A NEW METHOD TO ESTIMATE THE INTRINSIC TERM

IN ACTIVATION AND REACTION VOLUMES

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A simple formula is proposed to describe the effect of pressure on the rate and equilibrium constant of ionic reactions. The expression, given in Eq. (7), has been applied to known data and shown to provide a good description of the pressure effects on a variety of ionic reactions. The extrapolation of the relation to infinite pressure allows us to estimate the intrinsic volume changes.

Introduction

The measurement of pressure effect on reaction rate has become commonplace[1]. The resulting parameter, the activation volume. provides us with important information such as the transition state shift toward the final state with increasing steric hindrance[2], participation of solvent in the activation step[3], the existence of tunnelling[4], and so on.

When the polarity of the reactants and the transition state is small and there is no cage effect, the observed activation volume reflects the structural change of the reacting molecules themselves. Thus, the large negative activation volume observed for Diels-Alder reactions have been attributed to partial bond formation and secondary orbital interactions in the transition state[5]. Another example is the homolytic decomposition of 2.2′-azobisisobutyronitrile. The activation volume is +3.8 cm^3/mol and this value is the reflection of the two-bond scission mechanism[6].

However, in polar reactions the situation is not at all that simple. For example. the aquation of acidopentaamminecobalt(III) ions is believed to proceed by a dissociative mechanism[7]. Therefore, a simple analogy to the above organic reactions predicts positive activation volumes. The experiments by Swaddle and his co-workers[8] show that the reactions are moderately accelerated by pressure. This is due to a generally observed phenomenon called electrostriction. During the activation. separation of charge takes place and the solvent molecules around the reacting species are com-

1) T. Asano and W. J. le Noble, *Chem. Rev.*, 78, 407 (1978)
2) W. J. le Noble and T. Asano, *J. Am. Chem. Soc.*, 97, 1778 (1975)
3) G. Guastalla and T. W. Swaddle, *Can. J. Chem.*, 51, 821 (1973)
4) N. S. Isaacs, K. Javaid, and E. Rannala, *J. Chem. Soc. Perkin Trans. 2*, 709 (1978)
5) R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.*, 92, 7149 (1970)
6) R. C. Newman, *Acc. Chem. Res.*, 5, 381 (1972)
7) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, 1974
8) W. E. Jones, L. R. Carey, and T. W. Swaddle, *Can. J. Chem.*, 50, 2739 (1972)

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pressed by the electrostatic interactions. Therefore, the simple measurement of the kinetic effect of pressure was not enough to verify the dissociative nature of the reaction and Swaddle *et al.* measured the reaction volumes, along with the activation volumes, for a series of leaving ligands. The slope of the plot of ΔV^* against ΔV was 1.0 and this was taken as strong evidence for the proposed mechanism.

However, if one could eliminate the effect of the electrostriction from the observed activation volume and could estimate the volume change which reflects only the structural change of the reacting molecules, it would provide us with an immediate answer for the above problem. Such a procedure has been sought since the recognition of the importance of electrostriction. Unfortunately, however, two of the methods developed so far[9,10] are based on the solvent effect on the activation volume and, therefore, neither of them are applicable to the aquations mentioned above. In this paper, a new procedure to dissect activation volume is proposed and is applied to some known high pressure data. Recently, Inoue *et al.*[11,12] developed a somewhat similar method based on the continuum model. The two methods will be compared later.

General Consideration

The partial molar volume of an ionic solute may be exp essed by the equation[9,13]

$$\bar{V} = V_{int} + n(V_{solv} - V_{bulk}) \tag{1}$$

where V_{int} is the intrinsic volume of the solute, V_{bulk} is the molar volume of the bulk solvent, V_{solv} is the molar volume of the solvent in the solvation sphere, and n is the solvation number. Since solute-solvent interactions reach beyond the first solvation sphere, V_{solv} must be taken as an average molar volume for all the solvent molecules that are influenced by the presence of the solute and n is the total number of solvent molecules affected by one solute particle. When Eq. (1) is applicable to the initial and the transition states, the following equation is obtained,

$$\Delta V^* = \Delta V^*_{int} + \Delta n^*(V_{solv} - V_{bulk}) \tag{2}$$

where Δn^* equals the solvation number change during activation.

It is a well known fact that the isothermal compression of most liquids obeys the Tait equation,

$$V_P = V_1 \left(1 - C \ln \frac{B+P}{B+1} \right) \tag{3}$$

where V_P and V_1 are the molar volumes of the liquid at the external pressure P and 1 bar respectively, and B and C are parameters characteristic of the liquid. If one assumes that the solvent molecules in the solvation sphere behave like bulk solvent under the influence of the extra pressure ∂P,

9) Y. Kondo, M. Uchida, and N. Tokura, *Bull. Chem. Soc. Jpn.*, **41**, 992 (1968)

10) H. Hartmann, H. D. Brauer, H. Kelm, and G. Rinck, *Z. Phys. Chem. (Frankfurt am Main)*, **61**, 53 (1968)

11) H. Inoue, K. Hara, and J. Osugi, *This Journal*, **48**, 44 (1978)

12) H. Inoue, *This Journal*, **48**, 105 (1978)

13) F. J. Millero, A. L. Surdo, and C. Shin, *J. Phys. Chem.*, **82**, 784 (1978)

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$(V_{solv} - V_{bulk})$ at the external pressure P is given as below[14].

$$V_{solv} - V_{bulk} = CV_1 \ln \frac{B+P}{B+P+\delta P} \tag{4}$$

In this equation, δP is the average extra pressure for all of the solvent molecules under the influence of the electrostatic field of the solute and it may be estimated, for example, as follows.

The partial molar volume of potassium ion in water is 4.0 cm³/mol at 25°C if we assign -5.0 cm³/mol for the proton[16]. The intrinsic volume of K⁺ estimated by Hepler's equation[17] is 12.5 cm³/mol[18]. Since the ion is coordinated by four water molecules as found from the X-ray diffraction, if we assume arbitrarily the existence of eight water molecules in the outer solvation sphere(s), we get

$$4.0 = 12.5 + 12(V_{solv} - 18.1)$$

and V_{solv} becomes 17.4 cm³/mol. The pressure required to compress water to this molar volume is 980 bar. As can be seen from this example, if we consider δP as the average extra pressure for all of the solvent molecules influenced by the solute electrostatic field, it becomes a fairly low value, probably much lower than B for water, i.e., *ca.* 3 kbar. Therefore, in the pressure ranges usually used for kinetic investigations, from several hundred to several thousand bars, Eq. (4) may be approximated as follows,

$$V_{solv} - V_{bulk} = -CV_1 \frac{\delta P}{B+P} \tag{5}$$

The validity of this approximation will be discussed again later in this section.

Inserting Eq. (5) into Eq. (2) yields

$$\Delta V^* = \Delta V^*_{int} - \Delta n^* CV_1 \frac{\delta P}{B+P}$$

$$= \Delta V^*_{int} - \frac{\kappa}{B+P} \tag{6}$$

and by integrating this equation from pressure=1 to P, on the assumption that ΔV^*_{int} and δP are independent of pressure, Eq. (7) is obtained.

$$-\frac{RT}{P-1} \ln \frac{k_P}{k_1} = \Delta V^*_{int} - \frac{\kappa}{P-1} \ln \frac{B+P}{B+1} \tag{7}$$

If our model is a good description of the initial and the transition states and the approximations are valid, the plot of the left-hand side of the above equation against $1/(P-1) \ln (B+P)/(B+1)$ will be a straight line and ΔV^*_{int} will be obtained as its intercept with the ordinate.

If we integrate Eq. (4), the following equation is obtained,

14) A similar treatment was done by Gibson on aqueous salt solutions. See ref. 15.
15) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd ed., Reinhold, New York, p. 271 1950
16) F. J. Millero, *Chem. Rev.*, **71**, 147 (1971)
17) L. G. Hepler, *J. Phys. Chem.*, **61**, 1426 (1957)
18) Most of the estimates of the intrinsic volume are in the range of 10-14 cm³/mol.[16,19]
19) G. L. Madan, *Indian J. Chem.*, **11**, 1319 (1973)

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$$-\frac{RT}{P-1}\ln\frac{k_P}{k_1}=\Delta V^{\neq}{}_{\rm int}-\Delta n^{\neq}CV_1\frac{1}{P-1}[(B+P+\delta P)\ln(B+P+\delta P)$$

$$-(B+1+\delta P)\ln(B+1+\delta P)-(B+P)\ln(B+P)+(B+1)\ln(B+1)].\quad(8)$$

Since δP is an unknown, there is no simple way to estimate $\Delta V^{\neq}{}_{\rm int}$ from this equation. Therefore, to approximate Eq. (4) by Eq. (5) is one of the essentials in the present treatment. Although the second terms in Eq's (7) and (8) differ more than 10% if we assume B and δP are 3000 and 1000 bar respectively, they are in excellent linear correlation as depicted by

$$-\frac{\delta P}{P-1}\ln\frac{B+P}{B+1}=-0.025+\frac{1.24}{P-1}[(B+P+\delta P)\ln(B+P+\delta P)$$

$$-(B+1+\delta P)\ln(B+1+\delta P)-(B+P)\ln(B+P)+(B+1)\ln(B+1)],$$

and the correlation coefficient is 0.9999 when the points are taken at every 500 bar up to 5 kbar. Therefore, the extrapolation based on Eq. (7) will give the right $\Delta V^{\neq}{}_{\rm int}$ value.

When a solvent molecule is involved in the rate determining step as a reactant as in the aquation of Cr (III) ions, $\Delta V^{\neq}$ includes the molar volume of the bulk water as shown below.

$$\Delta V^{\neq}=\bar{V}^{\neq}-\bar{V}({\rm Cr})-V_{\rm bulk}$$

$$=V^{\neq}{}_{\rm int}-V_{\rm int}({\rm Cr})-\Delta n^{\neq}CV_1\frac{\delta P}{B+P}-V_{\rm bulk}$$

It is a necessary condition for the linearity between $-RT/(P-1)\ln k_P/k_1$ and $1/(P-1)\ln(B+P)/(B+1)$ that the molar volume of the bulk water be approximately expressed by

$$V_{\rm bulk}=\alpha+\frac{\beta}{B+P}\qquad\qquad(9)$$

The molar volume of water at 25°C calculated according to Eq. (9) with the parameters determined by the method of least squares ($\alpha=14.39\,{\rm cm^3/mol}$, $\beta=11400\,{\rm bar\,cm^3/mol}$) are compared with the experimental values in Table 1.

It can be seen in Table 1 that Eq. (9) reproduces the molar volume of water with fairly small errors. The difference between the two values are less than 0.2cm³/mol and it is well within the experimental error in activation volumes. The agreement improves considerably if the pressure range is narrower. For instance, if the molar volumes at every 200 bar up to 1 kbar are used in the calcula-

Table 1   Experimental and Calculated Molar Volumes of Water at 25°C

(cm³/mol)

P / bar	$V_{\rm exp}$	$V_{\rm calc}$
1	18.07	18.19
1000	17.36	17.24
2000	16.80	16.67
3000	16.36	16.29
4000	15.98	16.02
5000	15.66	15.82

tion, the error becomes less than 0.02 cm³/mol. Since α is the molar volume at infinite pressure. it may be considered as the intrinsic volume of water. It is true that α depends on the pressure range considered, e. g., 15.29 cm³/mol is obtained for the second case. but the amount of its change is less than 1 cm³/mol despite the large pressure range difference. And for our present purpose, i. e., to estimate ΔV^*_{int}, this difference may be considered small enough. Thus, Eq's (6) and (7) are supposed to hold true in the reactions which involve a water molecule as a reactant in the rate determining step.

Application to Known High Pressure Data

Aquations of Co (III) and Cr (III) Complexes: Swaddle and his co-workers measured the aquation rate constants for several pentaamminecobalt (III) and -chromium (III) complexes under pressure, and from the activation volume against reaction volume plot for various leaving groups, they assigned the dissociative mechanism to the cobalt complexes[8] and the associative mechanism to the chromium complexes[3]. Since the distance between the metal and the other ligands will change little during activation[20], the intrinsic volume of activation may be positive for the cobalt ions and negative for the chromium ions. Experimentally, this can be seen from the activation volume for the exchange of water with an aquo ion, because little solvation change is expected when the leaving group has no charge. Thus, Hunt and Taube[21] obtained +1.2 cm³/mol for $Co(NH_3)_5 OH_2^{3+}$. and Swaddle[2] and Stranks[22] obtained − 5.8 cm³/mol for $Cr(NH_3)_5 OH_2^{3+}$.

The literature data[3, 8] were treated by the present analytical method and the results are shown in Fig. 1. In most cases. the linearity obtained is satisfactory. The scattered points for nitropentaamminecobalt (III) ion is almost certainly the result of experimental error in the rate constant. The plot of ln k against pressure does not give a smooth line as in the other cases. Systematic deviation from the expected linearity is not observed. The intrinsic activation volumes are given in Table 2 along with the activation volumes at 1 bar calculated according to Eq. (10) and from the regression coefficients for Eq. (11).

$$\Delta V^* = \Delta V^*_{int} - \frac{\kappa}{B+1} \qquad (10)$$

$$\ln k = a + bP + cP^2 \qquad (11)$$

The predicted values for the intrinsic activation volume are born out. Positive values are obtained for the cobalt complexes and negative values for the chromium complexes. The magnitude of ΔV^*_{int} is also reasonable judging from the activation volumes of the water exchange reactions mentioned above. The fact that the slope of the plot is the largest for sulfatopentaamminecobalt (III) complex gives us further confidence in our analysis, because the net charge increase is four for this complex while for the others it is two.

20) D. R. Stranks, *Pure Appl. Chem.*, **38**, 303 (1974)

21) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958)

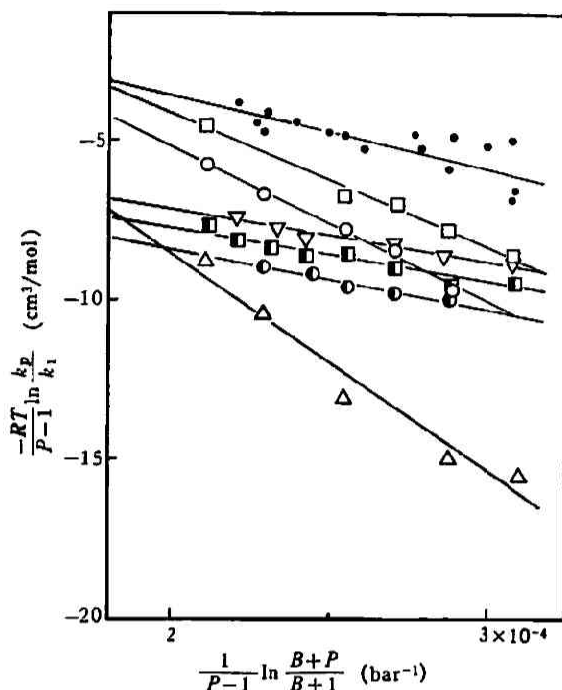22) T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc.*, **94**, 8357 (1972)

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Fig. 1 Plot to estimate ΔV_{int}^{*} for aquations of Co (III) and Cr (III) complexes in water at 25°C;

● $Co(NH_3)_5NO_3^{2+}$
○ $Co(NH_3)_5Cl^{2+}$
□ $Co(NH_3)_5Br^{2+}$
△ $Co(NH_3)_5SO_4^{+}$
◐ $Cr(NH_3)_5Cl^{2+}$
▮ $Cr(NH_3)_5Br^{2+}$
▽ $Cr(NH_3)_5I^{2-}$

Table 2 Analysis of the Data for the Aquations of Co (III) and Cr (III) Complexes according to Eq. (7)

substrate	ΔV_{int}^{*} cm³/mol	ΔV^{*} at 1 bar cm³/mol	
		Eq. (10)	Eq. (11)
$Co(NH_3)_5NO_3^{2+}$	+0.2	−6.4	−5.9
$Co(NH_3)_5Cl^{2+}$	+4.6	−11.8	−9.9
$Co(NH_3)_5Br^{2+}$	+4.0	−9.7	−8.7
$Co(NH_3)_5SO_4^{+}$	+5.4	−17.9	−17.0
$Cr(NH_3)_5Cl^{2+}$	−4.9	−10.9	−10.6
$Cr(NH_3)_5Br^{2-}$	−4.1	−10.2	−9.9
$Cr(NH_3)_5I^{2+}$	−4.2	−9.3	−9.2

Although it is not our primary aim to provide another method to estimate ΔV^{*} at 1 bar, any function which describes the relation between rate constant and pressure must give a reasonable activation volume. The extraction of the activation volume at 1 bar from high pressure rate constants has been controversial. Hyne et al.[23] examined several methods with their hydrolysis data and concluded that Eq. (11) was the best function to describe the data. In a recent report[24], several nonlinear functional forms including Eq. (11) were shown to provide virtually the same ΔV^{*} values for the hydrolysis of benzyl chloride with similar standard errors when the data base is extensive.

23) H. S. Golinkin, W. G. Laidlaw, and J. B. Hyne, Can. J. Chem., 44, 2193 (1966)
24) R. Lohmüller, D. D. Macdonald, M. Mackinnon, and J. B. Hyne, Can. J. Chem., 56, 1739 (1978)

Therefore, the values estimated by Eq. (10) were compared with those from Eq. (11). As can be seen from Table 2, the values obtained from Eq. (10) are slightly more negative than those obtained from Eq. (11). It has been widely known that although Eq. (11) describes experimental results with a high correlation coefficient, it tends to underestimate the differential coefficient. $(\partial \ln k/\partial P)_T$, at 1 bar. Therefore, the disagreement observed is probably caused, at least partially, by the nature of Eq. (11). However, the differences are 1 cm³/mol or less in the six out of seven cases calculated and they may be considered to be in good agreement.

Hydrolyses of Organic Halides: Solvolytic displacement reactions have been extensively studied under pressure, but most of them were done in mixed solvents of unknown compressibility. In addition, data for aqueous medium are usually available only for relatively low pressures. Probably, the most reliable work reported so far is that by Hyne and his co-workers[24]. Their data are plotted according to Eq. (7) in Fig. 2. The intrinsic activation volume is -2.4 cm³/mol in good agreement with an S_N2 mechanism. Another set of data on the hydrolysis of allyl chloride by Lateef and Hyne[25] gives a similar result. ΔV^*_{Int} is -2.9 cm³/mol in this case. This is also in agreement with the S_N2 mechanism.

The fact that the linearity between $-RT/(P-1)\ln k_p/k_1$ and $1/(P-1)\ln(B+P)/(B+1)$ is observed in these reactions and the fact that the extrapolated ΔV^*_{Int} values are reasonable judging from the reaction mechanism indicate that the molar volume of the substrate is given approximately by Eq. (12)

$$\bar{V} = \alpha + \frac{\beta}{B+P} \tag{12}$$

where B is the Tait equation parameter for water.

Generally speaking, the molar volume of neutral species in water decreases with increasing pressure and gradually levels off[26,27]. However, compared with the increase in the molar volume of ionic species, the change in the neutral one is much smaller. So, it is no surprise that the molar volume change with pressure is approximately represented as a hyperbola especially when the pres-
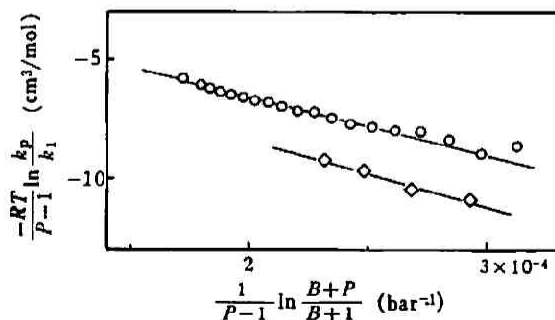

Fig. 2 Plot to estimate ΔV^*_{Int} for some hydrolysis reactions; ○ benzyl chloride at 30°C, ◇ ally chloride at 50.3°C

25) A. B. Lateef and J. B. Hyne, *Can. J. Chem.*, **47**, 1369 (1969)
26) A. A. Yayanos, *J. Phys. Chem.*, **76**, 1783 (1972)
27) H. Høiland, *Acta Chem. Scand.*, **27**, 2687 (1973)

sure range is narrow. In addition, polar solvent has larger B value, and the partial molar volume of a solute in such a solvent tends to be small[28, 29] and therefore, relatively incompressible. Eq. (12) satisfies this condition too, at least qualitatively, because the first differential coefficient of V with respect to pressure is inversely proportional to $(B+P)^2$. Furthermore, α is relatively insensitive to the B value, e.g., for water[30] we get 14.96 cm^3/mol as α if we use 2000 bar for B instead of 2996 bar. The difference in α obtained for these two widely variant B values is only 0.57 cm^3/mol.

Considering these facts, it may be justifiable to apply Eq. (7) to the hydrolysis reactions in water.

Ionization Equilibria in Water: When the present analysis is applied to ionization equilibria in water, the following equation is obtained.

$$-\frac{RT}{P-1} \ln \frac{K_P}{K_1} = \Delta V_{int} - \frac{\kappa}{P-1} \ln \frac{B+P}{B+1} \tag{13}$$

Several representative acid-base ionizations were analyzed according to this equation and the results are shown in Table 3 and Fig. 3. Except for carbonic acid, the intrinsic volume changes are relatively small as expected. The ionization of carbonic acid is actually a reaction of carbon dioxide and water,

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$
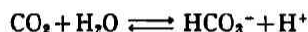
and the large negative intrinsic volume is the result of the covalent bond formation between carbon and oxygen atoms. On the contrary, the ionization volume of ammonia is mostly the result of the increase in the solvation. The relatively small but negative ΔV_{int} values for water, acetic acid, hydrogen sulfide, and ammonia might be the results of the shorter hydrogen bond length between water and ionic species compared with the one between neutral molecules. However, it is also plausible that these ΔV_{int} values results from the crudeness of the present model and must be considered close to zero.

Table 3 Intrinsic Reaction Volumes for Some Acid-Base Dissociation Equilibria in Water

acid or base	T °C	ΔV_{int} cm^3/mol	ref.
H_2O	25	-5.3	31
H_2S	25	-0.8	32
H_2CO_3	25	-14.8	33
CH_3COOH	25	-3.8	34
NH_3	45	-1.9	35

28) J. C. Gjaldbaek and J. H. Hildebrand, *J. Am. Chem. Soc.*, 72, 1077 (1950)
29) W. L. Masterton, *J. Chem. Phys.*, 22, 1830 (1954)
30) Since Eq's (9) and (12) are in the same form and there is little report of the *partial* molar volumes under pressure, water was just used as an illustrative example.
31) S. D. Hamann, *J. Phys. Chem.*, 67, 2233 (1963)
32) N. G. Sretenskaya, *Geokhimiya*, 430 (1977)
33) A. J. Read, *J. Solution Chem.*, 4, 53 (1975)
34) D. A. Lown, H. R. Thirsk, and Lord Wynne-Jones, *Trans. Faraday Soc.*, 66, 51 (1970)
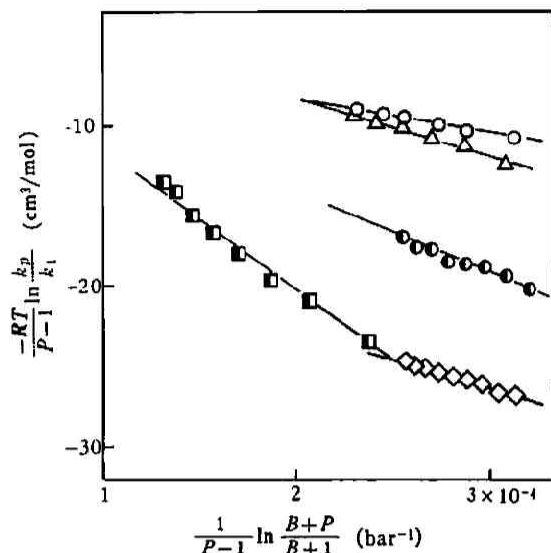35) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, 51, 1684 (1955)

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Fig. 3 Plot to estimate ΔV_{int} for some ioni-zation equilibria in water at 25°C : ○ aceitic acid, △ hydrogen sulfide, ◑ water, ◇ carbonic acid, ▣ ammonia (45°C)

Application to the Reactions in Nonaqueous Media : One of the reasons for the success of Eq. (7) in aqueous solutions is Eq. (12) is a good approximation for the molar volume of a neutral solute, probably because the compressibility of the solute is relatively small in aqueous solution as discussed above. In organic media, the thermal expansion volume[36] is much bigger and therefore, the com-
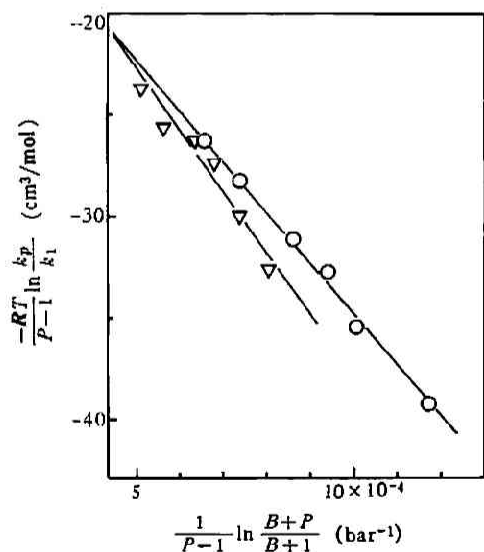

Fig. 4 Plot to estimate $\Delta V_{\text{int}}^{\ddagger}$ for the cycloaddi-tion of tetracyanoethylene with butyl vinyl ether at 30°C ; ▽ in acetonitrile, ○ in acetone
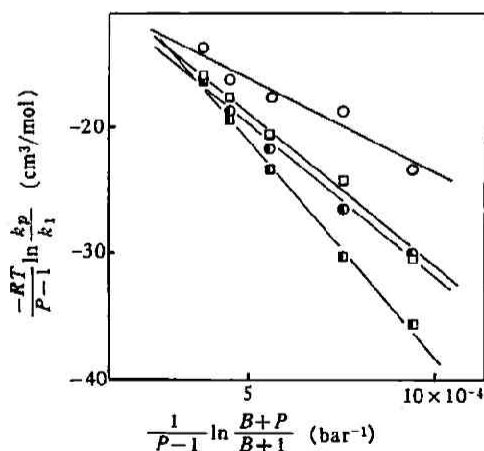

Fig. 5 Plot to estimate $\Delta V_{\text{int}}^{\ddagger}$ for the Menschutkin Reactions of 2,6-dialkylpyridine with methyl iodide ; ○ H, □ Me, ◑ Et, ▮ i-Pr

36) T. Asano and W. J. le Noble, *This Journal*, **43**, 82 (1973)

pressibility is higher. So we must expect that Eq. (12) becomes less accurate in organic solvents, especially in nonpolar ones. Several ionic reactions in relatively polar organic media were analyzed by the present method. Most of them show good linearity as depicted in Fig's 4, 5, and 6. The $\Delta V^{*}_{\text{Int}}$ and ΔV_{Int} values are listed in Table 4. It also includes the values for some other reactions not included in the Figures. The intrinsic activation volumes for the ionic cycloaddition of tetracyanoethylene (TCNE) with butyl vinyl ether is comparable with the value estimated by Fleischmann and Kelm [37] from the solvent effects on the activation volume, -14 cm³/mol.

It is interesting that the intrinsic term becomes less negative with increasing steric hindrance in the Menschutkin reactions of 2, 6-dialkylpyridines with methyl iodide. On the basis of $\Delta V^{*}/\Delta V$

Table 4   Intrinsic Activation or Reaction Volumes for Some Ionic Reactions in Polar Organic Media

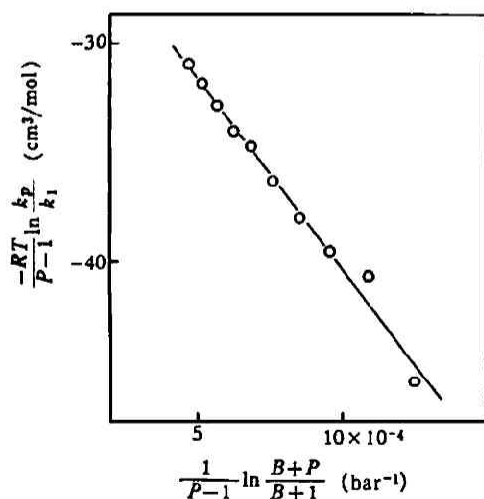| reaction	solvent	T °C	$\Delta V^{*}_{\text{Int}}$ or ΔV_{Int} cm³/mol	ref.
$TCNE + BuOCH - CH_2$	$MeCN$	30	-9.1	37
$TCNE + BuOCH = CH_2$	Me_2CO	30	-9.9	37
$Et_3N + EtI$	$PhNO_2$	50	-8.7	38
$Et_3N + EtI$	Me_2CO	50	-9.5	38
$C_5H_5N + MeI$	Me_2CO	25	-8.6	39
$2,6-Me_2C_5H_3N + MeI$	Me_2CO	25	-6.1	39
$2,6-Et_2C_5H_3N + MeI$	Me_2CO	25	-7.4	39
$2,6-i-Pr_2C_5H_3N + MeI$	Me_2CO	25	-3.4	39
ionization of Et_3N	$MeOH$	25	-14.0	11
ionization of piperidine	$MeOH$	25	-13.3	40

Fig. 6   Plot to estimate ΔV_{Int} for the ionization of triethylamine in methanol at 25°C

37) F. K. Fleischmann and H. Kelm, *Tetrahedron Lett.*, 3773 (1973)

38) H. Hartmann, H. D. Brauer, and G. Rinck, *Z. Phys. Chem. (Frankfurt am Main)*, **61**, 47 (1968)

39) W. J. le Noble and Y. Ogr, *Tetrahedron*, **26**, 4119 (1970)

40) S. D. Hamann and W. Strauss, *Discuss. Faraday Soc.*, **22**, 70 (1956)

values, le Noble and Asano[2] suggested some years ago that the transition state of this reaction shifts toward the final state with the increase in the steric hindrance. The increase in the slope of the plot with the steric hindrance is in accordance with this suggestion, because the later transition state means stronger solvation in the activated complex and, therefore, larger $\Delta n^{\ast}$. If that is the case, the present result may be understood as the longer C···I bond in the transition state with bulky alkyl groups.

The ionization of amines in methanol presents puzzling results. The intrinsic volume contraction is as large as 10 cm^3/mol. There is no adequate explanation for this phenomenon at present. However, it must be pointed out that similar results were obtained by Inoue et al[11]. as shown below.

Comparison of the Present Method with Inoue's: Recently Inoue et al.[11,12] derived equations which correlates high pressure rate or equilibrium constant with the dielectric constant of the reaction medium. According to their equation, the intrinsic activation volume is obtained by plotting $-RT/(P-1) \ln k_P/k_1$ against $(B'+1)/(P-1) \ln (B'+P)/(B'+1)$, where B' is the parameter for the Tait-type equation for the solvent dielectric constant, and extrapolating the relation to infinite pressure. In Table 5, the intrinsic terms calculated by their method are compared with the present results for some reactions. The agreements between the two values are good considering the approximations adopted and the big difference in their theoretical basis.

Table 5   Comparison of the the Intrinsic Volume Changes Estimated by the Two Methods

reaction	solvent,	T °C	$\Delta V_{int}^{\ast}$ or ΔV_{int} cm³/mol	
			(a)	(b)
$Co(NH_3)_5Cl^{2+}+H_2O$	H_2O	25	+4.6	+8.6
$Co(NH_3)_5Br^{2+}+H_2O$	H_2O	25	+4.0	+7.6
$Cr(NH_3)_5Cl^{2+}+H_2O$	H_2O	25	−4.9	−3.2
$Cr(NH_3)_5Br^{2+}+H_2O$	H_2O	25	−4.1	−2.4
$PhCH_2Cl+H_2O$	H_2O	30	−2.4	−0.9
$TCNE+BuOCH=CH_2$	MeCN	30	−9.1	−11.1
Et_3N ionization	MeOH	25	−14.0	−11.5
piperidine ionization	MeOH	25	−13.3	−11.2

a) By the present method.   b) By Inoue's method.

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