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.

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[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.

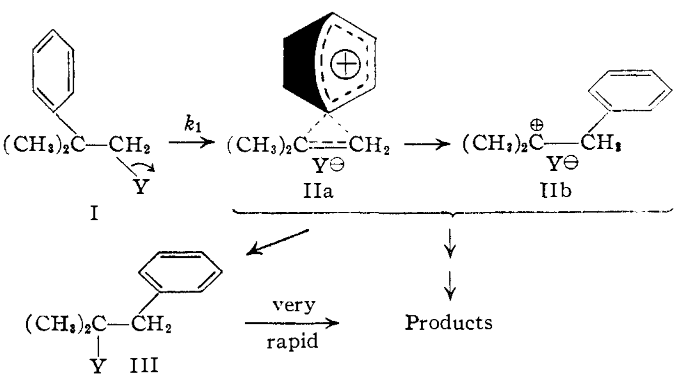
In the present paper we report and discuss the results of a study of rates of solvolysis of neophyl chloride and bromide in a variety of solvent mixtures.

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

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

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,

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[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).

TABLE I

RATES OF SOLVOLYSIS OF NEOPHYL CHLORIDE[a]

Solvent, vol. %[b]	$10^5 k$, sec.$^{-1}$ [c] 50.0°	75.0°	100.0°	$\Delta H^{\ddagger}$, kcal./mole (50°)	$\Delta S^{\ddagger}$, e.u. (50°)
EtOH-H_2O					
80	0.00035[d]	0.0068[e]	0.09[e]	26.0	−17
60	.00231	.0467		26.22	−12.5
50	.00592	.111		25.52	−12.8
40	.0171[f]	.278[f]		24.29	−14.5
30	.0529[g]	.745[g]		23.01	−16.2
20	.129[g,h]	1.78[g,h]		22.8	−15
MeOH-H_2O					
80	0.0011[d]	0.020[e]	0.245[e]	25.2	−17
70	.00255	.0491		25.79	−13.6
60	.00669	.1170		24.95	−14.3
50	.0170[f]	.272[f]		24.18	−14.8
40	.0394[f]	.585[f]		24.1	−13.5
30	.076[g,h]	1.27[g]		24.5	−11
AcOH-HCOOH					
100[i]	0.000047[d]	0.00136	0.0250	29.4	−10
75[j]	.00090[d]	.0201	0.296	27.12	−11.6
50[j]	.00509	.1079		26.65	− 9.6
25[j]	.01950	.382		25.95	− 9.1
HCOOH[k]	.0604	1.095		25.25	− 9.0
AcOH-H_2O[m]					
4.00 M H_2O	0.00039[d]	0.00869	0.127	27.05	−13.4
8.00 M H_2O	.00114[d]	.0228	0.306	26.17	−14.0
16.00 M H_2O	.00393	.0780		26.08	−11.9
50 vol. %	.0192	.335		24.93	−12.3
Dioxane-H_2O					
70	0.000124[d]	0.00278[n]	0.0411	27.2	−15
60	.00045	.01037		27.5	−12
50		.0363			
20	.065[n]	1.02[h]		24.5	−11
Me_2CO-H_2O					
75			0.0256[n]		
50		0.036[n]			

[a] Unless otherwise noted, initial concentration 0.03–0.04 M, with halide analysis being employed. [b] x vol. % A − B means x volumes of A plus 100 − x volumes of B, each at 25.0° before mixing. [c] Unless otherwise indicated, the overall average deviation was ±0.7% of k. [d] Extrapolated from the data at the other temperatures. [e] Initial rate constants; these rates drifted down in the course of the runs because of loss of hydrogen chloride by reaction with solvent. [f] Initial concentration 0.005–0.009 M. [g] Initial concentration 0.001–0.002 M; acidometric analysis used. [h] Average deviation ±4–5% of k. [i] Contained 0.068 M lithium acetate plus 0.01 M Ac_2O. [j] Contained 0.065 M lithium acetate and/or formate plus 0.01 M Ac_2O. [k] Contained 0.068 M lithium formate. [m] Contained 0.068 M lithium acetate. [n] Average deviation ±2–3% of k.

methanol and dioxane coalesce to form an excellent single straight line. The points for the acetic-formic acid mixtures form another line, equally straight, lying *ca.* 0.45 log unit below the first and almost exactly parallel with it.

The data for the acetic acid–water mixtures define a third straight line, lying below the first, but of higher slope, and headed for an intersection with it at the point for pure water. The parameters for the linear equations for these lines are listed in

$$\log k_{\mathrm{RX}} = a \log k_{\mathrm{R'Y}} + b \qquad (2)$$

The pattern of the observed dispersion is almost identical with those previously noted[9] for the bromide–chloride plots for the *t*-butyl and α-phenylethyl systems. Again, it is the carboxylic acid-containing solvents which are responsible for the dispersion.

Hydrogen Bonding Electrophilic Assistance to Ionization.—Considering reasons for the observed dispersion in the neophyl bromide–chloride plot, it is clear that it cannot be connected with ion pair return. We ascribe the dispersion to a leaving group specificity, the blend of specific and general solvent influences which make up ionizing power[8] for correlation of rates of solvolysis of a chloride being not quite suitable for a bromide. One probable difference between a bromide and a chloride is connected with the importance of hydrogen bonding to the leaving group in the solvolysis transition state. In fact, hydrogen bond considerations do predict qualitatively the observed dispersion pattern.

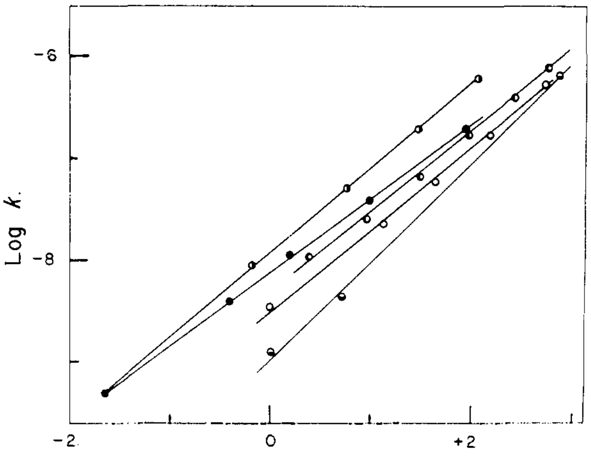

Fig. 1.—Plot of log k *vs.* Y for solvolysis of neophyl chloride at 50.0° in: EtOH-H_2O, ○; MeOH-H_2O, ◐; dioxane-H_2O, ◒; AcOH-H_2O, ●; AcOH-HCOOH, ◑.

Considering the contribution of specific hydrogen bonding electrophilic assistance to ionization, one would expect this to be more important in the carboxylic acid solvents than the aqueous alcohols. This statement is based on the known dependence

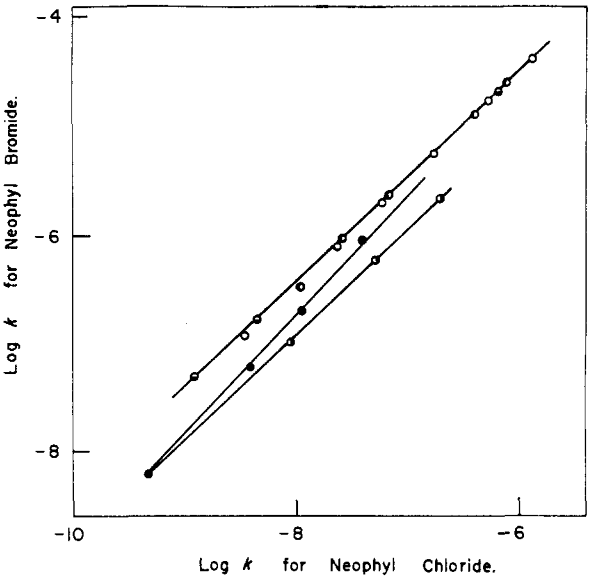

Fig. 2.—Plot of log k for solvolysis of neophyl bromide at 50.0° *vs.* log k for solvolysis of neophyl chloride at 50.0° in: EtOH-H_2O, ○; MeOH-H_2O, ◐; dioxane-H_2O, ◒; AcOH-H_2O, ●; AcOH-HCOOH, ◑.

TABLE II

RATES OF SOLVOLYSIS OF NEOPHYL BROMIDE[a]

Solvent, vol. %^{b}	$10^5 k$, sec.$^{-1}$ ^{c}		$\Delta H^{\ddagger}$, kcal./mole (50°)	$\Delta S^{\ddagger}$, e.u. (50°)
	50.0°	75.0°		
EtOH–H_2O				
90	0.0028	0.0608	26.8	−10
80	.0120	0.224	25.52	−11.4
60	.0794	1.357	24.74	−10.0
50	.2003	3.13	23.94	−10.7
40	.552^{f}	7.59^{f}	22.79	−12.2
30	1.73^{e}	19.7^{e}	21.10	−15.2
20	4.14^{d,e}	47.2^{d,e}	21.12	−13.4
H_2O		156^{d,e}		
MeOH–H_2O				
90	0.0101^{g}	0.21^{g}	26.5	− 8.7
80	.0333	0.600	25.21	−10.3
70	.0945	1.544	24.35	−10.9
60	.239	3.57	23.55	−11.5
50	.571^{e}	7.90^{e}	22.85	−12.0
40	1.27^{e}	17.0^{e}	22.54	−11.3
30	2.50^{e}	30.8^{d,e}	21.82	−12.2
AcOH–HCOOH				
100^{j}	0.00062^{k,i,p}	0.0157^{p}	28.3	− 9
75^{k}	.01304	0.213^{d}	26.4	− 9
50^{k}	.0591	1.107	25.50	− 8.3
25^{k}	.220	3.77	24.76	− 7.9
HCOOH^{m}	.677	10.76	24.08	− 7.8
AcOH–H_2O^{n}				
4.00 M H_2O	0.0060	0.122	26.2	−10
8.00 M H_2O	.0200	0.369	25.42	−10.7
16.00 M H_2O	.0896	1.498	24.55	−10.4
Dioxane–H_2O				
80		0.0247		
70	0.005^{p}	.099^{p}	26	−11
60	.017^{p}	.307^{p}	25.2	−12
50	.0755	1.21^{d}	24.1	−12
40	.261^{e}	3.87^{e}	23.48	−11.6
30	.797^{e}	11.1^{e}	23.16	−10.3
20	2.09^{d,e}	29.9^{d,e}	23.16	− 8.4
Me_2CO–H_2O				
75	0.0048^{h,q}	0.0820	24.7	−16
50	0.0833^{f}	1.271^{f}	23.71	−13.1

[a] Unless otherwise noted, initial concentration 0.03–0.04 M, with halide analysis being employed. [b] x vol. % A – B means x volumes of A plus 100 − x volumes of B, each at 25.0° before mixing. [c] Unless otherwise indicated, the over-all average deviation of the rates was ±0.7% of k. [d] Average deviation ±2–3% of k. [e] Initial concentration 0.001–0.003 M; acidometric analysis used. [f] Initial concentration 0.005–0.010 M. [g] Initial rate constants; these rates drifted down in the course of the runs due to loss of HBr by reaction with solvent. [h] Extrapolated from the data at the other temperatures. [i] At 100.0°, $10^5 k_0$ = 0.260.[p] [j] Contained 0.068 M lithium acetate plus 0.01 M Ac_2O. [k] Contained 0.065 M lithium acetate and/or formate, plus 0.01 M Ac_2O. [m] Contained 0.068 M lithium formate. [n] Contained 0.068 M lithium acetate. [p] Initial rate constants; these rates drifted up in the course of the runs; see Experimental section. [q] At 100.0°, $10^5 k$ = 0.95.

TABLE III

CORRELATION OF SOLVOLYSIS RATES WITH Y

Temp., °C.	Solvent range	No. of points	m	log k_0	r
	Neophyl chloride				
50.0	20–80 vol. % EtOH–H_2O	6	0.833	−8.535	0.055
75.0	20–80 vol. % EtOH–H_2O	6	.775	−7.203	.040
50.0	30–80 vol. % MeOH–H_2O	6	.790	−8.314	.028
75.0	30–80 vol. % MeOH–H_2O	6	.761	−7.029	.026
50.0	0–100% AcOH–HCOOH	5	.837	−7.929	.018
75.0	0–100% AcOH–HCOOH	5	.789	−6.572	.009
50.0	0–16 M H_2O in AcOH	4	.733	−8.110	.015
75.0	0–16 M H_2O in AcOH	4	.675	−6.776	.007
50.0	20–70 vol. % dioxane–H_2O	3	.961	−8.971	.057
75.0	20–70 vol. % dioxane–H_2O	4	.908	−7.615	.041
	Neophyl bromide				
50.0	20–90 vol. % EtOH–H_2O	7	0.811	−6.969	0.050
75.0	20–90 vol. % EtOH–H_2O	7	.752	−5.701	.044
50.0	30–90 vol. % MeOH–H_2O	7	.783	−6.774	.009
75.0	30–90 vol. % MeOH–H_2O	7	.712	−5.487	.013
50.0	0–100% AcOH–HCOOH	5	.822	−6.854	.009
75.0	0–100% AcOH–HCOOH	5	.761	−5.534	.005
50.0	0–16 M H_2O in AcOH	4	.826	−6.866	.011
75.0	0–16 M H_2O in AcOH	4	.746	−5.576	.022
50.0	20–70 vol. % dioxane–H_2O	6	.925	−7.369	.030
75.0	20–80 vol. % dioxane–H_2O	7	.834	−6.001	.051
50.0	50–75 vol. % Me_2CO–H_2O	2	.754	−7.122	
75.0	50–75 vol. % Me_2CO–H_2O	2	.729	−5.904	

TABLE IV

CORRELATION OF SOLVOLYSIS RATES WITH LOG k FOR NEOPHYL CHLORIDE,[a] *via* EQUATION 2

Temp.,^{a} °C.	Solvents	No. of points	a	b	r
	Neophyl bromide				
50.0	Aq. EtOH, MeOH, dioxane	15	0.977	1.367	0.017
75.0	Aq. EtOH, MeOH, dioxane	16	.956	1.205	.018
50.0	0–16 M H_2O in AcOH	4	1.123	2.242	.021
75.0	0–16 M H_2O in AcOH	4	1.126	2.047	.006
50.0	0–100% AcOH–HCOOH	5	0.980	0.918	.009
75.0	0–100% AcOH–HCOOH	5	0.975	0.862	.004
	α-Phenylethyl Chloride				
50.0	Aq. EtOH, MeOH, dioxane^{b}	10	1.199	6.399	0.023
50.0	0–16 M H_2O in AcOH	4	1.417	7.608	.017
50.0	25–100% AcOH–HCOOH	4	1.349	6.953	.032
	α-Phenylethyl bromide^{c}				
50.0	Aq. EtOH, MeOH, dioxane	9	1.158	5.526	0.037
50.0	0–8 M H_2O in AcOH	3	1.376	6.327	0.017

[a] 50° *vs.* 50°; 75° *vs.* 75°. [b] 30 vol. % EtOH–H_2O omitted; point far out of line. [c] Rates correlated with log k for neophyl bromide.

of hydrogen bond strength on the acidity of the proton donor. Also, one can expect the importance of hydrogen bonding to diminish in the order, RF > RCl > RBr > RI, judging by what is known regarding the variation of hydrogen bond strength with atomic size. These considerations lead to the observed qualitative behavior of bromides relative to chlorides.

One can attempt to place the whole matter on a more quantitative basis by dissecting the ionizing power **Y** into $\mathbf{Y}_G$, a measure of ionizing power based on general solvent functions, and $\mathbf{Y}_H$, a measure of ionizing power based on the specific short-range hydrogen-bonding electrophilic function of the solvent. The linear free energy relationship 1 may be rewritten in the form of equation 3

$$\log k = \log k_0 + m_G \mathbf{Y}_G + m_H \mathbf{Y}_H \qquad (3)$$

$$\log k_{RX} = \left[\log k_0^{RX} - \frac{m_G^{RX}}{m_G^{RCl}} \log k_0^{RCl}\right] + \frac{m_G^{RX}}{m_G^{RCl}} \log k_{RCl} + \left[m_H^{RX} - \frac{m_G^{RX}}{m_G^{RCl}}\, m_H^{RCl}\right]\mathbf{Y}_H \qquad (4)$$

where m_G is the compound parameter for the sensitivity of solvolysis rate to $\mathbf{Y}_G$, and m_H is the one for $\mathbf{Y}_H$. The term $m_G\mathbf{Y}_G$ accounts for change in log k due to change in general ionizing power of solvent while the term $m_H Y_H$ provides for the change in log k due to change in specific electrophilic ionizing power of the solvent.

If equation 3 is written for a halide RX and then also for the corresponding chloride, RCl, subtraction of one equation from the other and rearrangement of terms leads to equation 4. This equation represents the plot of log k for RX *vs.* log k for RCl. Consider such a plot for a series of aqueous alcohols. In such a series of solvents, Y_H could be expected to be relatively constant, since the specific hydrogen-bonding electrophilic solvent function is always being assumed by a similar hydroxylic molecule, namely, water or alcohol. We know, from comparisons of water and ethanol as solutes in nitromethane as solvent, that water and ethanol are equal within a factor of *ca.* 2 in effectiveness as specific electrophilic reagents.[10] On this basis, the plot of log k for RX *vs.* log k for chloride, RCl, is a line with slope m_G^{RX}/m_G^{RCl}.

For the series of acetic–formic acid solvents, Y_H can be expected again to be relatively constant at a higher value than for the aqueous alcohols. The plot of log k for RX *vs.* log k for chloride in the acetic–formic acid solvents is given by equation 4 as a straight line, again with a slope of m_G^{RX}/m_G^{RCl}. This general picture, therefore, does predict the parallel lines actually observed when log k for bromide is plotted against log k for chloride.

On the basis of equation 4 and the discussion, the vertical gap, $\log k_{RX}^{ROH} - \log k_{RX}^{RCOOH}$, between the two straight lines, one for aqueous alcohols and the other for acetic–formic acid mixtures, is given by equation 5

$$\log k_{RX}^{ROH} - \log k_{RX}^{RCOOH} = \left[\frac{m_G^{RX}}{m_G^{RCl}} m_H^{RCl} - m_H^{RX}\right][Y_H^{RCOOH} - Y_H^{ROH}] \quad (5)$$

On this basis, since $[Y_H^{RCOOH} - Y_H^{ROH}]$ is positive and approximately constant, the vertical gaps represent relative values of the quantity, $[(m_G^{RX}/m_G^{RCl})\, m_H^{RCl} - m_H^{RX}]$. These vertical gaps are itemized in Table V for the neophyl and also the *t*-butyl and α-phenylethyl bromides and chlorides.[9]

TABLE V

ANALYSIS OF DISPERSION IN BROMIDE–CHLORIDE PLOTS

R	Temp., °C.	m_G^{RBr}/m_G^{RCl}	$\log k^{ROH} - \log k^{RCOOH}$
Neophyl	50	0.98	0.45
t-Butyl	25	$0.93 \pm 0.01_5$	0.58 ± 0.05
α-Phenylethyl	25	0.93	0.80[a]

[a] Based on the point for acetic acid alone

In the neophyl case, as in the others, the quantity $\log k^{ROH} - \log k^{RCOOH}$ is positive for bromide. Although m_H^{RBr} was expected to be less than m_H^{RCl}, we now know it is also less than $(m_G^{RBr}/m_G^{RCl}) \cdot m_H^{RCl}$, namely, 0.98 m_H^{RCl}, 0.93 m_H^{RCl} and 0.93 m_H^{RCl}, for the neophyl, *t*-butyl and α-phenylethyl systems, respectively.

α-Phenylethyl *vs.* Neophyl.—It is instructive to plot log k for α-phenylethyl chloride *vs.* log k for neophyl chloride, as in Fig. 3. The points for the mixtures of water with ethanol, methanol and dioxane are found to coalesce to a considerable degree to form a fairly good single straight line, while those for the acetic acid–water mixtures and acetic–formic acid mixtures form separate lines of their own, of higher slope, lying below the first. The parameters for the equations for these lines are listed in Table IV. This plot is thus notably simpler than that for neophyl chloride *vs.* *t*-butyl chloride (Fig. 1), in which the ethanol–water, methanol–water and dioxane–water lines are widely dispersed. Thus, it is clear that neophyl chloride is more suitable for correlation of rates of solvolysis of the α-phenylethyl system than is the *t*-butyl system. This is not at all surprising on the basis of the similarity in the structural change from ground state to transition state in the neophyl and α-phenylethyl systems. In the one case, a phenyl group, in its anchimeric role, develops a delocalized charge, while, in the other, the α-phenyl group, through resonance, also develops a delocalized charge.

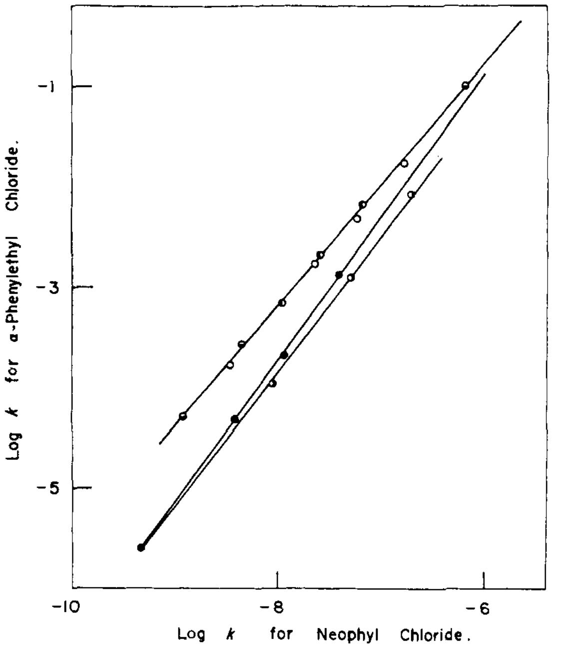

Fig. 3.—Plot of log k for solvolysis of α-phenylethyl chloride at 50.0° *vs.* log k for solvolysis of neophyl chloride at 50.0° in: EtOH-H_2O, ○; MeOH-H_2O, ◐; dioxane-H_2O, ⊖; AcOH-H_2O, ●; AcOH-HCOOH, ◑.

A plot of log k for α-phenylethyl bromide *vs.* log k for neophyl bromide is very similar to that for the chlorides. The parameters for the linear equations relating these data are listed in Table IV.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.—Over substantially all of the range of solvent variation covered for the neophyl halides, the principal contributor to increase in rate was found to be decrease in $\Delta H^{\ddagger}$, as much as 6 to 7 kcal./mole, whereas $\Delta S^{\ddagger}$ remained relatively constant at the level of -13.0 ± 1.9 e.u. for the chloride and -10.6 ± 1.4 e.u. for the bromide.

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

Employing the **A B C** classification set up in a previous paper in this series,[11] this places the bulk of the data on the borderline between the **B** and **C** regions. Comparison of these classifications for neophyl chloride and bromide in Table VI, together with those previously noted[7,9,11] for the *t*-butyl and α-phenylethyl halides, reveals a certain degree of family resemblance in the pattern of the variation of the thermodynamic quantities of activation with solvent variation.

TABLE VI

CLASSIFICATION OF THERMODYNAMIC BEHAVIOR

Solvent range	Class[a]
Neophyl chloride	
20–60% EtOH–H_2O	60 $^{\mathbf{C}}$ 85 $^{\mathbf{B}}$ 90
30–70% MeOH–H_2O	60 $^{\mathbf{C}}$ 75 $^{\mathbf{A}}$ 90
0–100% AcOH–HCOOH	0 $^{\mathbf{C}}$ 35 $^{\mathbf{B}}$ 100
0–50% AcOH–H_2O	0 $^{\mathbf{C}}$ 35 $^{\mathbf{B}}$ 75
Neophyl bromide	
20–90% EtOH–H_2O	25 $^{\mathbf{C}}$ 45 $^{\mathbf{B}}$ 70 $^{\mathbf{C}}$ 88 $^{\mathbf{A}}$ 91
30–90% MeOH–H_2O	20 $^{\mathbf{C}}$ 85
0–100% AcOH–HCOOH	0 $^{\mathbf{B}}$ 100
0–16 *M* H_2O in AcOH	0 $^{\mathbf{C}}$ 35 $^{\mathbf{B}}$ 55
20–70% dioxane–H_2O	65 $^{\mathbf{C}}$ 88 $^{\mathbf{B}}$ 95
50–75% Me_2CO–H_2O	55 $^{\mathbf{B}}$ 80

[a] Subscripts refer to mole percentage of fast component.

The increase in solvolysis rate arising from change of leaving group for the neophyl system from chloride to bromide is made up of an average decrease in $\Delta H^{\ddagger}$ of 1.3 ± 0.4 kcal./mole plus an average increase in $\Delta S^{\ddagger}$ of 2.4 ± 1.1 e.u. Thus, nearly 65% of the rate increase is due to decrease in the $\Delta H^{\ddagger}$ term. These results are quite similar to those previously noted for the *t*-butyl and α-phenylethyl systems.

As before,[9] 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. These comparisons are made in Table VII.

TABLE VII

CONTRIBUTION OF CHANGE IN ENTROPY AND ENTHALPY TO CHANGE IN FREE ENERGY OF ACTIVATION OF NEOPHYL BROMIDE AND CHLORIDE AT 50°

Solvent	k_{RBr}/k_{RCl}	$-T(\Delta S^{\ddagger}_{RCl} - \Delta S^{\ddagger}_{RBr})$, kcal./mole	$\Delta H^{\ddagger}_{RCl} - \Delta H^{\ddagger}_{RBr}$, kcal./mole	$\Delta F^{\ddagger}_{RCl} - \Delta F^{\ddagger}_{RBr}$ kcal./mole
EtOH–H_2O	33 ± 1	−0.8 ± 0.3	−1.4 ± 0.3	−2.2
MeOH–H_2O	34 ± 3	−1.0 ± .4	−1.4 ± .5	−2.4
Dioxane–H_2O	36 ± 4	−0.7 ± .5	−1.6 ± .4	−2.3
AcOH	13	− .3	−1.1	−1.4
HCOOH	11	− .4	−1.2	−1.6

From the data, it would appear that the reason for the low k_{RBr}/k_{RCl} ratios in the carboxylic acid-containing solvents is a combination of a decreased contribution of both the $\Delta(\Delta S^{\ddagger})$ and $\Delta(\Delta H^{\ddagger})$ terms, in approximately equal proportions.

Experimental Part

Neophyl Chloride and Bromide.—The samples employed were those previously described.[6]

Solvents.—Preparation of the solvents employed is described in detail in an earlier paper in this series.[12] In general, the solvents employed for the rate runs were from the same batches as those previously employed[12] to determine **Y**.

Kinetic Measurements and Experimental Results.—The techniques employed for the kinetic runs and analyses have been described previously.[12] In most cases, development of halide ion was followed. For a few of the highly aqueous alcohols and dioxanes, acidometric analysis was employed; these runs are suitably footnoted in Tables I and II. The data therein reported were based on an average of six points per run followed past 50–90% reaction. 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. Slight upward drifts during the course of the runs were observed for neophyl bromide in acetic acid and in 60 and 70% dioxane–water. Downward drifts observed for neophyl chloride in 80% EtOH–H_2O and 80% MeOH–H_2O and for neophyl bromide in 90% MeOH–H_2O apparently were due to loss of hydrogen halide arising from secondary reaction with the solvents. For these 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 the tables.

LOS ANGELES 24, CALIFORNIA

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[11] A. H. Fainberg and S. Winstein (Paper IV), THIS JOURNAL, **79**, in press.

[12] A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

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

Mechanisms of Elimination Reactions. Sulfur Isotope Effects in the Decomposition of Some Sulfonium Salts

BY WILLIAM H. SAUNDERS, JR., AND SMILJKO AŠPERGER

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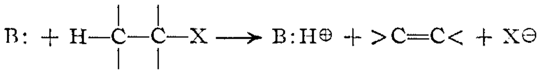
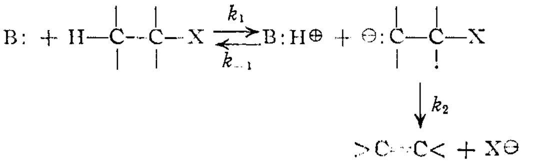
The $^{32}S/^{34}S$ isotope effect has been measured for the S_N1 decomposition of *t*-butyldimethylsulfonium iodide (I) in water and found to be *ca.* 1.8%. The E2 reaction of 2-phenylethyldimethylsulfonium bromide (II) with sodium hydroxide in water shows a much smaller isotope effect, *ca.* 0.15%. The mechanistic implications of these results are discussed.

Kinetic evidence on base-promoted elimination reactions is consistent with either a concerted process (mechanism 1) or a two-step process with a carbanion intermediate (mechanism 2). The question of the range of applicability of these two mech-



$$B: + H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \longrightarrow B:H^{\oplus} + {>}C{=}C{<} + X^{\ominus} \quad (1)$$



$$B: + H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B:H^{\oplus} + {}^{\ominus}:\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \xrightarrow{k_2} {>}C{=}C{<} + X^{\ominus} \quad (2)$$