Effect of Pressure on the Rate of Solvolysis. Hydrolysis of 1-Aryl-1-methylethyl Chlorides[1]

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The effect of pressure on the hydrolysis rates of 1-aryl-1-methylethyl chlorides were investigated, and the activation volumes, $\Delta V_0^{\neq}$, were calculated. Electron-donating substituents in an aryl group gave less negative $\Delta V_0^{\neq}$ values and electron-withdrawing substituents gave more negative $\Delta V_0^{\neq}$ values. The observed values of $\Delta V_0^{\neq}$ were found to correlate with σ^+. These observations are interpreted in terms of the dependence of the degree of solvation at the transition state of the reaction. The temperature dependence of $\Delta V_0^{\neq}$ is also discussed.

In recent years, the effect of pressure on the rates of organic reactions in solution has been extensively studied.[2] Rate measurements of reactions under high pressure allow us to estimate activation volumes, $\Delta V^{\neq}$, by means of the following expression;

$$\Delta V^{\neq} = -RT(\delta \ln k/\delta P)_T \qquad (1)$$

where $\Delta V^{\neq}$ is the partial molal volume change when a reactant(s) is converted into a transition-state species. An examination of the pressure effect on the kinetic rates can give a great deal of information about the transition states of the reactions. The general usefulness of the activation volume as a diagnostic probe of reaction mechanisms is well recognized.[3] The reaction constant, ρ, in the Hammett equation depends upon the reaction conditions; hence, a variation in the external pressure might influence the value of ρ. Equation 2[4] implies a linear correlation of $\Delta V^{\neq}$ with respect to σ;[5]

$$-\delta\Delta V^{\neq} = 2.303RT\sigma(\delta\rho/\delta P)_T \qquad (2)$$

where $\delta\,\Delta V^{\neq} = \Delta V_{\mathrm{X}}^{\neq} - \Delta V_{\mathrm{H}}^{\neq}$ and where $\Delta V_{\mathrm{H}}^{\neq}$ and $\Delta V_{\mathrm{X}}^{\neq}$ are activation volumes for unsubstituted and substituted substrates, respectively (the subscript x denotes a substituent). However, there have been only a few investigations of the substituent dependence of the activation volumes.[2d,6–10]

We undertook the present investigation in order to obtain fundamental data necessary for the estimation of the substituent dependence of the activation volume, for this is essential for getting detailed information about the transition states of organic reactions. The hydrolysis of 1-aryl-1-methylethyl chlorides in 90% aqueous acetone at 25.0 °C seems to be a suitable model reaction for the present purpose, because; a) this is a reaction in which a neutral molecule in an initial state leads to a highly dipolar transition state, b) the reaction mechanism is rather unambiguous, and c) the rate of reaction is known to give an excellent linear correlation with σ^+ and the value of ρ is considerably large.

Results and Discussion

The hydrolysis of 1-aryl-1-methylethyl chlorides in "90% aqueous acetone" (see Experimental section) at 25.0 °C were followed by a conductometric method under pressure. The first-order rate constants were calculated by the Guggenheim method[11] or by the usual first-order rate expression.[12] The results are summarized in Table 1. Logarithmic plots of the rate constants shown in Table 1 against Brown-Okamoto's σ^+ values exhibit an excellent linear relationship under pressure. Clearly $|\rho|$ decreases as the applied pressure increases.[13] Figure 1 shows a typical plot of log *k* (1-phenyl-1-methylethyl chloride) against pressure; this proves the linear relationship between log *k* and pressure in this case. With some electron-withdrawing substituents, the plots inclined to show slight convex curvature. In the present investigation, however, all the values of $\Delta V_0^{\neq}$, the activation volume at atmospheric pressure, were calculated by means of Eq. (1) and the following equation using the method of least-squares:

$$\ln k = a + bP \qquad (3)$$

Substituent Dependence of $\Delta V_0^{\neq}$. As has been

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[1] Organic Reactions under High Pressure. X. Part IX, see *Tetrahedron Lett.*, 1585 (1973).

[2] For recently reported solvolytic displacement reactions, see a) J. B. Hyne and co-workers, *Can. J. Chem.*, **48**, 2025, 2416, 2494 (1970); **49**, 2394, 3840 (1971). b) E. Whalley and co-workers, *ibid.*, **48**, 528, 2021 (1970). c) W. J. leNoble and A. Shurpik, *J. Org. Chem.*, **35**, 3588 (1970). d) C. Yamagami and A. Sera, *Chem. Lett.*, **1972**, 741.

[3] W. J. leNoble, "Progress in Physical Organic Chemistry," Vol. 5, p. 207, A. Streitwieser, Jr. and R. W. Taft Ed., Interscience Publisher, New York (1967).

[4] A. J. Ellis, W. S. Fyfe, R. I. Rutherford, A. Fischer, and J. Vaughan, *J. Chem. Phys.*, **31**, 176 (1959).

[5] In Eq. 2, the substituent constant *σ* is assumed to be independent of pressure. However, one can treat this pressure dependence problem on the Hammett equation in terms of a two variable (*σ* and P) problem. For similar treatment, see J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York (1963), p. 128.

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[9] K. J. Laidler and R. Martin, *Int. J. Chem. Kinet.*, **1**, 113 (1969).

[10] A. Fischer, B. R. Mann, and J. Vaughan, *J. Chem. Soc.*, **1961**, 1093.

[11] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1929).

[12] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York (1953), p. 27.

[13] The slope of the plot of *ρ* against pressure estimated by the least squares method is approximately 2×10^{-4}cm^2/kg.

Table 1. Hydrolysis rate constants of 1-aryl-1-methylethyl chlorides under pressure in 90% aqueous acetone at 25.0°C

Substituent	Pressure (kg/cm^2) 1	100	150	200	300	400	500	600	800	1000
	First-order rate constant$^{a)}$ (x10^{-5} s^{-1})									
4-Fluoro$^{b)}$	26.4		28.4	28.8$^{d)}$	30.0	31.4$^{d)}$	32.9	34.2$^{d)}$	37.3$^{d)}$	40.8
3-Methyl$^{b)}$	25.2		27.0	27.4$^{d)}$	28.5	29.9$^{d)}$	31.1	32.6$^{d)}$	35.5$^{d)}$	38.7
3-Isopropyl$^{b)}$	23.5		25.4	25.7$^{d)}$	27.0	28.1$^{d)}$	29.4	30.7$^{d)}$	33.5$^{d)}$	36.2
3-*t*-Butyl$^{b)}$	24.1		26.2	26.5$^{d)}$	28.3	29.0$^{d)}$	30.4	31.7$^{d)}$	34.6$^{d)}$	37.5
None$^{b)}$	12.3		13.3	13.5$^{d)}$	14.1	14.8$^{d)}$	15.8	16.3$^{d)}$	17.9$^{d)}$	19.8
3-Methoxy$^{b)}$	8.19		8.87	8.94$^{d)}$	9.34	9.75$^{d)}$	10.3	10.6$^{d)}$	11.6$^{d)}$	12.5
4-Chloro$^{c)}$	3.11			3.72		4.24		4.67		
4-Bromo$^{c)}$	2.35			2.93		3.38		3.74	4.33	
3-Methylthio$^{c)}$	1.92			2.33		2.71		2.95	3.28	
3-Fluoro$^{c)}$	0.284			0.351		0.396		0.446	0.499	
3-Iodo$^{c)}$	0.265			0.331		0.375		0.422	0.472	
3-Carboethoxy$^{c)}$	0.248			0.300		0.343		0.380	0.417	
3-Chloro$^{c)}$	0.212	0.246		0.272		0.302		0.350		0.457

a) Average of two or more experiments.
b) Calculated by the Guggenheim method.
c) Calculated by the usual first-order rate expression.
d) Extrapolated values from data at other pressures.

Table 2. Pressure effect on ρ-value for hydrolysis of 1-aryl-1-methylethyl chlorides

Pressure (kg/cm^2)	1	200	400	600	800
ρ	−4.55$^{a)}$	−4.48	−4.47	−4.41	−4.39
$r^{b)}$	0.999	1.000	1.000	1.000	0.999

a) H. C. Brown and Y. Okamoto reported $\rho = -4.54$, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).
b) Correlation coefficient.

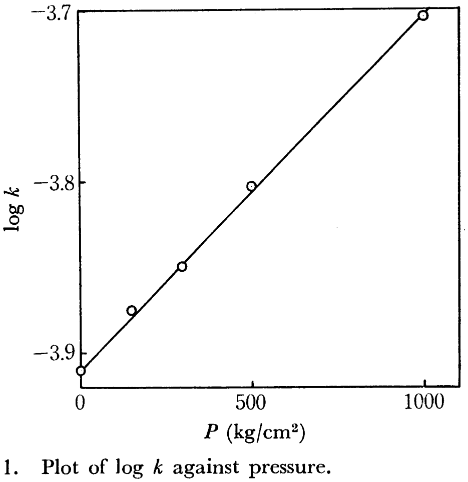

Fig. 1. Plot of log *k* against pressure.
Hydrolysis of 1-phenyl-1-methylethyl chloride in 90% aqueous acetone at 25.0 °C.

pointed out by Evans and Polanyi,[14] $\Delta V^{\ddagger}$ may conveniently be regarded as being constituted of two terms: $\Delta_1 V^{\ddagger}$, which represents a change in the volume of a reacting molecule(s) during an activation process, and $\Delta_2 V^{\ddagger}$, which is a corresponding change in the volume of the surrounding solvent molecules caused by their rearrangement. In a unimolecular ionization process, $\Delta_2 V^{\ddagger}$ is actually the dominating term.[3)]

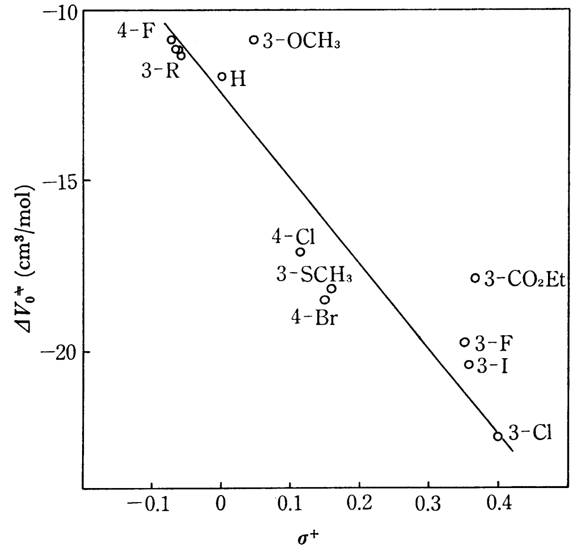

Fig. 2. Plot of $\Delta V_0^{\ddagger}$ against σ^+.

The values of $\Delta V_0^{\ddagger}$ in Table 3 are all negative and are found in the range from −10 to −25 cm^3/mol. The contribution of carbonium-ion-like species at the transition state of the present reaction is well established, and the stability of the transition state is governed by the degree of electronic charge delocalization by a given substituent. Negative values of $\Delta V_0^{\ddagger}$ for solvolytic reactions are usually referred to as "electrostriction". That is, a partially-charged transition-state species exerts an electrostatic attractive force on nearby polar solvent molecules; as a result, volume contraction occurs. Thus, the degree of charge delocalization should correspond to this electrostatic volume contraction in the transition state. Figure 2 shows such correlation, with a negative slope, between $\Delta V_0^{\ddagger}$ and σ^+ as anticipated by Eq. (2). The trend shown is qualitatively in good accordance with the above prediction; that is, the more the charge delocalization in

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[14] M. G. Evans and M. Polanyi, *Trans. Faraday. Soc.*, **31**, 875 (1935).

the transition state, the less negative the value of $\Delta V_0^{\ddagger}$ becomes.[15]

Temperature Dependence of $\Delta V_0^{\ddagger}$. A few data on the temperature dependence of the activation volume, $\delta\Delta V^{\ddagger}/\delta T$, have been previously reported,[16] and this parameter has been disucssed in terms of the difference in the degree of charge development. In general, $\delta\Delta V^{\ddagger}/\delta T$ is represented as the difference in the temperature dependence of the partial molal volumes between the transition state and the initial state;

$$\delta\Delta V^{\ddagger}/\delta T = \delta\bar{V}_t/\delta T - \delta\bar{V}_g/\delta T \qquad (4)$$

where $\bar{V}_t$ and $\bar{V}_g$ are the partial molal volumes of the transition state and the initial state, respectively.

In Table 4 the dependence of the rate of hydrolysis for 1-phenyl-1-methylethyl chloride on pressure at various temperatures is presented. The activation volumes thus obtained are also shown. As is shown, $\delta\Delta V_0^{\ddagger}/\delta T$ has a negative sign in the present reaction.[17] This implies, according to Eq. (4), that the electrostriction in the activation process results in a tight transition-state solvation shell whose volume is less responsive to temperature change (less expansive) than that of the initial state. Table 4 also shows that sign of $\delta\Delta S^{\ddagger}/\delta P$ seems to be positive, although the estimation of a numerical value of this parameter is, unfortunately, restricted. It seems that the pseudo-thermodynamic relationship;

$$-(\delta\Delta S^{\ddagger}/\delta P)_T = (\delta\Delta V^{\ddagger}/\delta T)_P \qquad (5)$$

is fulfilled.

Activation Volume—Activation Entropy Relationship. Electrostriction is a phenomenon where a strong electrostatic interaction exerts between an ion or a highly polar species and the surrounding solvent molecules. Therefore, the degree of freedom of the solvent molecules is restricted, resulting in a decrease in the entropy of the system. In fact, reactions which have large negative $\Delta V_0^{\ddagger}$ values are known to be characterized by large negative $\Delta S^{\ddagger}$ values. Accordingly, one can anticipate the presence of a rough proportionality between $\Delta V_0^{\ddagger}$ and $\Delta S^{\ddagger}$. Figure 3 shows a fairly good correlation between these two parameters. That the correlation holds in the present reaction strongly supports the validity of the application of the electrostriction theory in the present mechanistic representation of the reaction.

TABLE 3. SUBSTITUENT EFFECT ON $\Delta V_0^{\ddagger}$ FOR HYDROLYSIS OF 1-ARYL-1-METHYLETHYL CHLORIDES

Substituent	$\Delta V_0^{\ddagger\, a)}$ (cm^3/mol)	$\Delta S^{\ddagger\, a,b)}$ (e.u.)
4-Fluoro	−10.9	−11.7
3-Methyl	−11.2	−11.8
3-Isopropyl	−11.2	−10.2
3-*t*-Butyl	−11.4	−10.6
None	−12.0	−12.5
3-Methoxy	−10.9	−11.1
4-Chloro	−17.1	−13.6
4-Bromo	−18.5	−15.2
3-Methylthio	−18.2	−12.8
3-Fluoro	−19.7	−17.0
3-Iodo	−20.4	−16.1
3-Carboethoxy	−17.9	−11.9
3-Chloro	−22.5	−15.1

a) At 25 °C.
b) Taken from reported data, H. C. Brown and co-workers, *J. Amer. Chem. Soc.*, **79**, 1879, 1906, 1909 (1957); **80**, 4964, 4969 (1958).

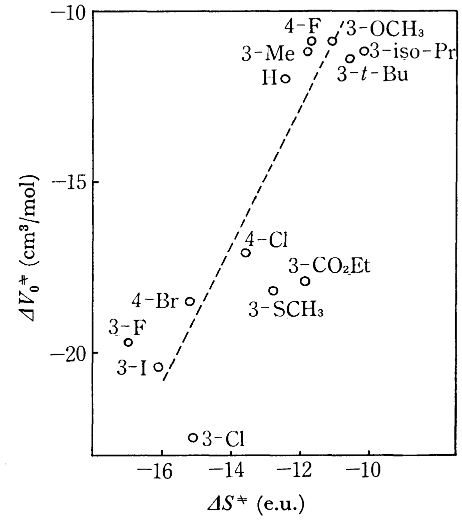

Fig. 3. Plot of $\Delta V_0^{\ddagger}$ against $\Delta S^{\ddagger}$.

TABLE 4. PRESSURE AND TEMPERATURE DEPENDENCE OF ACTIVATION PARAMETERS FOR HYDROLYSIS OF 1-PHENYL-1-METHYLETHYL CHLORIDE

Temperature (°C)	Pressure (kg/cm^2) First-order rate constant$^{a)}$ (x10^{-5} s^{-1}) 1	200	400	600	800	$\Delta V_0^{\ddagger}$ (cm^3/mol)
25.0	12.3	13.5	14.8	16.3	17.9	−12.0
35.0	36.1$^{b)}$	40.7	45.6	49.9	55.4	−12.8
40.0	59.0	65.5	73.5	79.0	91.7	−13.7
$\Delta H^{\ddagger}$ (kcal/mol)$^{c)}$	18.8	19.0	19.3	19.0	19.6	
$\Delta S^{\ddagger}$ (e.u.)$^{c)}$	−12.4	−12.4	−11.4	−12.1	−9.7	

a) Average of two or more experiments.
b) Taken from reported data, H. C. Brown *et al.*, *J. Amer. Chem. Soc.*, **79**, 1897 (1957).
c) At 25.0 °C.

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15) The position of the transition states along reaction coordinates might change a little with substituents. However, we ignore this small change and hence assume that the observed $\delta\Delta V_0^{\ddagger}$ reflects a difference in the solvation term, $\delta\Delta_2 V_0^{\ddagger}$.[14]

16) M. J. Mackinnon and J. B. Hyne, *Can. J. Chem.*, **49**, 3840 (1971).

17) The value of $\delta\Delta V_0^{\ddagger}/\delta T$ is roughly estimated as −0.1 cm^3 mol^{-1} degree^{-1}. The value indicates the intervention of a highly polar transition state.[16]

Experimental

Materials. The materials employed in the present experiment were prepared by the methods reported in the references quoted by Brown and his co-workers.[18] The purity of each material was found to be satisfactory by checking mp, n_D, NMR and IR spectra, and by elemental and glc analyses in the stage of the corresponding alcohol and/or olefin. These alcohols and olefins were converted into the corresponding tertiary chlorides by the method of Brown and Rei.[19] The products were directly used for the rate measurements without further purification.[20]

Solvent. Acetone was dried over anhydrous potassium carbonate and was then distilled at least twice. Commercially available conductivity water was employed and was stored out of contact with air. Brown and his co-workers[18] prepared the reaction solvent mixture by volume. However, in the present investigation, we employed "88.5% aqueous acetone (wt/wt)". This solvent was found to be kinetically equivalent to Brown's "90% aqueous acetone (v/v)"; that is, 1-phenyl-1-methylethyl chloride and 1-(4-fluorophenyl)-1-methylethyl chloride gave an identical solvolysis rate, respectively, in these two solvents.

High-Pressure Apparatus. The high-pressure apparatus is shown in Fig. 4. The pressure vessel is equipped with an electric head which is replaceable, if necessary, by a sampling assembly. The pressure-transmitting fluid was a silicon oil, KF-96 (200 cs, Shin-etsu Chem. Ind.), and pressure was applied by means of a hand-pump. The Bourdon gauge was reliable to ± 10 kg/cm^2 at 1000 kg/cm^2. The thermostat was controlled to 25.0 ± 0.015 °C or 35.0 and 40.0 ± 0.02 °C.

Kinetic Measurements. The conductivity cell employed throughout the experiment is shown in Fig. 4. A kinetic solution was prepared by mixing a weighed substrate with 90% aqueous acetone at ambient temperature ($[RX]_0 = 0.01$—0.04 mol/l). The cell was rinsed well with this solution, filled, and placed in the high-pressure vessel. The electric conductivity of the solution was then measured by means of Radiometer model CDM-3 and Yanagimoto model MY-8 conductivity outfits. The first readings were taken after the establishment of the thermal equilibria in the cell. A preliminary experiment using a thermocouple directly inserted into the cell showed that thermal equilibria in the cell were established after 12 min in the case of an applied pressure of 400 kg/cm^2 and a vessel temperature of 0 °C (pre-chilled vessel medium, *n*-hexane); 17 min, 700 kg/cm^2, 0 °C; 18 min, 700 kg/cm^2, 15 °C; 37 min, 700 kg/cm^2, 25 °C (in all cases, the bath temperature was kept at 25.0 °C).

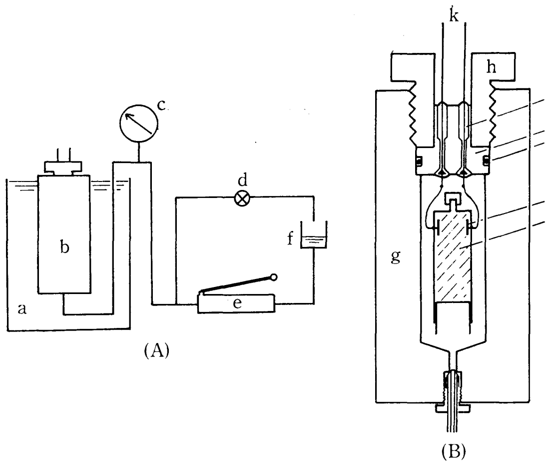

Fig. 4. High-pressure apparatus.
A) Schematic diagram of hydrostatic system. a: thermostatted bath, b: high-pressure vessel, c: Bourdon gauge, d: valve, e: pump, f: oil reservoir.
B) Diagram of pressure vessel. g: stainless steel vessel, h: gland nut, i: electric head, j: O-ring, k: electric leads, l: epoxy-resin, m: glass conductivity cell, n: platinum electrodes.

First-order rate constants were calculated by the Guggenheim method[11] or by the usual first-order rate expression[12] using the method of least-squares. In the former case, 10 pairs of readings were made for each run ($\Delta t \fallingdotseq$ two half lives). In the latter case, calibration plots of the conductance of the standard hydrogen chloride solution at several pressures against the concentrations (determined by titration) of hydrogen chloride in the solution were made. To obtain the "infinite titer", aliquots of the kinetic solution were added to an appropriate amount of 50% aqueous acetone; the solutions were then allowed to stand at ambient temperature for at least ten half lives, after which they were titrated with a standard alkaline solution, using methyl red as an indicator.

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[18] H. C. Brown and co-workers, *J. Amer. Chm. Soc.*, **79**, 1897, 1906, 1909 (1957); **80**, 4964, 4969 (1958).

[19] H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

[20] Reliability of this procedure, see H. C. Brown *et al.*, *J. Amer. Chem. Soc.*, **79**, 1897 (1957).