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Empirical Correlations of Partial Molar Volumes at Infinite Dilution of Organic Solutes and Transition States for S_N1 and S_N2 Ethanolysis of Alkyl Halides

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Activation volumes are measured to be −21 to −29 $cm^3\ mol^{-1}$ for the ethanolysis of t-butyl chloride and bromide and methyl bromide in ethanol at 318.15 K. Partial molar volumes at infinite dilution are measured for 34 organic solutes. Partial molar volumes of the transition states can be treated in the same way as those of common solutes, in which the partial molar volume of each solute is compared with that of an alkane having the same van der Waals volume. The volume changes caused by the molecularity of reaction and the intermolecular interaction during the activation process are discussed.

When we observe a chemical phenomenon, we imagine possible thermodynamic movements of the component molecules, which are operated by their inherent non-electrostatic and electrostatic forces. Many chemists are interested mainly in the electrostatic origin of the phenomenon, which is frequently referred to in terms of polarity and/or hydrophilicity. In many organic reactions, however, it is impossible to separate the electrostatic effect from the whole observed results. For simple and non-polar molecules such as He, Ne, Ar, Kr, and CH_4, the intermolecular pair potential Ψ can be expressed by the molecular diameter σ and the depth of minimum potential ε in the Lennard–Jones potential $\Psi = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, for example. The states of their pure liquids and mixtures can be reproduced by the computer simulation with the assignment of appropriate values of σ and ε to the molecules.[1] For simple polar molecules, it is also possible to reproduce the liquid properties by introducing an electrostatic pair potential such as $-\mu^4/(3kTr^6)$ to the above.[2] Nevertheless, the molecules with which organic chemists are frequently concerned are so complicated that C–C bonds rotate, alkyl chains are flexible, substituents are very polar, and so on. There remain many problems to be solved before such a physical or computational analysis will be performed for complex organic molecules. When we have sufficiently good computational procedures, the thermodynamic properties will be calculable. We can now measure them experimentally. Thus, an alternative to the simulation calculation is the development of empirical correlations for the thermodynamic properties of solutions of organic molecules. These correlations can then be used to elucidate the features of the organic reactions and their transition states.

For the volumetric behaviour, we have developed an empirical procedure which correlates the partial molar volumes at infinite dilution V^∞ with the molecular properties for aliphatic solutes.[3,4] The empirical correlations can be applied to elucidate the activation volumes $\Delta V^\ddagger$ and the partial molar volumes of the transition states $V^\infty(\ddagger)$. This treatment has already been examined experimentally for the S_N2 hydrolysis and ethanolysis of alkyl bromides.[4] The purpose of the present work is to apply this treatment to the S_N1 ethanolysis of t-butyl chloride and bromide. The mechanism of these reactions is well established[5] [equation (1*a*) for S_N1 and equation (1*b*) for S_N2

$$\mathrm{Bu^tX \longrightarrow [Bu^{t+\delta}\cdots X^{-\delta}]^\ddagger} \qquad (1a)$$

$$\mathrm{MeBr + EtOH \longrightarrow [Et(H)O^{+\delta}\cdots H_3C\cdots Br^{-\delta}]^\ddagger} \qquad (1b)$$

where X = Cl or Br. From the preliminary experiments, the ethanolysis of t-butyl bromide in ethanol at 333.15 K was found to be too fast to determine $\Delta V^\ddagger$, although V^∞ values were already known for many organic solutes at this temperature.[4] The reaction temperature of 318.15 K was selected at which the rate constants of the ethanolysis are moderate. Thus, measurements of the rates of S_N2 ethanolysis of methyl bromide were necessary to verify the applicability at this temperature. Our empirical treatment is given briefly as follows. Throughout the text, the volumetric unit of $cm^3\ mol^{-1}$ is omitted and a^{HC} is dimensionless.

The V^∞ of a solute can be resolved into the van der Waals volume V_w and the void partial molar volume V_{void}.[3] The

$$V^\infty = V_w + V_{void} \qquad (2)$$

difference in V_{void} of a solute from that of an alkane having the same V_w is defined as the solute–solvent interaction partial molar volume $V_{s\text{–}s}^{(HC)}$. Thus, V^∞ is composed of three terms

$$V_{s\text{–}s}^{(HC)} = V_{void} - V_{void}^{HC} \qquad (3)$$

according to equation (4). The V_{void} values for alkane solutes

$$V^\infty = V_w + V_{void}^{HC} + V_{s\text{–}s}^{(HC)} \qquad (4)$$

have a linear dependence on V_w in each of water at 298.15 K[3] and ethanol at 333.15 K[4] [equation (5) where a^{HC} and b^{HC} are

$$V_{void}^{HC} = (a^{HC} - 1)V_w + b^{HC} \qquad (5)$$

constants]. The $V_{s\text{–}s}^{(HC)}$ values reflect mainly hydrophilic properties of the solutes.[3,4]

The $\Delta V^\ddagger$ for a reaction is the difference in V^∞ between the transition state and the reactant(s) [equation (6) where Σ_g

$$\Delta V^\ddagger = V^\infty(\ddagger) - \Sigma_g V^\infty \qquad (6)$$

denotes the summation for the reactant(s)]. Thus, the $V^\infty(\ddagger)$ value can be determined by the measurements of $\Delta V^\ddagger$ and V^∞ for the reactant(s).[4] Substituting equation (4) into equation (6), $\Delta V^\ddagger$ can also be expressed by the three terms in equation (7*a*) where relationships (7*b–d*) hold. While Σ_g for the S_N2

$$\Delta V^\ddagger = \Delta_w V^\ddagger + \Delta_{void}^{HC} V^\ddagger + \Delta_{s\text{–}s}^{(HC)} V^\ddagger \qquad (7a)$$

$$\Delta_w V^\ddagger = V_w(\ddagger) - \Sigma_g V_w \qquad (7b)$$

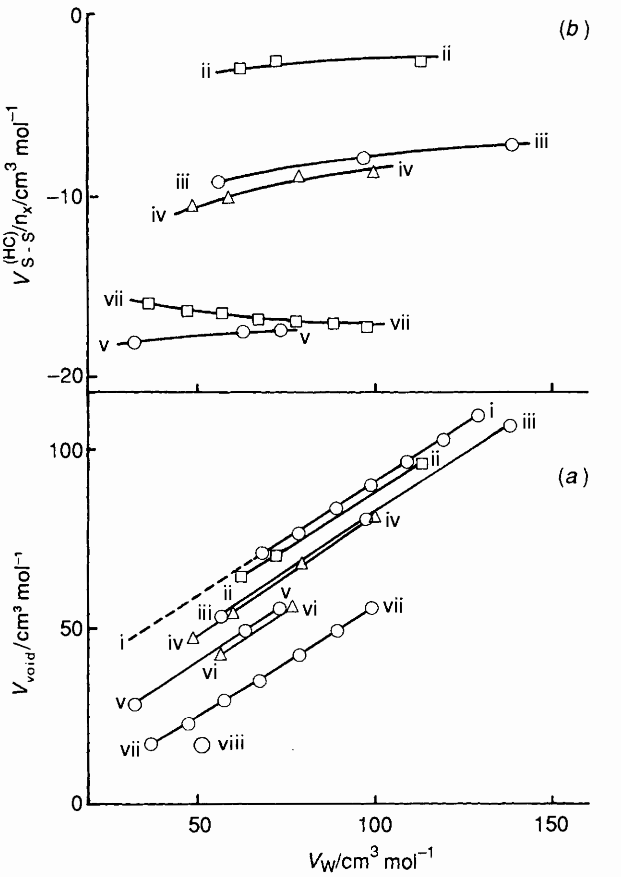

Figure. Plots of V_{void} (*a*) and $V^{(HC)}_{s\text{-}s}/n_x$ (*b*) against V_w for linear solute molecules in ethanol at 318.15 K. n_x Denotes the functional number, $n_x = 2$ for alkane-α,ω-diols and $n_x = 1$ for the others. Filled circle corresponds to pure ethanol. Different symbols are used only to identify the respective homologues: i, alkanes; ii, alkyl ethyl ethers; iii, alkyl chlorides; iv, alkyl bromides; v, alkyl alcohols; vi, cellosolves; vii, α,ω-alkanediols; viii, glycerine.

$$\Delta^{HC}_{void}V^{\ddagger} = V^{HC}_{void}(\ddagger) - \Sigma_g V^{HC}_{void} \qquad (7c)$$

$$\Delta^{(HC)}_{s\text{-}s}V^{\ddagger} = V^{(HC)}_{s\text{-}s}(\ddagger) - \Sigma_g V^{(HC)}_{s\text{-}s} \qquad (7d)$$

ethanolysis is the summation for alkyl halide and ethanol,[4] Σ_g for the S_N1 is that only for alkyl halide. Thus, the $\Delta^{HC}_{void}V^{\ddagger}$ for S_N1 and S_N2 ethanolysis of alkyl halides can be evaluated by equations (8*a*) and (8*b*), respectively, derived by substituting

$$\Delta^{HC}_{void}V^{\ddagger}(S_N1) = (a^{HC} - 1)\,\Delta_w V^{\ddagger} \qquad (8a)$$

$$\Delta^{HC}_{void}V^{\ddagger}(S_N2) = (a^{HC} - 1)\,\Delta_w V^{\ddagger} - b^{HC} \qquad (8b)$$

equation (5) into equation (7*c*) and using equation (7*b*). When the atomic geometry of the transition state is known or assumed, the $\Delta_w V^{\ddagger}$ can be calculated as the change(s) in overlapping volumes of van der Waals spheres of reacting atoms.[6,7] Then, the $\Delta^{(HC)}_{s\text{-}s}V^{\ddagger}$ can be evaluated by subtracting $\Delta_w V^{\ddagger}$ and $\Delta^{HC}_{void}V^{\ddagger}$ from the observed $\Delta V^{\ddagger}$. The values of $V^{\infty}(\ddagger)$, $V^{(HC)}_{s\text{-}s}(\ddagger)$ and $\Delta^{(HC)}_{s\text{-}s}V^{\ddagger}$ observed for the S_N2 hydrolysis and ethanolysis of alkyl bromides can satisfactorily be fitted to those of common solutes through the molecular properties symbolized in process (1*b*).[4]

The $\Delta V^{\ddagger}$ values for the alcoholysis of alkyl halides in the literature are *ca.* −18 to −30, but the differences of $\Delta V^{\ddagger}$ caused by differences between the S_N1 and S_N2 mechanisms are not so remarkable.[8] Rather large absolute values are estimated, $\Delta_w V^{\ddagger}$ −4.4 for S_N2 and 2.7 for S_N1 (see below). In equation (8*b*), the b^{HC} term is more significant than the $(a^{HC} - 1)\Delta_w V^{\ddagger}$ term: a^{HC} 1.53$_4$ and b^{HC} 9.9 in water at 298.15 K,[3] and a^{HC} 1.65$_6$ and b^{HC} 27.5 in ethanol at 333.15 K.[4] Thus, the $\Delta^{HC}_{void}V^{\ddagger}$ values are different according to the mechanism [equations (8*a*, *b*)]. This rough examination predicts an observable difference in $\Delta^{(HC)}_{s\text{-}s}V^{\ddagger}$ due to the mechanism, which may cancel the difference in $\Delta^{HC}_{void}V^{\ddagger}$.

Results

Activation Volume.—Table 1 lists the (pseudo-)first-order rate constants k_1 for the ethanolysis of t-butyl chloride and bromide and methyl bromide at 318.15 K at $\leqslant$ 98.1 MPa pressure.* The values of $\Delta V^{\ddagger}$ at 1 atm were determined by fitting the k_1 values to $\ln k_1 = c_1 + c_2P + c_3P^2$ for each of the reactions. They are −21 to −29 which are given in the last column of Table 1. These $\Delta V^{\ddagger}$ values are comparable with those for the alcoholysis of alkyl halides given in the literature,[8] and the difference in the mechanisms results in only a small difference in $\Delta V^{\ddagger}$.

Partial Molar Volume at Infinite Dilution.—The second column of Table 2 lists all the experimental results of V^{∞} for alkanes, alcohols, chlorides, bromides, ethers, glycols, and cellosolves as solutes in ethanol at 318.15 K. Table 2 also includes the results for the reactants of the ethanolysis.

The fourth column of Table 2 lists the values of V_{void} for all the solutes which were evaluated by equation (2) and the Bondi's tables of V_w.[7] The results for the solutes of linear molecules are plotted against V_w in the Figure (*a*). The linear dependence of V_{void} on V_w for alkane solutes is again proved under the present conditions. The empirical constants of equation (5) are a^{HC} 1.63$_7$ and b^{HC} 26.$_1$ in ethanol at 318.15 K. Both of these values are only slightly less than those at 333.15 K (1.65$_6$ and 27.$_5$).

When V_{void} at a constant V_w are compared for different series of solutes shown in the Figure (*a*), we obtain the sequence alkane > ether > alkyl halide > alcohol > glycol. Similar sequences were obtained for water at 298.15 K[3] and in ethanol at 333.15 K.[4] In the Figure, the difference in V_{void} for a polar solute from the point on the alkane line at its V_w is denoted by $V^{(HC)}_{s\text{-}s}$ [equation (3)]. The $V^{(HC)}_{s\text{-}s}$ values are listed in the fifth column of Table 2. The results for the linear solutes are plotted against V_w in Figure (*b*). Although showing minor dependences on V_w, the values averaged for homologous series of linear monofunctional solutes are as follows: 0 for alkanes according to the definition, −18 for alkyl alcohols, −8 for alkyl chlorides, −9 for alkyl bromides, and −2 for linear ethers. The $V^{(HC)}_{s\text{-}s}$ for the glycols divided by the functional number 2 show somewhat positive deviations from those for the linear alcohols with small V_w, and tend to approach the curve for the alcohols as V_w increases. Similar results were previously observed at 333.15 K for the homo-polyfunctional solutes of glycols, dibromides, and polyethers.[4]

For the polyfunctional solutes and the branched solutes studied, the additive values were estimated by reading off $V^{(HC)}_{s\text{-}s}$ of given functional groups at their V_w on the smoothed curves for corresponding monofunctional solutes shown in Figure 1(*b*). The deviations from the additive values are also given in the last column of Table 2. They are generally positive: 0 to 4 for glycols, 1 for cellosolves, and 12 for glycerine.

For the branched solutes, the $V^{(HC)}_{s\text{-}s}$ values are +3 for 2,2-dimethylalkanes, −15 to −18 for tertiary alcohols, and −4 to −7 for tertiary halides. Thus, the values for the branched solutes also tend to be a little more positive than those for the corresponding linear solutes.

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* 101 325 Pa = 1 atm.

Table 1. (Pseudo)-first-order rate constants under pressures and activation volumes for ethanolysis of alkyl halides at 313.15 K.

Substrate	Order of magnitude of k_1/s^{-1}	Pressure/MPa 0.1	24.5	49.0	73.5	98.1	$\Delta V^{\ddagger a}/\text{cm}^3\ \text{mol}^{-1}$
t-Butyl chloride	10^6k_1	1.4_7	1.8_9	2.3_8	2.8_1	3.3_1	−29
t-Butyl bromide	10^4k_1	0.6_0	0.7_6	0.8_9	1.0_5	1.2_2	−24
Methyl bromide	10^7k_1	2.2_8	—	3.2_9	—	4.6_2	−21

[a] Values at 1 atm (101325 Pa).

Partial Molar Volume of Transition State.—The $V^{\infty}(\ddagger)$ values are listed in the fourth column of Table 3, and were evaluated from the $\Delta V^{\ddagger}$ in Table 1 and the V^{∞} of the reactants in Table 2 according to equation (6). The results for S_N2 ethanolysis at 333.15 K[4] are also included in this table for comparison. For S_N2, $-4.4 < \Delta_w V^{\ddagger} < 0$ was derived in the previous work,[4] where the value −4.4 corresponds to 10% stretching of C–Br and C–O bond lengths in the transition state from their normal covalent bond lengths, which leads to a rather large $|\Delta_w V^{\ddagger}|$ value. For S_N1, $0 < \Delta_w V^{\ddagger} < 2.7$ is now derived, in which the value 2.7 corresponds to 40% stretching of C–Br in the transition state. The values of $V_{\text{void}}(\ddagger)$ and $V_{\text{s-s}}^{(\text{HC})}(\ddagger)$ for an arbitrary value of $\Delta_w V^{\ddagger}$ are listed in the sixth and seventh columns of Table 3, and those corresponding to the small and large $|\Delta_w V^{\ddagger}|$ are given in parentheses. The $V_{\text{s-s}}^{(\text{HC})}(\ddagger)$ are *ca.* −18 to −37. The results for S_N1 tend to be more negative than those for S_N2.

The values of $\Delta_{\text{void}}^{\text{HC}} V^{\ddagger}$ and $\Delta_{\text{s-s}}^{(\text{HC})} V^{\ddagger}$ are listed in the last two columns of Table 3. These values were calculated by equations (7) and (8*a*) or (8*b*). The $\Delta_{\text{s-s}}^{(\text{HC})} V^{\ddagger}$ for S_N1 are negative, from −24 to −33, while those for S_N2 are positive, from 2 to 12. Thus, $\Delta_{\text{s-s}}^{(\text{HC})} V^{\ddagger}$ are found to be different according to the mechanisms, as predicted in the introduction.

Discussion

Common Linear Solute.—Table 4 lists the excess partial molar volumes $V^{\infty} - V^{\text{M}}$ for alkanes in ethanol at 318.15 and 333.15 K, where V^{M} denotes the molar volume of pure solute at the same temperature. All the excess partial molar volumes are positive. However, those for alkanes in alkane solvents are negative although small in absolute value.[9] Thus, there exists an additional expansion during the dissolution of an alkane molecule into ethanol. The molecules of pure solvent ethanol, before the dissolution, are arranged in a structured framework, held together by co-operative hydrogen bonding. The observed volume increase during the dissolution is attributable to the breakdown of the solvent structure surrounding the alkane molecule. The $V^{\infty} - V^{\text{M}}$ in Table 4 increases with the size of the solute molecule. This is reasonable because the larger the solute molecule is, the more the solvent structure would be broken down.

The averaged $|V_{\text{s-s}}^{(\text{HC})}|$ for each of the polar linear homologues of the alcohols, bromides, glycols, and cellosolves is only a little less than that at 333.15 K. The small changes due to the difference in temperatures are almost equal to those expected from the thermal expansivity of pure ethanol.

The additive rule holds for $V_{\text{s-s}}^{(\text{HC})}$ of a long bifunctional solute $X(CH_2)_mY$, while $V_{\text{s-s}}^{(\text{HC})}$ of a short solute deviates from its additive value. This behaviour can easily be understood in the following way. When two polar groups X and Y are separated by a long polymethylene chain, the regions of surrounding solvent molecules that the respective groups influence are also independent, and then their effects are additive. When they approach each other, the regions are overlapped and their effects are no longer additive.

Common Branched Solute.—The positive $V_{\text{s-s}}^{(\text{HC})}$ of *ca.* 3 for 2,2-dimethylalkanes are more remarkable than those, *ca.* 1, for 2-methylalkanes. Those for 3-methylhexane and 4-methylheptane are small and negative, *ca.* $-0._3$.[4] $V^{\text{M}}_{\text{void}}$ ($= V^{\text{M}} - V_w$) was plotted against V_w by using the densities of pure alkanes.[10] Although $V^{\text{M}}_{\text{void}}$ for alkanes shows somewhat curved dependence on V_w,[9] increments of $V^{\text{M}}_{\text{void}}$ for 2-methyl- and 2,2-dimethylalkanes from those for corresponding alkanes are almost equal to the observed positive $V_{\text{s-s}}^{(\text{HC})}$. In the same way, decrements of $V^{\text{M}}_{\text{void}}$ similar to the negative $V_{\text{s-s}}^{(\text{HC})}$ are also derived for alkanes branched at 3- and higher positions. Such volumetric behaviour of pure alkanes has already been explained in terms of rotational modes of their molecules.[10a] Thus, $V_{\text{s-s}}^{(\text{HC})}$ depends on the framework of solute molecule.

In the previous work,[4] the deviation for each of the branched and polar solutes was shown to be rationalized by the branching form and the grade of substituent. Similarly, the deviation $0._2$ for t-pentyl alcohol can be expressed as the sum of the volume increment $3._2$ (2,2-dimethylbutane) and the volume reduction $-3._0$ due to the tertiary nature of the hydroxy group. The value $1._6$ for t-pentyl chloride is the sum of the same volume increment $3._2$ and the volume reduction $-1._6$ due to the tertiary nature of the chloro group. Unfortunately, the measurement of V^{∞} for 2,2-dimethylpropane solute was difficult due to its volatility at 313.15 K. As previously stated, the change in V^{∞} caused by the structures for alkane solutes can be approximated to the corresponding change in V^{M} of pure alkanes.[4] The V^{M} of pure 2,2-dimethylpropane is greater by *ca.* 7 than that of pure pentane. Thus, the deviations from additive values can be expressed as $(+7) + (-3._5)$ for t-butyl alcohol, $(+7) + (-1._8)$ for t-butyl chloride, and $(+7) + (-1._6)$ for t-butyl bromide. The contribution $-3._5$ due to the tertiary nature of t-butyl alcohol agrees well with $-3._0$ for t-pentyl alcohol, $-1._8$ for t-butyl chloride, and $-1._6$ for t-pentyl chloride.

As previously discussed,[4] we can visualize the following contributions to $V_{\text{s-s}}^{(\text{HC})}$: (*i*) functional groups, (*ii*) molecular framework or branching, (*iii*) grade (primary, secondary, *etc.*), (*iv*) distance between functional groups, and (*v*) obstruction of internal rotation.

Electrostriction of Transition State.—The partial charges in the transition states are *ca.* 0.2*e* for S_N2 and *ca.* 0.9*e* for S_N1 from solvent isotope effects.[11] With several assumptions for the geometries of the transition states, the quantities of the electrostriction were evaluated by the Kirkwood equation differentiated with respect to pressure.[4] The quantities derived as rather large values in absolute are −12 for S_N1 and −4 for S_N2. Thus, this simple electrostriction theory can explain the small difference in $V_{\text{s-s}}^{(\text{HC})}(\ddagger)$ between S_N1 and S_N2. However, the considerable values of $|V_{\text{s-s}}^{(\text{HC})}(\ddagger)|$ cannot be explained solely by this theory.

Property of S_N2 Transition State.—Now, we view the $V_{\text{s-s}}^{(\text{HC})}(\ddagger)$ obtained in this work for the S_N2 ethanolysis from the angle of the molecular property symbolized in process (1*b*). Since the transition state is also taken as a common solute, the

Table 2. Partial molar volumes at infinite dilution for organic solutes in ethanol at 313.15 K and their derivatives/cm^3 mol^{-1}.

Solute	V^{∞}	V_w[a]	V_{void}[b]	$V_{s-s}^{(HC)}$[c]	Deviation from additivity
Alkanes					
Hexane	$138._2$	68.3	$69._9$	0	—
Heptane	$154._5$	78.5	$76._0$	0	—
Octane	$171._4$	88.7	$82._7$	0	—
Nonane	$187._9$	99.0	$88._9$	0	—
Decane	$205._2$	109.2	$96._0$	0	—
Undecane	$221._6$	119.4	$102._2$	0	—
Dodecane	$238._4$	129.6	$108._8$	0	—
Alkyl alcohols					
Ethyl alcohol[d]	$60._0$	31.9	$28._1$	$-18._3$	—
Pentyl alcohol	$110._9$	62.6	$48._3$	$-17._7$	—
Hexyl alcohol	$127._8$	72.9	$54._9$	$-17._6$	—
Alkyl chlorides					
Butyl chloride	$108._5$	56.0	$52._5$	$-9._3$	—
Octyl chloride	$176._7$	96.9	$79._8$	$-8._0$	—
Dodecyl chloride	$244._5$	137.8	$106._7$	$-7._2$	—
Alkyl bromides					
Propyl bromide	$94._8$	48.5	$46._3$	$-10._7$	—
Butyl bromide	$112._1$	58.8	$53._3$	$-10._3$	—
Hexyl bromide	$146._9$	79.2	$67._7$	$-8._9$	—
Octyl bromide	$180._4$	99.7	$80._7$	$-8._9$	—
Alkyl ethyl ethers					
Ethyl propyl ether	$124._1$	61.7	$62._4$	$-3._0$	—
Butyl ethyl ether	$141._4$	72.0	$69._4$	$-2._6$	—
Ethyl octyl ether	$208._4$	112.9	$95._5$	$-2._5$	—
Alkane-α,ω-diols and glycerine					
Ethylene glycol	$53._6$	36.5	$17._0$	$-32._4$	$4._0$
Propane-1,3-diol	$68._4$	46.8	$22._6$	$-33._3$	$2._5$
Butane-1,4-diol	$85._1$	57.0	$28._1$	$-34._3$	$1._3$
Pentane-1,5-diol	$101._8$	67.2	$34._6$	$-34._3$	$1._1$
Hexane-1,6-diol	$118._5$	77.5	$41._0$	$-34._5$	$0._7$
Heptane-1,7-diol	$134._8$	87.7	$47._1$	$-34._9$	$-0._1$
Octane-1,8-diol	$151._0$	97.9	$53._1$	$-35._4$	$0._4$
Glycerine	$68._0$	51.4	$16._6$	$-42._2$	$11._2$
Cellosolves					
Ethylene glycol mono-ethyl ether	$98._0$	56.1	$41._9$	$-19._9$	$0._0$
Ethylene glycol mono-butyl ether	$132._0$	76.6	$55._4$	$-19._5$	$0._5$
Branched alkanes					
2,2-Dimethylbutane	$141._0$	68.2	$72._7$	$3._2$	$3._2$
2,2-Dimethylpentane	$157._3$	78.5	$78._9$	$2._8$	$2._8$
Branched alcohols					
t-Butyl alcohol	$97._2$	52.4	$44._8$	$-14._7$	$3._1$
t-Pentyl alcohol	$111._1$	62.6	$48._5$	$-17._5$	$0._2$
Branched chloride					
t-Butyl chloride	$114._8$	56.6	$58._2$	$-4._0$	$5._2$
t-Pentyl chloride	$128._1$	66.8	$61._3$	$-7._4$	$1._6$
Branched bromides					
t-Butyl bromide	$117._8$	58.9	$58._9$	$-4._7$	$5._4$

[a] Calculated by using Bondi's table in ref. 7. [b] Equation (2). [c] Equations (3) and (5) with constants $a^{HC} = 1.63_7$ and $b^{HC} = 26._1$. [d] Pure ethanol at 318.15 K.

$V_{s-s}^{(HC)}(\ddagger)$ must be expressed as a linear combination of the contributions (*i*)–(*v*) and an additional contribution (*vi*) of the partial charges.[4] Only a brief examination is given as follows, since the present $V_{s-s}^{(HC)}(\ddagger)$ value is similar to those at 333.15 K and the detailed examination is essentially the same as that described in the previous paper.[4]

The volumetric contribution due to the change in the molecular properties, resulting from the partial conversion of

Table 3. Volumetric behaviours/cm^3 mol^{-1} of the transition states and activation processes for S_N1 and S_N2 ethanolysis of alkyl halides in ethanol.

Substrate/mechanism	T/K	$\Sigma_g V^{\infty}$ [a]	$V^{\infty}(\ddagger)$ [b]	$V_w(\ddagger)$ [c]	$V_{void}(\ddagger)$ [c]	$V_{s\text{-}s}^{(HC)}(\ddagger)$ [c]	$\Delta_{void}^{HC} V^{\ddagger}$ [c]	$\Delta_{s\text{-}s}^{(HC)} V^{\ddagger}$ [c]
t-Butyl chloride/S_N1	318	115	86	$56.6 + A$ (57/59)	$29 - A$ (29/27)	$-33 - B$ ($-33/-37$)	$0 + C$ (0/2)	$-29 - B$ ($-29/-33$)
t-Butyl bromide/S_N1	318	118	94	$58.9 + A$ (59/61)	$35 - A$ (35/33)	$-29 - B$ ($-29/-33$)	$0 + C$ (0/2)	$-24 - B$ ($-24/-28$)
Methyl bromide/S_N2	318	120	99	$59.9 + A$ (60/56)	$39 - A$ (39/44)	$-25 - B$ ($-25/-18$)	$-26 + C$ ($-26/-29$)	$5 - B$ (5/12)
Methyl bromide/S_N2 [d]	333	123	97	$59.9 + A$ (60/56)	$37 - A$ (37/41)	$-30 - B$ ($-30/-23$)	$-28 + C$ ($-28/-31$)	$2 - B$ (2/9)
Propyl bromide/S_N2 [d]	333	158	132	$80.4 + A$ (80/76)	$51 - A$ (51/55)	$-29 - B$ ($-29/-22$)	$-28 + C$ ($-28/-31$)	$2 - B$ (2/9)
Butyl bromide/S_N2 [d]	333	174	150	$90.7 + A$ (91/86)	$59 - A$ (59/63)	$-28 - B$ ($-28/-21$)	$-28 + C$ ($-28/-31$)	$4 - B$ (4/11)

[a] $\Sigma_g V^{\infty} = V^{\infty}(RX) + V^{\infty}(EtOH)$ for S_N2 and $\Sigma_g V^{\infty} = V^{\infty}(RX)$ for S_N1. [b] $V^{\infty}(\ddagger) = \Sigma_g V^{\infty} + \Delta V^{\ddagger}$. [c] $A = \Delta_w V^{\ddagger}$, $B = a^{HC}\Delta_w V^{\ddagger}$, and $C = (a^{HC} - 1)\Delta_w V^{\ddagger}$. Values in parentheses: (for $\Delta_w V^{\ddagger} = 0$)/(for large $|\Delta_w V^{\ddagger}|$), large value: $\Delta_w V^{\ddagger} = 2.7$ for S_N1 and -4.4 for S_N2. [d] Ref. 4.

Table 4. Excess partial molar volumes/cm^3 mol^{-1} of n-alkenes infinitely diluted in ethanol.

	T/K	
Solute	318.15	333.15 [a]
C_6H_{14}	$2._9$	$2._3$
C_7H_{16}	$3._3$	$3._7$
C_8H_{18}	$4._0$	$3._5$
C_9H_{20}	$4._2$	$4._5$
$C_{10}H_{22}$	$5._2$	$6._1$
$C_{11}H_{24}$	$5._0$	$5._2$
$C_{12}H_{26}$	$5._3$	$5._6$

[a] Ref. 4.

the hydroxy group into a protonated ether in the transition state, is expressed as $\Delta(OH)$, and the contribution (*vi*) as $\Delta(\pm\delta)$.[4] The estimated contributions are: (*i*) $(-10)_{Br} + (-18)_{OH} + \Delta(OH)$, (*ii*) *ca.* 0, (*iii*) *ca.* 0, (*iv*) *ca.* 2, and (*v*) *ca.* 0. Then the total sum of (*i*)–(*vi*) $-26 + \Delta(OH) + \Delta(\pm\delta)$ is equal to the observed $V_{s\text{-}s}^{(HC)}(\ddagger)$ $-25 - 1.64\Delta_w V^{\ddagger}$, and, therefore, $\Delta(OH) + \Delta(\pm\delta) = 1 - 1.64\Delta_w V^{\ddagger}$. Introducing the limitations of $\Delta(\pm\delta) < 0$ and $\Delta(OH) < 15$ (the difference between ether and alcohol),[4] $(1 - 1.64\Delta_w V^{\ddagger})/15 < \Delta(OH) < 1$ is derived. Since $\Delta_w V^{\ddagger} < 0$ for S_N2, $(1 - 1.64\Delta_w V^{\ddagger})/15 > 1/15$. This suggests that the hydroxy group in the transition state is converted into ether by $>7\%$.

A positive $\Delta_{s\text{-}s}^{(HC)} V^{\ddagger}$ $5 - 1.64\Delta_w V^{\ddagger}$ arises from the fact that the negative $V_{s\text{-}s}^{(HC)}$ of the reactants $(-12)_{MeBr} + (-18)_{EtOH} = -30$ changes into a less negative value for the transition state $-25 - 1.64\Delta_w V^{\ddagger}$. Thus, the negative value for ethanol in the ground state makes a significant contribution to $\Delta_{s\text{-}s}^{(HC)} V^{\ddagger}$ and $\Delta V^{\ddagger}$. The EtOH molecule certainly forms hydrogen bonds with other surrounding EtOH molecules, and one of the lone pairs of OH in the transition state is employed for half-bond formation in order to form the ether bond.

Property of S_N1 *Transition State.*—The structure of the transition state for the S_N1 ethanolysis is similar to the ground state, and the component groups and atoms are the same. The $V_{s\text{-}s}^{(HC)}(\ddagger)$ (-33 or -29) $- 1.64\Delta_w V^{\ddagger}$ is composed of the contributions of (*i*) ($-9._3$ or $-10._3$), (*ii*) 7, (*iii*) ($-1._7$ or $-1._4$), (*iv*) *ca.* 0, (*v*) *ca.* 0, and (*vi*) $\Delta(\pm\delta)$, [where the values indicated as (*A* or *B*) are *A* for the substrate of the chloride and *B* for that of the bromide]. Thus, the relation of $\Delta(\pm\delta) = (-29$ or $-24) - 1.64\Delta_w V^{\ddagger}$ is derived. The large $|\Delta(\pm\delta)|$ suggests a probable change of the t-butyl moiety into a very hydrophilic group. The S_N1 reaction proceeds *via* a carbonium ion, the stability of which is explained by the hyperconjugation of the carbonium ion with nine peripheral hydrogen atoms in three methyl groups.[12] The partial carbonium charge in the transition state can disperse to the hydrogens, and this makes these C–H parts hydrophilic like the O–H group, although they behave only as proton donors. This could explain the large $|V_{s\text{-}s}^{(HC)}(\ddagger)|$, since the $V_{s\text{-}s}^{(HC)}$ of an alkyl alcohol which possesses only one hydroxy group is *ca.* -18.

Since the van der Waals radius of only one hydrogen atom, 0.1 nm, is much smaller than that of the whole t-butyl group, the electrostriction by the partial charge distributed on nine hydrogens is expected to give rise to the hydrophilicity of the transition state. The evaluation by the Born equation[13] gives the result *ca.* -6 if 0.9*e* is uniformly distributed on nine hydrogens, and *ca.* -50 if the charge is concentrated on only one hydrogen. The difference in electrostriction due to the charge distributions is caused by the electric charge square relation. Thus, the explanation using the electrostriction is probable, although it is difficult to estimate exactly the radius and the charge distribution.

The $\Delta_{s\text{-}s}^{(HC)} V^{\ddagger}$ for S_N1 corresponds to the difference in $V_{s\text{-}s}^{(HC)}$ between the transition state and the initial t-butyl halide as defined in equation (8*c*). In this comparison, the contributions (*i*)–(*v*) are almost cancelled, and the contribution (*vi*) $\Delta(\pm\delta)$ is dominant. Thus, the examination of $\Delta_{s\text{-}s}^{(HC)} V^{\ddagger}$ is essentially the same as that of $V_{s\text{-}s}^{(HC)}(\ddagger)$ described above.

Molecularity of Reaction.—In the conventional analysis, the $\Delta V^{\ddagger}$ is considered to consist of the structural term $\Delta_1 V^{\ddagger}$ and the solvation term $\Delta_2 V^{\ddagger}$.[8] The $\Delta_1 V^{\ddagger}$ is evaluated as the change of a cylindrical space with a cross section averaged for the reacting atoms. For a combination of two atoms, the initial length of the cylinder is assumed to be such that the van der Waals spheres of the atoms are in contact with each other, and then the cylinder shrinks to a given length at the transition state. If the van der Waals radius is defined as the distance to which two atoms approach without energy change (*cf.* the hard sphere potential, $\Psi = \infty$ for $r < \sigma$ and $\Psi = 0$ for $r \geqslant \sigma$) then the assumption of the initial length seems appropriate. However, this does not seem true for the condensed phase, see below.

As can be seen in Table 2, V_{void} are positive for all the solutes. Such a void space can be illustrated around the solute molecule and the solvent molecules also possess their own spaces. The void space is thought to be created by each of the solute molecules to equilibrate thermodynamically with the surrounding solvent molecules. When two atoms in such a liquid are in contact with each other, their void spaces overlap. Thus, there must be some volume reduction prior to the contact. In the case of a unimolecular decomposition, such a void volume change is much smaller than that for the above combination, since there is only an expansion of the void space including V_w. The difference b^{HC} between equations (8*a*) and (8*b*) seems to take such a void space into consideration. Thus, the $\Delta_{void}^{HC}V^{\ddagger}$ depends emphatically on the molecularity of reaction.

Equation (5) suggests that even a solute with $V_w = 0$ has the V_{void} of b^{HC}. Existence of such a point solute in the solution would obstruct the movement of the solvent molecules having energies at the given temperature and pressure. Thus, even a point solute would create some void space to equilibrate thermodynamically with solvent molecules. Although the quantitative definitions are different, there already exist some concepts similar to b^{HC}, such as the exclusion or free volume,[14] the scaled particle theory,[15] and κRT in the treatment by Yoshimura and Nakahara.[16] Thus, the $\Delta_{void}^{HC}V^{\ddagger}$ can be a measure for the volume change due to the translational change during the activation process in the liquid phase.

Experimental

Ethanolysis of t-butyl chloride was followed by use of GLC, where the molar ratios of produced t-butyl ethyl ether and isobutylene to the chloride were measured. $\ln(1 + [BuOEt]/[Bu^tCl] + [C_4{}']/[Bu^tCl]) = k_1t +$ constant. The column, serially connected PEG200 (15 wt%, 4 m) with Silicone DC 702 (15 wt%, 0.5 m), was used at 328 K. Ethanolysis of t-butyl bromide was too fast to be followed by the above GLC method, so that the electroconductimetry method of Guggenheim was applied. $\ln(1/R_{t+\Delta t} - 1/R_t) = -k_1t +$ constant. The value of Δt is a constant time interval arbitrarily chosen as *ca.* the half life of the bromide. Ethanolysis of methyl bromide was followed by the GLC method, in which the production rate of the ether was measured. $\ln(1 + [EtOMe]/[MeBr]) = k_1t +$ constant. Column PEG200 (15 wt%, 4 m) at room temperature. Initial concentrations were *ca.* 0.001 mol dm^{-3} for t-butyl halides and *ca.* 0.01 mol dm^{-3} for methyl bromide. The following GLC conditions were commonly used for the analyses in the reactions of t-butyl chloride and methyl bromide: support material UNIPORT-B of 40–60 mesh, N_2 carrier gas *ca.* 0.4 cm^3 s^{-1}, H_2 *ca.* 0.3 cm^3 s^{-1}, and air *ca.* 8.3 cm^3 s^{-1}.

The preparations of the materials, the measurements of V^{∞}, and the high-pressure apparatus were essentially the same as those described elsewhere.[3,4,17]

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