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

Correlation of Solvolysis Rates. IV.[1] Solvent Effects on Enthalpy and Entropy of Activation for Solvolysis of *t*-Butyl Chloride[2]

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In probing the basis of the success and limitations of linear free energy correlations of rates of solvolysis, the behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for solvolysis of *t*-butyl chloride toward solvent variation has been explored. The variation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with solvent has been scrutinized in the large variety of solvents reported on previously. In five of six pure solvents, $\Delta S^{\ddagger}$ for solvolysis of *t*-butyl chloride is relatively constant at *ca.* −3 e.u. On the other hand, water is uniquely set apart from the other solvents, $\Delta S^{\ddagger}$ now being 15 e.u. higher. A similarly anomalous position is occupied by the solvent water in solvolysis of other materials. With the aid of Henry's law constants for *t*-butyl chloride, the $\Delta\Delta F^{\ddagger}$ due to a solvent change can be dissected into separate effects on the ground state and transition state, namely, $\Delta\Delta F^0_v$ and $\Delta\Delta F^{\ddagger}_s$, respectively. Henry's law constants at several temperatures make possible the analogous dissection of the $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ terms. For changes of medium from one pure solvent to another in the case of *t*-butyl chloride solvolysis, $\Delta\Delta F^{\ddagger}_s$ tends to be of major importance. However, for the MeOH → HOH or EtOH → HOH solvent changes, $\Delta\Delta F^0_v$, related to the ground state, is of major importance. For solvolysis of *t*-butyl chloride in binary solvent mixtures, the behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ toward solvent composition tends to be complex. In this respect, the EtOH–HOH system is the most complex. For the various binary solvent systems, a linear relation between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ is the exception rather than the rule. An **ABC** classification system can be set up for characterizing the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior in solvolysis, and the symbolic terminology has been employed in summarizing and comparing the behavior of *t*-butyl chloride and a number of other substrates. As anticipated, the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior in *t*-butyl chloride solvolysis in binary solvent mixtures is poorly accounted for by a simple electrostatic treatment. Examination of Henry's law constants for *t*-butyl chloride in MeOH–HOH mixtures show that both ground state and transition state contributions to the $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values are important. Comparing the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior for *t*-butyl chloride with that for other substrates, it is evident that the various substances do not obey generalizations based solely on the nature of the solvent systems. Instead, as can be anticipated, the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior depends on substrate structure as well as on the nature of the solvent system. The pattern of behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for solvolysis of a substrate molecule determines the effect of temperature variation on the precision of the $m\mathbf{Y}$ correlation of the rates of solvolysis of that substrate molecule. This matter is treated analytically.

The thermodynamic quantities of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, for the solvolysis of the key substance, *t*-butyl chloride,[3] are of interest in probing the basis of the success and limitations of the linear free energy relationships[3] 1, 2 and 3. In relationship 1, $(k/k_0)_{\mathrm{RX}}$ is the ratio of first-order solvolysis rate constants of RX in a solvent and in a standard solvent, respectively, while $(k/k_0)_{\mathrm{RY}}$ is the analogous ratio for the substance RY. Relationship 3 makes use of a set of **Y** values for solvents equal to log (k/k_0) at 25° for the standard substance, *t*-butyl chloride. Thus, the **Y** values, or measures of solvent ionizing power, are based on a blend of specific and general solvent influences[3,4] appropriate to *t*-butyl chloride solvolysis.

$$\log\left(\frac{k}{k_0}\right)_{\mathrm{RX}} = m \log\left(\frac{k}{k_0}\right)_{\mathrm{RY}} \tag{1}$$

$$\Delta\Delta F^{\ddagger}_{\mathrm{RX}} = m\,\Delta\Delta F^{\ddagger}_{\mathrm{RY}} \tag{2}$$

$$\log\left(\frac{k}{k_0}\right) = \frac{-1}{2.303RT}\left(\frac{\partial\Delta F^{\ddagger}}{\partial \mathbf{Y}}\right)\mathbf{Y} = m\mathbf{Y} \tag{3}$$

A further interest in the thermodynamic quantities of activation of solvolysis is based on their possible utility in diagnosis of mechanism.[5] However, before any safe generalizations can be drawn regarding the connection between mechanism and $\Delta S^{\ddagger}$, for example, the dependence of $\Delta S^{\ddagger}$ on solvent composition for known mechanisms needs to be explored.

The variation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with solvent for the solvolysis of *t*-butyl chloride has been scrutinized in the large variety of solvents reported on in a previous paper.[3c] These results are reported and discussed in the present article.

Results

In Table I are summarized the first-order rate constants at 0° or 50° for solvolysis of *t*-butyl chloride in the various pure and mixed solvents. Most of the rate constants are new, a few representing duplication as indicated in the footnotes. In virtually all cases, the solvent mixtures were from the same batches as those employed to obtain the rates at 25.0° reported previously.[3c]

Also listed in the table are the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ calculated from the present and previous[3c] data. Based on the estimated probable error of the rate constants,[3c] $\Delta H^{\ddagger}$ is considered accurate to ±0.15 kcal./mole, and $\Delta S^{\ddagger}$ to ±0.5 e.u.

Some further comment on the present $\Delta H^{\ddagger}$ values is in order because reactions involving increase of charge, and therefore increased solvation, during passage into the transition state, commonly dis-

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Minneapolis, Minn., Sept. 16, 1955; page 52R of Abstracts.

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

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

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

[5] *E.g.*, S. Winstein and R. Heck, THIS JOURNAL, **78**, 4801 (1956).

TABLE I

RATES OF SOLVOLYSIS OF *t*-BUTYL CHLORIDE[a]

Solvent, vol. %[b]	Method[c]	10^5 *k*, sec.$^{-1}$[d] 0.00 ± 0.02°	10^5 *k*, sec.$^{-1}$[d] 50.00 ± 0.03°	$\Delta H^{\ddagger}$, kcal. mole (25°)	$\Delta S^{\ddagger}$, e.u. (25°)
EtOH–H_2O					
100	X		0.272[e]	26.13[f]	−3.2[f]
98	X	8.39[k]	0.509	24.46	−7.2
95	X	16.8[k]	1.125	23.58	−8.3
90	X		3.50	22.75	−8.7
80	X		18.5[g]	22.34[g]	−6.6[g]
70	X		68.9	21.90	−5.4
60	X		226	21.67	−3.7
50	H	1.353[h]		21.63[h]	−1.4[h]
45	H	2.75		21.05	−2.1
40	X	5.84			
40	H	5.76		20.32	−3.3
37.5	H	8.08		20.24	−3.0
35	H	11.10		20.20	−2.5
30	H	18.5		20.57	−0.1
25	H	25.9		21.20	+2.9
20	H	31.9		22.01	+6.3
15	H	39.7		22.61	+8.9
10	H	47.5		23.28	+11.7
5	H	58.0		23.48	+12.8
H_2O	H	72.7		23.22	+12.2
MeOH–H_2O					
100	X		2.10	24.88	−3.1
90	X		10.81	23.53	−4.0
80	X		44.9	22.40	−4.7
70	X		149	21.9	−4
70	H	0.249			
60	X	.922		21.63	−2.2
60	H	.932		21.64	−2.1
50	H	2.90		21.45	−0.6
40	H	7.69		21.33	+0.9
30	H	16.5		21.81	+4.2
20	H	26.5		22.79	+8.7
10	H	45.0		23.03	+10.7
AcOH–HCOOH					
100	X		0.669	25.80	−2.5
90	X	48.1[k]	2.90	24.52	−3.6
75	X		13.8	23.14	−4.7
50	X		103	22.13	−3.8
25	X	0.908		21.39	−3.1
HCOOH–H_2O					
100		3.73[l]		21.0[l]	−1.7[l]
95	X	4.97		20.78	−1.9
90	X	5.89		20.57	−2.4
80	X	7.74		20.23	−3.1
66²/₃	X	10.29		20.44	−1.7
33¹/₃	X	30.3		20.82	+1.8
14.29	X	57.0		21.09	+4.0
AcOH–H_2O					
0.50 *M* H_2O	X		1.061	25.13	−3.7
2.00 *M* H_2O	X		3.12	23.91	−5.3
4.00 *M* H_2O	X		8.11	23.14	−5.8
8.00 *M* H_2O	X		29.2	22.41	−5.5
16.00 *M* H_2O	X		161	21.53	−4.8
60	X	1.10		21.24	−3.4
50	X	2.73		21.30	−1.2
40	X	6.54		21.21	+0.2
25	X	21.1		21.55	+3.7
10	X	48.0			
Dioxane–H_2O					
90	X		0.156[i]	21.55	−18.5
80	X		2.61[i]	22.03	−11.5
70	X		18.28	22.01	−7.7
60	X		83	21.2	−7
50	H	0.748		21.08	−4.6
40	H	2.90		21.02	−2.1
30	H	9.10		21.21	+0.8
20	H	21.7		21.88	+5.0
10	H	43.3		22.48	+8.6
Me_2CO–H_2O					
90	X	2.92[k]	0.237	21.85	−16.8
80			3.68[j]	22.0[j]	−11[j]
70	X		21.5	21.16	−10.0
50	X	0.88		20.78	−5.4
30	H	10.96		20.41	−1.7
10	H	43.6		22.63	+9.1
Dioxane–HCOOH					
80	X	1.90[k]	0.1190	24.17	−11.0
60	X		4.29	23.07	−7.3
40	X		46.1	22.24	−5.1
20	X	0.58		21.7	−3
Formamide–H_2O					
100	X		74.6	22.36	−3.8
80	X	0.70		21.85	−1.9

[a] Initial concentration of 0.02–0.04 *M* when development of halide ion was followed; 0.001–0.005 *M* when acidometric analysis was employed. [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 herein reported that are constant is ±1.0% of *k*; the probable error *r* in log *k* is estimated to be 0.005. [e] Interpolation at 50.0° of data reported[3a] at other temperatures in EtOH containing several concentrations of KOAc, with simultaneous linear extrapolation to zero salt concentration, gives 0.278. [f] Calculation from data previously reported[3a] gives $\Delta H^{\ddagger}$ 25.53, $\Delta S^{\ddagger}$ −4.9. [g] Recalculation of data previously reported gives for $10^5 k$ at 50.0°: 18.4,[6] 18.2,[7] 16.7,[8] 18.5[9]; $\Delta H^{\ddagger}$: 22.37,[6] 22.60,[7] 21.80,[8] 22.59[9]; $\Delta S^{\ddagger}$: −6.5,[6] −5.8,[7] −8.5,[8] −5.8.[9] [h] Recalculation of data previously reported[6] gives for $10^5 k$ at 0°, 1.05; $\Delta H^{\ddagger}$ 22.35; $\Delta S^{\ddagger}$ +0.6. [i] Initial rates; upward drift in the course of the runs; see Experimental section of the previous paper.[3c] [j] Calculated from data of Hughes[6] at other temperatures. [k] Temperature 75.00°. [l] Extrapolated from data in the aqueous formic acid mixtures.

play[10–12] appreciable negative temperature coefficients of $\Delta H^{\ddagger}$. In the case of *t*-butyl chloride itself, in 76 wt. % EtOH–H_2O, Shorter and Hinshelwood[13] reported a change of activation energy of solvolysis with temperature. Also, Tommila[12] has reported, in a paper which became available to us since the present work was first presented,[1] a value of *ca.* −60 cal. per mole per degree for $\Delta C^{\ddagger}_p$ in the most highly aqueous acetone solvents.

In the present work, the thermodynamic quantities of activation are calculated, for the most part, from data at 25 and 50° in the low water regions and at 0 and 25° in the high water regions. Thus, most of the $\Delta H^{\ddagger}$ values correspond to an average temperature of either 37.5 or 12.5°. This switch from 37.5 to 12.5° has a perturbing effect on the plots of $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ *vs.* mole fraction solvent composition, but it does not affect the broad conclusions regarding complex behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ toward solvent variation. The most complex behavior is observed in the highly aqueous solvents, while the 37.5 to 12.5° temperature switch is made earlier.

$\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ Relations.—In order to obtain a point of departure in discussing the relative be-

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havior of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ toward solvent variation it is useful to inquire what relation would be required between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ to have the linear free energy relationship 3 obeyed strictly, not only at one temperature, but at other temperatures as well. In relation 3, **Y** is treated as temperature-invariant, **Y** values at 25° being employed.[3] Referring to eq. 3 and dissecting $\Delta F^{\ddagger}$ into the component $\Delta H^{\ddagger}$ and $-T\Delta S^{\ddagger}$ parts, one may express m as in eq. 4. For eq. 3 to be obeyed strictly at all

$$m = \frac{-1}{2.303RT}\,\frac{\partial \Delta H^{\ddagger}}{\partial \mathbf{Y}} + \frac{1}{2.303R}\,\frac{\partial \Delta S^{\ddagger}}{\partial \mathbf{Y}} \qquad (4)$$

temperatures, m must be a constant, independent of **Y**, at each temperature. For this to be true, both $(\partial \Delta H^{\ddagger}/\partial \mathbf{Y})$ and $(\partial \Delta S^{\ddagger}/\partial \mathbf{Y})$ must be constant. In other words, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ must be linear functions of **Y**. As a consequence, any pair of the quantities, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta F^{\ddagger}$ and **Y** are linearly related.[14]

Linear relations between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ have long been discussed.[16] Such linearity was anticipated by Evans and Polanyi[16a] on the basis of similar linear relations between entropy and enthalpy of solution for both ground and transition states. Such linearity may also be anticipated on the basis of electrostatic considerations, as will be brought out later in the manuscript. An excellent review of the success of such linear $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ relations through 1953 has been furnished recently by Leffler.[17] His review contains several examples of solvolysis with linear relations between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ as solvent is varied. A considerable body of pertinent solvolysis data has become available since 1953, and some of it is referred to in the present paper.

It is convenient to set up the set of linear relations between $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta F^{\ddagger}$ by starting with eq. 5. This expresses $\Delta H^{\ddagger}$ as linear in $\Delta F^{\ddagger}$, the

$$\Delta H^{\ddagger} = a(\Delta F^{\ddagger}) + d \qquad (5)$$

$$\Delta S^{\ddagger} = \left(\frac{a-1}{T}\right)\Delta F^{\ddagger} + d/T \qquad (6)$$

$$\Delta S^{\ddagger} = \left(\frac{a-1}{aT}\right)\Delta H^{\ddagger} + \frac{d}{aT} \qquad (7)$$

slope being a. On this basis, the slopes of the $\Delta S^{\ddagger}$ *vs.* $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$ plots are $(a-1)/T$ and $(a-1)/aT$, respectively, as expressed in eq. 6 and 7.

Pure Solvents.—Examination of the thermodynamic quantities of activation for the six pure solvents in which data are available is summarized in Table II. It is immediately obvious that $\Delta S^{\ddagger}$ is relatively constant at the level of *ca.* −3 e.u., actually −2.9 ± 0.6 e.u., for five of the solvents. On the other hand, water as solvent is uniquely set apart from the others, $\Delta S^{\ddagger}$ being some 15 e.u. higher. For the 5 solvents with relatively constant $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ is obviously fairly linear in $\Delta F^{\ddagger}$ with an a value in eq. 5 near unity. A least squares line with a equal to 0.96 reproduces the $\Delta H^{\ddagger}$ values with a probable error of 0.17 kcal./mole.

TABLE II

THERMODYNAMIC QUANTITIES OF ACTIVATION FOR SOLVOLYSIS OF *t*-BUTYL CHLORIDE IN PURE SOLVENTS

Solvent	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.	
HOH	23.22	+12.2	
HCOOH	21.0	−1.7	−2.9 ± 0.6
$HCONH_2$	22.36	−3.8	
MeOH	24.88	−3.1	
AcOH	25.80	−2.5	
EtOH	26.13	−3.2	

As brought out in Table III, a similar anomalous position is occupied by the solvent water in solvolysis of various materials, whether or not solvolysis mechanism resembles that for *t*-butyl chloride. In the case of methyl *p*-toluenesulfonate, Hyne and Robertson[18] measured rates in water and in a series of nine alcohols. For the alcohols, a plot of $\Delta S^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$ is quite linear. The point for water, however, falls far off the line.

Solvation of Ground and Transition States.—It is generally understood that the energy of activation for ionization of a substance such as *t*-butyl chloride is reduced to accessible values by solvation of the polar transition state. This is shown schematically as

$$\begin{tikzcd}
RX(g) \arrow[r, "\Delta F^{\ddagger}_{g}"] \arrow[rr, bend left, "\Delta F^{0}_{g}"] & \overset{\delta}{R}^{\ominus} - - - \overset{\delta}{X}^{\ominus}(g) \arrow[r] \arrow[d, "\Delta F^{\ddagger}_{s}"] & \overbrace{\underbrace{R^{\oplus}(g) + X^{\ominus}(g)}} \arrow[d, "\Delta F^{0}_{s}"] \\
RX(s) \arrow[u, "\Delta F^{0}_{v}"] \arrow[r, "\Delta F^{\ddagger}"] \arrow[rr, bend right, "\Delta F^{0}"'] & \overset{\delta}{R}^{\oplus} - - - \overset{\delta}{X}^{\ominus}(s) \arrow[r] & \overbrace{\underbrace{R^{\ominus}(s) + X^{\ominus}(s)}}
\end{tikzcd}$$

[the symbols (g) and (s) refer to gas and solution phases, respectively]. On this basis, $\Delta F^{\ddagger}$ for ionization in solution differs from $\Delta F^{\ddagger}_{g}$, the free energy of activation in the gas phase, by the sum of $\Delta F^{\ddagger}_{s}$, the large negative standard free energy of solution of the polar transition state, and ΔF^{0}_{v}, the molar standard free energy of vaporization of RX from the appropriate solvent. On the microscopic level, the $\Delta F^{\ddagger}_{s}$ and ΔF^{0}_{v} quantities are determined by interactions of solvent molecules with: (i) the transition state, (ii) the ground state and (iii) other solvent molecules.

The above analysis of $\Delta F^{\ddagger}$ is expressed in eq. 8. If one is interested in a solvent change, the $\Delta\Delta F^{\ddagger}$ associated with the solvent change may be expressed as in eq. 9 as the difference between the effects of the solvent change on the free energies of transition and ground states, respectively, namely,

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(14) It is important to note that the above conclusions are valid for *any* measure of solvolyzing power with which the logarithms of the rate constants are to be linearly correlated, whether this measure be **Y**, some function of the dielectric constant, or another "**Y**" based on some compound other than *t*-butyl chloride. The conclusions drawn apply to other linear free energy relationships employing a parameter invariant with temperature. An example of such a parameter is σ in Hammett's $\rho\ \sigma$ treatment.[15]

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(16) (a) A. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936); (b) R. P. Bell, *ibid.*, **33**, 496 (1937); (c) I. M. Barclay and J. A. Butler, *ibid.*, **34**, 1445 (1938).

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TABLE III

SOME $\Delta\Delta H^{\ddagger}$ AND $\Delta\Delta S^{\ddagger}$ VALUES AT 50°

Compound	EtOH → H_2O $\Delta\Delta H^{\ddagger}$, kcal./mole	EtOH → H_2O $\Delta\Delta S^{\ddagger}$, e.u.	MeOH → H_2O $\Delta\Delta H^{\ddagger}$, kcal./mole	MeOH → H_2O $\Delta\Delta S^{\ddagger}$, e.u.	$\Delta S^{\ddagger}$ H_2O, e.u.
Methyl *p*-toluenesulfonate[18]	−0.22	+ 5.1	−0.41	+3.7	−14.1
Ethyl benzenesulfonate[19,20]	− .34	+ 6.4	−1.14	3.1	−12.6
i-Propyl benzenesulfonate[21]	− .57	+11.3	−0.34	10.4	− 0.3
Methyl bromide[3b,22–24]	−3.1[a]	+11[a]			− 9.3
Ethyl bromide[3b,12,23]	−5.1[a]	+17[a]			− 7.1
Di-*i*-propyl phosphorochloridate[25]	+1.9	+16			−21.8
Benzyl chloride[26]	+0.2	+12			−12.5
α-Phenylethyl chloride[26]	*ca.* −3	*ca.* +12	*ca.* −2	*ca.* +10	*ca.* + 1
t-Butyl chloride	−2.91	+15.4	−1.66	+15.2	+12.0
Lithium chloride[b,28]	+4.3		+3.8		
Potassium chloride[b,27]			+3.0	+34.6	
Tetramethylammonium chloride[b,28]	−2.40		−2.06		

[a] 50 vol. % EtOH–H_2O → H_2O. [b] Change in ΔH^0 or ΔS^0 of solution.

$\Delta\Delta F^{\ddagger}_s + \Delta\Delta F^0_v$. Expressions for $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ corresponding to that for $\Delta\Delta F^{\ddagger}$ in eq. 9 may be put in the form of eq. 10 and 11.

$$\Delta F^{\ddagger} = \Delta F^{\ddagger}_g + \Delta F^{\ddagger}_s + \Delta F^0_v \quad (8)$$

$$\Delta\Delta F^{\ddagger} = \Delta\Delta F^{\ddagger}_s + \Delta\Delta F^0_v \quad (9)$$

$$\Delta\Delta H^{\ddagger} = \Delta\Delta H^{\ddagger}_s + \Delta\Delta H^0_v \quad (10)$$

$$\Delta\Delta S^{\ddagger} = \Delta\Delta S^{\ddagger}_s + \Delta\Delta S^0_v \quad (11)$$

Equivalent alternative forms of eq. 9 are eq. 12 and 13 which we have employed previously.[3a,c] In eq. 12, $(f_{RX}/f_{\ddagger})$ is the ratio of activity coefficients of RX and transition state, respectively, and k_0 is the rate constant in the standard solvent. Referring all activity coefficients to the gas phase leads[3a] to eq. 13. According to the latter equation, the specific solvolysis reaction rate constant, k, is proportional to the Henry's law constant, H_{RX}, of the alkyl halide molecule, and inversely proportional to the Henry's law constant of the solvolysis transition state, $H_{\ddagger}$. In these terms, $\Delta F^{\ddagger}_s$ is related to

$$k = k_0(f_{RX}/f_{\ddagger}) \quad (12)$$

$$k = \kappa(H_{RX}/H_{\ddagger}) \quad (13)$$

$$\Delta\Delta F^{\ddagger} = RT\,\Delta \ln H_{\ddagger} - RT\,\Delta \ln H_{RX} \quad (14)$$

$H_{\ddagger}$ and ΔF^0_v is related to H_{RX}. For a given solvent change, $\Delta\Delta F^{\ddagger}$ is given by eq. 14 as the sum of $RT\,\Delta \ln H_{\ddagger}$ and $-RT\,\Delta \ln H_{RX}$. From the observed $\Delta \ln k$ or $\Delta\Delta F^{\ddagger}$ value and $\Delta \ln H_{RX}$, which can be measured, $\Delta \ln H_{\ddagger}$ may be calculated.[3a] Thus the effects of solvent change on rate can be separated into the separate effects on ground and transition state, respectively.

For purposes of discussion and calculation, the transition state in a solvolytic ionization often has been approximated as the fully formed (and dissociated) pair of ions,[29–31] $R^{\oplus}$ and $X^{\ominus}$, the solvation of $R^{\oplus}$ being treated like that of an ordinary inorganic ion.[30–32] This amounts to substituting the standard free energy of ionization of RX in the gas phase, ΔF^0_g, for $\Delta F^{\ddagger}_g$, and the standard free energy of solution of the ionized RX, ΔF^0_s, for $\Delta F^{\ddagger}_s$ in eq. 8.

Interesting and instructive attempts to estimate rates of solvolysis in solution from the energetics of ionization in the gas phase and the calculated energetics of solvation of $R^{\oplus}$ and $X^{\ominus}$ have been made by Evans[30] and Franklin.[31] By employing the general method of Latimer, Pitzer and Slansky[33] for estimating enthalpy and entropy of solvation of trimethylcarbonium halides, Franklin[31] has actually been able to calculate rates of solvolysis of *t*-butyl halides in 80% ethanol which agree, partly fortuitously, to within *ca.* one power of ten with those observed.

Since $\Delta F^{\ddagger}_s$ is so important in reducing free energy of activation to the observed $\Delta F^{\ddagger}$, predictions regarding the behavior of $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ have often been based on the behavior of ΔF^0_s, ΔH^0_s and ΔS^0_s of ordinary salts.[34] For example, regarding the level of $\Delta S^{\ddagger}$ values, negative values are usually anticipated[35] because of the large negative ΔS^0_s values in solvation of ordinary salts. Because of the much greater importance of $\Delta F^{\ddagger}_s$ over ΔF^0_v in determining $\Delta F^{\ddagger}$ in eq. 8, a further impression has apparently developed that, for solvent changes, the $\Delta\Delta F^{\ddagger}_s$, $\Delta\Delta H^{\ddagger}_s$ and $\Delta\Delta S^{\ddagger}_s$ quantities will be much more important than $\Delta\Delta F^0_v$, $\Delta\Delta H^0_v$ and $\Delta\Delta S^0_v$ in determining the $\Delta\Delta F^{\ddagger}$, $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ quantities associated with the solvent change. Comparing the transition state with ordinary salts, one would then anticipate a parallelism between $\Delta\Delta F^{\ddagger}$, $\Delta\Delta H^{\ddagger}$ or $\Delta\Delta S^{\ddagger}$, and $\Delta\Delta F^0_s$, $\Delta\Delta H^0_s$ and $\Delta\Delta S^0_s$, respectively, of ordinary salts.

Comparing the observed facts with predictions based on analogy with ordinary salts, we may first

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TABLE IV

DISSECTION OF $\Delta\Delta F^{\ddagger}$ VALUES IN SOLVOLYSIS OF *t*-BUTYL CHLORIDE INTO GROUND STATE AND TRANSITION STATE CONTRIBUTIONS

Solvent, vol. %	Temp., °C.	log $(p/N)^a$	log $(p/M)^b$	Δ log (p/M)	$\Delta\Delta F^{\ddagger}$	$\Delta\Delta F^{\ddagger}$s	$\Delta\Delta F^0{}_v{}^c$
MeOH	0	2.634	1.231[d]	0	0	0	0
70.5% MeOH–H_2O	0	3.951	2.400[d]	1.169	−2.79[e]	−1.33	−1.46
60.5% MeOH–H_2O	0	4.292	2.703[d]	1.472	−3.50[e]	−1.66	−1.84
49.5% MeOH–H_2O	0	4.723	3.127[d]	1.896	−4.12[e]	−1.75	−2.37
MeOH	25	3.350	1.959[d]	0	0	0	0
90.17% MeOH–H_2O	25	3.697	2.245[d]	0.286	−1.08[e]	−0.69	−0.39
80.09% MeOH–H_2O	25	4.043	2.545[d]	.586	−2.01[e]	−1.21	− .80
70.45% MeOH–H_2O	25	4.390	2.846[d]	.887	−2.80[e]	−1.59	−1.21
H_2O	25	6.699	4.957[f]	2.998	−6.25	−2.16	−4.09
AcOH	25	3.090	1.849[f]	−0.110	+0.75	+0.60	+0.15
AcOH–Ac_2O N_{AcOH}0.042	25	2.895	1.869[f]	− .090	3.00[g]	2.88	.12
EtOH	25	3.037	1.807[f]	− .152	1.28	1.07	.21
EtOH	25	2.799	1.569[h]	− .390	1.28	0.75	.53
90% EtOH–H_2O	25	3.225	1.897[h]	− .062	−0.47	− .55	.08
80% EtOH–H_2O	25	3.778	2.371[h]	.412	−1.49	− .89	− .56
70% EtOH–H_2O	25	4.210	2.739[h]	.780	−2.30	−1.24	−1.06
60% EtOH–H_2O	25	4.772	3.246[h]	1.287	−3.02	−1.26	−1.76
50% EtOH–H_2O	25	5.260	3.686[h]	1.727	−3.75	−1.39	−2.36
40% EtOH–H_2O	25	5.761	4.143[h]	2.184	−4.59	−1.61	−2.98

[a] log H_{RX}, p being vapor pressure in mm. and N being mole fraction, respectively, of *t*-butyl chloride. [b] log H_{RX}, molarity, M, of *t*-butyl chloride being employed instead of mole fraction, N. [c] $-RT\,\Delta\ln(p/M)$. [d] Based on data of Olson, Ruebsamen and Clifford.[37] [e] Based on data of Fainberg and Winstein.[3c] [f] Calculated from data of Grunwald and Winstein.[3a] [g] Based on the assumed[3a] $E^{\ddagger} = 26.4$ kcal./mole. [h] Calculated from the interpolated values of Olson and Halford.[36]

look at the $\Delta S^{\ddagger}$ values. These are generally negative for solvolysis of *t*-butyl chloride in most solvents, and this is true also for other substrates listed in Table III, most of them being substances whose solvolysis is not limiting.[3b] However, that $\Delta S^{\ddagger}$ is not always negative[10,35] is shown by the high positive $\Delta S^{\ddagger}$ value for *t*-butyl chloride in water and highly aqueous solvents.[1,12]

Going on to compare the effects of the solvent change, MeOH → HOH, with the expectations based on $\Delta\Delta F^0{}_s$, $\Delta\Delta H^0{}_s$ or $\Delta\Delta S^0{}_s$ of ordinary salts, it is, of course, obvious that $\Delta\Delta F^{\ddagger}$ has the expected sign based on such an analogy. Further, $\Delta\Delta S^{\ddagger}$ is substantially positive just as are the $\Delta\Delta S^0{}_s$ values for salts. Because of the relatively low entropy of water with its relatively highly organized liquid structure,[27,35] substantial positive $\Delta\Delta S^0{}_s$ values are observed for ordinary salts, this being +35 e.u. for potassium chloride (Table III). For all the substances listed in Table III, regardless of the preference for solvolysis mechanism, positive values of $\Delta\Delta S^{\ddagger}$ are the rule. In the case of *t*-butyl chloride, it is interesting specifically to compare the observed $\Delta\Delta S^{\ddagger}$ of +15 e.u. with the value of $\Delta\Delta S^0{}_s$ for trimethylcarbonium chloride of +31 e.u. given by Franklin's treatment.[31]

Comparing $\Delta\Delta H^{\ddagger}$ for the solvent change, MeOH → HOH, with $\Delta\Delta H^0{}_s$ for salts, we note that $\Delta\Delta H^{\ddagger}$ is −1.7 kcal./mole (−2.9 for EtOH → H_2O), while $\Delta\Delta H^0{}_s$ for lithium or potassium chloride has the opposite sign. However, $\Delta\Delta H^0{}_s$ does have a negative sign (−2.1 kcal./mole) for tetramethylammonium chloride, which might be expected[32] to be a better model for trimethylcarbonium chloride than lithium or potassium chloride. Again, it is interesting to compare the $\Delta\Delta H^{\ddagger}$ value of −1.7 kcal./mole with the $\Delta\Delta H^0{}_s$ value obtained for the model for trimethylcarbonium chloride employed by Franklin.[31] For the latter value, Franklin's treatment gives +3.8 kcal./mole.

With *t*-butyl chloride as the substrate in solvolysis, there are sufficient available data on Henry's law constants[3a,36,37] to indicate from the outset that $\Delta\Delta F^{\ddagger}$ values due to solvent change cannot be discussed on the basis of $\Delta\Delta F^{\ddagger}{}_s$ values alone. In Table IV is given the dissection of $\Delta\Delta F^{\ddagger}$ values into the component $\Delta\Delta F^{\ddagger}{}_s$ and $\Delta\Delta F^0{}_v$ parts. In this table, all the $\Delta\Delta F$ values are referred to methanol as the standard solvent. Focusing attention on the pure solvents for the moment, it may be seen that $\Delta\Delta F^{\ddagger}$ does tend to be associated mainly with a corresponding change in $\Delta\Delta F^{\ddagger}{}_s$, except for the change to water as solvent. For solvent changes such as MeOH → HOH or EtOH → HOH, $\Delta\Delta F^0{}_v$ values, relating to effects on the ground state, are of major importance.[38] For these solvent changes, $\Delta\Delta F^0{}_v$ is *ca.* twice as large as $\Delta\Delta F^{\ddagger}{}_s$.

How difficult it is to calculate the effect of solvent change on rate from first principles may be illustrated for the MeOH → HOH change by combining Franklin's $\Delta\Delta F^0{}_s$ value[31] (which is used as an approximation to $\Delta\Delta F^{\ddagger}{}_s$) with the $\Delta\Delta F^0{}_v$ value given by Henry's law constants. $\Delta\Delta F^0{}_s$, evaluated as $\Delta\Delta H^0{}_s - T\Delta\Delta S^0{}_s$, is −5.5 kcal./mole at 25°.

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(38) The $\Delta\Delta F^0{}_v$ value for the solvent change, MeOH → H_2O, is in principle separable into $\Delta\Delta H^0{}_v$ and $\Delta\Delta S^0{}_v$ values from data on the temperature coefficients of the Henry's law constants. However, as far as we know, the necessary data are unavailable. On the basis of the behavior of other halides, for example, chloroform, the $\Delta\Delta F^0{}_v$ value for *t*-butyl chloride may be due mainly to the entropy term [E. Grunwald, Thesis, U.C.L.A., 1947; A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 349].

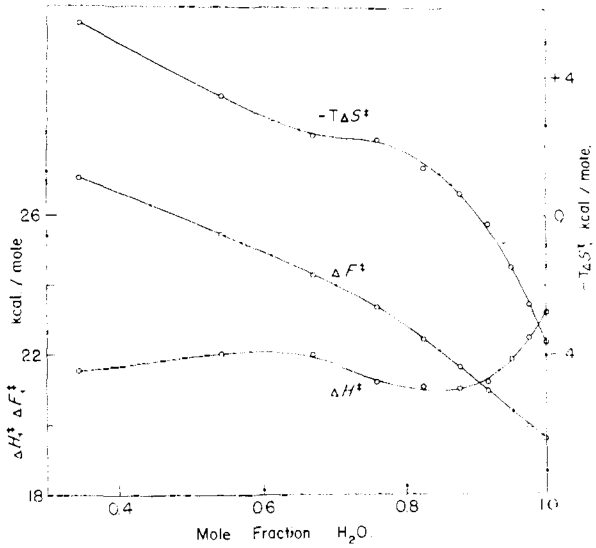

Fig. 1.—Plot of $\Delta H^{\ddagger}$, $\Delta F^{\ddagger}$, and $-T\Delta S^{\ddagger}$ vs. mole fraction H_2O for solvolysis of *t*-butyl chloride in dioxane–H_2O mixtures at 25.0°.

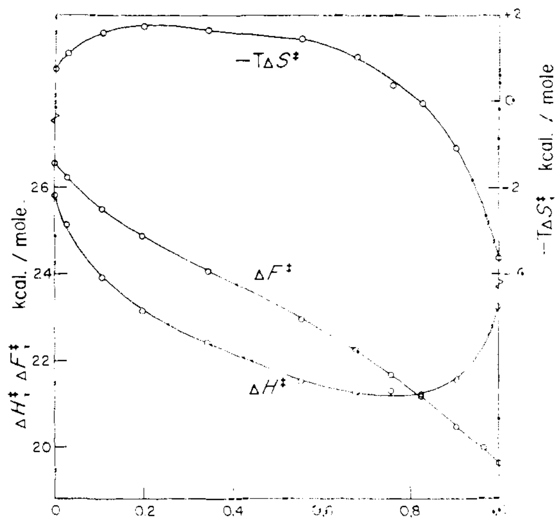

Fig. 2.—Plot of $\Delta H^{\ddagger}$, $\Delta F^{\ddagger}$ and $-T\Delta S^{\ddagger}$ vs. mole fraction H_2O for solvolysis of *t*-butyl chloride in AcOH–H_2O mixtures at 25.0°.

Addition of $\Delta\Delta F^0_v$ gives -9.6 kcal./mole for $\Delta\Delta F^{\ddagger}$, -6.2 kcal./mole being the observed value. The discrepancy corresponds to a factor of $10^{2.5}$ in rate.

Binary Solvents; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ vs. Mole Fraction.—Thermodynamic quantities of activation for solvolysis of *t*-butyl chloride have now been made available for the complete composition ranges of a number of binary solvent pairs. These data permit an examination of the variation of the thermodynamic quantities of activation in solvolysis with solvent composition, and they reveal a number of striking features. Some of these features become apparent when $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $-T\Delta S^{\ddagger}$ are plotted against mole fraction of the more rapid component of each binary solvent pair, as in Figs. 1, 2 and 3. There exists a considerable diversity of behavior of the thermodynamic quantities of activation toward solvent composition for the various binary solvent systems.

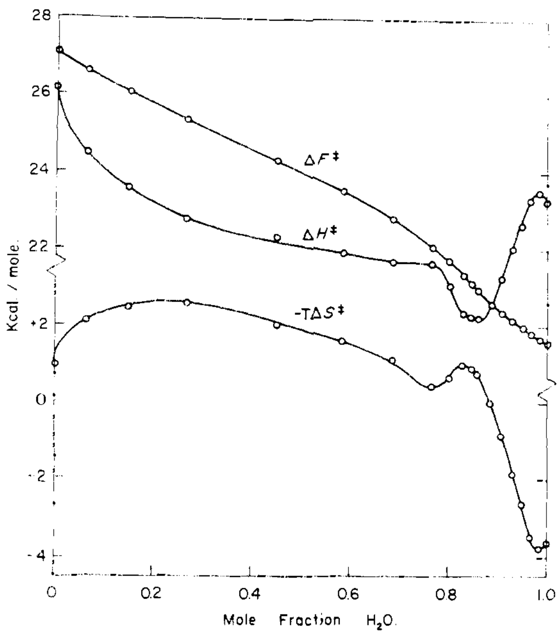

Fig. 3.—Plot of $\Delta H^{\ddagger}$, $\Delta F^{\ddagger}$ and $-T\Delta S^{\ddagger}$ vs. mole fraction H_2O for solvolysis of *t*-butyl chloride in EtOH–H_2O at 25.0°.

The behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for solvolysis of *t*-butyl chloride is most simple in the non-aqueous solvent pairs. In mixtures of acetic and formic acids, substantially the entire contribution to the increase in rate in going from acetic to formic acid is a 5.8 kcal./mole decrease in $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ remaining almost constant at -3.2 ± 0.8 e.u. The latter, however, does show a shallow minimum at 75% AcOH–HCOOH. In dioxane–formic acid mixtures, decrease in $\Delta H^{\ddagger}$ and increase in $\Delta S^{\ddagger}$ are *ca.* equally responsible for increase in rate as the formic acid content is increased.

Still a different behavior is apparent in the solvent mixtures involving water plus an "inert" solvent, *e.g.*, acetone–water and dioxane–water mixtures. Here the principal contribution to increase in rate is made by increasing $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ being roughly constant. This is shown graphically for the dioxane–water mixtures in Fig. 1. The character shown by $\Delta H^{\ddagger}$, involving a weak maximum at *ca.* 60 mole % water and a marked minimum at 85 mole % water, is real, being well outside of experimental error.

The situation becomes more complex for acetic acid–water mixtures, as shown in Fig. 2. Here $\Delta H^{\ddagger}$ passes through a minimum at *ca.* 75 mole % water, and $-T\Delta S^{\ddagger}$ through a maximum at *ca.* 20 mole % water. This plot is fairly characteristic of those solvent mixtures in which both components are hydroxylic. Thus, the plots for formic acid–water and methanol–water mixtures are quite similar, and even ethanol–water, discussed further below, shows a resemblance. With acetic acid–water mixtures, the principal contribution to increasing rate over the first two-thirds of the solvent range is from the decrease in $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ being relatively constant. In contrast, in the high water region, the effect of $\Delta S^{\ddagger}$ becomes increasingly important, sufficiently so as to outweigh by far the actual reversal of the trend in $\Delta H^{\ddagger}$.

The most complex behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is observed in ethanol–water mixtures. Thus, while $\Delta F^{\ddagger}$ is a monotonically decreasing, relatively characterless function of solvent composition, $\Delta H^{\ddagger}$ and $-T\Delta S^{\ddagger}$ go through some remarkable reversals. Roughly describing the behavior, from pure ethanol to *ca.* 85 mole % water, the chief contribution to decrease in $\Delta F^{\ddagger}$ is decrease in $\Delta H^{\ddagger}$. In the last 15 mole % of water, an enormous increase in $\Delta S^{\ddagger}$ dominates the picture, more than compensating for the reversal in the trend of $\Delta H^{\ddagger}$. In this case, $\Delta H^{\ddagger}$ drops six kcal./mole over the first 85 mole %, then rises three kcal./mole in the last 15 mole % of water. The $\Delta S^{\ddagger}$ value remains relatively constant at −4.6 ± 2.2 e.u. over the first 85 mole %, and then abruptly rises more than 15 e.u. in going the rest of the way to pure water.[39]

Complex behavior of $\Delta H^{\ddagger}$ toward solvent variation has also been reported by Tommila[21,40] for hydrolysis of methyl, ethyl and *i*-propyl benzenesulfonates in acetone–water and dioxane–water mixtures. In a paper which became available to us since our work was first presented,[1] Tommila and co-workers[12] report a complex pattern of $\Delta H^{\ddagger}$ *vs.* solvent composition for hydrolysis of ethyl bromide, *t*-butyl bromide and *t*-butyl chloride in aqueous acetones. Further, Hyne and Robertson[18] have observed shallow minima in $\Delta H^{\ddagger}$ near pure water for solvolysis of methyl benzenesulfonate in aqueous methanol, ethanol and 2-propanol.

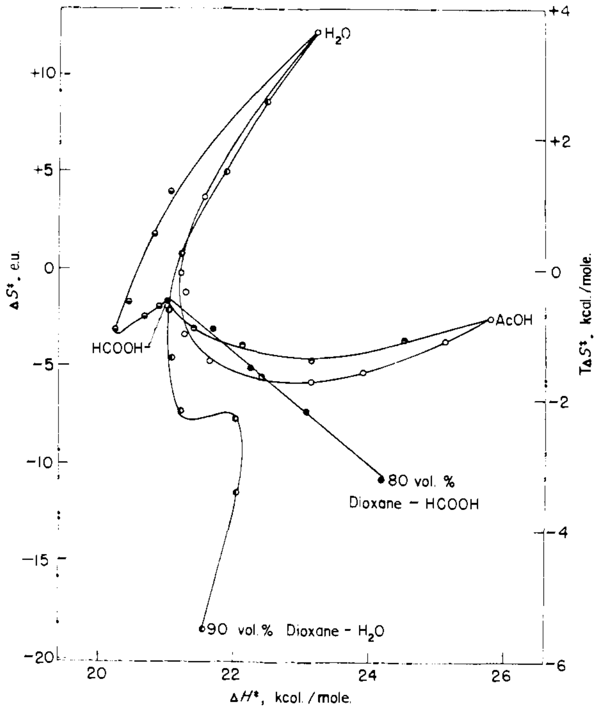

Fig. 4.—Plot of $\Delta S^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$ for solvolysis of *t*-butyl chloride at 25.0°: ○, AcOH–H_2O; ◓, AcOH–HCOOH; ◒, HCOOH–H_2O; ●, dioxane–HCOOH; ◐, dioxane–H_2O.

A B C Classification.—When $\Delta S^{\ddagger}$ is plotted *vs.* $\Delta H^{\ddagger}$, as in Figs. 4, 5 and 6, for solvolysis of *t*-butyl chloride in the various binary solvent systems, rather complex curves are obtained, the most complex being the plot for the ethanol–water mixtures in Fig. 6. For discussion, comparison and tabulation purposes, it is convenient to set up a symbolic terminology for characterizing the behavior of the thermodynamic quantities of activation toward solvent variation.

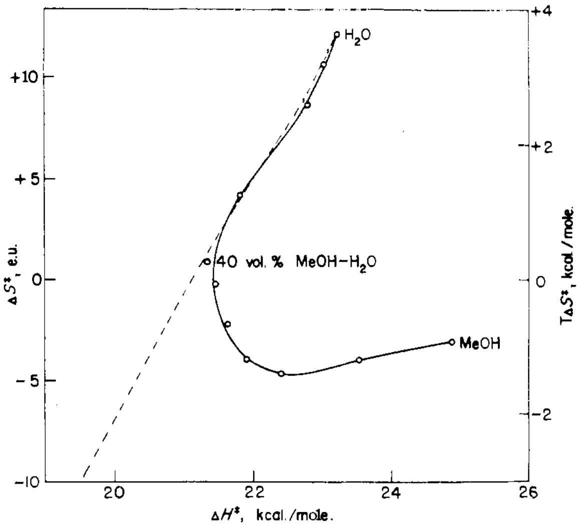

Fig. 5.—Plot of $\Delta S^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$ for solvolysis of *t*-butyl chloride in MeOH–H_2O mixtures. Dashed line calculated on the basis of electrostatic considerations; circles are experimental data.

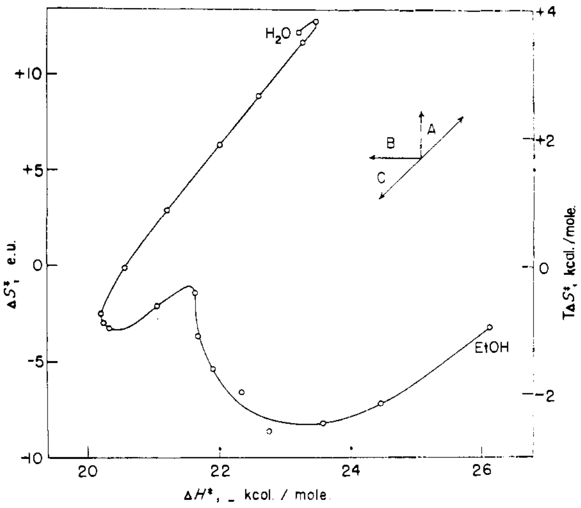

Fig. 6.—Plot of $\Delta S^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$ for solvolysis of *t*-butyl chloride in EtOH–H_2O mixtures at 25.0°.

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(39) The variations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with solvent composition are not independent of each other. One limitation on the independence of their variation can be derived from the observation that $\Delta F^{\ddagger}$ decreases monotonically as N_{H_2O} changes from 0 to 1. Mathematically, this can be expressed by the inequality, $d\Delta F^{\ddagger}/dN_{H_2O} < 0$. Substitution of $(\Delta H^{\ddagger} - T\Delta S^{\ddagger})$ for $\Delta F^{\ddagger}$ and rearrangement of terms lead to the inequality, $d\Delta H^{\ddagger}/dN_{H_2O} < d(T\Delta S^{\ddagger})/dN_{H_2O}$. This expresses the requirement that, whatever variation the slope of $\Delta H^{\ddagger}$ *vs.* N_{H_2O} goes through, it is always exceeded algebraically by the slope of the curve of $T\Delta S^{\ddagger}$ *vs.* N_{H_2O}. Thus, changes in slope of one curve are always accompanied by related changes in slope of the other.

(40) E. Tommila and E. Merikallio, *Suomen Kemistilehti*, **26B**, 79 (1953).

TABLE V

SUMMARY OF THERMODYNAMIC CLASSIFICATION SCHEME

Class	$\partial\Delta H^{\ddagger}/\partial\Delta F^{\ddagger}$	$\partial\Delta S^{\ddagger}/\partial\Delta F^{\ddagger}$	$\partial\Delta S^{\ddagger}/\partial\Delta H^{\ddagger}$	$\partial\Delta F^{\ddagger}/\partial N$	a	m_2/m_1
A	−	−	+	−	<0	$>1 \rightarrow 1$
B	+	−	−	−	$0 \rightarrow 1$	$1 \rightarrow T_1/T_2$
C	+	+	+	−	>1	$(T_1/T_2) \rightarrow < (T_1/T_2)$
D	−	−	+	+		
E	+	−	−	+		
F	+	+	+	+		

TABLE VI

CORRELATION OF SOLVOLYSIS RATES WITH **Y** AND THE **A B C** CLASSIFICATION

Compound	Temp., °C.	Solvent range	No. of points	m	$\log k_0$	r^a	Class
t-Butyl chloride	50.0	All solvents	69	0.974	−3.716	0.043	
		0–100% EtOH–H_2O	19	.974	−3.698	.052	${}_{0}\mathbf{C}_{25}\mathbf{B}_{75}\mathbf{C}_{85}\mathbf{A}_{100}$
		0–100% MeOH–H_2O	11	.983	−3.693	.041	${}_{0}\mathbf{C}_{35}\mathbf{B}_{75}\mathbf{A}_{100}$
		0–100% AcOH–HCOOH	6	.926	−3.676	.012	${}_{0}\mathbf{C}_{35}\mathbf{B}_{100}$
		0–100% HCOOH–H_2O	8	1.070	−3.990	.027	${}_{0}\mathbf{C}_{35}\mathbf{A}_{100}$
		0–100% AcOH–H_2O	11	0.961	−3.676	.044	${}_{0}\mathbf{C}_{20}\mathbf{B}_{85}\mathbf{A}_{100}$
		0–90 vol. % dioxane–H_2O	10	1.007	−3.774	.027	${}_{35}\mathbf{A}_{60}\mathbf{B}_{85}\mathbf{A}_{100}$
		0–90 vol. % Me_2CO–H_2O[d]	7	1.009	−3.779	.038	${}_{30}\mathbf{A}_{50}\mathbf{B}_{90}\mathbf{A}_{100}$
		0–80 vol. % dioxane–HCOOH	5	0.960	−3.723	.004	${}_{35}\mathbf{B}_{100}$
Neopentyldimethylcarbinyl chloride[9]	25.0	70–90 vol. % EtOH–H_2O	4	.856	−3.704	.007	
	50.0	70–90 vol. % EtOH–H_2O	4	.855	−2.411	.009	${}_{25}\mathbf{B}_{60}$
Dineopentylmethylcarbinol chloride[9]	25.0	80–100 vol. % EtOH–H_2O	4	.665	−2.302	.008	
	50.0	80–100 vol. % EtOH–H_2O	4	.612	−1.186	.013	${}_{0}\mathbf{C}_{45}$
Di-isopropyl phosphorochloridate[25]	25.0	0–100% EtOH–H_2O[b]	5	.376	−3.426	.037	
	50.0	0–100% EtOH–H_2O	4	.411	−2.688	.047	${}_{0}\mathbf{A}_{100}$
Ethyl dichloroacetate[41]	35.0	50–70 vol. % Me_2CO–H_2O	3	.701	−7.284	.013	
	45.0	50–80 vol. % Me_2CO–H_2O	4	.622	−6.903	.007	${}_{65}\mathbf{C}_{80}$
Methyl benzenesulfonate[18]	50.0	0–100% EtOH–H_2O, MeOH–H_2O	18	.220	−4.503	.025	
	75.0	0–100% EtOH–H_2O, MeOH–H_2O	15	.217	−3.511	.028	
	50.0	0–100% EtOH–H_2O	13	.214	−4.502	.024	${}_{0}\mathbf{B}_{85}\mathbf{A}_{100}$
	75.0	0–100% EtOH–H_2O	10	.211	−3.516	.027	
	50.0	0–100% MeOH–H_2O	6	.235	−4.516	.012	${}_{0}\mathbf{B}_{85}\mathbf{A}_{100}$
	75.0	0–100% MeOH–H_2O	6	.230	−3.508	.011	
Ethyl benzenesulfonate[19,40]	25.0	0–80 wt. % Me_2CO–H_2O 0–90 wt. % dioxane–H_2O	15	.440	−6.553	.028	
	50.0	0–80 wt. % Me_2CO–H_2O 0–90% wt. % dioxane–H_2O	16	.440	−5.335	.029	
	25.0	0–80 wt. % Me_2CO–H_2O	7	.441	−6.562	.035	
	50.0	0–80 wt. % Me_2CO–H_2O	7	.441	−5.338	.034	${}_{5}\mathbf{C}_{20}\mathbf{A}_{80}\mathbf{B}_{95}\mathbf{A}_{100}$
	25.0	0–90 wt. % dioxane–H_2O	9	.440	−6.543	.024	
	50.0	0–90 wt. % dioxane–H_2O	10	.440	−5.333	.029	${}_{20}\mathbf{A}_{55}\mathbf{B}_{90}\mathbf{C}_{95}\mathbf{A}_{100}$
	50.0	0–100% EtOH–H_2O, MeOH	5	.284	−4.819	.052	
n-Propyl benzenesulfonate[19,21]	25.0	0–90 wt. % Me_2CO–H_2O	7	.454	−6.816	.044	${}_{25}\mathbf{A}_{70}\mathbf{C}_{90}\mathbf{A}_{100}$
	50.0	0–90 wt. % Me_2CO–H_2O	7	.450	−5.617	.031	
Ethyl bromide[c,12]	40.0	0–85 wt. % Me_2CO–H_2O	20	.339	−6.787	.031	
	60.0	0–85 wt. % Me_2CO–H_2O	20	.364	−5.950	.030	${}_{35}\mathbf{A}_{72}\mathbf{C}_{94}\mathbf{A}_{100}$

[a] Probable error of the fit.[42] [b] The value for 60% EtOH–H_2O was far out of line and was omitted. [c] Based on **Y** values calculated or interpolated from Tommila's[12] data on solvolysis rates of *t*-butyl chloride in presumably the same solvents. [d] Tommila, *et al.*,[12] recently have reported solvolysis data for *t*-butyl chloride in 18 Me_2CO–H_2O mixtures at several temperatures. Their data are in essential agreement with those reported in this and the previous paper[3c] in the high water region (N_{H_2O} = 0.83 to 1.00), but differ seriously from our data in the low water region.

The classification system may be defined with the aid of a plot of $\Delta S^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$ as shown in the inset in Fig. 6. In such plots, arrowheads may be placed on the curves to indicate the direction of increasing **Y** or increasing mole fraction of the more rapid component of a binary solvent set, *e.g.*, N_{H_2O}. When the $\Delta S^{\ddagger}$ axis is laid out in units of $T\Delta S^{\ddagger}$ (kcal./mole), as in Figs. 4, 5 and 6, a line of unit slope is a line of constant $\Delta F^{\ddagger}$. Values of $\Delta F^{\ddagger}$ decrease as one crosses these iso-free energy lines from the lower right-hand side of the plot to the upper left. Since $\Delta F^{\ddagger}$ decreases continuously, the plot of $\Delta S^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$, however it changes direction, is constrained to cut each 45° line once and only once. In general, it can do this in one of three ways: **A**, both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ increase; **B**, $\Delta H^{\ddagger}$ decreases while $\Delta S^{\ddagger}$ increases; **C**, both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ decrease. These classes are given in Table V along with the signs of $(\partial\Delta H^{\ddagger}/\partial\Delta F^{\ddagger})$, $(\partial\Delta S^{\ddagger}/\partial\Delta F^{\ddagger})$ and $(\partial\Delta S^{\ddagger}/\partial\Delta H^{\ddagger})$. For classes **A** and **C**, the sign of $\partial(\Delta S^{\ddagger})/\partial(\Delta H^{\ddagger})$ is positive, while for class B, the sign is negative.

When a linear relation obtains between the thermodynamic quantities of activation, classes **A**, **B** and **C** are prescribed by definite boundary values of the slope a in eq. 5 relating $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$. Thus, a is less than 0 for **A**, between 0 and 1 for **B** and greater than 1 for **C**.

Classes **A**, **B** and **C** suffice for neutral solvolysis of neutral substrates, for which solvolysis rate in-

TABLE VII

LINEAR FITS OF THERMODYNAMIC DATA TO $\Delta H^{\ddagger} = a\Delta F^{\ddagger} + d$

Compound	Temp., °C.	Solvent range	Class	n[a]	r,[b] kcal./mole	d, kcal./mole	a
t-Butyl chloride	25.0	EtOH, AcOH, MeOH, $HCONH_2$, HCOOH	$\mathbf{B}$	5	0.17	0.14	0.96
		90–100 vol. % EtOH–H_2O	${}_{0}\mathbf{C}_{27}$	4	.31	−24.63	1.86
		50–90 vol. % EtOH–H_2O	${}_{27}\mathbf{B}_{76}$	5	.08	13.56	0.36
		35–50 vol. % EtOH–H_2O	${}_{76}\mathbf{C}_{83}\mathbf{B}_{86}$	5	.11	− 9.09	1.39
		0–35 vol. % EtOH–H_2O	${}_{86}\mathbf{A}_{100}$	8	.19	75.00	−2.63
		80–100 vol. % MeOH–H_2O	${}_{0}\mathbf{C}_{35}$	3	.01	− 7.12	1.24
		40–80 vol. % MeOH–H_2O	${}_{35}\mathbf{B}_{75}$	5	.08	13.24	0.38
		0–40 vol. % MeOH–H_2O	${}_{75}\mathbf{A}_{100}$	5	.15	50.18	−1.37
		0–70 vol. % MeOH–H_2O	${}_{50}\mathbf{A}_{100}$	7	.04	50.34[c]	−1.39[c]
		70–100 vol. % MeOH–H_2O	${}_{0}\mathbf{A}_{50}$	4	.02	75.51[c]	−2.48[c]
		0–100% AcOH–HCOOH	${}_{0}\mathbf{C}_{35}\mathbf{B}_{100}$	6	.22	0.23	0.95
		75–100 vol. % AcOH–HCOOH	${}_{0}\mathbf{C}_{35}$	3	.01	− 9.25	1.32
		0–75 vol. % AcOH–HCOOH	${}_{35}\mathbf{B}_{100}$	4	.07	5.42	0.72
		0–100% HCOOH–H_2O	${}_{0}\mathbf{C}_{35}\mathbf{A}_{100}$	8	.49	39.69	−0.90
		80–100 vol. % HCOOH–H_2O	${}_{0}\mathbf{C}_{35}$	4	.05	−25.42	2.16
		14.3–80 vol. % HCOOH–H_2O	${}_{35}\mathbf{A}_{93}$	4	.03	34.22	−0.66
		0–14.3 vol. % HCOOH–H_2O	${}_{93}\mathbf{A}_{100}$	2	..	153.62	−6.66
		80–100 mole % AcOH–H_2O	${}_{0}\mathbf{C}_{20}$	4	.09	−16.24	1.58
		45–80 mole % AcOH–H_2O	${}_{20}\mathbf{B}_{55}$	3	.02	2.23	0.84
		15–45 mole % AcOH–H_2O	${}_{55}\mathbf{B}_{85}$	4	.07	18.02	0.15
		0–15 mole % AcOH–H_2O	${}_{85}\mathbf{A}_{100}$	3	.31	48.71	−1.31
		0–90 vol. % dioxane–H_2O	${}_{35}\mathbf{A}_{60}\mathbf{B}_{85}\mathbf{A}_{100}$	10	.49	23.79	−0.09
		70–90 vol. % dioxane–H_2O	${}_{35}\mathbf{A}_{60}$	3	.11	26.47	−0.18
		60–70 vol. % dioxane–H_2O	${}_{60}\mathbf{B}_{75}$	2	..	2.81	0.79
		40-60 vol. % dioxane–H_2O	${}_{75}\mathbf{B}_{85}$	3	.02	18.63	0.11
		0–30 vol. % dioxane–H_2O	${}_{92}\mathbf{A}_{100}$	4	.10	50.70	−1.41
		0–30 vol. % dioxane–H_2O[c]	${}_{92}\mathbf{A}_{100}$	4	.11	47.24[c]	−1.22[c]
		30–50 vol. % dioxane–H_2O[c]	${}_{83}\mathbf{A}_{92}$	3	.10	60.51[c]	−1.86[c]
		0–90 vol. % Me_2CO–H_2O	${}_{30}\mathbf{A}_{50}\mathbf{B}_{90}\mathbf{A}_{100}$	7	.72	23.77	−0.09
		0–80 vol. % dioxane–HCOOH	${}_{35}\mathbf{B}_{100}$	5	.04	9.66	0.53
Neopentyldimethyl carbinyl chloride[9]	50.0	70–90 vol. % EtOH–H_2O	${}_{25}\mathbf{B}_{60}$	3	.01	21.52	.03
Dineopentylmethyl carbinyl chloride[9]	50.0	80–100 vol. % EtOH–H_2O	${}_{0}\mathbf{C}_{45}$	4	.14	− 2.31	1.03
1-Chloro-2-methyl-propan-2-ol[43]	85.1	0–80 vol. % EtOH–H_2O	${}_{45}\mathbf{A}_{100}$	5	.22	42.89	−0.59
2,3-Dichlorodioxane[44]	25.0	0–75 vol. % dioxane–H_2O	${}_{60}\mathbf{B}_{100}$	5	.14	6.10	0.66
	25.0	0–90 vol. % Me_2CO–H_2O	${}_{30}\mathbf{B}_{100}$	10	.16	7.83	0.57
Methyl chloromethyl ether[45]	25.0	dioxane–alcohol benzene–alcohol CCl_4–alcohol	${}_{5}\mathbf{A}_{100}$				
		0–80 vol. % dioxane–2-chloroethanol	${}_{25}\mathbf{A}_{100}$				
Ethyl chloromethyl ether[45]	25.0	40–80 vol. % dioxane–EtOH	${}_{25}\mathbf{A}_{70}$				
Dichlorodimethyl ether[45]	25.0	0–80 vol. % dioxane–EtOH	${}_{25}\mathbf{A}_{100}$				
p-Nitrobenzyl bromide[46]	50.0	50–90 wt. % dioxane–H_2O	${}_{35}\mathbf{A}_{85}$	3	.13	58.37	−1.51
Benzoyl chloride[47]	25.0	60–95 vol. % Me_2CO–H_2O	${}_{20}\mathbf{A}_{75}$	5	.14	65.41	−2.34
Methanesulfonyl chloride[48]	50.0	50–85 wt. % dioxane–H_2O	${}_{45}\mathbf{C}_{85}$	7	.13	32.67	2.08
Diisopropyl phosphorochloridate[25]	50.0	0–100 vol. % EtOH–H_2O[d]	${}_{0}\mathbf{A}^{d}_{100}$	5	.27	27.04	−0.63
Ethyl dichloroacetate[41]	50.0	50–70 vol. % Me_2CO–H_2O	${}_{65}\mathbf{C}_{80}$	3	.06	−45.12	2.14
Methyl *p*-toluenesulfonate[18]	50.0	9 pure alcohols	$\mathbf{A}$	9	.57	129.21	−4.12
Ethyl bromide[h,12]	50.0	0–85 wt. % Me_2CO–H_2O	${}_{35}\mathbf{A}_{75}\mathbf{C}_{94}\mathbf{A}_{100}$				
Ethyl benzenesulfonate[19,40]	50.0	92.5–98 wt. % Me_2CO–H_2O	${}_{5}\mathbf{C}_{20}$	4	.06	−28.59	1.69
		0–92.5 wt. % Me_2CO–H_2O	${}_{20}\mathbf{A}_{80}\mathbf{B}_{95}\mathbf{A}_{100}$	9	.24	28.32	−0.29
		0–95 wt. % dioxane–H_2O	${}_{20}\mathbf{A}_{55}\mathbf{B}_{90}\mathbf{C}_{95}\mathbf{A}_{100}$	10	.35	24.86	−0.16
		0–95 vol. % C_6H_6–EtOH	${}_{10}\mathbf{A}_{100}$	8	.29	79.68	−2.16
		0–80 vol. % Me_2CO–EtOH	${}_{25}\mathbf{A}_{100}$	9	.12	25.43	−0.165

TABLE VII (*continued*)

Compound	Temp., °C.	Solvent range	Class	n^a	r,[b] kcal./mole	d, kcal./mole	a
n-Propyl benzenesulfonate[21]	50.0	56–90 wt. % $Me_2CO–H_2O$	$_{25}\mathbf{A}_{70}$	3	.21	37.06	−0.59
		27.2–56 wt. % $Me_2CO–H_2O$	$_{70}\mathbf{C}_{90}$	3	.03	−21.22	1.58
		0–27.2 wt. % $Me_2CO–H_2O$	$_{90}\mathbf{A}_{100}$	3	.30	58.40	−1.52
i-Propyl benzene sulfonate[19,21]	50.0	0–99 wt % $Me_2CO–H_2O$	$_{3}\mathbf{C}_{15}\mathbf{A}_{45}\mathbf{B}_{95}\mathbf{A}_{100}$				
		0–98 wt. % dioxane–H_2O	$_{10}\mathbf{A}_{65}\mathbf{B}_{95}\mathbf{A}_{100}$	8	.57	30.51	−0.37
		0–70 vol. % C_6H_6–i-PrOH	$_{35}\mathbf{A}_{100}$	5	.12	49.78	−1.07
		0–50 vol. % C_6H_6–EtOH	$_{65}\mathbf{A}_{100}$	4	.06	48.93	−1.02
Water[g,49]	25.0	0–70 wt. % dioxane–H_2O	**A**	4	.05	16.83	−0.17
Formic acid[g,49]	25.0	0–82 wt. % dioxane–H_2O	**B**	5	.16	− 1.60	.34
Acetic acid[g,49,50]	25.0	0–82 wt. % dioxane–H_2O	**A**	5	.11	1.01	− .16
		0–20 wt. % MeOH–H_2O	**B**	3	.04	− 3.31	.50
Propionic acid[g,49]	25.0	0–82 wt. % dioxane–H_2O	**A**	5	.18	0.74	− .11
Hydrogen chloride[27]	25.0	0–100% MeOH–H_2O	$_{0}\mathbf{A}_{80}\mathbf{C}_{100}$	11	.22	−21.46[e]	−0.48
Sodium chloride[27]	25.0	0–100% MeOH–H_2O	$_{0}\mathbf{A}_{85}\mathbf{B}_{100}$	11	.76	0.89[e]	−0.05

[a] No. of pieces of data fitted. [b] Probable error of the linear fit.[42] [c] Calculated by the electrostatic approximation (see text). [d] No experimental data between 0 and 60 vol. % EtOH–H_2O. [e] ΔH^0 and ΔF^0 of solution. [g] Ionization. [h] Based on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ calculated from first-order rate constants.

creases monotonically as **Y** or N of the more rapid solvent component increases; *i.e.*, $(\partial\Delta F^{\ddagger}/\partial N)$ is negative. For the sake of generality, classes **D, E** and **F**, where $(\partial\Delta F^{\ddagger}/\partial N)$ is positive, are included and defined in Table V.

In the example shown in Fig. 5, it is clear that in traversing the iso-free energy lines of decreasing value in going from methanol to water, the plot starts in the **C** class, shifts to B, and then to **A**. This leads to a convenient shorthand description of the data, **C B A**. It is useful to append subscripts to the letters designating the solvent range covered for each class, in terms of mole % of the more rapid component. Thus, for the methanol–water case, the complete description of the relative contributions of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to the solvolysis rate of t-butyl chloride is given as $_{0}\mathbf{C}_{35}\mathbf{B}_{75}\mathbf{A}_{100}$. This type of designation is particularly useful where only restricted portions of solvent ranges have been investigated.

In Table VI and VII are listed these classifications for the present data on t-butyl chloride, as well as for a number of compounds for which sufficient data were available from the literature. In most cases, the solvent compositions at which a transition from one class to another occurs could not be accurately estimated; for this reason, the figures designating solvent composition were in most cases rounded off to the nearest 5 mole %. As a further simplification, only the major and unambiguously established regions of the curves are described. Thus the complex plot in Fig. 6 for t-butyl chloride in ethanol–water, which might be described exhaustively as $_{0}\mathbf{C}_{25}\mathbf{B}_{75}\mathbf{CBABC}_{100}$, is adequately described as $_{0}\mathbf{C}_{25}\mathbf{B}_{75}\mathbf{C}_{85}\mathbf{A}_{100}$.

Complex $\Delta S^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$ Plots.—The relation between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ in solvolysis of t-butyl chloride is a simple linear one only for the dioxane–formic acid mixtures, the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior being **B**.

Most of the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ plots are rather complex, as could be anticipated from the plots of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ *vs.* mole fraction illustrated in Figs. 1–3. Any minimum or maximum in a plot of $\Delta S^{\ddagger}$ or $\Delta H^{\ddagger}$ *vs.* N_{H_2O}, for example, represents a change in sign of $(\partial\Delta S^{\ddagger}/\partial\Delta F^{\ddagger})$. As is clear from Table V, this is associated with a change in symbolic classification, for example, from **C** to **B** or **B** to **A**.

Even though the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ plots for solvolysis of t-butyl chloride in the binary solvent sets are complex, segments, sometimes large segments, of the curves may be approximated by a linear relation. Such plots with several linear segments have been employed by Tommila[12] for t-butyl chloride and ethyl bromide in aqueous acetones. In Table VII is summarized the treatment of the present t-butyl chloride data on the basis of such linear segments. Also included in the table is the analogous treatment of some of the data from the literature for solvolysis of other compounds. Further, the table includes similar analysis of the thermodynamic data for ionization of water and several carboxylic acids, as well as the data for solvation of sodium chloride and hydrogen chloride.

In acetone–water or dioxane–water mixtures, the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior, although complex, tends to be barely **A** over-all and near the **AB** border. At the high water end of the solvent spectrum the behavior is **A**. In the binary mixtures of two hydroxylic solvents, the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior for t-butyl chloride displays the following general pattern. Starting with the pure slower solvent and adding the faster solvent component, almost always water, the initial $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior is uniformly **C**. At the high water end of the solvent spectrum, the behavior is uniformly **A**. However, at the fast end of the AcOH–HCOOH solvent spectrum, the behavior is **B**, the over-all behavior in the AcOH–HCOOH solvent system tending to be at the **BC** border.

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Attempted Electrostatic Treatment for $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ Behavior.—It is interesting to inquire how far a simple electrostatic view would go to account for the behavior of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ toward solvent change. Using Kirkwood's simplified treatment for the dependence of the activity coefficient of a dipolar molecule[51] on the dielectric constant (D) of the medium on both ground and transition states in solvolysis of *t*-butyl chloride, one can write eq. 15 to express the dependence of $\Delta F^{\ddagger}$ on D.[52] In this equation, $\Delta F^{\ddagger}_0$ is the hypothetical value in the medium of unit dielectric constant and A is a function of the dipole moments and radii of the ground and transition state molecules, these being assumed to be independent of medium. Since we are interested in change of medium, it is convenient to put eq. 15 into the form of eq. 16. In the latter, $\Delta\Delta F^{\ddagger}$ due to a medium change is expressed as proportional to the change in the quantity $[(D - 1)/(2D + 1)]$.

$$\Delta F^{\ddagger} = \Delta F^{\ddagger}_0 - A[(D - 1)/(2D + 1)] \qquad (15)$$

$$\Delta\Delta F^{\ddagger} = -A\,\Delta[(D - 1)/(2D + 1)] \qquad (16)$$

$$\Delta\Delta S^{\ddagger} = A\,\Delta\left[\frac{3D}{(2D + 1)^2}\,\frac{\mathrm{d}\ln D}{\mathrm{d}T}\right] \qquad (17)$$

$$\Delta\Delta H^{\ddagger} = A\,\Delta\left[\frac{3DT}{(2D + 1)^2}\,\frac{\mathrm{d}\ln D}{\mathrm{d}T} - \frac{(D - 1)}{(2D + 1)}\right] \qquad (18)$$

Since $\Delta S^{\ddagger}$ equals $-(\partial\Delta F^{\ddagger}/\partial T)$ and $\Delta F^{\ddagger}$ equals $(\Delta H^{\ddagger} - T\Delta S^{\ddagger})$, it is easy to derive expressions for $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ predicted by the simplified electrostatic model being employed.[10,35,45,53] It is most convenient for our present purposes to cast these expressions in the form of eq. 17 and 18, focusing our attention on $\Delta\Delta S^{\ddagger}$ and $\Delta\Delta H^{\ddagger}$ due to a change in medium.

The constant A in eq. 15–18 can be evaluated as the slope of the plot of $\Delta F^{\ddagger}$ *vs.* $(D - 1)/(2D + 1)$. Corresponding plots of log k *vs.* $[(D - 1)/(2D + 1)]$ are given for *t*-butyl chloride in several solvent mixtures in a previous paper.[3c] The term d(log D)/dT can be evaluated from a plot of log D *vs.* T.

For methanol–water mixtures, the plot of $\Delta F^{\ddagger}$ *vs.* $(D - 1)/(2D + 1)$ is satisfactorily linear over 0–60 vol. % MeOH–H_2O.[3c] The corresponding A value is 658 kcal./mole. Using pure water as origin, $\Delta\Delta S^{\ddagger}$ and $\Delta\Delta H^{\ddagger}$ values for the MeOH–H_2O mixtures were calculated with the aid of eq. 17 and 18. The resulting plot of the derived $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values is given as the dashed line in Fig. 5. From this plot, it is clear that good agreement with the experimental data is obtained from 0 to 40% MeOH–H_2O. However, the electrostatic prediction fails badly in the range beyond 40%.

The quantitative agreement between the prediction and the experimental data is shown by the a and d values for eq. 5, listed in Table VII. Thus, the calculated values of a and d for the range 0–70 vol. % MeOH–H_2O are −1.39 and 50.34, respectively. The corresponding experimental values in the 0–40 vol. % MeOH–H_2O region are −1.37 and 50.18. The divergence at lower water concentration is then shown by the experimental data for the 40–80 vol. % MeOH–H_2O region, a and d being +0.38 and 13.24, respectively.

An attempt to apply the electrostatic approach starting from 100% MeOH fails completely, the electrostatic view predicting **A**, instead of the **C** behavior actually observed.

The same treatment applied to the data for *t*-butyl chloride in the dioxane–water mixtures gave similar results. For this solvent mixture, the plot of $\Delta F^{\ddagger}$ *vs.* $(D - 1)/(2\,D + 1)$ is strongly curved all the way to pure water.[3c] However, employing the limiting slope at pure water for the calculation led to the prediction listed in Table VII for the solvent range 0–50% dioxane–H_2O. It is apparent that the agreement with the experimental data is fairly good over the range 0–30%, but it becomes poor beyond this range.

Considering other applications of the simplified electrostatic treatment, it was applied with fair success by Salomaa[45] to the trend of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values in solvolysis of α-chloromethyl ether in a series of alcohol–benzene mixtures, such as *n*-BuOH–C_6H_6. Bensley and Kohnstam[10] found the simple electrostatic viewpoint failed to account for the behavior of $\Delta S^{\ddagger}$ and also the temperature coefficient of $\Delta H^{\ddagger}$ in solvolysis of benzal chloride and benzotrichloride. Similarly, in certain bimolecular reactions, Caldin and Peacock[53] found that the electrostatic viewpoint gives a poor account of the trends in $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ as solvent varies.

Differential Solvation of Ground and Transition States in Solvent Mixtures.—It is rather obvious from the outset that the differential solvation of the transition and ground states in solvolysis cannot be accounted for completely by a simple electrostatic treatment. The latter predicts a small decrease in log H of the weakly dipolar *t*-butyl chloride molecule as D of solvent is increased. Instead, log H rises steeply as water is added to ethanol or methanol (Table IV). Thus, there is a large effect due to solvent-solute interactions for *t*-BuCl of a type not included in the electrostatic model. It is very unlikely that terms due to this effect should exactly cancel between ground and transition states, since the latter is so much more polar. In binary solvent mixtures, the $\Delta F^{\ddagger}_s$ and ΔF^0_v quantities, as well as the related enthalpy and entropy terms are determined by a more complicated set of interactions than in the case of pure solvents. In binary solvent mixtures, there are involved possible interactions with two kinds of solvent molecules on the part of both the ground state and transition state. Solvent–solvent interactions are also more complicated.

In the last respect mentioned above, alcohol–water mixtures are probably the most complex binary solvent sets. Thus, for ethanol–water and methanol–water mixtures, the enthalpy and excess entropy of mixing go through pronounced minima, while the excess free energy of mixing goes through a maximum as solvent composition is varied.[54] In methanol–water mixtures at 25°, there is a viscosity maximum at 27 mole % methanol, while there are minima in equivalent conductance at 33 and 42

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mole % methanol for tetraethylammonium and potassium chlorides, respectively.[55] Of related interest is that the apparent acidity function of ethanol–water mixtures based on *m*- and *p*-nitroaniline as indicators goes through a pronounced minimum as solvent composition is varied.[56]

Considering solvolysis of *t*-butyl chloride in the ethanol–water and methanol–water mixtures, the separation of $\Delta\Delta F^{\ddagger}$ values into $\Delta\Delta F^{\ddagger}_s$ and $\Delta\Delta F^0_v$ components with the aid of Henry's law constants (eq. 14) makes it clear that progressive addition of water to ethanol or methanol gives rise to important contributions of both $\Delta\Delta F^{\ddagger}_s$ and $\Delta\Delta F^0_v$ terms. The data are summarized in Table IV. Just as in the case of the gross change from methanol to water, solvent effects cannot be discussed on the basis of $\Delta\Delta F^{\ddagger}_s$ alone.

Considering the behavior of the thermodynamic quantities of activation in *t*-butyl chloride solvolysis in aqueous alcohol as solvent is varied, it is quite evident that the monotonic change in $\Delta F^{\ddagger}$ with solvent composition is composed of monotonic changes in both ΔF^0_v and $\Delta F^{\ddagger}_s$. Thus, for aqueous methanols, Olson, Ruebsamen and Clifford[37] have reported that log H_{RX}, which determines ΔF^0_v, is a nearly linear function of vol. % water. Similarly, over the range examined, H_{RX} is nearly linear in **Y**. Another way to put it is that log k is nearly linear in log H_{RX} for quite a range of solvent composition, as was pointed out some years ago.[3a] By the same token, log $H_{\ddagger}$ is linear in **Y** over the same range of solvent composition.

There are many indications that ΔF^0_s of ordinary salts, if these be taken as models for the transition state in solvolysis, are monotonic functions of solvent composition for aqueous alcohols. Thus, the log of the solubility of sodium or potassium chloride is a smooth, nearly linear function of mole fraction in methanol–water mixtures.[57] As pointed out by Hudson and Saville,[32] the free energy of solvation of potassium chloride is a nicely linear function of **Y** for aqueous methanols at 25°, the slope or m value being 1.50.

When it comes to accounting for the complex behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for solvolysis of *t*-butyl chloride toward composition of aqueous methanols, data are available to apportion $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values into ground state and transition state components only for the first portion of the MeOH → HOH solvent spectrum. For this range of aqueous methanols, Olson, Ruebsamen and Clifford[37] have measured H_{RX} at both 0 and 25°, permitting the calculation of $\Delta\Delta H^{\circ}_v$ and $\Delta\Delta S^{\circ}_v$. As summarized in Table VIII, one calculates for the solvent change, MeOH → 70.5% MeOH—H_2O, a $\Delta\Delta H^{\circ}_v$ of the same sign and of about the same magnitude as the observed $\Delta\Delta H^{\ddagger}$. The corresponding $\Delta\Delta S^{\circ}_v$ is *ca.* -10 e.u., which requires a compensating $\Delta\Delta S^{\ddagger}_s$ of +9 e.u. to make up the $\Delta\Delta S^{\ddagger}$ of −1 e.u.

For the range of solvent composition for which the necessary data are available, it is quite evident that both the ground state and transition state are important in determining the trends in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as water is added to methanol. The $\Delta\Delta H^{\circ}_v$ starts down properly so as to account largely for $\Delta\Delta H^{\ddagger}$, but it is not known whether it will turn up at high water concentrations so as to account for the minimum in $\Delta H^{\ddagger}$.

TABLE VIII

SEPARATION OF $\Delta\Delta F^{\ddagger}$, $\Delta\Delta H^{\ddagger}$ AND $\Delta\Delta S^{\ddagger}$ INTO GROUND STATE AND TRANSITION STATE CONTRIBUTIONS

Thermodynamic quantity	Solvent change MeOH → 70.5% MeOH	MeOH → HOH
$\Delta\Delta F^{\ddagger}$, kcal./mole	−2.80	−6.25
$\Delta\Delta F^{\ddagger}_s$, kcal./mole	−1.59	−2.16
$\Delta\Delta F^0_v$, kcal./mole	−1.21	−4.09
$\Delta\Delta H^{\ddagger}$, kcal./mole	−3.0	−1.66
$\Delta\Delta H^{\ddagger}_s$, kcal./mole	+1.2 (−0.1)[a]	(+3.8)[b]
$\Delta\Delta H^0_v$, kcal./mole	−4.2 (−2.9)[a]	
$\Delta\Delta S^{\ddagger}$, e.u.	−1	+15.2
$\Delta\Delta S^{\ddagger}_s$, e.u.	+ 9 (+5)[a]	(+31)[b]
$\Delta\Delta S^0_v$, e.u.	−10 (−6)[a]	

[a] On the basis of a plot of log (p/N) *vs.* vol. % MeOH–HOH, Olson, Ruebsamen and Clifford[37] stated that the value of log (p/N) for 70.5% MeOH–HOH appeared to be high by several per cent. The use of the lower figure gives rise to the values in parentheses. [b] Values of $\Delta\Delta H^{\circ}_s$ and $\Delta\Delta S^{\circ}_s$ for trimethylcarbonium chloride from Franklin's treatment.[31]

Examining the behavior of ΔH°_s of ordinary salts in aqueous alcohols as a possible guide to the behavior of $\Delta H^{\ddagger}_s$ in solvolysis, it turns out that ΔH°_s of sodium chloride, potassium chloride and potassium bromide do display rather complex behavior. The ΔH°_s values go through a maximum[27,58] at *ca.* 80 mole % water in methanol–water mixtures, approximately the same composition at which the $\Delta H^{\ddagger}$ values for solvolysis of *t*-butyl chloride go through a minimum. We are aware of no such data on tetramethylammonium chloride, a better model[32] for trimethylcarbonium chloride than the alkali halides. In any case, the behavior of the ΔH°_s values of salts in methanol–water mixtures suggests that $\Delta H^{\ddagger}_s$ for the transition state could be expected to show complex behavior as composition is varied.

It is evident that complete data on H values for *t*-butyl chloride and other substances would make possible a complete dissection of $\Delta\Delta F^{\ddagger}$, $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values for solvent changes into ground state and transition state contributions. These data, together with information on partial molal enthalpies and entropies of the solvent components, would lead the way to a better understanding of the differential solvation of ground and transition states in solvolysis of organic substrates in mixed solvents. For solvolysis of several substances, Tommila[12] and Robertson[18] have actually attempted qualitative explanations of the $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ trends with solvent change, without recourse to any information on H values of the substrates and thermodynamic data on the solvent components. In our opinion, it is preferable to postpone such discussion until necessary thermodynamic data are available. We hope to collect such data in collaboration with Professor R. L. Scott of this department.

$\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ Behavior of Other Substrates.—Surveying the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior in solvolysis of

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(55) N. G. Foster and E. S. Amis, *Z. physik. Chem.*, **7**, 360 (1956).

(56) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1976 (1948).

(57) G. Akerlof and H. E. Turk, THIS JOURNAL, **57**, 1746 (1935).

(58) R. L. Moss and J. H. Wolfenden, *J. Chem. Soc.*, 118 (1939).

substrates other than *t*-butyl chloride, summarized in Tables VI and VII, it will be seen that the simplest behavior is displayed in binary mixtures of an "inert" and an organic hydroxylic solvent. Just as for *t*-butyl chloride in dioxane–formic acid mixtures, a linear relation between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ obtains in solvolysis of several α-chloroethers[45] and ethyl benzenesulfonate[19,40] in binary solvent systems such as benzene–alcohol, dioxane–alcohol and acetone–alcohol mixtures. The $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior is **A** in all of these cases, in contrast with the **B** behavior for *t*-butyl chloride in dioxane–formic acid mixtures. For benzhydryl bromide[59] in dioxane–ethanol mixtures, we have also observed a linear **B** behavior.

When the binary solvent set consists of mixtures of an "inert" solvent with water, the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior tends to be more complicated than when the hydroxylic component is an alcohol. As with *t*-butyl chloride, other substances tend to display an over-all **A** behavior in most cases, and an **A** behavior at the high water end of the binary solvent spectrum. However, there are exceptions to this generalization, 2,3-dichlorodioxane,[44] for example, displaying a relatively linear **B** behavior up to pure water in dioxane–water and acetone–water.

In ionization reactions bearing some analogy to solvolysis, the ΔS°, ΔH° behavior of water and several carboxylic acids in dioxane–water mixtures, tends to be near the **A B** border. It is **A** for water,[49] acetic acid[49] and propionic acid,[49] but **B** for formic acid.[49]

Table VII provides little opportunity to compare the behavior of other substances with that of *t*-butyl chloride in binary mixtures of two hydroxylic solvents. The initial **C** behavior as water is added to ethanol is not displayed by diisopropyl phosphorochloridate,[25] but it is shown by dineopentylmethylcarbinyl chloride.[9] In other papers of this series, it is reported that the initial **C** behavior as water is added to another hydroxylic solvent is general for *t*-butyl bromide,[60a] α-phenylethyl chloride[26b] and bromide,[60a] neophyl chloride and bromide[60b] and benzhydryl chloride.[59] The **A** behavior at the high water end of ethanol–water mixtures is displayed by 1-chloro-2-methyl-2-propanol[43] and diisopropyl phosphorochloridate,[25] although data are too sparse in the latter case to guarantee the relationship. As far as behavior in acetic–formic acid mixtures goes, the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior of α-phenylethyl chloride,[26b] neophyl chloride[60b] and neophyl bromide[60b] is near the **BC** border, analogous to the behavior of *t*-butyl chloride. The behavior is **C** with initial addition of formic acid to acetic acid in the case of the first two substances, but barely **B** with neophyl bromide.[60b]

In the methanol–water system, the behavior of acetic acid ionization[50] and hydrogen and sodium chloride solvation[27] may be compared with *t*-butyl chloride solvolysis. For addition of water to methanol, hydrogen and sodium chlorides show an initial **A** behavior, while at the high water end of the solvent spectrum, hydrogen chloride is **C**, sodium chloride is **B**, while acetic acid is also **B**.

It is evident that the $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ behavior of organic substrates in solvolysis, and the ΔH°, ΔS° behavior of organic acids in ionization, do not obey generalizations based solely on the nature of the solvent systems. Instead, the behavior depends on substrate structure as well as on the nature of the solvent system. This is not surprising; in fact, one should expect[12] the thermodynamics of differential solvation of transition state relative to ground state in solvolysis to vary with substrate structure. For example, comparing *t*-butyl chloride with 2,3-dichlorodioxane, the latter substance has ether oxygen atoms for hydrogen-bonding of the ground state to hydroxylic solvent molecules. For 2,3-dichlorodioxane the change in solvation from ground state to transition state in acetone–water mixtures, for example, would not be expected to be comparable to that for *t*-butyl chloride.

Obviously, by paying heed to substrate structure as well as the nature of the binary solvent system, one could expect to formulate useful generalizations regarding $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior in solvolysis and related reactions. We are hoping to carry on further investigations on the nature and scope of such generalizations.

m*Y and Temperature.**—If the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior in solvolysis of two substances, RX and RY, is the linear one of eq. 5, linear free energy relations 1 and 2 would be obeyed if $\Delta H^{\ddagger}_{\mathrm{RX}}$ were linear in $\Delta H^{\ddagger}_{\mathrm{RY}}$, as expressed in eq. 19. Also, the *mY**

$$\Delta\Delta H^{\ddagger}_{\mathrm{RX}} = (a_{\mathrm{RX}}/a_{\mathrm{RY}})m\ \Delta\Delta H^{\ddagger}_{\mathrm{RY}} \qquad (19)$$

relation 3 would be obeyed strictly at every temperature, even though **Y** is kept constant at the 25° value.

It is quite clear that a linear relation between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ does not obtain in general for *t*-butyl chloride, nor for other substrate molecules whose solvolysis rates are correlated quite successfully by the *m***Y** relation 3. Less stringent relations exist among the $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ quantities which account for the fair success of relation 3. This has been treated briefly already[1,26b] and will be dealt with more fully later.

The pattern of behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for solvolysis of a substrate molecule determines the effect of temperature variation on the precision of the *m***Y** correlation of the rates of solvolysis of that substrate molecule. It is helpful to treat the matter analytically as follows.

Differentiation of eq. 4 with respect to temperature, approximating $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as temperature invariant, leads to relation 20 between $(\mathrm{d}m/\mathrm{d}T)$ and $(\partial\Delta H^{\ddagger}/\partial \mathbf{Y})$. This equation is essentially one derived in a previous discussion[3a] of the temperature dependence of *m*. With the aid of eq. 3 which states that $(\partial\Delta F^{\ddagger}/\partial \mathbf{Y})$ is equal to $-2.303RTm$, eq. 20 may be transformed to 21. The latter expresses the relation between $(\mathrm{d}m/\mathrm{d}T)$ and $(\partial\Delta H^{\ddagger}/\partial\Delta F^{\ddagger})$. When there is a linear relation between $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$, as expressed by eq. 5, $(\partial\Delta H^{\ddagger}/\partial\Delta F^{\ddagger})$ has the value *a*, and eq. 21 may be rewritten in the form of 22. Approximating *a* as invariant with temperature and integrating gives relation 23 between the ratio, (m_2/m_1), of *m* values

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[59] S. Winstein, A. H. Fainberg and E. Grunwald, THIS JOURNAL, **79**, 4146 (1957).

[60] (a) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1602 (1957); (b) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608 (1957).

at the higher and lower temperatures, respectively, and the ratio of the two temperatures.

It is instructive to note the special forms taken by relation 23 at the **AB** and **BC** borders. At the **AB** border, $a = 0$, $\Delta H^{\ddagger}$ being invariant to solvent change.

$$\frac{\mathrm{d}m}{\mathrm{d}T} = \frac{1}{2.303RT^2}\frac{\partial \Delta H^{\ddagger}}{\partial \mathbf{Y}} \tag{20}$$

$$\frac{\mathrm{d}m}{\mathrm{d}T} = \frac{-m}{T}\frac{\partial \Delta H^{\ddagger}}{\partial \Delta F^{\ddagger}} \tag{21}$$

$$\mathrm{d}\ \ln m/\mathrm{d}\ \ln T = -a \tag{22}$$

$$\frac{m_2}{m_1} = \left(\frac{T_1}{T_2}\right)^a \tag{23}$$

In this case, m_2/m_1 is unity. At the **BC** border, $a = 1$ and $\Delta S^{\ddagger}$ is constant. Here, (m_2/m_1) is T_1/T_2. The ranges of (m_2/m_1) values are summarized in Table V for each of the **A**, **B**, **C** regions.

To illustrate the role that temperature plays in determining the precision of $m\mathbf{Y}$ fits of rates of solvolysis, it is instructive to examine the $m\mathbf{Y}$ fits of the data for *t*-butyl chloride at 50° summarized in Table VI. These involve simply plots of log *k* at 50° against **Y** values at 25°. They simulate the hypothetical case of a substrate whose solvolysis rates correlate perfectly with **Y** at 25°, and whose solvolysis rates are now correlated with the $m\mathbf{Y}$ relation at 50°.

If the thermodynamic quantities of activation in solvolysis of *t*-butyl chloride followed the linear pattern of eq. 5, all of the data at 50° would be fitted perfectly by the $m\mathbf{Y}$ relation. The slope of the log *k* *vs.* **Y** line would no longer be 1.000, in general, but it would be calculable by relation 23. Thus, the probable error of the $m\mathbf{Y}$ fit of the data for *t*-butyl chloride at 50°, namely, 0.043 in log *k*, is entirely attributable to effects from varied patterns of $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior in the different solvents.

If, instead of considering all solvents together, the eight binary solvent sets are considered separately, the $m\mathbf{Y}$ plot is dispersed into eight separate lines, the corresponding slopes ranging from 0.926 in AcOH–HCOOH mixtures all the way to 1.070 in HCOOH–H_2O mixtures, the corresponding intercepts varying from −3.676 to −3.990. This dispersion of lines illustrates the extent to which temperature effects can influence the magnitudes of the parameters of the $m\mathbf{Y}$ relation.

For certain of the binary solvent mixtures, *e.g.*, AcOH–HCOOH and dioxane–HCOOH, the thermodynamic quantities of activation are fitted quite well by the linear relation 5 over the entire range of solvent composition studied. This result is reflected in the excellence of the $m\mathbf{Y}$ fits of the data in these binary solvent mixtures.

For a number of the other binary solvent mixtures, however, the complexity of the variation of the thermodynamic quantities of activation with solvent composition necessitated breaking up these solvent mixtures into several ranges (Table VII). For the EtOH–H_2O mixtures, it was necessary to fit eq. 5 to four separate regions of solvent composition in going from pure ethanol to pure water; values of *a* ranging from +1.86 to −2.63 were thus obtained. Calculation of the slopes of the $m\mathbf{Y}$ plot of the data for *t*-butyl chloride at 50° in EtOH–H_2O *via* eq. 23 for these different regions of solvent composition yielded values ranging from 0.862 in the 90–100 vol. % EtOH–H_2O region to 1.236 in the 0–35 vol. % EtOH–H_2O region. Thus, the slope of 0.974 obtained for the entire range is clearly a compromise average value which covers up considerable curvature arising from temperature effects.

Where the thermodynamic quantities of activation obey relation 5 moderately well, one can calculate the slope *m* of the log *k* *vs.* **Y** plot at one temperature from the value at another temperature with the aid of relation 23. How this works in actual practice is shown for *t*-butyl chloride in Table IX for those binary solvent sets for which relation 5 fits $\Delta H^{\ddagger}$ with a probable error less than 0.5 kcal./mole (Table VII). For these four binary solvent sets, the calculated (m_2/m_1) values for $(T_2/T_1) = (323/298)$ agree essentially perfectly with the analytical values from the $m\mathbf{Y}$ fit of the solvolysis data.

TABLE IX

CALCULATION OF VARIATION OF *m* WITH TEMPERATURE FOR *t*-BUTYL CHLORIDE SOLVOLYSIS

$(T_2/T_1 = 323/298)$

Solvent range	m_2/m_1 Obsd.[a]	m_2/m_1 Calcd.[b]
0–100% AcOH–HCOOH	0.926	0.926
0–100% HCOOH–HOH	1.070	1.075
0–90% dioxane–HOH	1.007	1.007
0–80% dioxane–HCOOH	0.960	0.958

[a] From *m* **Y** plot. [b] From equation 23.

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