1.5276[18]). The average of 37 solvolysis infinity values indicated a purity of 98.7 ± 0.3%.

Solvents.—Preparation of the solvents is described in detail in a preceding paper[1a]; in general, the solvents employed for the rate runs described in this paper were from the same batches as those employed[1a] to determine **Y**.

Kinetic Measurements and Experimental Results.—The techniques employed for the kinetic runs and analyses have been described previously.[1a] The new data reported in Table I were based on an average of six points per run followed past 50–80% reaction. The observed kinetics in all cases were first order within experimental error; the overall average deviation was ±1.0% of k. The estimated probable error, r, in log k is 0.005.

LOS ANGELES 24, CALIFORNIA

---

[18] J. W. Breitenbach and A. Maschin, *Z. physik. Chem.*, **A187**, 181 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Correlation of Solvolysis Rates. VI. *t*-Butyl and α-Phenylethyl Bromides[1]

BY ARNOLD H. FAINBERG AND S. WINSTEIN

RECEIVED SEPTEMBER 21, 1956

As part of a detailed examination of the basis, scope and limitations of linear free energy relationships for the correlation of solvolysis rates, attention is now focused on effects arising from change of leaving group from chloride to bromide. To this end, rates of solvolysis of *t*-butyl and α-phenylethyl bromides have been determined in an extensive series of solvent compositions. Plots of log k_{RBr} *vs.* log k_{RCl} for both series show a strikingly similar pattern; the points for the non-carboxylic acid-containing solvent mixtures, *e.g.* mixtures of water with ethanol, methanol and dioxane, form a very good single straight line, while those for the carboxylic acid-containing solvents, *e.g.* acetic acid–water mixtures, form other lines for each binary pair, equally straight, but lying below the first. Possible reasons for the exceptionally low values for the bromide–chloride ratios of solvolysis rates in the carboxylic acid-containing solvents are discussed. The relative contributions of $\Delta(\Delta H^{\ddagger})$ and $\Delta(\Delta S^{\ddagger})$ to increase in solvolysis rate arising from the change of chloride to bromide are contrasted for the various solvent mixtures.

In the preceding paper,[2] concerned with the correlation of solvolysis rates of α-phenylethyl chloride by the linear free energy relationship[3] represented by equation 1

$$\log k = \log k_0 + m\mathbf{Y} \qquad (1)$$

a tendency toward dispersion of points into separate lines, one for each solvent pair, was noted. This illustrated one of the limitations[3] of the $m\mathbf{Y}$ relation, arising from one type of change of structure of the substrate.

In the present work, we have focused our attention on effects arising from a change of leaving group from chloride to bromide. To this end, we have measured the rates of solvolysis of *t*-butyl and α-phenylethyl bromides in a wide range of solvents.

Results.—In Tables I and II are summarized all of the available first-order rate constants for the solvolysis of these compounds in mixtures of water with ethanol, methanol, acetic acid and dioxane. In addition, for *t*-butyl bromide rate constants for acetic–formic acid and acetone–water mixtures are listed.

Most of the data in Tables I and II are new; those which are cited from the literature are suitably footnoted, as are several entries which duplicate previously reported results. The Tables also list the values of the thermodynamic quantities of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

mY Plots and Y Values.—When the data for *t*-butyl bromide at 25.0°, in 28 solvent compositions, are fitted to equation 1 by the method of least squares, values of $m = 0.924$ and $\log k_0 = -3.494$ are obtained. However, the probable error[10] of the fit, $r = 0.155$, now obtained with this large variety of solvents is considerably larger than that previously listed[3a,b] for data in five ethanol–water mixtures. Reference to the plot of log k for *t*-butyl bromide at 25° *vs.* **Y**, shown in Fig. 1, reveals that most of this error is contributed by the inclusion of the data for the solvent mixtures containing acids, acetic acid–water and acetic–formic acid mixtures. These two binary sets form excellent straight lines of their own, falling considerably below the line defined by the non-acid-containing solvent mixtures. The latter set, involving mixtures of water with ethanol, methanol, dioxane and acetone, now gives a much improved fit, r being 0.044 at 25°.

It is nevertheless true, as previously observed[2] for α-phenylethyl chloride, that there is a still further improvement in the fit when each solvent pair is taken separately. Table III lists the parameters m and log k_0 of equation 1, as well as the probable error of the fit, r, for each of these solvent groupings. The mean value of r for the five separate lines for *t*-butyl bromide corresponding to individual solvent pairs is 0.015 at 0° and 0.010 at 25°. These compare favorably with the estimated probable error of 0.01 in log k for the experimental data for the bromide, and they demonstrate that the lines are quite linear.

A further indication of the linearity of the separate lines for the data at 25° is the fact that the lines all intersect each other at very close to the same point and that this point corresponds to a value of **Y** near that of pure water.[17] These equations thus furnish a means of estimating the solvolysis rate of *t*-butyl bromide in pure water at 25.0°. These extrapolations are summarized in

---

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

[2] A. H. Fainberg and S. Winstein, THIS JOURNAL, **79**, 1597 (1957).

[3] (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).

[4] (a) M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2065 (1948); (b) E. D. Hughes, C. K. Ingold, S. Masterman and B. J. McNulty, *ibid.*, 899 (1940).

TABLE I

RATES OF SOLVOLYSIS OF t-BUTYL BROMIDE[a]

Solvent vol. %[b]	Method[c]	$10^5 k$, sec.$^{-1}$ [d]			$\Delta H^{\ddagger}$, kcal./mole (25°)	$\Delta S^{\ddagger}$, e.u. (25°)
		0.0°	25.0°	50.0°		
EtOH–H_2O						
100	X	0.0089[e]	0.440[f]	11.85[f]	24.64[f]	−0.4[f]
90	X	0.199[e]	6.62[g]	128.3	22.10	−3.5
80	X	1.19[h]	35.8[i]		21.46[i]	−2.3[i]
70	H	4.22	131.6		21.67	+1.0
60		13.1[j]	378[j]		21.17[j]	+1.4[j]
50	H	49.5	1276		20.44	+1.4
40	H	205	4170		18.92	−1.4
H_2O		2400[p]	77000[p]		21.9	+14
MeOH–H_2O						
100	X	0.0845[e]	3.44	79	23.40	−0.5
90	X	0.60[e]	19.5	370	21.9	−2
80	X		87			
70	H	11.2	314		20.97	+0.4
60	H	37.9	940		20.2	0
50	H	111.2				
40	H	282				
AcOH–HCOOH[k]						
100	X	0.0063[e]	0.302[l]	7.90[l]	24.41	−1.9
50	X		53.3			
HCOOH[m]	X		958			
AcOH–H_2O[k]						
0.50 M H_2O	X			12.8[l]		
2.00 M H_2O	X	0.0524[e]	1.98	42.6	22.91	−3.2
4.00 M H_2O	X	.190[e]	6.14	116	21.89	−4.4
8.00 M H_2O	X	.998[e]	27.6	457	20.90	−4.8
Dioxane–H_2O						
90	X	0.025[e]	0.63[l]	9.5[l]	20.2	−15
80	X		7.9[l]			
70	X		45.5			
70	H	1.82	46.2		20.36	−5.5
60	H	8.84	212		19.99	−3.7
50	H	37.1	857		19.73	−1.8
40	H	128.6	2807		19.36	−0.7
30	H	358				
Me_2CO–H_2O[n]						
83.0 mole %			0.157			
78.2 mole %		0.0126[o]	.304		20.0[o]	−17[o]
68.5 mole %		.043[o]	1.06		20.1[o]	−14[o]
58.9 mole %		.157	3.55		19.67	−12.7
49.1 mole %		.542	12.5		19.67	−10.2
39.4 mole %		1.85	42.4		19.63	−7.9

[a] Initial concentration 0.017–0.035 M where halide analysis was employed; 0.004–0.007 M where acidometric analysis was used. [b] x vol. % A − B means x volumes of A plus 100 − x volumes of B, each at 25° before mixing. [c] H = acidometric analysis; X = halide analysis. [d] The average deviation of all of the new rates herein reported that were constant was ±1.2% of k. [e] Extrapolated from the data at the other temperatures. [f] Calculation from data previously reported[4] gives for 10^5k at 25.0°, 0.451; at 50.0°, 11.2; $\Delta H^{\ddagger}$ 23.94; $\Delta S^{\ddagger}$ −2.7. [g] Previously reported[6] 7.17. [h] Previously reported at 0.1°, 1.16,[5] 1.12.[6] [i] Calculation from data previously reported gives for 10^5 k at 25°, 37.8,[6] 36.6,[6] 35.8,[7] 35.8,[8] 36.6[5]; $\Delta H^{\ddagger}$ 22.22,[6] 21.79[5]; $\Delta S^{\ddagger}$ +0.4,[6] −1.2.[5] [j] Calculated from data reported at other temperatures by Bateman, *et al.*[5] [k] Contained 0.065–0.068 M lithium salts (acetate and/or formate) plus 0.01 M Ac_2O. [l] These are initial rate constants; the rates drifted up in the course of these runs; see the Experimental section. [m] Contained 0.068 M lithium formate. [n] Calculated from data previously reported by Cropper, Spieth and Olson[9] at other temperatures. [o] These are rough estimates based on data reported[9] over a temperature interval of 5.2°. [p] Extrapolated values; see text.

---

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

(6) K. A. Cooper and E. D. Hughes, *ibid.*, 1183 (1937).

(7) O. T. Benfey, E. D. Hughes and C. K. Ingold, *ibid.*, 2494 (1952).

(8) H. C. Brown and A. Stern, THIS JOURNAL, **72**, 5068 (1950).

(9) W. H. Cropper, F. Spieth and A. R. Olson, *ibid.*, **76**, 6248 (1954).

(10) See reference 3c, footnote 13.

(11) J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1208 (1952).

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

TABLE II

RATES OF SOLVOLYSIS OF α-PHENYLETHYL BROMIDE[a]

Solvent, vol. %[b]	Method[c]	$10^5 k$, sec.$^{-1}$ [d] 0.0°	25.0°	50.0°	$\Delta H^{\ddagger}$, kcal./mole (25°)	$\Delta S^{\ddagger}$, e.u. (25°)
EtOH–H_2O						
100	X	0.0199[f]	0.628	11.62[e]	21.74	−9.4
90	X	.195[f]	4.92	75.3	20.30	−10.1
80	X	.764[f]	19.1	289	20.23	−7.7
70	H	2.27	62.0		20.81	−3.4
60	H	6.51	175		20.72	−1.6
50	H	23.1	539		19.79	−2.5
45	H	48.1	974		18.89	−4.4
40	H	110	1547		16.52	−11.4
H_2O		2600[k]	56000[k]		19.2	+5
MeOH–H_2O						
100	X	0.17[f]	5.1	90	21.5	−6
90	X	0.92[f]	22.8	344	20.2	−7.5
80	X		81			
70	H	11.31	264		19.79	−3.9
60	H	34.6	760		19.41	−3.1
50	H	98.6	1896		20.18	+1.3
AcOH[i]	X	17.0[g,h]	0.040[f]	1.05[h]	24.5	−6
AcOH–H_2O[j]						
0.500 *M* H_2O	X	0.0018[f]	0.0772	1.892	23.90	−6.3
2.00 *M* H_2O	X	.0101[f]	0.364	7.55	22.63	−7.5
4.00 *M* H_2O	X	.0417[f]	1.36	25.8	21.96	−7.1
8.00 *M* H_2O	X	.272[f]	7.5	125	20.90	−7.3
Dioxane–H_2O						
90	X	0.00297[f]	0.0734	1.104	20.16	−19.0
80	X	.038[f]	1.00	15.8	20.6	−13.
70	H	.282[f]	6.92	103	20.16	−9.9
60	H	1.44	34.6		19.97	−7.4
50	H	7.32	164		19.53	−5.8
40	H	33.3	685		18.99	−4.7
30	H	133.5	2680		18.83	−2.6

[a] Initial concentration 0.017–0.034 *M* where halide analysis was employed; 0.002–0.006 *M* where acidometric analysis was used. [b] *x* vol. % A − B means *x* volumes of A plus 100 − *x* volumes of B, each at 25.0° before mixing. [c] H = acidometric analysis; X = halide analysis. [d] The average deviation of all of the new rates reported herein that were constant was ±1.0% of *k*. [e] Extrapolation to 54.9° gives $10^5 k = 19.5$; previously reported[4] at this temperature, 19.2. [f] Extrapolated from the data at the other temperatures. [g] At 74.82°. [h] These are initial rate constants; the rates drifted up during the course of these runs; see Experimental section. [i] Contained 0.068 *M* LiOAc + 0.01 *M* Ac_2O. [j] Contained 0.068 *M* LiOAc. [k] Extrapolated value; see text.

Table IV. The five aqueous solvent pairs yield a remarkably small range of values of log *k*, −0.05 to −0.17, averaging $-0.11_5 \pm 0.02_5$ (*k* 0.77 ± 0.04 sec.$^{-1}$).

In order to make the corresponding extrapolations at 0.0°, it is necessary to calculate the least squares fits of log *k* for *t*-butyl bromide *vs.* log *k* for *t*-butyl chloride at this temperature. The parameters for these equations are listed in Table V. The values for log *k* in water for the bromide at 0.0° extrapolated with these equations are listed in Table IV; they average −1.62 ± 0.04 (*k* 0.024 ± 0.002 sec.$^{-1}$).

Turning now to the data for α-phenylethyl bromide, a plot of log *k* for this compound against **Y** shows even greater dispersion of lines corresponding to separate solvent pairs than was previously observed[2] for the chloride. Again, treating the lines separately gives fairly good fits, as can be seen in Table III. However, in exact analogy with the chloride, the lines for the ethanol-water and dioxane-water mixtures show noticeably more curvature than those for methanol-water and acetic acid-water.

Sufficient data are available for the solvolysis of *t*-butyl nitrate in ethanol-water mixtures[11] and in dioxane-water mixtures[12] to make visible dispersion of lines arising from change of leaving group from chloride to nitrate. The parameters for the equations for these lines are listed in Table III. These are also listed for *t*-amyl chloride[15–17] and *t*-amyl bromide[4a,8,13a,14] based on data from the literature.

Among the data available from the literature on rates of solvolysis of the compounds treated in Table III are several rates in solvent compositions for which **Y** values based on solvolysis rates for *t*-butyl chloride are as yet undetermined. For these cases, the equations, the parameters for which are listed in Table III, yield estimates of **Y** = −2.42 and −2.72 in 78.2 and 83.0 mole % Me_2CO-H_2O, respectively (from solvolysis data for *t*-butyl bromide[9]); **Y** = −2.97 in 95 wt. % = 79.5 mole % dioxane-water (from solvolysis data for

TABLE III

CORRELATION OF SOLVOLYSIS RATES WITH **Y**

Temp., °C.	Solvent range	No. of points	*m*	log k_0[a]	*r*
	t-Butyl bromide				
0.0	All solvents	27	1.001	−4.918	0.166
25.0	All solvents	28	0.924	−3.494	.155
0.0	All solvents except those containing acids	23	.953	−4.821	.090
25.0	All solvents except those containing acids	22	.917	−3.383	.044
0.0	40–100 vol. % $EtOH–H_2O$	7	1.017	−4.967	.028
25.0	40–100 vol. % $EtOH–H_2O$	7	0.941	−3.455	.012
0.0	40–100 vol. % $MeOH–H_2O$	6	1.010	−4.942	.018
25.0	60–100 vol. % $MeOH–H_2O$	5	0.947	−3.426	.007
25.0	0–100% AcOH–HCOOH	3	.946	−3.972	.014
0.0	0–8 *M* H_2O in AcOH	4	1.200	−5.236	.005
25.0	0–8 *M* H_2O in AcOH	4	1.067	−3.780	.012
50.0	0–8 *M* H_2O in AcOH	5	0.963	−2.537	.009
0.0	30–90 vol. % dioxane–H_2O	6	.931	−4.718	.016
25.0	40–90 vol. % dioxane–H_2O	6	.921	−3.336	.008
0.0	39–69 mole % $Me_2CO–H_2O$[b]	4	.930	−4.661	.006
5.12	20–60 mole % $Me_2CO–H_2O$[b]	5	.936	−4.359	.013
25.0	39–69 mole % $Me_2CO–H_2O$[b,g]	4	.913	−3.308	.006
	α-Phenylethyl bromide				
0.0	All solvents	25	1.123	−5.415	0.321
25.0	All solvents	26	1.031	−3.955	.294
0.0	40–100 vol. % $EtOH–H_2O$	8	0.872	−5.048	.078
25.0	40–100 vol. % $EtOH–H_2O$	8	.817	−3.642	.047
0.0	50–100 vol. % $MeOH–H_2O$	5	.873	−4.797	.025
25.0	50–100 vol. % $MeOH–H_2O$	6	.843	−3.388	.011
0.0	0–8 *M* H_2O in AcOH	5	1.375	−5.825	.007
25.0	0–8 *M* H_2O in AcOH	5	1.245	−4.364	.003
50.0	0–8 *M* H_2O in AcOH	5	1.135	−3.129	.007
0.0	30–90 vol. % dioxane–H_2O	7	1.038	−5.513	.050
25.0	30–90 vol. % dioxane–H_2O	7	1.014	−4.136	.036
	t-Butyl nitrate				
0.0	60–90 vol. % $EtOH–H_2O$[c]	2	0.938	−4.957	
25.0	60–90 vol. % $EtOH–H_2O$[c]	2	.892	−3.503	
25.0	60–85 wt. % dioxane–H_2O[d]	3	.820	−3.412	0.001
25.0	All solvents	5	.839	−3.442	.046
	t-Amyl chloride				
25.0	60–80 vol. % $EtOH–H_2O$[e]	2	0.871	−4.818	
	t-Amyl bromide				
25.0	MeOH, 80–100 vol. % $EtOH–H_2O$[f]	4	0.862	−3.233	0.026

[a] Units of *k*, sec.$^{-1}$. [b] Based on the data of Cropper, Spieth and Olson.[9] These equations yield **Y** values of −2.42 and −2.42 for 78.2 and 83.0 mole % $Me_2CO–H_2O$, respectively. [c] Based on data of Baker and Easty.[11] [d] Based on data of Lucas and Hammett.[12] This equation yields a **Y** value of −2.97 for 95 wt. % dioxane–H_2O (N_{H_2O} 0.2047). [e] Based on the average of data reported by several authors.[15–17] [f] Based on the average of data reported by several authors.[4a,8,13a,14] Assuming negligible dispersion, this equation yields **Y** values of −2.73 and −3.26 for *i*-PrOH and *t*-BuOH, respectively, based on data of Brown and Moritani.[14] [g] This equation reproduces the data of Tommila, *et al.*,[16] over the range of 10 to 38 mole % $Me_2CO–H_2O$ with an average deviation of 0.033 in log *k*. However, in the range of 50 to 85 mole % $Me_2CO–H_2O$, the data of Tommila, *et al.*,[16] are in very marked disagreement with those calculated from the data of Olson, *et al.*,[9] listed in Table I. The latter are supported by data reported by Hughes, *et al.*,[13b,c] in 90 and 95 vol. % $Me_2CO–H_2O$.

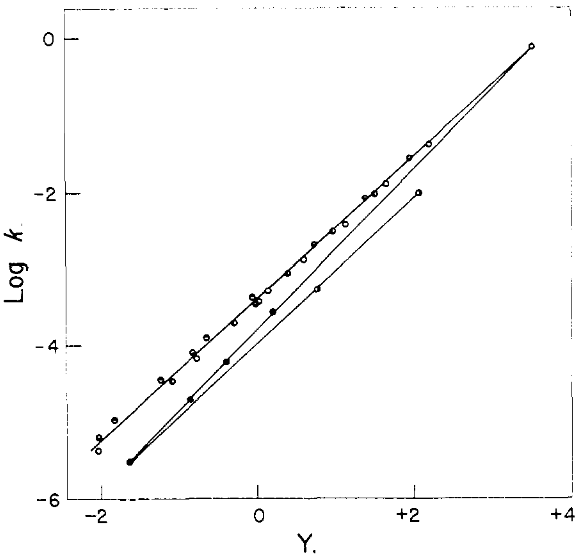


Fig. 1.—Plot of log *k*. *vs*. **Y** for solvolysis of *t*-butyl bromide at 25.0° in: $EtOH–H_2O$, ○; $MeOH–H_2O$, ◐; dioxane–H_2O, ◒; $Me_2CO–H_2O$, ◓; AcOH–HCOOH, ◑; $AcOH–H_2O$, ●.

t-butyl nitrate[12]); and **Y** = −2.73 and −3.26 for *i*-PrOH and *t*-BuOH, respectively (from solvolysis data of *t*-amyl bromide[14]).

Effect of Leaving Group.—The data for the *t*-butyl system show that, even with the structure of R in RX held constant, change in X gives dispersion of lines in the log *k* *vs*. **Y** plots. For the α-phenylethyl system, the effects due only to change in leaving group can be isolated by plotting log *k* for the bromide *vs*. log *k* for the chloride, as shown in Fig. 2. Here it is seen that the points corresponding to mixtures of water with ethanol, methanol and dioxane form an excellent single straight line, while those for the acetic acid–water mixtures form another line, equally straight, lying below the first. The latter line has the higher slope and is headed for an intersection with the first line at the point for pure water. The parameters for the equations for these lines at several temperatures are listed in Table V; the small values of *r* demonstrate the excellent linearity. As before, these equations permit the estimation of the sol-

TABLE IV

ESTIMATION OF RATE OF SOLVOLYSIS OF *t*-BUTYL AND α-PHENYLETHYL BROMIDES IN WATER

Solvent pair	log *k* (estimated)[a] at 0.0°	log *k* (estimated)[a] at 25.0°	log ($k_{25.0}/k_{0.0}$)
	t-Butyl bromide		
$EtOH–H_2O$	−1.69	−0.17	1.52
$MeOH–H_2O$	−1.63	− .12	1.51
Dioxane–H_2O	−1.61	− .12	1.49
$AcOH–H_2O$	−1.56	− .05	1.50
$Me_2CO–H_2O$		− .12	
Average	−1.62 ± 0.04	−0.115 ± 0.025	1.505 ± 0.01
	α-Phenylethyl bromide		
Aq. EtOH, MeOH, dioxane	−1.62	−0.265	−1.36
$AcOH–H_2O$	−1.53	− .230	−1.30
Average	−1.58 ± 0.04	−0.25 ± 0.02	−1.33 ± 0.03

[a] Estimated by extrapolation, employing the equations log $k_{RBr} = a \log k_{RCl} + b$, and the log k_{RCl} values.

---

(13) E. D. Hughes and B. J. McNulty, *J. Chem. Soc.*, 1283 (1937); (b) K. A. Cooper and E. D. Hughes, *ibid.*, 1183 (1937); (c) L. C. Bateman, E. D. Hughes and C. K. Ingold, *ibid.*, 960 (1940).

(14) H. C. Brown and I. Moritani, THIS JOURNAL, **76**, 455 (1954).

(15) (a) V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953); **76**, 1603 (1954); (b) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953); (c) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949); *ibid.*, **73**, 1317 (1951).

(16) E. Tommila, M. Tiilikainen and A. Voipio, *Ann. Acad. Sci. Fennicae*, **65**, 3 (1955).

(17) This is in contrast with an earlier conclusion of Cropper, Spieth and Olson.[9]

TABLE V

CORRELATION OF SOLVOLYSIS RATES OF ALKYL BROMIDES WITH CHLORIDES, *via* THE EQUATION $\log k_{RBr} = a \log k_{RCl} + b$

R	Temp.,[a] °C.	Solvent range	No. of points	a	b	r
t-Butyl[b]	0.0	Aq. EtOH, MeOH, dioxane	19	0.942	1.323	0.047
	.0	40–100% EtOH–H_2O	7	.944	1.270	.028
	.0	40–100% MeOH–H_2O	6	.945	1.338	.006
	.0	30–90% dioxane–H_2O	6	.922	1.286	.006
	.0	0–8 *M* H_2O in AcOH	4	1.067	1.791	.019
α-Phenylethyl	0.0	Aq. EtOH, MeOH, dioxane	17	0.910	0.812	.031
	25.0	Aq. EtOH, MeOH, dioxane[c]	18	.926	.957	.016
	50.0	Aq. EtOH, MeOH, dioxane[c]	16	.943	1.057	.018
	0.0	0–8 *M* H_2O in AcOH	5	1.074	1.340	.016
	25.0	0–8 *M* H_2O in AcOH	5	1.077	1.192	.013
	50.0	0–8 *M* H_2O in AcOH	5	1.081	1.067	.003

[a] For the solvolysis rates of both bromides and chlorides. [b] The corresponding parameters at 25.0° are readily calculated from the proper entries in Table III, noting that $a = m$ and $b = 5.033\ m + \log k_0$. [c] Excludes 40 vol. % EtOH–H_2O, which appears to be far out of line.

volysis rates of α-phenylethyl bromide in water at these temperatures; these extrapolations are summarized in Table IV.

Figure 2, in which α-phenylethyl bromide is compared with the chloride, shows a marked resemblance to Fig. 1 in which *t*-butyl bromide is compared with *t*-butyl chloride. In both cases, it is the acid-containing solvents which are chiefly responsible for the dispersion of lines arising from change in leaving group. This resemblance is not accidental: similar examples will be presented in subsequent papers in this series. This result can be stated in another way: the ratios of solvolysis rates for bromides to chlorides are much lower in the acid-containing solvents than in the nucleophilic solvents. These ratios are listed for the pure solvents for the *t*-butyl and α-phenylethyl systems in Table VI. The bromide–chloride ratio for the *t*-butyl system in acetic acid is hardly more than one-quarter that in ethanol, a solvent of comparable ionizing power; for the α-phenylethyl system, it is less than one-sixth.

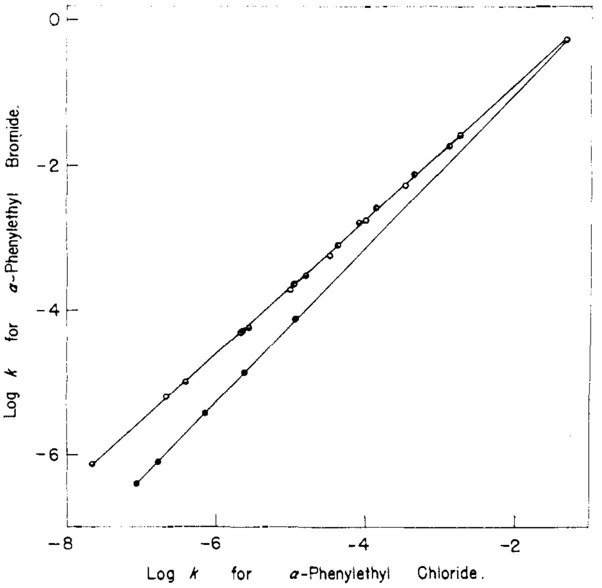


Fig. 2.—Plot of log *k* for solvolysis of α-phenylethyl bromide at 25.0° *vs.* log *k* for solvolysis of α-phenylethyl chloride at 25.0° in: EtOH–H_2O, ○; MeOH–H_2O, ◐; dioxane–H_2O, ◒; AcOH–H_2O, ●.

TABLE VI

COMPARISON OF BROMIDE WITH CHLORIDE IN PURE SOLVENTS AT 25.0°. CONTRIBUTIONS OF CHANGE IN ENTROPY AND ENTHALPY OF ACTIVATION TO CHANGE IN FREE ENERGY

Solvent	k_{RBr}/k_{RCl}	$\Delta S^{\ddagger}_{RBr}$, e.u.	$\Delta S^{\ddagger}_{RCl} - \Delta S^{\ddagger}_{RBr}$, e.u.	$-T(\Delta S^{\ddagger}_{RCl} - \Delta S^{\ddagger}_{RBr})$, kcal./mole	$\Delta H^{\ddagger}_{RCl} - \Delta H^{\ddagger}_{RBr}$, kcal./mole	$\Delta F^{\ddagger}_{RCl} - \Delta F^{\ddagger}_{RBr}$, kcal./mole
			t-Butyl			
H_2O	27	+14	−2.2	0.7	1.3	2.0
MeOH	46	−0.5	−2.6	.8	1.5	2.3
EtOH	51	− .4	−2.8	.8	1.5	2.3
AcOH	14	−1.9	−0.6	.2	1.4	1.6
			α-Phenylethyl			
H_2O	12	+5	−4.0	1.2	0.4	1.6
MeOH	23	−6	−2.8	0.8	1.0	1.8
EtOH	29	−9.4	−1.6	.5	1.5	2.0
AcOH	4.6	−6	−0.5	.15	0.75	0.9

Several possible reasons can be visualized for the low bromide–chloride ratios in acetic acid solvent:

(i) The blend of specific and general solvent influences which make up ionizing power[3] for correlation of rates of solvolysis of chlorides is not quite suitable for correlating solvolysis rates of bromides; *i.e.*, there is some specificity associated with leaving group.

(ii) The titrimetric rate constants, k_t, are not equal to the rate constants for ionization to the first intermediate, k_1, values of which are more apt to follow a simple linear free energy relationship than composite rate constants such as k_t. To the extent that ion pair return[18] diminishes the titrimetric rate from the rate of ionization to some lower value, we can expect it to be more serious in acetic acid than in the other solvents and also more serious for bromides than for chlorides. This combination would thus contribute to the dispersion observed in the plots of $\log k_{RBr}$ *vs.* $\log k_{RCl}$.

(iii) Nucleophilic character of the solvent is important to solvolysis rate of the compounds in question because their solvolysis is not limiting.[3b]

---

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

This would contribute to the dispersion observed in log k_{RBr} *vs.* k_{RCl} plots if nucleophilic character of solvent were more important for bromide than chloride.

In the next paper in this series, a bromide-chloride comparison is made for a system where bromide-chloride dispersion can be due only to (i) above.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.—In a previous paper in this series,[19] an **ABC** classification was set up to describe the relative contributions of changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to change in rate arising from variation in solvent composition. In Table VII are listed these classifications for *t*-butyl and α-phenylethyl bromides. Comparison with those previously noted for *t*-butyl[19] and α-phenylethyl[2] chlorides reveals a marked similarity in the pattern of the variation of the thermodynamic quantities of activation with solvent composition.

TABLE VII

CLASSIFICATION OF THERMODYNAMIC BEHAVIOR

Compound	Solvent range	Class
t-Butyl bromide	40–100% EtOH–H_2O	0 ^{C} 25 ^{B} 70 ^{C} 85
	60–100% MeOH–H_2O	0 ^{C} 20 ^{B} 60
	0–8 *M* H_2O in AcOH	0 ^{C} 35
	40–90% diox.–H_2O	35 ^{A} 65 ^{B} 90
	39–83 mole % Me_2CO–H_2O	20 ^{A} 30 ^{B} 60
α-Phenylethyl bromide	40–100% EtOH–H_2O	0 ^{C} 25 ^{A} 60 ^{C} 80
	50–100% MeOH–H_2O	0 ^{C} 20 ^{B} 60 ^{A} 75
	0–8 *M* H_2O in AcOH	0 ^{C} 10 ^{B} 35
	30–90% diox.–H_2O	35 ^{A} 55 ^{B} 90

For both the *t*-butyl and α-phenylethyl systems, in all of the solvent compositions examined, the increase in solvolysis rate arising from change of leaving group from chloride to bromide is made up of a decrease in $\Delta H^{\ddagger}$ plus an increase[20] in $\Delta S^{\ddagger}$, the $\Delta H^{\ddagger}$ contribution being a little larger than that of $\Delta S^{\ddagger}$. Thus, for the *t*-butyl system, on the average, $\Delta H^{\ddagger}$ for the bromide is lower by 1.2 ± 0.3 kcal./mole and $\Delta S^{\ddagger}$ is higher by 2.9 ± 1.2 e.u. than for the chloride. For the α-phenylethyl system, the corresponding comparison shows that $\Delta H^{\ddagger}$ is lower by 0.8 ± 0.4 kcal./mole and $\Delta S^{\ddagger}$ is higher by 2.5 ± 1.4 e.u.

A more detailed examination of these relative contributions reveals significant differences between those found for the carboxylic acid-containing solvents as opposed to the others. This comparison is made for the pure solvents in Table VI. These differences provide a thermodynamic basis for the dispersion of lines in the log k_{RBr} *vs.* log k_{RCl} plots. Thus, for the *t*-butyl system, the change in $\Delta H^{\ddagger}$ is quite comparable in magnitude for all four pure solvents, water, methanol, ethanol and acetic acid—*ca.* 1.4 ± 0.1 kcal./mole. However, the essential difference between acetic acid and the other solvents, the reason for the low $k_{t\text{-BuBr}}/k_{t\text{-BuCl}}$ ratio and thus for the dispersion of lines in the log $k_{t\text{-BuBr}}$ *vs.* log $k_{t\text{-BuCl}}$ plot, is clearly seen to be the greatly decreased contribution of the $\Delta(\Delta S^{\ddagger})$ term in acetic acid (0.6 e.u.) as compared with the value of 2.5 ± 0.3 e.u. for the other three solvents. One consequence of this difference is that $\Delta(\Delta H^{\ddagger})$ is *ca.* 65% of $\Delta(\Delta F^{\ddagger})$ for water, methanol and ethanol, while it is *ca.* 85% for acetic acid.

The situation for the α-phenylethyl system is somewhat more complex, in that there is considerable variation in both the magnitude and relative contributions of the changes in $\Delta H^{\ddagger}$ in the four pure solvents to change in $\Delta F^{\ddagger}$. Compensating variations in $\Delta(\Delta S^{\ddagger})$ for water, methanol and ethanol tend to bring these solvents into line with each other. However, $\Delta(\Delta S^{\ddagger})$ for acetic acid is much too small to compensate. Again, it is this factor which is principally responsible for the low k_{Br}/k_{Cl} ratio.

Experimental Part

***t*-Butyl Bromide.**—Anhydrous hydrogen bromide was passed into *t*-butyl alcohol to yield *t*-butyl bromide, b.p. 72.6–72.7° (752 mm.), $n^{20}D$ 1.4299, $n^{25}D$ 1.4265; reported[23] b.p. 73.3° (760 mm.), $n^{15}D$ 1.4306.

α-Phenylethyl Bromide.—Anhydrous hydrogen bromide was passed into α-phenylethyl alcohol, b.p. 102.5–103.0° (20 mm.), to yield α-phenylethyl bromide, b.p. 97° (20 mm.), $n^{20}D$ 1.5636, $n^{25}D$ 1.5610, reported b.p. 98–99° (20 mm.),[24] $n^{20}D$ 1.5612.[25] This material was 94.3 ± 0.7% pure, based on solvolysis infinities.

Solvents.—Preparation of the solvents was described in detail in a previous paper.[3c] In most cases, the solvents employed for the rate runs reported in this paper were from the same batches as those employed[3c] to determine **Y**.

Kinetic Measurements and Experimental Results.—The techniques employed for the kinetic runs and analyses have been described previously.[3c] The new data reported in Tables I and II were based on an average of six points over a reaction range past 50 to 80% reaction. The average deviation for all of the rate constants which were constant was ±1.2% of *k* for *t*-butyl bromide and ±1.0% of *k* for α-phenylethyl bromide. The observed kinetics were first order within experimental error for all of the solvent compositions employed except those specifically footnoted in Tables I and II. For those that drifted in the course of the runs, initial rate constants were estimated by linear extrapolation to zero reaction of plots of integrated rate constant *vs.* percentage reaction; these are the values listed in Tables

TABLE VIII

UPWARD DRIFTS IN RATE CONSTANTS DURING SOLVOLYSIS

Compound	Solvent	Temp., °C.	Increase in *k* per 0.01 *M* reaction, %
t-Butyl bromide	90% diox.–H_2O	25.0	6
	90% diox.–H_2O	50.0	4
	80% diox.–H_2O	25.0	3
	AcOH	25.0	4.3
	AcOH	50.0	4.4
	AcOH + 0.5 *M* H_2O	50.0	4
α-Phenylethyl bromide	AcOH	50.0	2
	AcOH	75.0	3

---

(19) A. H. Fainberg and S. Winstein, THIS JOURNAL, **79**, in press.

(20) Evans and Hamann[21] previously noted that the values for $\Delta S^{\ddagger}$ for several bromides were larger than those for the corresponding chlorides. They also called attention to a similar difference between the entropies of solution of the gaseous bromide and chloride ions in aqueous methanol.[22]

(21) A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 40 (1951).

(22) W. L. Latimer and C. M. Slansky, THIS JOURNAL, **62**, 2019 (1940).

(23) J. Timmermans and Y. Delcourt, *J. chim. phys.*, **31**, 100 (1934).

(24) C. L. Arcus, A. Campbell and J. Kenyon, *J. Chem. Soc.*, 1510 (1949).

(25) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560** 1 (1948).

I and II. The magnitudes of the drifts expressed in percentage change in the integrated rate constant per 0.01 mole of reaction are listed in Table VIII. These drifts appear to be salt effects and will be treated further in a subsequent paper.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

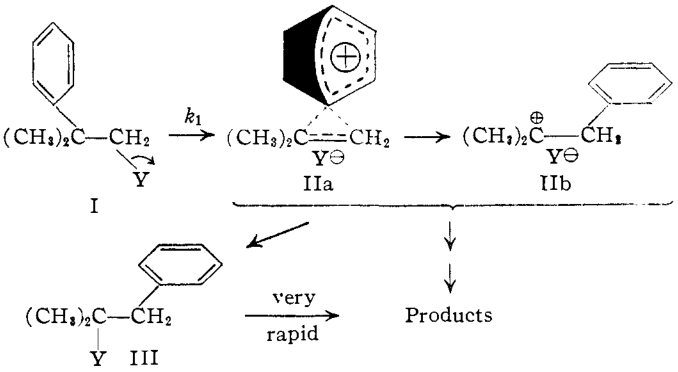
Correlation of Solvolysis Rates. VII. Neophyl Chloride and Bromide[1]

BY ARNOLD H. FAINBERG AND S. WINSTEIN

RECEIVED SEPTEMBER 21, 1956

Rates of solvolysis of neophyl chloride and bromide are reported in a variety of solvents. For the neophyl system, in which solvolysis proceeds by way of an anchimerically assisted ionization, the observed first-order titrimetric solvolysis rate constant, k_t, is equal to the ionization rate constant, k_1. Therefore, any failure of the linear free energy relationship, $\log k_{RX} = a \log k_{RY} + b$, to correlate rates of solvolysis of neophyl bromide with those of neophyl chloride must be due to genuine failure of the relationship to account for rates of ionization to the first intermediate, rather than to the fact that k_t is a composite quantity, dependent on the extent of ion-pair return. The plot of log k for neophyl bromide *vs.* log k for the chloride does, in fact, show a dispersion of the data into a pattern of lines quite analogous to that previously observed for the bromide–chloride comparison for the *t*-butyl and α-phenylethyl systems. This dispersion is ascribed to a leaving group specificity to which the principal contribution arises from specific hydrogen bonding electrophilic assistance to ionization.

In other work, it has been shown that solvolysis of neophyl derivatives I proceeds very predominantly by way of an anchimerically assisted ionization involving aryl participation.[2,3] Ion pair return[4] of cationic intermediates II to the covalent condition would give rise to very reactive tertiary derivatives III which will survive only briefly. Therefore, the observed first-order titrimetric solvolysis rate constant, k_t, measures[5] the ionization rate constant, k_1. For this reason, as in the study of salt effects,[6] neophyl derivatives are rather unique control substances for testing the scope and limitations of linear free energy relationships in the correlation of solvolysis rates. Any failure of a linear free energy relationship for the correlation of rates of solvolysis of a neophyl derivative must be due to a genuine failure of the relationship to account for rates of ionization to the first intermediate rather than to the fact that k_t is a composite quantity.



In the present paper we report and discuss the results of a study of rates of solvolysis of neophyl chloride and bromide in a variety of solvent mixtures.

Results.—In Tables I and II are summarized the first-order rate constants for the solvolysis of neophyl chloride and bromide in a large variety of solvent mixtures at several temperatures. All of the data in these tables are new; their over-all probable error is estimated to be less than 0.01 in log k or 2% in k. Also listed are the values of the thermodynamic quantities of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

Correlation of Solvolysis Rates with Y.—In Fig. 1 is plotted log k for the solvolysis of neophyl chloride *vs.* **Y**. It is clear from this plot that the data cannot be treated satisfactorily with a single line expressed by equation 1

$$\log k = \log k_0 + m\mathbf{Y} \tag{1}$$

for all solvent mixtures. However, it is also obvious that there is a strong tendency for the data for each solvent pair to form a separate line. This dispersion of the m**Y** plot into separate lines for each binary solvent mixture is similar to that previously observed for α-phenylethyl chloride.[7] Therefore, as before, the data for each solvent pair are treated separately. Table III lists the parameters m and log k_0 of equation 1, as well as the probable error of the fit, r, for each set of binary solvent mixtures for neophyl chloride. On the whole, the fits obtained by this modification of the original[8] m**Y** relation are quite satisfactory for many purposes.

A similar dispersion of a plot of log k for neophyl bromide *vs.* **Y** into lines corresponding to separate solvent pairs is obtained; these data are also treated analytically in Table III.

Bromide-Chloride Comparison.—As before,[9] effects due only to change in leaving group can be isolated by plotting log k for neophyl bromide *vs.* log k for neophyl chloride, as shown in Fig. 2 for the data at 50.0°. In this plot, the points corresponding to mixtures of water with ethanol,

---

(1) Research sponsored by the Office of Ordnance Research, U. S. Army.

(2) S. Winstein, *et al.*, THIS JOURNAL, **74**, 1113 (1952).

(3) R. Heck, unpublished work.

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

(5) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952).

(6) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956).

(7) A. H. Fainberg and S. Winstein (Paper V), *ibid.*, **79**, 1597 (1957).

(8) (a) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); (b) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(9) A. H. Fainberg and S. Winstein (Paper VI), *ibid.*, **79**, 1602 (1957).