b.p. 80-100° (1 mm.), 246° (760 mm.), m.p. 15°, n^{20}_D 1.569.

Anal. Calcd. for $C_{11}H_{11}N$: N, 8.9. Found: N, 8.9.

N-Methylpyrrole.—A mixture of 40% aqueous methylamine (219 g., 3.2 moles), I (80 g., 0.57 mole), glacial acetic acid (15 drops) and concentrated hydrochloric acid (9 drops) was heated slowly with stirring to 44°, then the heat source was removed. After 30 minutes at that temperature, the mixture became homogeneous. The mixture was maintained at 44° for another hour then allowed to stand at room temperature overnight. The reaction mixture was cooled in an ice-bath and acidified by the careful addition of 18% hydrochloric acid. The mixture was thrice extracted with ether and the combined organic layers were dried over anhydrous potassium carbonate, filtered and distilled to give the product, 21 g. (46% yield), b.p. 114°, $n^{23.5}_D$ 1.4855.

N-Cyclohexylpyrrole.—Cyclohexylamine (75 g., 0.75 mole) and I (75 g., 0.53 mole) were treated with acetic acid (9 drops) and concentrated hydrochloric acid (5 drops) while nitrogen was swept slowly through the stirred mixture. The vent gas from the condenser was passed through a scrubber which contained 350 ml. of 2.8 *N* hydrochloric acid solution. After the mixture was heated at 70 ± 5° for 4 hr., 1.0 mole of dimethylamine had been liberated. Potassium carbonate (1 g.) was added and distillation of the reaction mixture gave (a) b.p. 53–60° (17 mm.), 17 g., n^{20}_D 1.4589 (recovered amine); (b) b.p. 60° (17 mm.) to 62° (1 mm.), 8.5 g., n^{20}_D 1.5060 (intermediate cut, contained product contaminated with 10% recovered amine); (c) b.p. 62–63° (1 mm.), 48 g., n^{20}_D 1.5111; (d) residue, 18 g., polymeric.

Anal. (Cut c) Calcd. for $C_{10}H_{15}N$: N, 9.4. Found: N, 9.4.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES, AND FLORIDA STATE UNIVERSITY]

Correlation of Solvolysis Rates. VIII. Benzhydryl Chloride and Bromide. Comparison of *m*Y and Swain's Correlations[1]

BY S. WINSTEIN, ARNOLD H. FAINBERG AND E. GRUNWALD

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In this paper are reported rates of solvolysis of benzhydryl chloride and bromide and the correlation of these and other data in the literature by means of the *m*Y relation. The dispersion of log *k vs.* Y plots into separate lines for each solvent pair, observed previously with *t*-butyl, α-phenylethyl and neophyl halides, is even more marked with the benzhydryl halides. The contributing causes of such dispersion include structural limitations of the *m*Y relation with respect to variation of both the R and X parts of RX. The leaving group specificity is especially marked with F, fluorides tending to be very fast in carboxylic acid solvents. Ion pair return, which depresses the observed solvolysis rate below the ionization rate by variable amounts depending on the nature of the solvent, contributes to the observed dispersion in some cases. Swain and Mosely's conclusion that the solvolysis of *t*-butyl chloride is not limiting and that gradation of mechanism continues far past *t*-butyl as structure is varied so as to make solvolysis more nearly limiting is based to a large extent on the solvolytic behavior in the series *n*-BuBr, *t*-BuCl, $(C_6H_5)_3CF$. In the view of Swain and Mosely, the unusually high rate of solvolysis of trityl fluoride in acetic acid is caused by the change in structure of the R part of RX from *t*-Bu to $(C_6H_5)_3C$. *In our view*, it is caused instead by the change of X in RX from Cl to F. Examination of $(k_{ROH}/k_{AcOH})_Y$ values for a whole group of substances supports the designation of *t*-butyl chloride solvolysis in the common solvents as limiting. The relations between Grunwald and Winstein's two-parameter, Swain, Dittmer and Kaiser's three-parameter and Swain, Mosely and Bown's four-parameter correlations of solvolysis rates are discussed and the numerical fits obtained are compared.

The three preceding papers of this series[2-4] were concerned with the correlation of the rates of solvolysis of *t*-butyl, α-phenylethyl and neophyl halides by the linear free energy relationship[5] 1.

$$\log k = \log k_0 + mY \quad (1)$$

A marked dispersion of the data into separate lines, one for each solvent pair, was noted. In this paper we examine new data for benzhydryl chloride and bromide and related data from the literature which show this dispersion to an even greater degree.

The point of view adopted in this paper is somewhat different from that of 1948.[5a] In the original *m*Y treatment,[5a] the intent was to separate the total effect of solvent change into a variable **Y**, characteristic of the solvent, and a variable *m*, characteristic solely of RX. With the limited data then available, this approach succeeded for aliphatic compounds. However, the data for α-phenylethyl and benzhydryl chloride could not be fitted to the **Y** values for the aliphatic compounds in all of the solvent pairs with a single value of *m*. This was, of course, a manifestation of dispersion[2-4,5d] of lines and was recognized as a limitation of the *m*Y relationship. It was handled by introducing a second set of **Y** values with which it was possible to correlate the data for both compounds and which was recommended for general use with α-aryl derivatives. The parameter *m* was still considered constant for any one RX.

As more data became available,[2-4,5d,6] the limitations of the original *m*Y treatment became more and more apparent, and the pattern of dispersed lines evolved. To fit the data in the next higher approximation, *m* is a function of both RX *and* of the solvent pair.[2-4,5d] Since the burden of accounting for the structural limitations of the original *m*Y treatment[5a] has thus been shifted on to *m*, there is no advantage in retaining more than one set of **Y** values. The set based on *t*-butyl chloride[5c] has therefore been used in this paper.

On the basis of the new findings, the use of sol-

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[1] Research sponsored by the Office of Ordnance Research, U. S. Army.

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[4] A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608 (1957).

[5] (a) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); (b) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951); (c) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956); (d) S. Winstein, Discussion at 13th National Organic Chemistry Symposium of the American Chemical Society, Ann Arbor, Mich., June 17, 1953.

[6] L. Wilputte-Steinert and P. J. C. Fierens, *Bull. soc. chim. Belges*, **64**, 277, 287, 299, 308 (1955).

volysis rates to detect limiting solvolysis[5a,b,7] has been re-examined, and the *m*Y correlation of solvolysis rates has been compared with other correlations recently proposed by Swain and coworkers.[8,9]

Results

Table I lists all of the first-order rate constants now available for the solvolysis of benzhydryl chloride and bromide in mixtures of water with ethanol, methanol, acetic acid, dioxane and acetone, and in mixtures of acetic and formic acids. About two-thirds of the data are new; the others duplicate previous values or are taken directly from literature sources.

TABLE I

SPECIFIC RATES OF SOLVOLYSIS[a] OF BENZHYDRYL CHLORIDE AND BROMIDE

Solvent, vol. %[b]	$10^5 k$, sec.$^{-1}$[c]		$\Delta H^{\ddagger}$, kcal./mole (25°)	$\Delta S^{\ddagger}$ e.u. (25°)
	25.0°	50.0°		
	Benzhydryl chloride[d]			
EtOH–H_2O				
100	5.41[e]	89.0	20.84[e]	−7.9[e]
95	19.2[10]			
90	48.7[f]			
80	172[10]			
MeOH–H_2O				
100	83.3	25.2[g]	19.8	−6
96.7	145[9a]			
90	374			
AcOH–HCOOH				
100[h]	0.526[i]			
100[m]	0.611	12.41	22.45	−6.9
95[h]	2.18[k]			
90[h]	7.6[k]			
85.3[h]	23.5[k]			
75[j]	300[k]			
AcOH–H_2O[v]				
0.50 M H_2O	1.434	25.4	21.41	−8.9
2.00 M H_2O	9.43	137	19.89	−10.2
4.00 M H_2O	52[k]			
Dioxane–H_2O[n]				
90	0.168[p]	2.40	19.76	−18.7
80	2.67	41.2	20.35	−11.2
70	20.4	315[q]	20.4	−7
60	128			
Me_2CO–H_2O				
90	0.460[11]	5.80[11]	18.8	−20
80	7.27[r]	113[s]	20.4	−9
70	32.0[11]			
50	1650[13]			
i-PrOH	0.57[12]			
	Benzhydryl bromide[d]			
AcOH[m,u]	1.67	31.9	22.00	−6.6
AcOH–H_2O[v]				
0.50 M H_2O	4.2	72.8	21.2	−7
2.00 M H_2O	32.6			
Dioxane–H_2O				
90	4.35			
80	56			
70	377			
Me_2CO–H_2O				
90	18[13]	201[11b]	17.8	−16
80	153[14]			
70	1200[13]			
Dioxane–EtOH[w]				
60	4.60	0.263[t]	17.93	−18.2
40	18.6	.93[t]	18.83	−12.4
20	52.5	2.24[t]	19.82	−7.0
EtOH	124	4.66[t]	20.63	−2.6

[a] Unless otherwise noted, halide analysis was employed. [b] x vol. % $A - B$ means x volumes of A plus $100 - x$ volumes of B, each at 25° before mixing. [c] The over-all average deviation of the rates which were constant was ±1.0% of k. [d] Unless otherwise noted, initial concentration 0.02–0.03 M. [e] Recalculation of data previously reported gives at 25.0°, $10^5 k = 5.63$,[15] 5.30,[17] 5.72,[16] 5.75,[10] 4.85[18]; $\Delta H^{\ddagger}$ 21.99,[15] 19.16,[10] 20.69[18]; $\Delta S^{\ddagger}$ −4.2,[15] −13.6,[10] −8.9.[18] [f] Previously reported[10] 49.3. [g] At 15.0°, reported by Benfey, Hughes and Ingold.[14] [h] Contained 0.032 M lithium acetate and/or formate, plus 0.01 M Ac_2O. [i] Calculated for 0.032 M lithium acetate from data[19] at other salt concentrations. [j] Contained 0.065 M lithium acetate and/or formate plus 0.01 M Ac_2O. [k] Initial rate constants; these rates drifted down during the runs; see Experimental section. [m] Contained 0.068 M lithium acetate plus 0.01 M Ac_2O. [n] Böhme and Schürhoff[20] report data at several temperatures in eight solvent compositions covering the range 60–95 wt. % dioxane–H_2O. [p] Initial rate constant; the rate drifted up in the course of the run; see Experimental section. [q] Average deviation ±3%, followed over the range 50–90% reaction. [r] This value is the average of data previously reported.[11,21,22] [s] Calculated from data previously reported[11,21,22] at 0.0°. [t] At 0.0°. [u] $10^5 k$ at 40.0° = 10.60. [v] Contained 0.068 M lithium acetate. [w] Acidimetric analysis employed; initial concentration of benzhydryl bromide 0.010–0.012 M.

Table I also lists the values of the thermodynamic quantities of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The solvent range covered by these data is narrower than in the case of the *t*-butyl,[3,23] α-phenylethyl[2,3] and neophyl halides,[4] because of the difficulty of determining solvolysis rates in the highly aqueous solvents. The region in which the varia-

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(22) E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

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tion of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with solvent composition had previously been found to be the most complex for other compounds[2,3,23] had, unfortunately, to be omitted.

The general level of $\Delta S^{\ddagger}$ for benzhydryl chloride in ethanol, methanol and the acetic and aqueous acetic acid solvents is -8 ± 1 e.u.; this value compares with -4 and -9 for *t*-butyl and α-phenylethyl chlorides, respectively, in the same solvents.

For benzhydryl chloride, in acetic acid–water mixtures, the increase in rate in going from anhydrous acetic acid to acetic acid 2 *M* in water involves principally a decrease in $\Delta H^{\ddagger}$, this being opposed by a much smaller decrease in the entropy term. Employing the ABC classification scheme set up in an earlier paper[23] to describe the relative contributions of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to change in rate due to solvent variation, this behavior can be described as C. In the aqueous dioxanes and acetones, the increase in rate arising from increase in water content is principally the result of a large increase in $\Delta S^{\ddagger}$, opposed by a much smaller increase in the $\Delta H^{\ddagger}$ term; this behavior is A. The trends observed with benzhydryl chloride are quite analogous to those previously found for *t*-butyl,[23] α-phenylethyl[2] and neophyl[4] chlorides over the same ranges of solvent composition.

For the four solvents for which comparison can be made, the increase in rate arising from change of leaving group from chloride to bromide is made up of an average decrease in $\Delta H^{\ddagger}$ of 0.5 ± 0.3 kcal./mole plus an average increase in $\Delta S^{\ddagger}$ of 3 ± 2 e.u. Again, these results are similar to those previously noted for the *t*-butyl,[3] α-phenylethyl[3] and neophyl[4] systems.

For benzhydryl bromide in 0–60% dioxane–ethanol, *ca.* two-thirds of the increase in rate with increasing ethanol content is contributed by increase in $\Delta S^{\ddagger}$, the remainder being furnished by decrease in $\Delta H^{\ddagger}$. For these data, which fall into the B class, $\Delta S^{\ddagger}$ is quite accurately linear in $\Delta H^{\ddagger}$. Salomaa[24] has previously reported linear relations between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ for solvolysis of several α-haloethers in dioxane–ethanol mixtures; however, in contrast with our results, his data describe an A behavior.

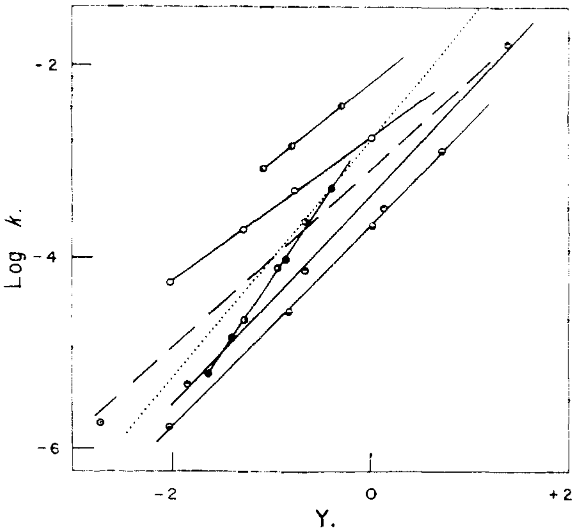

Fig. 1.—Plot of log *k* *vs.* Y for solvolysis of benzhydryl chloride at 25.0° in: EtOH-H_2O, O; MeOH-H_2O, ◐; *i*-PrOH, ⊙; dioxane-H_2O, ◒; Me_2CO-H_2O, ◓; AcOH-H_2O, ●; AcOH-HCOOH, ◑. The dashed line is the least squares line for all of the data; the dotted line is given by equation 5, based on Swain, Mosely and Bown's compound parameters.

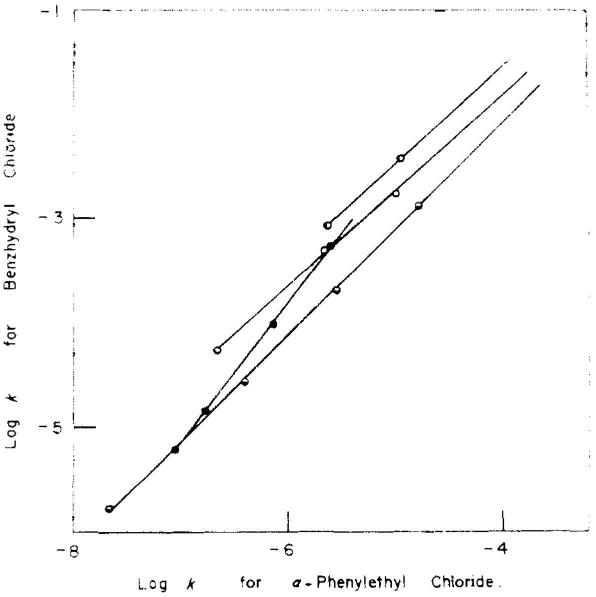

Fig. 2.—Plot of log *k* for solvolysis of benzhydryl chloride at 25.0° *vs.* log *k* for solvolysis of α-phenylethyl chloride at 25.0° in: EtOH-H_2O, O; MeOH-H_2O, ◐; dioxane-H_2O, ◒; AcOH-H_2O, ●.

mY Plots.—When the data for benzhydryl chloride at 25.0°, in 24 solvent compositions, are fitted to equation 1 by the method of least squares, values of $m = 0.927$ and $\log k_0 = -3.062$ are obtained. However, the probable error of the fit,[25] r, equal to 0.408, is very large for this whole group of solvents. The plot in Fig. 1 of log *k* for benzhydryl chloride *vs.* Y shows clearly that each solvent pair should be considered separately. Thus, the four points for dioxane-water in the 60–90 vol.% range form an excellent straight line lying below those for ethanol-water and methanol-water mixtures, while the lines for the carboxylic acid-containing mixtures start low and cut across the others with very much higher slopes. The parameters m and $\log k_0$ of equation 1, together with the probable error of the fit,[25] r, for the separate lines for each solvent pair are listed in Table II for benzhydryl chloride. With this modification of the original[5a] mY relation, the average r is now 0.02, quite satisfactory for correlative and interpolative purposes. However, for extrapolation these relations should be applied with caution if high accuracy is desired. While curvature of the lines is almost imperceptible in the ranges covered, it is obvious that at least some

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TABLE II

CORRELATION OF SOLVOLYSIS RATES WITH Y

Compound	*n*	Solvent range	Temp., °C.	*m*	log k_0[a]	*r*
$(C_6H_5)_2$ CHCl	24	All solvents	25	0.927	−3.062	0.408
	4	80–100% EtOH–H_2O	25	.740	−2.763	.002
	3	90–100% MeOH–H_2O	25	.820	−2.181	.005
	4	85–100% AcOH–HCOOH[b]	25	1.713	−2.477	.009
	4	0–4 *M* H_2O in AcOH[c]	25	1.561	−2.660	.016
	3	0–2 *M* H_2O in AcOH[c]	50	1.351	−1.697	.007
	3	50–90% Me_2CO–H_2O[f]	25	1.106	−3.332	.053
	2	80–90% Me_2CO–H_2O	50	1.09	−2.21	...
	4	60–90% Dioxane–H_2O[d]	25	1.049	−3.668	.024
	3	70–90% Dioxane–H_2O	50	1.037	−2.517	.004
$(C_6H_5)_2$CHBr	4	0–4 *M* H_2O in AcOH[c]	25	1.687	−2.017	.008
	3	0–2 *M* H_2O in AcOH[c]	50	1.448	−1.118	.006
	3	70–90% Me_2CO–H_2O	25	0.913	2.099	.085
	3	70–90% Dioxane–H_2O	25	.954	−2.442	.008
$(C_6H_5)_2$CHF[9a]	2	50–80% EtOH–H_2O	25	.98	−6.56	...
$(C_6H_5)_3$CF[9a,26,27]	2	69.5–96.7% MeOH–H_2O	25	.77	−2.84	...
	3	40–100% EtOH–H_2O	25	.890	−3.530	.044
	4	40–70% Me_2CO–H_2O[e]	25	1.58	−5.02	.13
$(C_6H_5)_3COC_6H_4NO_2$[9a]	2	40–80% EtOH–H_2O	25	0.57	−3.35	...
$(C_6H_5)_3COOCC_6H_5$[13]	2	50–60% Me_2CO–H_2O	25	.79	−4.02	...
$(C_6H_5)_3COOCCH_3$[9a]	2	69.5–96.7% MeOH–H_2O	25	.48	−2.86	...
$(C_6H_5)_3COOCCH_3$[9a]	2	60–80% EtOH–H_2O	25	.50	−3.28	...
	2	50–80% Me_2CO–H_2O	25	.83	−4.28	...
$(C_6H_5)_3$CSCN[9a]	2	69.5–96.7% MeOH–H_2O	25	.39	−2.96	...
	3	50–80% Me_2CO–H_2O	25	.261	−3.076	.010
$(C_6H_5)_3$SiF[27]	5	50–83.4% Me_2CO–H_2O	45	.468	−5.587	.038

[a] *k* in sec.$^{-1}$. [b] Containing 0.038 *M* lithium acetate and/or formate. [c] Containing 0.068 *M* lithium acetate. [d] This equation reproduces the data of Böhme and Schürhoff,[20] reported for a mole ratio of [RCl]/[H_2O] of 1/500 in 60–90 wt. % dioxane–H_2O, with a probable error $r = 0.037$. [e] Data in 80 and 85% Me_2CO–H_2O lie considerably above this line. [f] The point for 70% Me_2CO–H_2O is far out of line and was omitted in this calculation.

of the lines for the aqueous solvents must curve very considerably in the higher water region, since they must all intersect at pure water.

Although the data listed in Table I for benzhydryl bromide cover a more limited solvent range than for the chloride, they suffice to show that the plot of log *k* for the bromide *vs.* Y involves even greater dispersion than was found for the chloride. This is in line with the previous observation[3] comparing the α-phenylethyl halides. Again, treating the data for each solvent pair separately, the fits are satisfactory, as is shown in Table II.

Also listed in Table II are the values of *m* and log k_0 for a number of related compounds, including benzhydryl and triphenylsilyl fluorides and five trityl derivatives, for which suitable data are available from the literature. The data are not sufficient in most cases to test adequately the validity of equation 1 for each of the solvent pairs.[28] Nevertheless, on fitting the data to equation 1, the phenomenon of dispersion is again observed. The dispersion of the lines from each other, and of individual points for other solvent pairs from these lines is large, for trityl acetate rivaling and for trityl fluoride exceeding that shown by benzhydryl chloride in Fig. 1.

Dispersion of *m*Y Plots.—It is clear from this and preceding papers in this series that dispersion of the plots of log *k* *vs.* Y into separate lines for each binary solvent pair is a general phenomenon. There are definite structural limitations to the linear free energy relationship 1. For one thing, the structure of the R part of RX cannot be varied indiscriminately without introducing marked dispersion. Thus, it already has been noted[4] that the plot of log *k* for α-phenylethyl chloride *vs.* log *k* for *t*-butyl chloride (*i.e.*, *vs.* Y) shows much more dispersion and curvature of lines than a plot of log *k* for α-phenylethyl chloride *vs.* log *k* for neophyl chloride. In the former comparison, only one of the compounds possesses a phenyl group to delocalize charge in the transition state, while in the latter case, both compounds have a phenyl group. Thus it can be anticipated that a plot of log *k* for benzhydryl chloride *vs.* log *k* for α-phenylethyl chloride will show much less dispersion than the plot *vs.* Y; this is shown in Fig. 2. The parameters for the equations for the lines in this plot are presented in Table III.

The lines for the ethanol–, methanol– and dioxane–water mixtures can be extrapolated to yield an average value of log $k = 0.7 \pm 0.2$ for benzhydryl chloride in pure water at 25°. The probable reason for the high initial slope for the acetic acid–water line is discussed below; from Fig. 2 it would appear that this line must curve strongly downward to meet the other lines at the point for pure water.

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[26] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 246 (1953).

[27] C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, *ibid.*, **71**, 965 (1949).

[28] The lines for trityl thiocyanate in 50–80% Me_2CO–H_2O and for trityl fluoride in 40–100% EtOH–H_2O are quite good; that for trityl fluoride in aqueous acetone shows considerable positive curvature, particularly in the low water region (Table II, footnote *e*).

TABLE III

CORRELATION OF SOLVOLYSIS RATES AT 25.0° *via* THE EQUATION LOG $k_{RX} = a \log k_{R'Y} + b$

RX	RY	Solvent range	No. of points	a	b	r
$(C_6H_5)_2CHCl$	$C_6H_5CHClCH_3$	80–100% EtOH–H_2O	3	0.910	1.814	0.031
$(C_6H_5)_2CHCl$	$C_6H_5CHClCH_3$	90–100% MeOH–H_2O	2	.955	2.313	. . .
$(C_6H_5)_2CHCl$	$C_6H_5CHClCH_3$	60–90% dioxane–H_2O	4	.973	1.737	.045
$(C_6H_5)_2CHCl$	$C_6H_5CHClCH_3$	0–4 *M* H_2O in AcOH	4	1.335	4.203	.014
$(C_6H_5)_2CHBr$	$(C_6H_5)_2CHCl$	EtOH, 80% Me_2CO–H_2O,[a] 70–90% dioxane–H_2O	5	0.938	1.058	.019
		0–2 *M* H_2O in AcOH	3	1.085	0.880	.000

[a] The points for 70 and 90% Me_2CO–H_2O appear to be out of line and were omitted from this calculation.

Another structural limitation to the *m*Y relation is a leaving group specificity, the blend of solvent influences for correlation of, *e.g.*, a chloride being not quite appropriate for, *e.g.*, a bromide. This was illustrated most clearly with the neophyl halides in the preceding paper.[4] As before,[3,4] the effect of variation of leaving group can be isolated by plotting log k for benzhydryl bromide *vs.* log k for the chloride as in Fig. 3. From this plot, it is seen that the dispersion of lines for the mixtures of water with ethanol, dioxane and acetone is minor; it is the acetic acid-containing solvents that show large dispersion, bromide appearing to be too slow in rate with respect to chloride by as much as one power of ten. The parameters for the equations of these lines are listed in Table III.

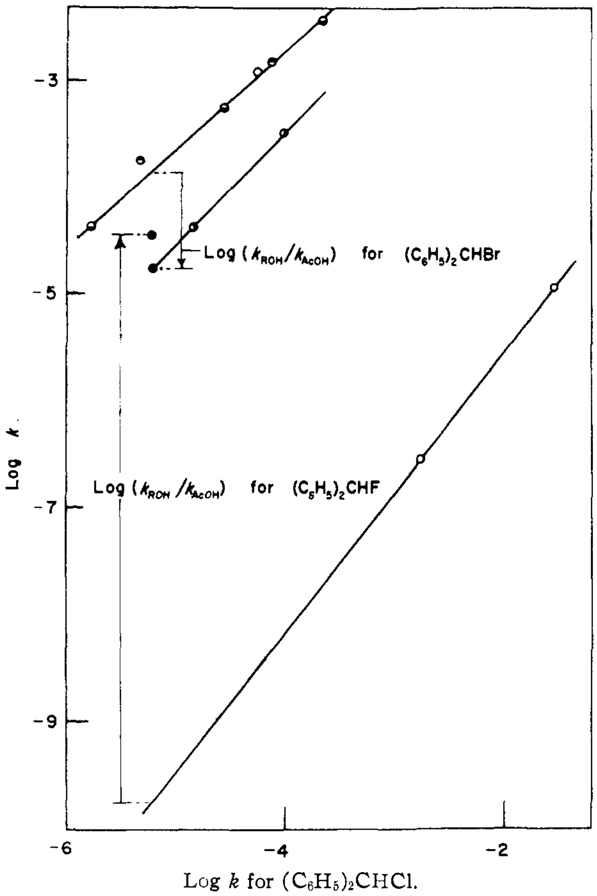

Fig. 3.—Plot of log k for benzhydryl bromide and fluoride *vs.* log k for benzhydryl chloride at 25.0° in: EtOH–H_2O, ○; dioxane–H_2O, ◒; Me_2CO–H_2O, ◓; AcOH, ●; AcOH–H_2O, ◑.

As in the case of the neophyl halides,[4] a useful measure of the effect of the leaving group specificity is the quantity log k_{ROH} − log k_{AcOH}, the vertical gap between the aqueous alcohol line and the acetic acid point in a plot of log k for bromide *vs.* log k for chloride. This is given in Table IV along with the analogous information for the *t*-butyl, α-phenylethyl and neophyl halides. For the neophyl system, data on the toluenesulfonate are available[19] and, as shown in Table IV, the sign for log k_{ROH} − log k_{AcOH} is negative instead of positive as in the case of the bromide. In other words, using chloride as standard, neophyl *p*-toluenesulfonate tends to be relatively fast in acetic acid while the bromide tends to be slow.

TABLE IV

VERTICAL GAPS, LOG k_{ROH} − LOG k_{AcOH}, IN PLOTS OF LOG k_{RX} *vs.* LOG k_{RCl}

RX	Temp., °C.	log k_{ROH} − log k_{AcOH}
Neophyl OTs[19]	50	−0.30
Neophyl Br	50	+ .45
t-Butyl Br	25	.52
α-Phenylethyl Br	25	.80
Benzhydryl F	25	−5
Benzhydryl Br	25	+0.93

The importance of the leaving group specificity is most strikingly demonstrated by the plot of log k for benzhydryl fluoride *vs.* benzhydryl chloride in Fig. 3. Benzhydryl fluoride is relatively very fast in acetic acid, log k_{ROH} − log k_{AcOH} being estimated as −5.

Previously[4] it seemed reasonable to discuss the leaving group specificity in terms of the importance of hydrogen bonding to the leaving group in the solvolysis transition state. On this basis, the data in Table IV suggest that the importance of hydrogen bonding falls off in the order F >> OTs > Cl > Br. This order is a reasonable one, the position of F in this series being in line with the well-known tendency for fluorine to hydrogen bond. Another indication of the tendency for strong interaction between fluorine and a proton donor in solvolysis is the acid catalysis observed with fluorides.[29,30]

In this connection, it is instructive to note that a large fluoride specificity is *not* evident with the *p*-

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[29] W. T. Miller, Jr., and J. Bernstein, THIS JOURNAL, **70**, 3600 (1948).

[30] N. B. Chapman and J. L. Levy, *J. Chem. Soc.*, 1677 (1952).

nitrobenzoyl system, the ratio $(k_{\mathrm{ROH}}/k_{\mathrm{AcOH}})_{\mathrm{Y}}$ for the fluoride being closely similar to that for the chloride. This is shown in Table V, which also contains other data required in subsequent sections. The data appear to indicate that carbon–halogen bond breaking is not involved in the rate-determining step, the solvolysis presumably involving an addition mechanism.[43]

TABLE V

SUMMARY OF COMPOUND PARAMETERS IN CORRELATION OF SOLVOLYSIS OF VARIOUS SUBSTANCES

Compound	Temp., °C.	c_1	c_2	m		
				EtOH–H$_2$O	AcOH–HCOOH	$(k_{\mathrm{ROH}}/k_{\mathrm{AcOH}})_{\mathrm{Y}}$
p-O$_2$NC$_6$H$_4$COF[9a]	25	1.67	0.49	0.53[a]	0.57	10,000
p-O$_2$NC$_6$H$_4$COCl[9a]	25	1.09	.21	.33	.35	13,000
MeBr[5b,33,34,35]	50	0.80	.27	.26	..	300[b]
EtOTs[5b,31,32]	50	.65	.24	.25	.42	70
EtBr[5b,33,36,37]	55	.80	.36	.34	..	80[b]
n-BuBr[33,38]	75	.77	.34	.33	..	....
C$_6$H$_5$CH$_2$OTs[5b]	25	.69	.39	.39	..	30
i-PrOBs[5a,31,40]	70	.63	.48	.40	.55	6
i-PrBr[5b,33,39,41]	50	.90	.58	.52	.56[c]	40
t-BuCl	25	(1.00)	(1.00)	(1.00)	(1.00)	(1)
t-BuBr	25	[d]	[d]	0.94	0.95	3
(CH$_3$)$_3$CCH(OBs)CH$_3$[5a,31,40]	70	0.76	0.87	.64	.72[e]	0.4
2-Br–C$_6$H$_{10}$OBs[5b]	50	.80	.87	.70	.83	1.0
Neophyl OTs[19]	50	..	..	.50	.63	0.4
Neophyl Cl[4]	50	..	..	.83	.84	0.5
Neophyl Br[4]	50	..	..	.81	.82	1.0
1-Bromobicyclo[2.2.2]octane[f]	100	.96	.99	.88	.92	0.7
C$_6$H$_5$CHClCH$_3$[2]	25	..	..	.97	1.19	5
C$_6$H$_5$CHBrCH$_3$[3]	25	..	..	.82	..	30
(C$_6$H$_5$)$_2$CHF[9a]	25	.32	1.17	.98	..	0.0002
(C$_6$H$_5$)$_2$CHCl	25	1.24	1.25	.74	1.71	20
(C$_6$H$_5$)$_2$CHBr	25	..	..	..	..	90
(C$_6$H$_5$)$_3$CF[7b]	25	0.37	1.12	0.89	..	0.0008

[a] Using the data for 40 and 100% EtOH–H$_2$O only; the point for 80% EtOH–H$_2$O appears to be far out of line. [b] $(k_{\mathrm{ROH}}/k_{\mathrm{HCOOH}})_{\mathrm{Y}}$. [c] At 100°. [d] Swain, Mosely and Bown[9a] omitted the data for t-butyl bromide from their calculations, stating "they appeared to interfere with convergence of the successive approximation procedure employed." [e] Rate in formic acid at 70.0° estimated from rate reported[31] at 25.13° by assuming $\Delta S^{\ddagger} = +1.5$ e.u.; the value found[40] for acetic acid. [f] Given by Streitwieser,[42] who calculated it from unpublished data of W. E. Doering and M. Finkelstein.

Superimposed on the dispersion arising from variations in structure discussed above is the disturbance arising from ion pair return.[44] This phenomenon, first demonstrated in the acetolysis and rearrangement of α,α-dimethylallyl chloride,[45] involves return to the covalent condition of a varying fraction of the ion pair intermediates. Where such return exists, the "titrimetric" solvolysis rate constant, k_t, is only a fraction, F, of the true ionization rate constant, k_1. In the solvolysis of *exo*-norbornyl bromide, for instance, the ionization rate, measured polarimetrically,[46] exceeds the titrimetric rate by a factor of 24 in acetic acid but only 5 in 80% ethanol. With *threo*-3-phenyl-2-butyl p-toluenesulfonate, the ionization rate exceeds the titrimetric one by a factor of 4.6 in acetolysis but only 1.2 in formolysis.[47]

Since **Y** is a measure of solvent ionizing power, equation 1 is designed to correlate rates of ionization to the first intermediate in solvolysis rather than composite titrimetric rate constants, k_t. When ion pair return is involved, k_t falls below the true ionization rate to a degree which bears no necessary relation to the ionizing power of the solvent. For example, ion pair return is serious in solvolysis of α,α-dimethylallyl chloride[45] in acetic acid, but it is absent in ethanol, a solvent with a closely similar **Y** value.

With the benzhydryl halides, there is evidence that ion pair return strongly influences the titrimetric rate. Unpublished exploratory work employing thiocyanate ion as a carbonium ion-trap in the acetolysis of benzhydryl chloride and bromide suggests that the true ionization rate of these compounds in acetic acid is at least 10 times the titrimetric solvolysis rate for the chloride and 15–20 times that for the bromide. For α-phenylethyl chloride and bromide, the corresponding factors are

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(31) S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1120 (1952).

(32) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

(33) L. C. Bateman and E. D. Hughes, *J. Chem. Soc.*, 940, 945 (1940).

(34) L. C. Bateman, K. A. Cooper, E. D. Hughes and C. K. Ingold, *ibid.*, 925 (1940).

(35) E. A. Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **A220**, 386 (1953).

(36) E. Grunwald and S. Winstein, THIS JOURNAL, **69**, 2051 (1947).

(37) I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 164, 171 (1956).

(38) M. L. Bird, E. D. Hughes and C. K. Ingold, *ibid.*, 255 (1943).

(39) E. D. Hughes, C. K. Ingold and V. G. Shapiro, *ibid.*, 225 (1936).

(40) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, THIS JOURNAL, **74**, 1113 (1952).

(41) W. S. Coburn, E. Grunwald and H. P. Marshall, *ibid.*, **75**, 5735 (1953).

(42) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(43) See reference 5c, footnote 41.

(44) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, THIS JOURNAL, **78**, 328 (1956).

(45) W. G. Young, S. Winstein and H. Goering, *ibid.*, **73**, 1958 (1951).

(46) E. Clippinger and S. Winstein, unpublished work.

(47) S. Winstein and K. C. Schreiber, THIS JOURNAL, **74**, 2165 (1952).

3 and 7. Thus, ion pair return would appear to account for part of the apparent slowness of these bromides in acetic acid when compared with the corresponding chloride. It also accounts for a part of the over-all slowness of these compounds in acetic acid relative to other solvents in which ion pair return plays a lesser role. It is significant in this connection that similar experiments with *t*-butyl chloride indicate that its titrimetric acetolysis rate is very close to, if not identical with, its rate of ionization.

The pattern of the plots of log *k* for benzhydryl chloride *vs.* Y and *vs.* log *k* for α-phenylethyl chloride in Figs. 1 and 2 is consistent with some disturbance from ion pair return. For example, the very high slopes observed for the acetic acid–water lines, as compared with those for the non-acid containing solvent mixtures, would arise from decreasing[46] ion pair return as the water content of the mixtures is increased. Furthermore, the relatively complete elimination of return at an intermediate solvent composition would be expected to give rise to the downward curvature in the acetic acid–water line that appears to be required in Fig. 2, in order for this line to intersect those for the other aqueous solvents at the point for pure water.

Limiting Solvolysis.—In the view of Swain and Mosely,[7] solvolysis of *t*-butyl chloride is not limiting, the gradation of mechanism continuing far past *t*-butyl as structure is varied to favor such solvolysis. Their conclusion is based to a large extent on the gradation in solvolytic behavior in the structural series *n*-BuBr, *t*-BuCl, $(C_6H_5)_3CF$. Trityl fluoride[7b] fails to yield a single line in an *m*Y plot and the rate in acetic acid is anomalously fast, being *ca.* 10^3 times as fast in this solvent as in aqueous alcohol with a corresponding Y value (Table V). This relatively high rate in acetic acid was in line with Swain's expectations based on the trend in the $(k_{\mathrm{ROH}}/k_{\mathrm{AcOH}})_{\mathrm{Y}}$ ratio from *n*-BuBr to *t*-BuCl (Table V) and appeared to confirm his views.

In our view, the very low value of $(k_{\mathrm{ROH}}/k_{\mathrm{AcOH}})_{\mathrm{Y}}$ for trityl fluoride compared to *t*-butyl chloride is caused primarily by the change in departing group from Cl to F rather than by the change in R from *t*-butyl to trityl. The theory that solvolysis rates of fluorides in acetic acid are relatively very fast due to specific hydrogen bonding[4] has already been explored and is consistent with the data for the benzhydryl system (Table IV). It is significant that trityl fluoride is relatively fast in acetic acid by a factor similar to that for benzhydryl fluoride (Table V). In fact, in a plot of log *k* for trityl fluoride *vs.* log *k* for benzhydryl fluoride, the point for acetic acid lies within 0.2 log unit of the ethanol–water line. On the other hand, in contrast with the fluoride, benzhydryl chloride is not relatively fast, but in fact relatively slow, in acetic acid (Table V).

In previous work, which was restricted to OTs, Cl and Br leaving groups,[5b] the approach to limiting character of solvolysis was judged from the $(k_{\mathrm{ROH}}/k_{\mathrm{AcOH}})_{\mathrm{Y}}$ ratios, which were used as measures of $(\partial \log k/\partial N)_{\mathrm{Y}}$. While the dispersion in *m*Y plots makes this ratio not as quantitative a criterion as it was formerly believed, it is still useful in a semi-quantitative fashion if one omits the fluorides. As is brought out in Table V, $(k_{\mathrm{ROH}}/k_{\mathrm{AcOH}})_{\mathrm{Y}}$ drops from *ca.* 10^4 to 1 as structure is varied in the direction of more limiting solvolysis from *p*-nitrobenzoyl chloride through methyl bromide, ethyl bromide, benzyl *p*-toluenesulfonate and isopropyl bromide to *t*-butyl chloride. The ratio is also *ca.* unity (within a very small factor) for pinacolyl, *trans*-2-bromocyclohexyl and neophyl arylsulfonates, neophyl chloride and bromide, and 1-bromobicyclo[2.2.2]octane. Since *t*-butyl chloride is no more sensitive to nucleophilic character of solvent than these compounds, with their unique structural features favoring limiting solvolysis, the indications are strong that *t*-butyl chloride solvolysis is also limiting in the usual solvents.

As brought out earlier in this paper, $(k_{\mathrm{ROH}}/k_{\mathrm{AcOH}})_{\mathrm{Y}}$ ratios increase again as structure is varied through the α-phenylethyl and benzhydryl chlorides and especially the bromides. This apparent increased sensitivity to nucleophilic character is logically ascribed, not to the ionization step in the solvolysis of these materials, but rather to ion pair return.

Swain, Mosely and Bown's Four-parameter Equation.—In principle, one could hope to correlate all solvolysis rates with one equation, including those in which there is nucleophilic participation by solvent. Such an equation[48] is 3, which is an integrated form of equation 2 employed by Winstein, Grunwald and Jones[5b] in their discussion of the contributions of nucleophilic character, *N*, and ionizing power, Y, to solvolysis rate. Thus, if the partial derivatives in equation 2 are constant at *l* and *m*, respectively, equation 2 leads to the integrated form 3.

$$\mathrm{d}\log k = \left(\frac{\partial \log k}{\partial N}\right)_{\mathbf{Y}} \mathrm{d}N + \left(\frac{\partial \log k}{\partial\, \mathbf{Y}}\right)_{N} \mathrm{d}\mathbf{Y} \quad (2)$$

$$\log\,(k/k_0) = lN + m\mathbf{Y} \quad (3)$$

$$\log\,(k/k_0) = c_1d_1 + c_2d_2 \quad (4)$$

While Winstein, Grunwald and Jones[5h] were interested in relative values of $(\partial \log k/\partial N)_{\mathrm{Y}}$, or *l*, for different substances, they employed the integrated form of equation 2 only where *lN* was regarded as either negligible (Lim.) or as relatively constant. An example of the latter is the solvolysis of *n*-butyl bromide in a series of aqueous alcohols. As a measure of $(\partial \log k/\partial N)_{\mathrm{Y}}$, there was employed the ratio $(k_{\mathrm{ROH}}/k_{\mathrm{RCOOH}})_{\mathrm{Y}}$.

Swain and co-workers[9a] have attempted recently a general correlation of solvolysis rates with the aid of the four-parameter equation 4. Formally, this is simply equation 3 with different notation for the compound and solvent parameters. However, there do exist some differences of viewpoint.

Swain stresses specific solvation of the leaving group and the reacting carbon atom, each by an individual solvent molecule in an electrophilic or nucleophilic role, respectively. The parameters d_1 and d_2 are measures of solvent nucleophilic and electrophilic character, respectively, and c_1 and c_2

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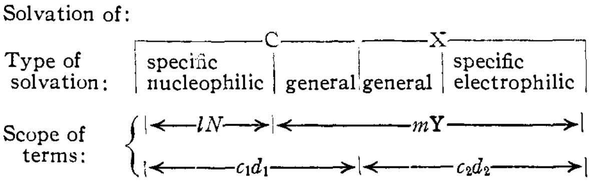
(48) In view of the structural limitations discussed above and in the previous paper,[4] it would seem that really successful fits would require more than two terms on the right-hand side of equation 3. For example, dissection[4] of the *m*Y term into two contributing terms already makes three terms necessary.

are measures of substrate sensitivity to these solvent characteristics. There apparently exists a difference in the kind of solvation meant to be accommodated by the lN and $m\mathrm{Y}$ terms, on the one hand, and the c_1d_1 and c_2d_2 terms, on the other. It is helpful to first divide solvation[49] into solvation of carbon and solvation of X and also to classify solvent functions[50] into (i) general and (ii) specific short range nucleophilic or electrophilic ones. Then the difference in intended meaning of the lN and $m\mathrm{Y}$ or the c_1d_1 and c_2d_2 terms may be depicted by the scheme.



Swain's use of the term nucleophilic character, measured by d_1, is broader than ours. We restrict the term nucleophilic to covalent solvation, according to the original more conventional usage, while Swain uses it for electrostatic as well as covalent solvation.[51]

A substantial body of solvolysis data has been processed on the basis of equation 4 by Swain, Mosely and Bown.[9a] The data covered a wide range of nucleophilic participation, either by solvent or by a neighboring group, and covered various departing groups, including F, OTs, Cl and Br. The conditions imposed were $d_1 = d_2 = 0.00$ for 80% ethanol, $c_1 = c_2 = 1.00$ for *t*-butyl chloride, $c_1/c_2 = 3.00$ for methyl bromide and $c_1/c_2 = 0.333$ for trityl fluoride. There are a number of fundamental difficulties associated with this treatment. (1) The *a priori* choice of c_1/c_2 values for methyl bromide and trityl fluoride is, in effect, an arbitrary assumption regarding the reaction mechanism for these compounds. (2) The treatment makes no allowance for ion pair return; the rate constants used in the treatment are titrimetric rate constants, k_t, whereas the rate constants which one might hope to be able to correlate are $k_1 = k_t/F$. Although F may vary from unity to small values, no provision is made for such a variation. (3) No allowance is made for leaving group specificity.[4]

Although Swain, Mosely and Bown's measures of fit of the four-parameter equation were generally satisfactory,[9a] this indication of the success of their treatment is to some extent illusory. For most of the solvents they treated, d_1 values are within the narrow range of -0.2 ± 0.2. For these solvents, the contribution of the c_1d_1 term in equation 4 tends to be negligible for many substances. In Table VI are listed some compounds for which this is true. Omitting the acetic acid or formic acid solvent, the rate constants may be fitted with the c_2d_2 term alone with a mean deviation of ± 0.25 in the log k for the 9 compounds, in contrast with ± 0.20 using both the c_2d_2 and c_1d_1 terms. The c_2d_2 term alone does essentially as well as both terms for the nucleophilic solvents for this group of compounds, which includes benzoyl chloride, *t*-butyl chloride, benzhydryl chloride and trityl fluoride. Thus, c_2d_2 is essentially equal to $m\mathrm{Y}$ in the treatment employing equation 1. In fact, the c_2 values tend to be equal to the m values of the $m\mathrm{Y}$ correlation in aqueous alcohol mixtures. Table V shows this near identity of c_2 and m values for MeBr, EtOTs, EtBr, *n*-BuBr, $C_6H_5CH_2OTs$ and *i*-PrBr. The only commonly employed solvents with significantly lower nucleophilic character are acetic and formic acids, with d_1 values of -4.6 ± 0.2. More often than not, the rate constant in only one of these solvents was available. Therefore, this one solvent often constituted the only one where the c_1d_1 term was really significant. In such cases, the d_1 value used for this solvent was essentially responsible for setting the c_1 value. Without additional solvents to cover a more substantial range of d_1 values, a good test of the four-parameter equation is not obtained.

TABLE VI

COMPARISON OF THE FITS OF SWAIN'S FOUR-PARAMETER EQUATION WITH THOSE OBTAINED EMPLOYING ONLY THE c_2d_2 TERM

Compound	No. of solvents[a]	No. of solvents omitted	Average deviation 4-parameter equation 4	Average deviation $\log(k/k_0) = c_2d_2$
C_6H_5COCl	11	1	±0.23	±0.23
p-$CH_3C_6H_4COCl$	3	1	±0.28	±0.27
2-$CH_3OC_6H_{10}OBs$	3	1	± .09	± .18
2-$BrC_6H_{10}OBs$	3	1	± .11	± .22
$(C_6H_5)_2CHCl$	7	2	± .16	± .29
$(C_6H_5)_3CSCN$	6	0	± .09	± .10
$(C_6H_5)_3COC_6H_4NO_2$	3	1	± .09	± .09
$(C_6H_5)_3CF$	6	1	± .28	± .34
t-BuCl	11	4	± .25	± .34
	Weighted average		± .20	± .25

[a] Includes all solvents except those containing carboxylic acid, for which the d_1 term is large and cannot be neglected.

Because of the fundamental difficulties associated with the treatment, the derived c_1 parameters must be regarded as completely empirical and as having no mechanistic significance as measures of substrate sensitivity to nucleophilic character of the solvent.[5d] This fact also has been pointed out by Swain, Mosely and Bown,[9a] but we wish to emphasize it by means of further examples. Thus, according to the c_1 substrate parameter, sensitivity to nucleophilic character increases in the order: MeBr = EtBr < *i*-PrBr < *t*-BuCl. Also, it increases as structure is changed from isopropyl to pinacolyl *p*-bromobenzenesulfonate. Furthermore, according to c_1 values, solvolysis of *trans*-2-bromocyclohexyl *p*-bromobenzenesulfonate, with neighboring bromine playing the close-range nucleophilic role, is just as sensitive to nucleophilic character of solvent as is the solvolysis of methyl bromide. Just as striking a discrepancy is supplied by the case of the bridgehead bromide, 1-bromobicyclo[2.2.2]octane, studied by Doering and Finkelstein.[52] Thus, according to the c_1 values, solvolysis of this substance is more sensitive to nu-

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[49] R. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 604 (1935).

[50] E. Gelles, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2918 (1954).

[51] See comment of V. J. Shiner, Jr., THIS JOURNAL, **75**, 2925 (1953), footnote 17.

[52] W. E. Doering and M. Finkelstein, unpublished work cited by Streitwieser.[41]

cleophilic character of solvent than is the solvolysis of methyl bromide.

The four-parameter equation offers little assistance with the problem of dispersion of lines which has been treated in this and preceding papers.[2–4] For the sake of illustration, the case of benzhydryl chloride will be examined more closely. For this substance, c_1 and c_2 are essentially equal,[9a] being 1.24 and 1.25, respectively (Table V). For *t*-butyl chloride, $c_1 = c_2 = 1.00$, by definition. The plot of log k for benzhydryl chloride *vs.* **Y** is therefore predicted by equation 4 to have the form 5, using an average value $c_1 = c_2 = 1.245$. Thus, one single straight line should encompass all solvent mixtures. This line is shown in Fig. 1 by a dotted line. Obviously, the observed dispersion is not anticipated.

$$\log k = \log k_0 + 1.245\mathbf{Y} \qquad (5)$$

Comparison of Numerical Fits.—In this section we compare the fit of the modified $m\mathbf{Y}$ treatment with that of the four-parameter equation and also with the "special two-parameter equation" 6 of Swain, Dittmer and Kaiser.[9b] Equation 6 was

$$\log (k/k_0)_{\mathrm{RX}} = \log (k/k_0)_{\mathrm{MeBr}} + ab \qquad (6)$$

proposed as an alternative to equation 4; a is a compound parameter and b is a solvent parameter.[53]

Swain and co-workers[9] have tested the "goodness of fit" of their equations by means of a variable, Φ, which evaluates the deviations from the equations in relation to the variation of the data. By this criterion their correlations were satisfactory for both of their equations. When the same criterion is used to evaluate the modified $m\mathbf{Y}$ treatment, the correlation is nearly perfect, Φ being close to 100%.

An alternative measure of fit is the probable error, r, which evaluates the deviations regardless of the variation of the data and discounts the adjustable parameters.[54] While Φ is more useful when one wishes to find out whether or not a given equation will correlate a set of data, the probable error is more useful, after the correlation has been demonstrated, in testing whether or not the data are being fitted within their experimental error. For the rate constants reported in this and preceding papers in this series, the probable error in log k is about 0.01. However, since data from other sources are also used, we estimate that a perfect correlation might yield a somewhat larger r, probably not exceeding 0.02.

In the initial correlation[5a,b] of solvolysis rates with the two-parameter equation 1, in which all rate constants for a given compound were fitted to a single line, 74 values of log (k/k_0) were fitted with 38 constants with a probable error of 0.06; the two worst fits were off by 0.27 and 0.13 unit in log k.

Using the same basis for comparison, Swain, Mosely and Bown[9a] correlated a much wider range of compounds and solvents with the 4-parameter equation. They fitted 146 values of log (k/k_0) with 86 constants with a probable error of 0.20; of these, 11 values were fitted to worse than 0.40 and an additional 23 to between 0.20 and 0.40 in log k. The 15 rate constants for *t*-butyl chloride were fitted with a probable error of 0.30. Ten rate constants for benzhydryl chloride were fitted with a probable error of 0.30, not much improved over the 0.40 obtained by the single $m\mathbf{Y}$ line treatment of the 24 pieces of data listed in Table I.

For the 91 values of log (k/k_0) fitted by Swain, Dittmer and Kaiser's correlation[9b] (34 parameters plus 19 values of log (k/k_0) for methyl bromide required), a value of $r = 0.20$ was obtained; 10 rates were fitted to worse than 0.40 in log k and an additional 21 to between 0.20 and 0.40.

The modified $m\mathbf{Y}$ treatment, employing separate lines for each solvent pair, applied to all of the data reported and summarized in this and preceding[2–4,5c,23] papers fits 760 values of log k with 372 constants[55] with a probable error of *ca.* 0.025 in log k. This modification of the original $m\mathbf{Y}$ relation permits inclusion of many cases of non-limiting solvolysis, even in solvent mixtures of varying nucleophilic character such as acetic acid–water. For comparison, application of Swain, Mosely and Bown's four-parameter correlation[9a] to this same set of data would have required 434 constants.

In our opinion, equations 4 and 6 may be useful for obtaining fairly rough estimates of rate constants over a rather wide range of compounds and solvents. The modified $m\mathbf{Y}$ treatment comes close to fitting data within their experimental error and is most suitable for accurate fitting over a more narrow range of compounds and solvents.

Experimental Part

Benzhydryl Chloride.—The method of Farinacci and Hammett[16] was used to prepare the benzhydryl chloride, b.p. 137° (5.0 mm.), f.p. 17.8°, f.p. depression to half frozen 0.4°, $n^{20}\mathrm{D}$ 1.5959, $n^{25}\mathrm{D}$ 1.5937; reported b.p. 146.5–147.6° (6 mm.),[16] f.p. 17.6°,[56] $n^{19.5}\mathrm{D}$ 1.5959.[57] An average of 49 solvolysis infinities gave a purity of 98.7 ± 0.4%. The material was quite stable when stored *in vacuo* in the solid state at 5°.

Benzhydryl Bromide.—Treatment of a pentane solution of benzhydrol, m.p. 65.5–66.5°, with anhydrous hydrogen bromide, as described by Courtot[58] gave benzhydryl bromide, b.p. 151–153° (5 mm.), m.p. 38.2°. Alternatively, diphenylmethane, b.p. 114° (5 mm.), f.p. 24.6–24.8°, was brominated[59] to give benzhydryl bromide, b.p. 153–156° (5 mm.), m.p. 36.2–37.4°. Recrystallization from pentane followed by distillation at 107° (0.7 mm.) raised the f.p. to 38.7°, f.p. depression to half frozen 0.4°. Other authors[58–63] have reported f.p.'s ranging from 42 to 46°.

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(53) It should be noted that equation 6 contains one more parameter than equation 1. This becomes evident when equation 1 is written in the form

$$\log (k/k_0)_{\mathrm{RX}} = m \log (k/k_0)_{\mathrm{BuCl}}$$

Inasmuch as we regard equation 1 as a two-parameter equation, we regard equation 6 as a three-parameter equation.

(54) $r = 0.6745\sqrt{\Sigma d^2/(n - f)}$, where d_i is the absolute value of the difference between the ith calculated and experimental value, n is the number of pieces of data being fitted, and f is the number of adjustable parameters employed.

(55) These include 130 values of **Y**, all of which can be calculated from the 40 parameters required for the power series for **Y** in terms of mole fraction of fast component (Table II of ref. 5c).

(56) A. Weissberger and R. Sängewald, *Z. physik. Chem.*, **B20**, 149 (1933).

(57) V. Grignard and K. Ono, *Bull. soc. chim.*, [4] **39**, 1594 (1926).

(58) C. Courtot, *Ann. chim.*, [9] **5**, 80 (1916).

(59) C. Friedel and M. Balsohn, *Bull. soc. chim.*, [2] **33**, 339 (1880).

(60) W. M. Budde and S. J. Potempa, THIS JOURNAL, **74**, 258 (1952).

(61) J. U. Nef, *Ann.*, **298**, 232 (1897).

(62) N. P. Buu-Hoï, *ibid.*, **556**, 8 (1944).

(63) O. O. Orazl and J. Meseri, *Annales assoc. quim. Argentina*, **37**, 263 (1949); *C. A.*, **44**, 5829b (1950).

An average of 39 solvolysis infinities gave a purity of 99.3 ± 0.3% for the sample employed.

Solvents.—Preparation of solvents was described in detail in an earlier paper in this series[5c]; in general, the solvents employed for the rate runs herein reported were from the same batches as those employed[5c] to determine Y.

Kinetic Measurements.—The techniques employed for the kinetic runs and halide analysis have been described previously.[5c] Some hydrolysis was found to occur in the case of the benzhydryl halides during the extraction procedure (*e.g.*, 2% hydrolysis in forty shakes of a 5-ml. aliquot of 0.032 *M* benzhydryl chloride in AcOH in 25 ml. of pentane with 10 ml. of H_2O; *ca.* 3% hydrolysis for the bromide under the same conditions). However, it was shown, for benzhydryl chloride, that if rigorous standardization[64] of the extraction procedure[5c] is adhered to, the amount of hydrolysis during extraction is proportional to the concentration of unreacted organic halide present. Under this circumstance, it can be shown that, as long as, in the calculation of the integrated rate constant, all points, and particularly the zero point, are based on the concentration of halide ion obtained *via* the extraction procedure, this hydrolysis has no effect on the magnitude of the rate constants. Thus, if *f* is the fraction of unreacted RX hydrolyzed during the extraction

$$(a - fa)/[(a - x) - f(a - x)] = a(1 - f)/[(a - x)(1 - f)] = a/(a - x)$$

and, therefore, the integrated rate constant $k = (2.303/t) \log [a/(a - x)]$ is unaffected by such hydrolysis.

TABLE VII

DRIFTS IN RATE CONSTANTS DURING SOLVOLYSIS OF BENZHYDRYL CHLORIDE AT 25°

Solvent	Change in *k* per 0.01 *M* reacn., %
90% Dioxane–H_2O	+3
100% AcOH[a]	0
95% AcOH–HCOOH[b]	−5
90% AcOH–HCOOH[b]	−8
85% AcOH–HCOOH[b]	−11
75% AcOH–HCOOH[a]	−16
4 *M* H_2O in AcOH[a]	−5

[a] Contained 0.068 *M* lithium acetate and/or formate.
[b] Contained 0.038 *M* lithium acetate and/or formate.

Experimental Results.—The new data reported in Table I were based on an average of 7 points per run followed past 50 to 80% of completion. The average deviation for all of the rates which were first order within experimental error was ±0.9% for benzhydryl chloride and ±1.0% for the bromide. For the rate runs which drifted, the entries in Table I, suitably footnoted, are the estimated initial rates. These estimates were made empirically by linear extrapolation to zero reaction of a plot of integrated rate constant *versus* percentage reaction. The magnitudes of these drifts, expressed empirically as percentage change in *k* per 0.01 *M* reaction calculated from the true zero of reaction time, are listed in Table VII. The drifts are manifestations of opposing salt effects, and they will be considered more fully in a later paper.

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(64) The extent of hydrolysis was shown to depend on the number of shakes employed in the first aqueous extraction.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

The Solvolyses of Some Tertiary Halides in Dimethylformamide and N-Methylpropionamide

BY SIDNEY D. ROSS AND MORTIMER M. LABES

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The solvolyses of *t*-butyl bromide and dimethylneopentylcarbinyl chloride have been studied in both N-methylpropionamide and dimethylformamide, and *t*-butyl chloride has been studied in the latter solvent. The results obtained are discussed in terms of current mechanisms for solvolytic reactions.

There has been considerable interest recently in dimethylformamide as a medium for organic reactions.[1] The attractive properties of dimethylformamide are its exceptional solvent power for both organic and inorganic compounds and its high polarity, as indicated by its dielectric constant of 36.71 at 25°.[2] In this latter respect, N-methylpropionamide, which has received very little attention, perhaps because it is not available commercially, is of even greater interest, since its dielectric constant at 30° is 164.3,[2] a value more than twice that of the dielectric constant of water.

Because of these highly polar characteristics, dimethylformamide and N-methylpropionamide might be expected to be particularly effective solvents for S_N1 solvolyses.[3] To explore this possibility, we have studied the rates of solvolysis of three tertiary, aliphatic halides, *t*-butyl chloride, *t*-butyl bromide and dimethylneopentylcarbinyl chloride, in these two solvents. Since the inception of this work, some results on the reaction of *t*-butyl bromide in dimethylformamide have appeared in the literature.[1d]

Experimental

Materials.—Eastman Kodak Co. White Label *t*-butyl bromide and *t*-butyl chloride were distilled from phosphorus pentoxide prior to use, b.p.'s 72–73° and 50–51°, respectively. Dimethylneopentylcarbinyl chloride was prepared by the procedure described in the literature[4]; b.p. 51.5–53° at 28 mm., $n^{20}D$ 1.4308. Eimer and Amend, C.P. sodium bromide was dried in a vacuum oven over phosphorus pentoxide for two days prior to use. Eastman Kodak Co. White Label tetraethylammonium bromide was crystallized from isopropyl alcohol and dried *in vacuo*. Tetraethylammonium nitrate was prepared by adding equivalent nitric acid to a 10% aqueous solution of tetraethylammonium hydroxide (Eastman Kodak Co.). The solution was concentrated by distillation at a water-pump vacuum, and the salt which crystallized was recrystallized two times from isopropyl alcohol and dried *in vacuo;* m.p. 280° dec.[5]

N,N-Dimethylformamide (du Pont technical grade) was

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