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[Contribution from the Department of Chemistry,  
Massachusetts Institute of Technology]

Displacement Reactions. XIII.<sup>1</sup> Correlation of Rates of

Solvolysis with a Special Two-Parameter Equation

(1) Paper XI<sup>2</sup> serves as an introduction to this paper. Further details and discussion may be found in reference 7. The work carried out by Miss Kaiser (kinetics on picryl chloride and phenacyl bromide) was supported by the Office of Naval Research.

(2) C. G. Swain, R. B. Mosely, D. E. Bown, I. Allen and D. C. Dittmer, J. Am. Chem. Soc., 76, 600 (1954).

By C. Garúner Swain, Donald C. Dittmer<sup>3</sup>

and Lore E. Kaiser

(3) National Science Foundation Fellow, 1952-1953.

A special two-parameter equation,  $\log (k/k^\circ)_A - \log (k/k^\circ)_{A^\circ} =$

$a \log b$ , is tested, where  $k$  is the first-order rate constant for solvolysis of any organic chloride or bromide (A) or of the standard compound, methyl bromide (A<sup>o</sup>), in any solvent,  $k^\circ$  is the corresponding rate constant in a standard solvent (80% ethanol) at the same temperature,  $a$  is a constant depending only on the chloride or bromide and  $b$  is a constant depending only on the solvent. Values of  $a$  are reported for 15 compounds ranging from picryl chloride to *t*-butyl chloride, and values of  $b$  for 19 solvents ranging from triethylamine to formic acid. These were determined from the equation and a total of 124  $\log (k/k^\circ)$  values by the method of least squares. The minimum, mean and maximum ranges in observed rates for compounds are factors of 10,  $2 \times 10^3$  and  $3 \times 10^6$  respectively. The mean and maximum errors in the calculated rates are factors of 1.5 and 7.6.

A special two-parameter equation was presented in paper XI<sup>2</sup>

$$\log \left( \frac{k}{k^\circ} \right)_A - \log \left( \frac{k}{k^\circ} \right)_{A^\circ} = a + b \quad (1)$$

where  $k$  is the first-order rate constant for solvolysis of any organic chloride or bromide (A) or of the standard compound, methyl bromide (A<sup>o</sup>), in any medium,  $k^\circ$  is the corresponding rate constant in a standard medium at the same temperature,  $a$  is a constant depending only on the chloride or bromide and  $b$  is a constant depending only on the solvent.

As the standard solvent we chose 80% ethanol-20% water by volume because more data were available for it than for any other solvent. Table I lists  $\log k_0$  in 80% ethanol for all of the 15 compounds not previously given in Table I of paper XII.<sup>4</sup>

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(4) G. G. Swain, R. B. Mosely and D. E. Bown, J. Am. Chem. Soc., 76, 000 (1954).

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Table II lists 42 of the 124  $\log (k/k^\circ)$  values which were used. The other 82  $\log (k/k^\circ)$  values are for the compounds listed in Table III in the solvents listed in Table IV, and may be found in Table II of paper XII.<sup>4,5</sup> One-half (62) of the 124 values were measured in this laboratory.

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(5) The  $\log (k/k^\circ)$  values for  $\alpha$ -phenylethyl chloride used in this treatment were the correctly calculated ones (cf. footnote j in Table II of paper XII<sup>4</sup>). The omissions were  $\log (k/k^\circ)$  values for 40% ethanol, 83.3% formic acid and 97.5% acetic anhydride and the value for  $p$ -nitrobenzoyl chloride in acetic acid.

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Table I

ADDITIONAL RATES IN 80% ETHANOL

<u>Compound<sup>a</sup></u>	<u>log<sub>10</sub> k°, sec.<sup>-1</sup></u>	<u>Temp., °C.</u>	<u>Ref.</u>
PicCl	-5.30	50	6
φCOCH <sub>2</sub> Br	-5.80	50	6
<u>i</u> -BuBr	-7.61	50	7
<u>t</u> -BuBr	-3.44	25	8

<sup>a</sup>Pic = picryl (2,4,6-trinitrophenyl);

φ = C<sub>6</sub>H<sub>5</sub> or p-substituted C<sub>6</sub>H<sub>4</sub>;

Me = Et, Pr, Bu = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>.

Table II  
RELATIVE RATES OF SOLVOLYSIS

<u>Compound<sup>a</sup></u>	<u>Solvent<sup>b</sup></u>	<u>log (k/k<sup>o</sup>)</u>	<u>Tem., °C.</u>	<u>Ref.</u>
PiOCl	MeOH, 96.7	-0.22	50	6
"	MeOH, 69.5	- .02	50	6
"	EtOH	- .50	50	6
"	EtOH, 50	- .09	50	6
"	Me <sub>2</sub> CO, 90	-1.01	50	6
"	Me <sub>2</sub> CO, 70	-0.44	50	6
"	Me <sub>2</sub> CO, 50	- .36	50	6
φCOCH <sub>2</sub> Br	MeOH, 96.7	-0.29	50	6
"	MeOH, 69.5	+ .26	50	6
"	EtOH	- .93	50	6
"	EtOH, 50	+ .27	50	6
"	Me <sub>2</sub> CO, 90	- .73	50	6
"	Me <sub>2</sub> CO, 70	- .13	50	6
"	Me <sub>2</sub> CO, 50	+ .15	50	6
MeBr	Et <sub>3</sub> N	+1.85	50	7
"	<u>n</u> -BuNH <sub>2</sub>	+4.66	50	7
"	C <sub>5</sub> H <sub>5</sub> N	+3.57	50	7
"	φNH <sub>2</sub>	+3.54	50	7
<u>i</u> -BuBr	<u>n</u> -BuNH <sub>2</sub>	+3.07	50	7
"	C <sub>5</sub> H <sub>5</sub> N	+2.11	50	7
"	φNH <sub>2</sub>	+2.53	50	7
<u>n</u> -BuBr	Et <sub>3</sub> N	-1.14	75	7
"	<u>n</u> -BuNH <sub>2</sub>	+2.72	75	7
"	C <sub>5</sub> H <sub>5</sub> N	+2.12	75	7
"	φNH <sub>2</sub>	+2.35	75	7

(Table II continued)

<u>Compound</u>	<u>Solvent</u>	<u>log (k/k<sup>o</sup>)</u>	<u>Temp., °C.</u>	<u>Ref.</u>
$\phi\text{CH}_2\text{Cl}$	$\text{Et}_3\text{N}$	-1.47	50	7
"	$n\text{-BuNH}_2$	+2.70	50	7
"	$\text{C}_5\text{H}_5\text{N}$	+1.75	50	7
"	$\phi\text{NH}_2$	+2.75	50	7
$\phi_2\text{CHCl}$	$\text{Et}_3\text{N}$	< -10	25	7
"	$n\text{-BuNH}_2$	-3.23	25	7
"	$\text{C}_5\text{H}_5\text{N}$	-3.95	25	7
"	$\phi\text{NH}_2$	-0.16	25	7
"	$\text{MeOH}$	-0.31	25	9
$t\text{-BuBr}$	$\text{EtOH}$	-1.81	25	10
"	$\text{EtOH}, 90$	-0.71	25	8
"	$\text{EtOH}, 60$	+1.02	25	8
"	$\text{Me}_2\text{CO}, 90$	-1.46	25	11
"	$\text{Me}_2\text{CO}, 80$	-0.52	25	8
"	$\text{Me}_2\text{CO}, 70$	+ .15	25	11
$t\text{-BuCl}$	$\text{Me}_2\text{CO}, 90$	-1.85	25	9
"	$\text{Me}_2\text{CO}, 70$	+0.13	25	9

<sup>a</sup>See footnote a of Table I.

<sup>b</sup>Number after solvent is % by volume based on volumes before mixing with water; when no number is given solvent was anhydrous and pure; Me, Et, Bu,  $\phi$ , Ac =  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_4\text{H}_9$ ,  $\text{C}_6\text{H}_5$  and  $\text{CH}_3\text{CO}$ . The amine solvents were always 95.2% amine - 4.8% benzene based on volumes before mixing.

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- (6) Data supplied by Miss Lore E. Kaiser.
- (7) D. C. Dittmer, Ph.D. Thesis, M.I.T., September, 1953; C. G. Swain and D. C. Dittmer, J. Am. Chem. Soc., 76, 6000 (1954).
- (8) L. C. Bateman, K. Cooper, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 925 (1940).
- (9) S. Winstein, private communication.
- (10) E. D. Hughes, C. K. Ingold, S. Masterman and B. J. McNulty, J. Chem. Soc., 899 (1940).
- (11) L. Bateman, M. Church, E. D. Hughes, C. K. Ingold and N. Taber, ibid., 979 (1940).
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The compounds correlated are all chlorides or bromides, but include p-nitrobenzoyl, methyl, benzhydryl and t-butyl. The solvents are especially varied, including n-butylamine, triethylamine, alcohols, water and anhydrous formic acid.

We used the method of least squares in a simple iterative procedure to obtain the best values of a and b (see method of calculation below). To make the solution unique three conditions were imposed arbitrarily as follows.

$$\underline{b} = 0.00 \text{ for } 80\% \text{ EtOH}$$

$$\underline{a} = 0.00 \text{ for MeBr}$$

$$\underline{a} = 1.00 \text{ for } \underline{t}\text{-BuCl}$$

A renormalization to any other arbitrary assignment (any Y) may be made easily using the equations

$$\underline{a}^* = \underline{\lambda} \underline{a}$$

$$\underline{b}^* = \underline{b}/\underline{\lambda}$$

for new values (denoted by superscript stars). When data for a secondary standard  $A^{\circ 1}$  are used instead of data for  $A^{\circ}$ , the equation becomes

$$\log (\underline{k}/\underline{k}^{\circ})_A - \log (\underline{k}/\underline{k}^{\circ})_{A^{\circ 1}} = (\underline{a} - \underline{\Delta}) \underline{b}$$

where  $\underline{\Delta} = \log (\underline{k}/\underline{k}^{\circ})_{A^{\circ 1}} - \log (\underline{k}/\underline{k}^{\circ})_{A^{\circ}}$ .

The minimum, mean and maximum ranges in  $\log \left(\frac{k}{k^0}\right)_{\text{obs.}}$  values for one compound are 1.0, 3.3 and 6.4 corresponding to variations of  $1 \times 10^1$ ,  $2 \times 10^3$  and  $3 \times 10^6$  in the observed rate itself. The mean and maximum errors out of  $12^4 \log \left(\frac{k}{k^0}\right)_{\text{calc.}} - \log \left(\frac{k}{k^0}\right)_{\text{obs.}}$  values are 0.18 and 0.88 corresponding to factors of 1.52 (for the mean) and 7.6 (for benzhydryl chloride in 90% acetone) in  $k$  itself. Measures of fit ( $\bar{\rho}$ ) for typical compounds were listed in paper XI;<sup>2</sup> for solvents,  $\bar{\rho} = 97\%$  for triethyl amine, 97% for water, 95% for formic acid, 63% for acetic acid and 85% for ethanol.

Method of Calculation.- Crude  $b$  values were first obtained for solvents in which the rates with both methyl bromide and *t*-butyl chloride were measured, by use of the equation

$$\log \left(\frac{k}{k^0}\right)_{\text{t-BuCl}} - \log \left(\frac{k}{k^0}\right)_{\text{MeBr}} = b$$

which is true because  $a = 1.00$  for *t*-BuCl. Crude  $a$  values were then determined using equation 1 and any solvent for which  $b$  had been obtained. Crude  $b$  values were then determined for the other solvents in which methyl bromide was not studied by using the equation

$$\log \left(\frac{k}{k^0}\right)_A - \log \left(\frac{k}{k^0}\right)_{\text{t-BuCl}} = (a - 1.00) b$$

and any compound A for which  $a$  had been obtained.

The values of  $a$  and  $b$  determined in this way depend on the particular solvents and compounds used in calculating them, since the experimental error is finite and different for each  $\log \left(\frac{k}{k^0}\right)$  value. To minimize the effect of experimental errors, better values of  $b$  for all solvents were obtained by the method of least squares from the crude values of  $a$ , with equal weighting of all the usable  $\log \left(\frac{k}{k^0}\right)$  values.

$$\underline{b} \sum_i \underline{a}_i^2 - \sum_i \underline{a}_i \left[ \log\left(\frac{k}{k^\circ}\right)_{A_i} - \log\left(\frac{k}{k^\circ}\right)_{\text{MeBr}} \right] = 0$$

$$\underline{b} \sum_i (\underline{a}_i - 1.00)^2 - \sum_i (\underline{a}_i - 1.00) \left[ \log\left(\frac{k}{k^\circ}\right)_{A_i} - \log\left(\frac{k}{k^\circ}\right)_{\text{t-BuCl}} \right] = 0$$

Then better values of  $\underline{a}$  were obtained in the same way by the least-squares method from the better  $\underline{b}$  values.

$$\underline{a} \sum_j \underline{b}_j^2 - \sum_j \underline{b}_j \left[ \log\left(\frac{k}{k^\circ}\right)_A - \log\left(\frac{k}{k^\circ}\right)_{\text{MeBr}} \right] = 0$$

$$(\underline{a} - 1.00) \sum_j \underline{b}_j^2 - \sum_j \underline{b}_j \left[ \log\left(\frac{k}{k^\circ}\right)_A - \log\left(\frac{k}{k^\circ}\right)_{\text{t-BuCl}} \right] = 0$$

These least-squares procedures can be repeated to give still slightly better values of the parameters, but the result proved not worth the effort in the few cases tried.

Tables III and IV give the  $\underline{a}$  and  $\underline{b}$  values obtained.

Table III

CONSTANTS FOR COMPOUNDS,  $R_1R_2R_3CX$ 

<u>Compound</u> <sup>a</sup>	<u>No. of Reactions</u>	<u>a</u>	<u>R<sub>1</sub>-, R<sub>2</sub>-, R<sub>3</sub>-, X</u>
PicCl	8	-0.42	-C(NO <sub>2</sub> )=OH-C(NO <sub>2</sub> )=CH-(NO <sub>2</sub> )=, Cl
NO <sub>2</sub> φCOCl	7	- .37	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -, O=, Cl
φCOCH <sub>2</sub> Br	8	- .04	C <sub>6</sub> H <sub>5</sub> CO-, H-, H-, Br
MeBr	10	(0.00)	H-, H-, H-, Br
φCOCl	12	+ .06	C <sub>6</sub> H <sub>5</sub> , O=, Cl
EtBr	5	.15	CH <sub>3</sub> -, H-, H-, Br
<u>i</u> -BuBr	4	.16	(CH <sub>3</sub> ) <sub>2</sub> CH-, H-, H-, Br
<u>n</u> -BuBr	12	.18	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -, H-, H-, Br
φCH <sub>2</sub> Cl	8	.19	C <sub>6</sub> H <sub>5</sub> -, H-, H-, Cl
MeφCOCl	5	.41	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -, O=, Cl
<u>i</u> -PrBr	5	.42	CH <sub>3</sub> -, CH <sub>3</sub> -, H-, Br
φCHClMe	5	.64	C <sub>6</sub> H <sub>5</sub> -, CH <sub>3</sub> , H-, Cl
φCHCl	13	.78	C <sub>6</sub> H <sub>5</sub> -, C <sub>6</sub> H <sub>5</sub> -, H-, Cl
<u>t</u> -BuBr	7	.93	CH <sub>3</sub> -, CH <sub>3</sub> -, CH <sub>3</sub> -, Br
<u>t</u> -BuCl	15	(1.00)	CH <sub>3</sub> -, CH <sub>3</sub> -, CH <sub>3</sub> -, Cl

<sup>a</sup>See footnote a of Table I.

Table IV

## CONSTANTS FOR SOLVENTS

<u>Solvent</u> <sup>a</sup>	<u>No. of Reactions</u>	<u>b</u>	<u>Dielectric Constant</u>
Et <sub>3</sub> N	3	-17.27	3.2
n-BuNH <sub>2</sub>	5	-10.15	5.4
C <sub>2</sub> H <sub>5</sub> N	5	- 9.66	12.4
φNH <sub>2</sub>	5	- 4.78	7.3
MeOH	6	- 0.94	33.7
EtOH	14	- .74	23.2
Me <sub>2</sub> CO, 90	7	- .72	24.6
EtOH, 90	4	- .52	28.0
MeOH, 96.7	6	- .51	34.2
EtOH, 80	15	(0.00)	33.9
Me <sub>2</sub> CO, 80	7	+ .04	30.9
Me <sub>2</sub> CO, 70	7	.42	36.5
AcOH	5	.57	9.7
MeOH, 69.5	5	.61	47.3
EtOH, 60	4	.88	44.7
Me <sub>2</sub> CO, 50	8	1.02	49.5
EtOH, 50	8	1.14	51.3
H <sub>2</sub> O	4	2.95	79.2
HCOOH	6	4.00	58.5

<sup>a</sup>See footnote b of Table II.

<sup>b</sup>These constants, measured at or near 20°C., were taken from Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1923, Ed. 5, Vol. 2, p. 1035 ff. or "Tables Annuelles de Constantes et Données Numerique," Hermann et Cie., Paris, 1937, Vol. XI, Section 22, pp. 6, 29.

The difference in free energies of two solvolytic reactions for a compound, A, is

$$\begin{aligned} (\Delta F_{II}^* - \Delta F_I^*)_A &= 2.303 \frac{RT}{T} \log \left( \frac{k_{II}}{k_I} \right)_A = (\Delta E_{P_{II}}^* - \Delta E_{P_I}^*)_A \\ &+ (\Delta E_{Z_{II}}^* - \Delta E_{Z_I}^*)_A - 2.303 \frac{RT}{T} \log \left( \frac{Q_{II}^* Q_I}{Q_{II} Q_I^*} \right)_A \end{aligned} \quad (2)$$

In this equation I and II refer to two different solvents,  $\Delta F^*$  is a free energy of activation,  $R$  is a gas constant,  $T$  is the absolute temperature,  $k_{II}$  is the first-order rate constant for the reaction of A with solvent II,  $k_I$  is the first-order rate constant for the reaction of A with solvent I,  $\Delta E_P^*$  is the difference in potential energies per mole between reactants and transition state,  $\Delta E_Z^*$  is the difference in zero-point vibrational energies per mole between reactants and transition state,  $Q^*$  is a partition function for a transition state, and  $Q$  is a partition function for the ground state.

An expression exactly like equation 2 can be written for a standard compound,  $A^\circ$ . If the zero-point vibrational energy terms and the partition function terms in both equations are, to a first approximation, assumed equal, and the equations subtracted one from the other, equation 3 is obtained.

$$\log \left( \frac{k_{II}}{k_I} \right)_A - \log \left( \frac{k_{II}}{k_I} \right)_{A^\circ} = \frac{\Delta \Delta E_P^*}{2.303 \frac{RT}{T}} \quad (3)$$

If the term involving  $\Delta \Delta E_P^*$  in equation 3 can be represented as a product of two parameters, one  $a$ , corresponding to the potential energy change contributed by the compound and the other  $b$ , corresponding to the potential energy change contributed by the solvent (relative to standard compound and standard solvent), the desired equation is obtained

$$\log \frac{k_{II}/R_I}{A} - \log \frac{k_{II}/R_I}{A^\circ} = \underline{a} \underline{b}$$

where  $k_I = k^\circ$ .

As is commonly done in two-parameter linear free-energy relationships, we consider one parameter (b) as an independent variable, independent of temperature. The other parameter (a) is not an accurate inverse function of absolute temperature (as is  $\rho$  in the Hammett equation),<sup>7</sup> but nevertheless probably will not deviate very far from this in practice.

Significance of a and b Values.- Table III compares the value of a with the substituents on the carbon atom at which reaction occurs. Generally, the value of a increases as the electron-supplying ability of the substituents increase. The substituents with nitro groups have the smallest a values; this is expected since nitro groups are electron-attracting. The compounds with the most positive a values bear alkyl or aryl substituents which are electron-donating.

The step-wise replacement of the hydrogens in methyl bromide with methyl groups results in an increase in a. A phenyl group is more effective in increasing the value of a than a methyl group; this may indicate a shift in electron distribution from the phenyl ring toward the reaction site, a resonance effect rather than an inductive effect.

It should be remembered that a may be a function of temperature and the nature of the leaving group in addition to being a function of the polar effects exerted by the substituents on the reaction.

Table IV compares the value of b with dielectric constant of the solvent. Dielectric constant is important in the determination of electrical effects transmitted through a medium. There is a more-or-less general increase in b with increasing dielectric constant, the most notable exception being acetic acid. There seems to be also a trend from basic to acidic solvents as b becomes more positive. The relative greater acidities of aniline, acetic acid and formic acid in comparison with their neighbors in the table may explain why these compounds have greater b values than their

dielectric constants would indicate. It is noted also that as the solvents become more aqueous the  $\rho$  values become greater.

When the product  $\rho \sigma$  is positive the rate of reaction of a given compound in a given solvent relative to the rate in 80% ethanol-20% water is greater than the relative rate for methyl bromide. This condition occurs in the reactions of the strongly nucleophilic solvents (solvents with a negative  $\rho$ ) with compounds with strongly electron-withdrawing substituents (compounds with a negative  $\sigma$ ) and in the reactions of solvents with pronounced electrophilic character (solvents with a positive  $\rho$ ) with compounds with electron-supplying substituents (compounds with a positive  $\sigma$ ).

Limitations of the Correlation.- To ensure that the zero-point vibrational energies and partition functions will always change in the same way from one solvent to another, the correlation must be restricted to compounds with leaving groups of similar electronegativity, polarizability and bond energy. The carbon-chlorine and carbon-bromine bond energies are close to each other (66.5 and 54.0 kcal) whereas the carbon-fluorine bond energy is considerably larger (107.0 kcal.).<sup>12</sup> For these reasons the

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(12) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, Ed. 2, p. 53.

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inclusion of chlorides and bromides in the correlation was justified, but the inclusion of fluorides was not. Sulfonate esters and trityl thiocyanate were likewise excluded because they differ too much from chloride and bromide.

By changing the standard compound to a sulfonate ester, a fluoride or a thiocyanate, it may prove possible to correlate the rates of solvolysis of organic sulfonates, fluorides or thiocyanates. At present there is not enough data to determine the extent of the applicability of equation 1 when it is restricted to other types of leaving groups.

Picryl chloride is less well correlated than the other compounds,

possibly because of excessive solvent interaction with the polar nitro groups or because of excessive resonance in the transition state for reaction with the more nucleophilic solvents.

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