

tion required about 1 hr., and after an additional hour at  $-40^\circ$  all the lithium appeared to have reacted. The temperature was kept at  $-40^\circ$  during the hour required for the addition, with stirring, of a solution of 24.6 g. (0.1 mole) of *p*-tolyl disulfide in 60 ml. of ether. The mixture was allowed to warm to room temperature and was filtered through cotton. The ether solution was extracted five times with 50-ml. portions of water, dried over anhydrous magnesium sulfate and the solvent removed on the steam-bath. Vacuum distillation of the 25.5-g. residue gave 9.2 g. (52%) of a fraction boiling at  $78-80^\circ$  (0.3 mm.),  $n_D^{25}$  1.5600. Truce and Simms<sup>8</sup> reported b.p.  $83-86^\circ$  (2 mm.),  $n_D^{20}$  1.5634. The infrared spectrum of our product, which is contaminated with *cis* isomer, matched most of the peaks listed by Truce and Simms.<sup>8</sup>

Oxidation of 3.0 g. of *trans*-2-*p*-tolylthio-2-butene with 30% hydrogen peroxide in acetic acid gave 2.90 g. of crystals, m.p.  $44-46^\circ$ . Recrystallization gave material identical with that obtained by treating I with base. Infrared analysis indicates that the original mixture contained 90% of *trans*- and 10% of *cis*-2-*p*-tolylsulfonyl-2-butene.

*cis*-2-*p*-Tolylthio-2-butene.—Using a procedure identical with that as above, 14 g. (0.103 mole) of *cis*-2-bromo-2-butene was converted to the lithium compound and treated with *p*-tolyl disulfide. Vacuum distillation gave 11.0 g. (62%) of crude *cis*-2-*p*-tolylthio-2-butene, b.p.  $67-69^\circ$  (0.3 mm.),  $n_D^{25}$  1.5580.

*Anal.* Calcd. for  $C_{11}H_{14}S$ : C, 74.09; H, 7.86. Found: C, 73.90; H, 7.76.

Oxidation of 3.0 g. (0.017 mole) of crude *cis*-*p*-tolylthio-2-butene with 10 ml. of 30% hydrogen peroxide in 30 ml. of acetic acid for 1 hr. at  $70-80^\circ$  was enough to eliminate the yellow color of the sulfide. The solution was poured into 100 ml. of ice-water and the resulting white crystals, collected on a filter, were washed and dried. The crude material melted at  $44-47^\circ$ , and infrared analysis showed that it consisted of 75% of *cis*- and 25% *trans*-2-*p*-tolylsulfonyl-2-butene.

*trans*- and *cis*-2-(*p*-Tolylsulfonyl)-cyclopentyl Brosylates (V and VI).—These esters were prepared from the corresponding sulfone alcohols and *p*-bromobenzenesulfonyl chloride by the method described above.

*trans*-2-(*p*-Tolylsulfonyl)-cyclopentyl *p*-bromobenzenesulfonate melted at  $130-131^\circ$ .

*Anal.* Calcd. for  $C_{13}H_{19}O_3S_2Br$ : C, 47.06, H, 4.16. Found: C, 46.69; H, 3.81.

*cis*-2-(*p*-Tolylsulfonyl)-cyclopentyl *p*-bromobenzenesulfonate melted at  $136-137^\circ$ .

*Anal.* Calcd. for  $C_{13}H_{19}O_3S_2Br$ : C, 47.06; H, 4.16. Found: C, 47.16; H, 3.94.

**Kinetic Measurements.**—Pseudo first-order rates were measured conductometrically using a large excess of trimethylamine in 50% aqueous dioxane buffered with amine salt. Second-order rate constants were obtained by plotting the observed first-order rate constants from three different dilutions of buffer stock against amine concentration. The slope of such a plot is equal to the second-order rate constant. A typical set of data is given in Table II for the reaction of V at  $50^\circ$ . The concentration of trimethylamine used in this run is 0.0222 *M*. The trimethylamine *p*-toluenesulfonate concentration was 0.0002 *M*. Using the value 3000 ohms as the infinity reading a plot of time vs.  $\log(R/R - R_\infty)$  gave a slope of  $1.09 \times 10^{-3}$ ;  $k_1 = 2.303 \times 1.09 \times 10^{-3} = 2.50 \times 10^{-3}$  sec.<sup>-1</sup>.

TABLE II

REACTION OF *trans*-2-*p*-TOLYLSULFONYLCYCLOPENTYL BROSYLATE WITH TRIMETHYLAMINE IN 50% AQUEOUS DIOXANE AT  $50^\circ$

Time, sec.	Resistance ohms	$\log \frac{R/R - R_\infty}{R_\infty}$	Time, sec.	Resistance ohms	$\log \frac{R/R - R_\infty}{R_\infty}$
34	7400	0.226	211	4800	0.426
55	6900	.248	250	4550	.468
70	6600	.264	303	4300	.520
85	6250	.284	351	4100	.572
116	5800	.316	405	3900	.638
140	5450	.347	500	3700	.723
177	5100	.384	1019	3210	.723
			$\infty$	3000	1.185

Similar runs with amine concentrations of 0.0645 and 0.0443 *M* gave  $k_1$  values of  $7.54 \times 10^{-3}$  and  $4.96 \times 10^{-3}$ , respectively. A plot of these  $k_1$  values against amine concentrations gave a straight line with a slope equal to  $1.13 \times 10^{-1}$ . The second-order constants for V at 25 and  $40^\circ$  were  $2.42 \times 10^{-2} M^{-1} \text{sec.}^{-1}$  and  $6.24 \times 10^{-2} M^{-1} \text{sec.}^{-1}$ , respectively.

A plot of the logarithm of these second-order rate constants against the reciprocal of the absolute temperature gave a line with a slope of  $2.58 \times 10^3$ ;  $E_a = 4.58 \times 2.58 \times 10^3 = 11.8$  kcal.

$$\Delta S^\ddagger = -R \left[ \ln \frac{kT}{h} - \ln k_2 - \left( \frac{E_a - RT}{RT} \right) \right] = -26.4 \text{ e. u.}$$

EVANSTON, ILLINOIS

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

## Correlation of Solvolysis Rates. V.<sup>1</sup> $\alpha$ -Phenylethyl Chloride<sup>2</sup>

BY ARNOLD H. FAINBERG AND S. WINSTEIN

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Rates of solvolysis of  $\alpha$ -phenylethyl chloride are reported for an extensive series of solvent compositions. These are employed for a detailed examination of the scope and limitations of the linear free energy relationship for the correlation of solvolysis rates,  $\log k = \log k_0 + mY$ . The data are not fit very satisfactorily by a single  $\log k$  vs. *Y* line. However, there is a strong tendency for dispersion into rather satisfactory separate lines for each binary solvent set. The linearity of these lines appears to depend in part on roughly linear relations between the enthalpy and entropy of activation of  $\alpha$ -phenylethyl chloride and the corresponding quantities for *t*-butyl chloride, respectively.

**Introduction.**—In the present article are reported the results of a study of the rates of solvolysis of  $\alpha$ -phenylethyl chloride in an extensive series of solvents to disclose more clearly the scope and

limitations of the linear free energy relationship<sup>3</sup> represented by equation 1.

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

In this equation,  $k$  and  $k_0$  are the first-order solvolysis rate constants for a certain substance,  $RX$ , in a solvent and in the standard solvent, 80%

(1) Previous papers in this series, A. H. Fainberg and S. Winstein: (a) (III) *THIS JOURNAL*, **78**, 2770 (1956); (b) (IV), in press.

(2) (a) Research sponsored by the Office of Ordnance Research, U. S. Army; (b) some of the material of this paper was presented before the 128th Meeting of the American Chemical Society at Minneapolis, Minn., Sept. 16, 1955, p. 52R, Abstracts of Papers.

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

TABLE I  
 RATES OF SOLVOLYSIS OF  $\alpha$ -PHENYLETHYL CHLORIDE<sup>a</sup>

Solvent, vol. % <sup>b</sup>	10 <sup>3</sup> <i>k</i> , sec. <sup>-1</sup> <sup>c</sup>			$\Delta H^\ddagger$ , kcal./mole (50°)	$\Delta S^\ddagger$ , e.u. (50°)
	0.0°	25.0°	50.0°		
<b>EtOH-H<sub>2</sub>O</b>					
100 <sup>d</sup>		0.0216	0.480	23.25	-11.0
90		.212	3.84	21.54	-12.2
80 <sup>e</sup>		.987	16.90	21.11	-10.6
70		3.35	56.0	20.92	-8.8
60		10.35	169	20.74	-7.2
50		34.2	486	19.7	-8
40	6.62 <sup>f</sup>	137	1770 <sup>f</sup>	19.0	-8
30	32.1 <sup>f</sup>	490 <sup>f</sup>	4900 <sup>f</sup>	17.0	-12
20		1230 <sup>f</sup>			
10		2750 <sup>f</sup>			
H <sub>2</sub> O	211.4	4800 <sup>g</sup>	67000 <sup>f</sup>	19.6	+1
<b>MeOH-H<sub>2</sub>O</b>					
100 <sup>h</sup>		0.226	4.65	22.51	-8.8
90		1.09	19.67	21.52	-9.0
80		4.29	71	20.81	-8.7
70		14.3	208	19.88	-9.4
60	1.79	44.7	678 <sup>f</sup>	20.18	-6.1
50		134			
<b>AcOH-HCOOH</b>					
100 <sup>i</sup>		0.00870	0.253 <sup>k</sup>	25.12	-6.5
75		0.560	11.2	22.3	-8
50		7.18	127	21.34	-5.9
25	1.56	47.8	860 <sup>f</sup>	21.5	-2
<b>HCOOH-H<sub>2</sub>O</b>					
100 <sup>l</sup>		223			
100	14.7 <sup>m</sup>	338 <sup>m</sup>		19.66	-3.9
50 <sup>l</sup>		957			
<b>AcOH-H<sub>2</sub>O<sup>n</sup></b>					
0.50 M H <sub>2</sub> O		0.0167	0.443	24.46	-7.4
2.00 M H <sub>2</sub> O		.0716	1.60	23.12	-9.0
4.00 M H <sub>2</sub> O		.240	4.98	22.58	-8.5
8.00 M H <sub>2</sub> O		1.135	21.1	21.73	-8.2
16.00 M H <sub>2</sub> O		8.18	136	20.88	-7.2
<b>Dioxane-H<sub>2</sub>O<sup>n</sup></b>					
90		0.00217	0.0398	21.64	-21.0
80		.0386	.757	22.14	-13.6
70		.275	5.24	21.92	-10.4
60		1.57	27.3	21.20	-9.4
50		8.22	124	20.13	-9.7
30	7.96 <sup>r</sup>	186 <sup>r</sup>	2650 <sup>f</sup>	19.78	-4.7
20	27.7 <sup>r</sup>	678 <sup>r</sup>	10100 <sup>f</sup>	20.11	-1.0
10		2050 <sup>r</sup>			
<b>Me<sub>2</sub>CO-H<sub>2</sub>O</b>					
80			9.04 <sup>s</sup>		
60			135 <sup>t</sup>		
<b><math>\mu</math>-C<sub>7</sub>F<sub>7</sub>COOH-AbOH<sup>v</sup></b>					
100		ca. 90 <sup>q</sup>			
50		ca. 0.4 <sup>q</sup>			

<sup>a</sup> Initial concentration 0.01-0.035 *M*; development of chloride ion was followed, unless otherwise indicated. <sup>b</sup> *x* vol. % A - B means *x* volumes of A plus 100 - *x* volumes of B, each at 25.0° before mixing. <sup>c</sup> The average deviation of all of the rates reported herein which were constant was  $\pm 1.0\%$  of *k*; the estimated probable error *r* in log *k* is 0.005. <sup>d</sup> Calculation from data previously reported<sup>5</sup> gives for 10<sup>3</sup>*k* at 25.0°, 0.0165; at 50.0°, 0.458;  $\Delta H^\ddagger$  24.81;  $\Delta S^\ddagger$  -6.3. <sup>e</sup> Calculation from data previously reported<sup>6</sup> gives for 10<sup>3</sup>*k* at 25.0°, 0.998; at 50.0°, 16.36;  $\Delta H^\ddagger$  21.41,  $\Delta S^\ddagger$  -11.7. <sup>f</sup> Extrapolated from the data at other temperatures. <sup>g</sup> Estimated value; see text. <sup>h</sup> Extrapolation to 70.0° gives 10<sup>3</sup>*k* = 38.0; previously reported<sup>7</sup> at this temperature, 43.5. <sup>i</sup> The AcOH and AcOH-HCOOH mixtures contained a slight excess of Ac<sub>2</sub>O (less than 0.01 *M*), as well as 0.068 *M* lithium acetate and/or formate; see ref. 1a for details. <sup>j</sup> At 74.82°, 10<sup>3</sup>*k* = 4.40. <sup>k</sup> Previously reported<sup>8</sup> for AcOH + 0.2 *M* LiOAc at 50.0°, 10<sup>3</sup>*k* = 0.322. <sup>l</sup> Contained 0.065 *M* lithium formate. <sup>m</sup> Polarimetric rates reported by Bodendorf and Böhme.<sup>9</sup> <sup>n</sup> Contained 0.068 *M* lithium acetate. <sup>o</sup> Böhme and Schürhoff<sup>10</sup> report solvolysis rate constants for  $\alpha$ -phenylethyl chloride in a number of aqueous dioxane mixtures at several temperatures. Their data are internally inconsistent, and cannot be compared satisfactorily with the data listed here. <sup>p</sup> Contained 0.068 *M* lithium acetate and/or heptafluorobutyrate. <sup>q</sup> These values are rough estimates of initial rates; in spite of a more than twofold excess of lithium salts, these runs proceeded to an equilibrium at about 50% reaction. <sup>r</sup> Initial concentration 0.001-0.005 *M*; acidometric analysis employed. <sup>s</sup> At 70.0°, data of Hughes, *et al.*<sup>7</sup> <sup>t</sup> At 67.0°, data of Hughes, *et al.*<sup>7</sup>

ethanol, respectively;  $m$  is the compound parameter measuring sensitivity of solvolysis rate to  $Y$ , the measure of ionizing power of the solvent. The latter has been set<sup>3a</sup> equal to  $\log(k/k_0)$  for  $t$ -butyl chloride at 25°,  $Y$  representing the blend of specific and general solvent influences appropriate to  $t$ -butyl chloride solvolysis. Another instructive way to write the relationship of equation 1 is in the form<sup>3a</sup> of equation 2, where  $(f_{RX}/f_{\pm})$

$$\log \left( \frac{f_{RX}}{f_{\pm}} \right)_{RX} = m \log \left( \frac{f_{RX}}{f_{\pm}} \right)_{BuCl} = mY \quad (2)$$

represents the ratio of activity coefficients of the solvolyzing molecule and the transition state, respectively, activity coefficients being unity in the standard solvent.

$\alpha$ -Phenylethyl chloride was included in an earlier<sup>3a</sup> treatment of solvolysis rates with the aid of equation 1, but data in only five solvents were involved. Even these data indicated an important limitation<sup>3</sup> of equation 1, since the  $Y$  values employed for the aqueous acetones were based on benzhydryl chloride instead of  $t$ -butyl chloride.

**Results.**—In Table I are summarized the first-order rate constants for the solvolysis of  $\alpha$ -phenylethyl chloride in mixtures of water with ethanol, methanol, formic acid, acetic acid and dioxane and in mixtures of acetic acid with formic acid and with heptafluorobutyric acid. The table comprises all of the available data which can be plotted against the  $Y$  values given in a preceding paper in this series.<sup>1a</sup> Most of the data in Table I are new; those which are cited from the literature are suitably footnoted, as are several entries which duplicate previously reported results. The table also lists values of the thermodynamic quantities of activation,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ .

**$mY$  Correlations.**—When the data in 35 solvents at 25° are fitted to equation 1 by the method of least squares, employing the  $Y$  values based on  $t$ -butyl chloride,<sup>1a</sup> the probable error of the fit,<sup>11</sup>  $r$ , is 0.190, considerably larger than previously listed<sup>3a</sup> for the data in five solvents. Even though the rates being correlated cover a range of over six powers of ten, we regard such a fit as rather unsatisfactory. When one examines the plot of  $\log k$  for  $\alpha$ -phenylethyl chloride at 25° vs.  $Y$ , shown in Fig. 1, it is immediately obvious that there is a strong tendency for the data for each solvent pair to form a separate line. This general dispersion, which we have already commented on elsewhere,<sup>12</sup> was, of course, not apparent in the previous<sup>3a</sup> correlation of rates which involved so few solvents and employed  $Y$  values for aqueous acetones based on benzhydryl chloride.<sup>13</sup>

(4) L. Wilputte-Steinert and P. J. C. Fierens, *Bull. soc. chim. Belges*, **64**, 287 (1955).

(5) G. Baddeley and J. Chadwick, *J. Chem. Soc.*, 368 (1951).

(6) A. M. Ward, *ibid.*, 445 (1927).

(7) E. D. Hughes, C. K. Ingold and A. D. Scott, *ibid.*, 1201 (1937).

(8) J. Steigman and L. P. Hammett, *THIS JOURNAL*, **59**, 2536 (1937).

(9) K. Bodendorf and H. Böhme, *Ann.*, **516**, 1 (1935).

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

(11) See ref. 1a, footnote 13.

(12) S. Winstein, Discussion at the 13th National Organic Chemistry Symposium of the American Chemical Society, Ann Arbor, Mich., June 17, 1953.

(13) The previous<sup>3a</sup> correlation involved several numerical errors

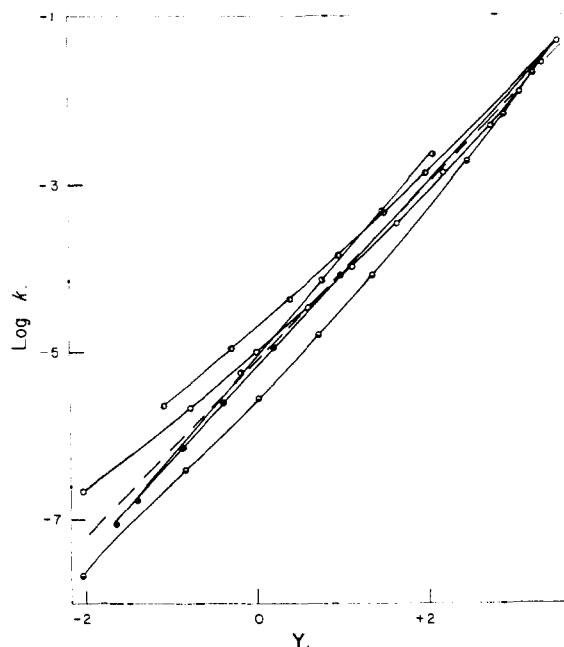


Fig. 1.—Plot of  $\log k$  for solvolysis of  $\alpha$ -phenylethyl chloride at 25.0° vs.  $Y$  in: EtOH-H<sub>2</sub>O, ○; MeOH-H<sub>2</sub>O, ●; dioxane-H<sub>2</sub>O, ◐; AcOH-H<sub>2</sub>O, ●; AcOH-HCOOH, ◑. The dashed line is the least squares line for all of the data.

Treatment of each solvent pair separately is obviously much superior from the standpoint of closeness of fit. Table II lists the parameters  $m$  and  $\log$

TABLE II  
CORRELATION OF SOLVOLYSIS RATES OF  $\alpha$ -PHENYLETHYL CHLORIDE WITH LINEAR EQUATIONS IN  $Y$

Temp., °C.	Solvent range	No. of points	$m$	$\log k_0$	$r$
25.0	10-100 vol. % EtOH-H <sub>2</sub> O	10	0.966	-4.939	0.084
50.0	30-100 vol. % EtOH-H <sub>2</sub> O	8	.856	-3.702	.056
25.0	50-100 vol. % MeOH-H <sub>2</sub> O	6	.912	-4.693	.021
50.0	60-100 vol. % MeOH-H <sub>2</sub> O	5	.831	-3.448	.023
25.0	0-16 M H <sub>2</sub> O in AcOH <sup>c</sup>	6	1.136	-5.180	.015
50.0	0-16 M H <sub>2</sub> O in AcOH <sup>a</sup>	6	1.045	-3.887	.005
25.0	0-100% AcOH-HCOOH <sup>a</sup>	5	1.194	-5.073	.024
50.0	25-100 vol. % AcOH-HCOOH <sup>a</sup>	4	1.135	-3.743	.010
25.0	10-90 vol. % dioxane-H <sub>2</sub> O	8	1.136	-5.493	.081
50.0	20-90 vol. % dioxane-H <sub>2</sub> O	7	1.088	-4.257	.067
25.0	50-100 vol. % HCOOH-H <sub>2</sub> O <sup>d</sup>	2	1.073	-4.856	
70.0	60 <sup>b</sup> -80 vol. % Me <sub>2</sub> CO-H <sub>2</sub> O <sup>e</sup>	2	0.88	-3.45	
25.0	All solvent compositions	35	1.056	-5.094	.190
50.0	All solvent compositions	29	0.974	-3.843	.200

<sup>a</sup> Solvents contain 0.065-0.068 M lithium acetate and/or formate. <sup>b</sup> Estimated at 70.0° from data at 67.0°. <sup>c</sup> Data of Hughes, *et al.*<sup>7</sup>

$k_0$  of equation 1, as well as the probable error of the fit,  $r$ , for each set of binary solvent mixtures, as well as for all of the solvent compositions taken together. Separate lines for each binary pair at 25° reduce  $r$  from 0.190 to an average value of 0.045; at 50°,  $r$  is reduced from 0.200 to an average value of 0.032. These represent a four- to six-fold improvement in the fit over that obtained by treating all solvent compositions together. Considering the wide range of rates correlated (five to six pow-

ers in the extrapolation of rate constants from 70 or 67 to 50°. The solvents involved were EtOH, MeOH, and 60 and 80 vol. % Me<sub>2</sub>CO-H<sub>2</sub>O. The correct values for these solvents are listed in Table I.

ers of ten for the ethanol-water and dioxane-water mixtures), the fits obtained by this modification of the original<sup>3a</sup>  $mY$  relation are quite satisfactory for many purposes.

A still closer scrutiny of the plots in Fig. 1 reveals that the lines for certain of the binary pairs show systematic curvature, not very marked in the case of the methanol-water and acetic acid-water mixtures but rather appreciable for the ethanol-water and dioxane-water mixtures. The curvature of plots of  $\log k$  vs.  $Y$  may be treated by the parabolic fit of the data to equation 3 as summarized in Table III. On this basis, the slope of

$$\log k = a + bY + cY^2 \quad (3)$$

$$\frac{d \log k}{dY} = b + 2cY \quad (4)$$

the  $\log k$  vs.  $Y$  plot is given by equation 4,  $b$  being the slope at  $Y = 0$ . The measure of curvature is  $c$ ,  $2c$  being the change in slope per unit change in  $Y$ . Also, the sign of  $c$  determines the direction of curvature.

TABLE III

FIT OF RATES OF SOLVOLYSIS OF  $\alpha$ -PHENYLETHYL CHLORIDE AT 25.0° TO THE QUADRATIC EQUATION 3

Solvent range	$a$	$b$	$c$	$(n-f)^a$	$r^{11}$
50-100% MeOH-H <sub>2</sub> O	-4.708	+0.883	+0.0237	3	0.006
10-100% EtOH-H <sub>2</sub> O	-5.034	.889	.0450	7	.016
10-80% dioxane-H <sub>2</sub> O <sup>b,c</sup>	-5.581	1.033	.0538	4	.013
0-16 M H <sub>2</sub> O in AcOH	-5.162	1.118	-.0251	3	.001

<sup>a</sup>  $(n-f)$  is the number of independent checks of each equation, equal to the number of pieces of data fitted ( $n$ ), minus the number of independent parameters ( $f$ ) employed in the equation, equal to 3 for the quadratic fits. <sup>b</sup> The rate constant for 90% dioxane-water calculated using this equation is 60% larger than the value experimentally observed; since this far exceeds the experimental error of the rate run, this indicates that the curve for dioxane-water inflects downward in the low water region. <sup>c</sup> This equation reproduces the data of Wilputte-Steinert and Fierens<sup>4</sup> in four dioxane-water compositions with an average deviation of 0.020 in  $\log k$ , based on  $Y$  values calculated from their nominal solvent compositions.

The plot of  $\log k$  vs.  $Y$  is most strongly curved for the dioxane-water mixtures; the data of Table III show that the slope changes from 0.94 in 80% dioxane-water to 1.41 in pure water. For the ethanol-water mixtures, the slope increases continuously from 0.71 in ethanol to 1.20 in water. For both these binary solvent pairs, the probable error of the fit of the data to equation 1 is relatively large (*ca.* 0.08). This is very much reduced by the quadratic fit, as is clear from Table III. The curvature is not nearly so serious for the methanol-water mixtures, the slope changing from 0.83 in methanol to 1.05 in water. For the acetic acid-water mixtures, the indications are that the total slope variation is within *ca.*  $\pm 0.07$  of 1.10. For this solvent mixture, the linear fit of  $\log k$  to  $Y$  is already excellent. The linear fit of the data for the acetic-formic acid mixtures is likewise excellent.

For the four binary solvent sets treated by equation 3, the average value of the probable error of the fit,  $r$ , is 0.009, not much larger than the estimated probable error in  $\log k$ , *ca.* 0.005.

On the basis of equation 3, it becomes possible to make a reasonable estimate of the solvolysis rate of  $\alpha$ -phenylethyl chloride in pure water at 25.0°.

For this purpose, the data for the dioxane-water mixtures appears to be the most dependable,<sup>14</sup> the quadratic extrapolation giving a value of  $4.8 \times 10^{-2}$  sec.<sup>-1</sup>. This compares with a value of  $4.7 \times 10^{-2}$  sec.<sup>-1</sup> recently estimated by Wilputte-Steinert and Fierens<sup>4</sup> from data at 0 and 5°.

The dispersion and curvature of lines in the  $\log k$  vs.  $Y$  plots observed in the present work must be ascribed, at least in part, to the failure of differential solvation of transition and ground state substrate molecules to be accounted for exactly by the simple linear free energy relations 1 or 2. Evidently, the change of R (in RX) from *t*-Bu to C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>), the latter with a benzene ring to delocalize charge,<sup>3a,15</sup> is not permitted for strict adherence to the original form of equation 1. As long as the data do not conform to one  $\log k$  vs.  $Y$  line, it is convenient that there is dispersion into rather satisfactory lines for each binary solvent set. This makes it possible to fit the data rather well with a linear treatment for each solvent pair.

It is interesting that dispersion of lines strictly analogous to that observed in solvolysis has been reported by Marshall and Grunwald<sup>16</sup> in fitting the effect of solvent change on acid dissociation of anilinium ions with the aid of the relation  $\log (f_B/f_{BH}) = mY_0$ , in aqueous dioxanes, aqueous ethanol and aqueous methanols.

$\Delta H^\ddagger$  and  $\Delta S^\ddagger$ .—As was previously noted for *t*-butyl chloride,<sup>1b</sup> the relative contribution of the entropy and enthalpy terms to the solvolysis rates shows remarkable changes as solvent composition is varied. For the solvent ranges 40-100% ethanol-water, 70-100% methanol-water and 0-16 M water in acetic acid, the principal contribution to increase in rate, as water content of these solvent pairs is increased, is furnished by decrease in  $\Delta H^\ddagger$ . For example  $\Delta H^\ddagger$  decreases by more than 6 kcal./mole from pure ethanol to 40% ethanol-water. For these solvent ranges,  $\Delta S^\ddagger$  remains relatively constant at a level of *ca.*  $-9 \pm 1$  e.u. However, at still higher water contents, the indications are that increase in the entropy term becomes the principal contributor to increase in rate,  $\Delta S^\ddagger$  rising to a level of *ca.*  $+1$  e.u. in pure water.

For the dioxane-water mixtures, increase in  $\Delta S^\ddagger$  is chiefly responsible for increase in rate, both in the 70-90% dioxane-water region and in the high water region past 50%, while decrease in  $\Delta H^\ddagger$  plays the chief role in the 50-70% dioxane-water region. The above changes are graphically illustrated in Fig. 2, in which  $\Delta S^\ddagger$  is plotted against  $\Delta H^\ddagger$  for several of the binary solvent mixtures.

In the previous paper in this series,<sup>1b</sup> an A B C classification was set up to describe the relative contributions of changes in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  to changes in rate. For the A designation, increase in  $\Delta S^\ddagger$  is the principal contributor to increase in

(14) This statement is based on the precision of the fit of the quadratic equation to the experimental data in the high water region. The methanol-water quadratic extrapolation gives  $4.6 \times 10^{-2}$  sec.<sup>-1</sup>, while that for ethanol-water is  $4.2 \times 10^{-2}$  sec.<sup>-1</sup>. The quadratic acetic acid-water fit appears to overcorrect when compared to the linear fit; the average value for the two extrapolations is  $4.5 \pm 1.7 \times 10^{-2}$  sec.<sup>-1</sup>.

(15) L. Wilputte-Steinert and P. J. C. Fierens, *Bull. soc. chim. Belges*, **64**, 308 (1955).

(16) H. Marshall and E. Grunwald, *This Journal*, **76**, 2000 (1954).

rate, this change being opposed by increase in  $\Delta H^\ddagger$ . For the **C** class, the exact opposite obtains, while for the **B** class, decrease in  $\Delta H^\ddagger$  and increase in  $\Delta S^\ddagger$  both act to increase rate. The range of solvent composition included in each class is designated by numerical subscripts appended to the classification symbols, these subscripts being mole per cent. of fast component. With the aid of this classification scheme, further clarified by the inset in Fig. 2, the complex behavior of the thermo-

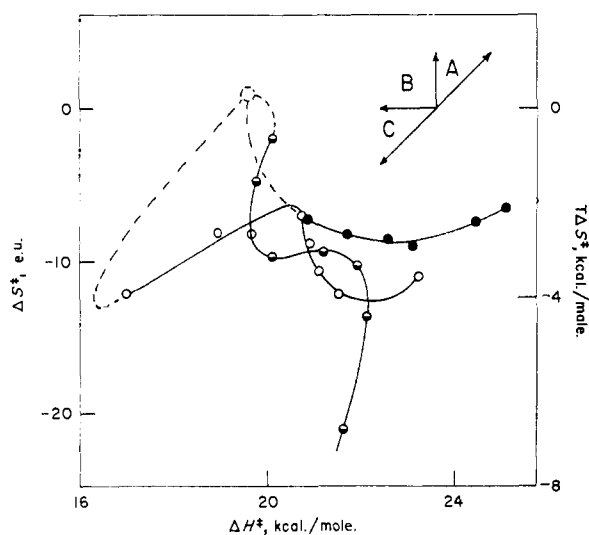


Fig. 2.—Plot of  $\Delta S^\ddagger$  vs.  $\Delta H^\ddagger$  for solvolysis of  $\alpha$ -phenylethyl chloride at 50.0°: in EtOH-H<sub>2</sub>O, O; dioxane-H<sub>2</sub>O, ◐; AcOH-H<sub>2</sub>O, ●.

dynamic quantities of activation is summarized in Table IV. These classifications for  $\alpha$ -phenylethyl chloride strongly resemble those previously found for *t*-butyl chloride.<sup>1b</sup> This resemblance is shown below to have a strong bearing on the thermodynamic basis for the success of the *mY* relation.

TABLE IV  
SUMMARY OF THE BEHAVIOR OF  $\Delta H^\ddagger$  AND  $\Delta S^\ddagger$  OF SOLVOLYSIS OF  $\alpha$ -PHENYLETHYL CHLORIDE

Solvent range	Class <sup>a</sup>	$N^b = 0$	$\frac{\Delta S^\ddagger}{N^b}$ e.u.	$N^b = 1$
40-100% EtOH-H <sub>2</sub> O	0 C 25 B 70 C 90	-11.0	+1	
60-100% MeOH-H <sub>2</sub> O	0 C 50 A 60	-8.8	+1	
0-16 M H <sub>2</sub> O in AcOH	0 C 10 B 55	-6.5	+1	
20-90% diox.-H <sub>2</sub> O	35 C 60 B 90 A 95			
25-100% AcOH-HCOOH	0 C 35 B 65 A 85			

<sup>a</sup> Subscripts denote mole per cent. of the fast component (water or formic acid). <sup>b</sup> Mole fraction of fast component.

**Thermodynamic Basis of the *mY* Relation.**—The present data support the previous<sup>1b</sup> conclusion that except for limited ranges of solvent variation, it is not a linear relation between the entropy and enthalpy of activation that is responsible for the observed successes of the linear free energy relation 1. Such a linear relation is required if equation 1 is to hold strictly at more than one temperature, **Y** being temperature independent but *m* varying with temperature. If, however, the linear free energy relationship is written in the form of equation 5, in

which  $\log k_{RX}$  is compared with  $\log k_{t\text{-BuCl}}$  at the

$$\log k_{RX} = m \log k_{t\text{-BuCl}} + \log k_0 \quad (5)$$

same temperature, there is no necessary relation between  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  for a given compound. However, one way<sup>2b</sup> in which 5 can hold rigorously at more than one temperature is for equations 6 and 7

$$\Delta H^\ddagger_{RX} = m\Delta H^\ddagger_{t\text{-BuCl}} + c \quad (6)$$

$$\Delta S^\ddagger_{RX} = m\Delta S^\ddagger_{t\text{-BuCl}} + c' \quad (7)$$

to be satisfied. These equations require that  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for **RX** each be linear in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for *t*-butyl chloride, both slopes being equal to the *m* of equation 5. It should be noted that in this treatment, *m* is treated as temperature independent, instead of **Y** previously.

The data for  $\alpha$ -phenylethyl and *t*-butyl<sup>1b</sup> chlorides indicate a certain amount of success for equations 6 and 7 in accounting roughly for the success of the linear free energy relations. As illustrated in Fig. 3, a plot of  $\Delta S^\ddagger$  for the solvolysis of

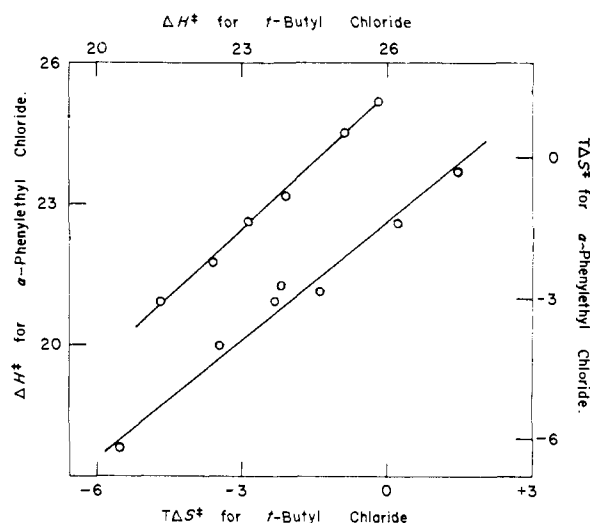


Fig. 3.—Plot of the thermodynamic quantities of activation for  $\alpha$ -phenylethyl vs. *t*-butyl chloride; upper curve,  $\Delta H^\ddagger$  for AcOH-H<sub>2</sub>O; lower curve,  $T\Delta S^\ddagger$  for dioxane-H<sub>2</sub>O.

$\alpha$ -phenylethyl chloride in dioxane-water mixtures is fairly linear in  $\Delta S^\ddagger$  for *t*-butyl chloride for the same solvents. The slope of this plot is 0.84, while that of the linear free energy correlation is 1.14. For this solvent pair, the  $\Delta H^\ddagger$  vs.  $\Delta H^\ddagger$  plot is much less significant, since change in  $\Delta H^\ddagger$  is a relatively negligible contributor to change in  $\Delta F^\ddagger$ . On the other hand, for the acetic acid-water mixtures, for which  $\Delta S^\ddagger$  is relatively constant over the explored range of solvent composition, it is more pertinent to look at  $\Delta H^\ddagger$  for  $\alpha$ -phenylethyl chloride vs.  $\Delta H^\ddagger$  for *t*-butyl chloride. As shown in Fig. 3, the plot is quite linear, with a slope of 0.96; this compares with 1.14 for the linear free energy correlation.

### Experimental Part

**$\alpha$ -Phenylethyl Chloride.**—The material employed had the following physical properties: b.p. 82.0° (20 mm.).  $n_D^{20}$  1.5277,  $n_D^{25}$  1.5250 [reported b.p. 83-84° (19 mm.),<sup>17</sup>  $n_D^{20}$

(17) D. R. Read and W. Taylor, *J. Chem. Soc.*, 681 (1940).

1.5276<sup>18</sup>). The average of 37 solvolysis infinity values indicated a purity of  $98.7 \pm 0.3\%$ .

**Solvents.**—Preparation of the solvents is described in detail in a preceding paper<sup>18</sup>; in general, the solvents employed for the rate runs described in this paper were from the same batches as those employed<sup>18</sup> to determine **Y**.

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

**Kinetic Measurements and Experimental Results.**—The techniques employed for the kinetic runs and analyses have been described previously.<sup>1a</sup> 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  $\pm 1.0\%$  of  $k$ . The estimated probable error,  $r$ , in  $\log k$  is 0.005.

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

## Correlation of Solvolysis Rates. VI. *t*-Butyl and $\alpha$ -Phenylethyl Bromides<sup>1</sup>

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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  $\alpha$ -phenylethyl bromides have been determined in an extensive series of solvent compositions. Plots of  $\log k_{\text{RBr}}$  vs.  $\log k_{\text{RC1}}$  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,<sup>2</sup> concerned with the correlation of solvolysis rates of  $\alpha$ -phenylethyl chloride by the linear free energy relationship<sup>3</sup> represented by equation 1

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

a tendency toward dispersion of points into separate lines, one for each solvent pair, was noted. This illustrated one of the limitations<sup>3</sup> of the  $mY$  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  $\alpha$ -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  $m = 0.024$  and  $\log k_0 = -3.494$

are obtained. However, the probable error<sup>10</sup> of the fit,  $r = 0.155$ , now obtained with this large variety of solvents is considerably larger than that previously listed<sup>3a,b</sup> 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<sup>2</sup> for  $\alpha$ -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.<sup>17</sup> 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, F. 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).