solvent than it is in the former.

Solvolysis rates often depend very strongly on solvent composition. It is experimentally difficult and frequently too tedious for a researcher's purpose to reproduce mixed solvents with high accuracy. Thus in any correlation of such rates taken from different authors or from the same authors at different times, one may quite rightly expect to assign sizeable deviations to experimental errors. For example, where we have attempted to compare our work with results reported in the literature we have found that we must allow for discrepancies of 0.02 to 0.03 unit in N_W in aqueous acetone, whereas an error of 0.026 unit in N_W will produce in the specific rate of solvolysis of *t*-butyl chloride an error of a factor of 1.5.[19] This factor is the average deviation reported for the Swain–Dittmer correlation, and so one might conclude that the correlation fits a large amount of the data treated very nearly within the limits of experimental error. For this reason we point out that two so closely related compounds as *t*-butyl chloride and *t*-butyl bromide show real deviations which are outside the average deviation. Thus, some doubt is cast on the usefulness of the correlation as a basis for theory, but we do not wish to underestimate the value of such correlations in organizing large quantities of information for use in estimating orders of magnitudes of rates.

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[17] C. G. Swain and D. C. Dittmer, THIS JOURNAL, **75**, 4627 (1953).

[18] Data taken from E. D. Hughes, *J. Chem. Soc.*, 255 (1935); L. C. Bateman, K. A. Cooper, E. D. Hughes and C. K. Ingold, *ibid.*, 925 (1940).

[19] The value of reporting solvent compositions in terms of some easily measured rates is illustrated here.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

The Products of Solvolysis of *t*-Butyl Chloride in Aqueous Methanol Solutions[1,2]

BY FRANCES SPIETH, WILLIAM C. RUEBSAMEN AND A. R. OLSON

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Methods of analyzing for isobutene, methyl *t*-butyl ether and *t*-butyl alcohol in aqueous methanol solutions are described. These methods are then used to determine the fractions of these substances that are produced in the solvolysis of *t*-butyl chloride in aqueous methanol solutions at several compositions and temperatures.

The products of solvolysis of *t*-butyl chloride in aqueous methanol solutions are methyl *t*-butyl ether, *t*-butyl alcohol and isobutene. The purpose of the work presented here has been to determine quantitatively the fractions of the several products at various solvent compositions.

Bateman, Hughes and Ingold[3] determined the ratio of methyl *t*-butyl ether to *t*-butyl alcohol by a fractional distillation method. We have determined these products by a distribution method. The distribution coefficients of methyl *t*-butyl ether and *t*-butyl alcohol between 20 weight per cent. methanol in water and carbon tetrachloride are sufficiently different so that an analysis of each layer for total concentration of *t*-butyl compounds enables one to calculate the proportion in which the two compounds are present. The analysis for *t*-butyl compounds was based on the quantitative precipitation of a complex containing one molecule of isobutene to seven atoms of mercury (in a mercuric salt) and subsequent volumetric determination of mercury in the precipitate. The analytical method was conceived and developed from previously published work.[4–7]

Determinations of the fraction of isobutene

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[1] This work was supported in part by the Office of Naval Research. United States Navy.

[2] This is the second in a series of papers dealing with the solvolysis of *t*-butyl compounds in aqueous organic solvents; see Cropper, Spieth and Olson, THIS JOURNAL, **76**, 6248 (1954).

[3] L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 884 (1938).

[4] G. Deniges, *Compt. rend.*, **126**, 1043, 1145, 1277 (1898); *Bull. soc. chim., Paris*, [3] **19**, 384 (1898).

[5] A. Newton and E. J. Buckler, *Ind. Eng. Chem., Anal. Ed.*, **12**, 251 (1940).

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