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Pressure Effect on Dimerization Equilibria of a Series of Substituted Nitrosobenzenes in Solution

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High Pressure / Liquids / Solutions / Statistical Mechanics / Thermodynamics

The effect of pressure was studied on the dimerization reactions of six di- and tri-substituted nitrosobenzenes in carbon tetrachloride at 25°C. The obtained configurational volume changes for the prototype one bond formation reactions are in the range of -17 to -21 $cm^3\ mol^{-1}$ at 6.13 MPa. The volume changes were interpreted in terms of the perturbation theory of liquid; they were dominated by the volume change in the reference system composed of hard spheres. Small differences between the observed and theoretical reference volume changes were ascribed to the perturbation due to electrostatic interactions between the solute and solvent; the perturbation volume changes were estimated by the Kirkwood theory of dipolar solvation.

1. Introduction

Activation and reaction volumes have been investigated extensively for a variety of chemical reactions in solution to get insight into the reaction mechanism [1]. We can say that in most cases, the measured volume changes have been interpreted on the basis of the following additivity scheme:

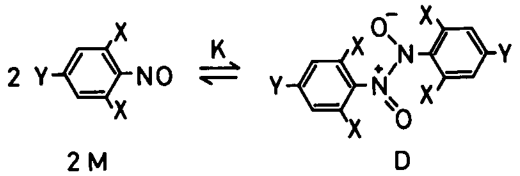
$$\Delta V = \Delta V_{\mathrm{ref}} + \Delta V_{\mathrm{per}} \tag{1}$$

where ΔV_{ref} is the volume change accompanying a reference reaction which is subjected to no "specific" solute-solvent interactions, and ΔV_{per} is the volume change due to perturbation through some additional (attractive) interactions. The simple scheme of this form which seems to stem from Evans and Polanyi [2] has been used for half a century without its fundamental scrutiny. Although the "intrinsic volume change" has been assigned to the first term, this primitive interpretation is physically unrealistic as pointed out in the previous work [3]. Thus it is important to study at the molecular level the significance of the first term in Eq. (1) by applying an equilibrium statistical mechanical method to a simple nonionic reaction as chosen here.

To understand the usefulness of Eq. (1), it is essential to evaluate the reference volume change. This important task, has been neglected and left unsolved because it requires a deep understanding of the liquid state where a model reaction takes place. We are not allowed to take a close look at the effect of solvation on the volume change which may be assigned to the second term in Eq. (1) until the reference volume change is established according to a liquid theory.

Although the first term in Eq. (1) is regarded as being dominated by the volume change due to the bond formation or breakage in reacting molecules themselves, a key role is played just by their molecular packing in solution [4]. This important fact has led us to evaluate the reference volume change according to the theory of liquids composed of hard spheres [3, 5]. This approach to the volumetric problem of our interest is in line with the van der Waals picture of liquid [6] and also with our empirical view on the importance of the "steric effect" on the chemical reaction.

The simpler the reaction we choose the more efficient our comparative study of theory and experiment on the volumetric aspect of the reaction in solution. In this respect a dimerization reaction meets our requirements. The substituted nitrosobenzenes which are in equilibrium with the dimer (N,N′-dioxyazobenzene) of the trans form [7−9] as



(2)

$X = Cl,\ Br,\ CH_3$
$Y = H,\ X$

are chosen here for the following reasons: (1) this nonionic reaction can be regarded as a prototype one bond formation reaction, (2) this is so simple that the liquid theory can be applied to the volumetric study, and (3) this dimerization has no experimental troubles in contrast to the dimerization of nitrogen dioxide. The latter reaction that is the only simple dimerization so far studied at high pressure [10] has the disadvantages: the reactant or product suffers from some decomposition and the equilibrium lies so far to the dimer side.

2. Experimental

2.1. Materials

Substituted nitrosobenzenes were prepared by oxidizing the corresponding anilins [11]. 2,6-Dichloronitrosobenzene (DCNB), 2,4,6-trichloronitrosobenzene (TCNB), 2,6-dibromonitrosobenzene (DBNB), and 2,4,6-tribromonitrosobenzene (TBNB) were purified by sublimation, and 2,6-dimethylnitrosobenzene (DMNB) and 2,4,6-trimethylnitrosobenzene (TMNB) were purified by recrystallization from ethanol to avoid their decomposition during sublimation. Carbon tetrachloride was purified by the usual method.

2.2. Equilibrium Measurement

The equilibrium concentration of the monomer was monitored with a spectrophotometer (Shimadzu UV-240) through the absorption band around 750 nm due to the nitrosobenzene; the dimer has no absorption in this region. The concentration measurement at high pressure was carried out at pressure intervals of 24.5 MPa up to 122.6 MPa using the high pressure optical cell described elsewhere [4b]. The temperature was controlled to ±0.1 °C at 25 °C by circulating thermostated water. The variation of the concentration of the nitrosobenzene with pressure was corrected with the aid of the equation of state of carbon tetrachloride [12]. The equilibrium measurements were performed at least at four different concentrations.

The reliability of the obtained volume change for reaction (2) depends on the precision of the absorption measurement at high pressure. Consequently we took care of the following: (i) the base line shift associated with the way of setting the high pressure cell in the spectrophotometer and (ii) the uncertainty of the optical path length. The base line shift was corrected by that in the range of 400–500 nm where neither the monomer nor the dimer has no appreciable absorption. The path length, which varied to a small extent from one run to another, was checked according to the monomer absorbance at 0.1 MPa. After these corrections the reproducibility of the absorbance at high pressure was ±0.001. The increase in the optical path length due to an increase in pressure was neglected because the effect was estimated to be at most 0.1% at the highest pressure.

3. Results

When the nitrosobenzene monomers (M) are in equilibrium with the dimers (D) as expressed by Eq. (2), the following relationship holds:

$$A/c = -2KA^2/\varepsilon dc + \varepsilon d \qquad (3)$$

where A is the absorbance of the monomer in equilibrium, c is the concentration reduced to the monomer (denoted by [M] + 2[D]), ε is the extinction coefficient of the monomer, d the path length (ca. 10 mm) and K is the equilibrium constant in the molarity scale (mol dm^{-3}) given by [D]/[M]^2.

According to Eq. (3) a plot of A/c against A^2/c shows a straight line, and we can obtain the extinction coefficient and the equilibrium constant from the intercept and slope; note that in the case of the dimerization of nitrogen dioxide [10], the pressure dependence of ε could not be examined. Such a plot for TCNB is shown in Fig. 1. The intercept (the extinction coefficient) changes little with increasing pressure but the slope decreases; the latter trend indicates the increase in the equilibrium constant as a result of the application of pressure. The values of the equilibrium constants thus obtained for the six nitrosobenzenes are summarized in Table 1 together with the relevant parameters. The error of the equilibrium constants for the substituted nitrosobenzenes is less than 5% except for DCNB and DMNB. Since such nitrosobenzenes as DCNB and DMNB have a larger equilibrium constant, its uncertainty amounts to 10%; in this case, the left-hand side of Eq. (3) is small compared with the magnitude of the first term on the right-hand side, so the slope and intercept of the plot have a larger uncertainty.

The volume change accompanying the dimerization reaction is obtained by differentiating the equilibrium constant with respect to pressure as

$$\Delta V = -\kappa_T RT - RT\frac{\partial \ln K}{\partial P} \qquad (4)$$

$$= -\kappa_T RT + \Delta V^{\mathrm{conf}} \qquad (5)$$

Table 1
Equilibrium constants and extinction coefficients for the substituted nitrosobenzenes at 25 °C in carbon tetrachloride at high pressures

P/MPa	K/mol^{-1} dm^3	$\lambda_{\max}$/nm	ε/mol^{-1} dm^3 cm^{-1}
	2,4,6-trichloronitrosobenzene		
0.1	24.2 ± 0.2	780	43.9 ± 0.1
24.5	31.2 ± 0.4	782	45.3 ± 0.2
49.0	38.7 ± 0.8	782	45.9 ± 0.3
73.5	48.1 ± 1.3	783	46.7 ± 0.4
98.1	57.9 ± 0.9	784	47.1 ± 0.3
122.6	70.7 ± 1.0	784	47.8 ± 0.2
	2,4,6-tribromonitrosobenzene		
0.1	1.50 ± 0.10	772	39.0 ± 0.2
24.5	1.98 ± 0.06	773	39.8 ± 0.1
49.0	2.38 ± 0.09	775	40.3 ± 0.1
73.5	2.81 ± 0.07	775	40.6 ± 0.1
98.1	3.48 ± 0.11	776	41.1 ± 0.1
122.6	4.04 ± 0.10	777	41.3 ± 0.1
	2,4,6-trimethylnitrosobenzene		
0.1	25.6 ± 0.2	800	50.9 ± 0.2
24.5	33.7 ± 1.3	800	52.8 ± 0.5
49.0	43.4 ± 0.8	800	54.3 ± 0.3
73.5	56.0 ± 2.8	800	56.0 ± 0.8
98.1	67.3 ± 2.0	800	56.5 ± 0.6
122.6	82.5 ± 2.4	800	57.6 ± 0.6
	2,6-dichloronitrosobenzene		
0.1	44.0 ± 1.1	773	41.3 ± 0.3
24.5	54.8 ± 2.7	773	42.1 ± 0.5
49.0	61.9 ± 4.3	774	41.4 ± 0.7
73.5	79.0 ± 4.7	775	42.2 ± 0.7
98.1	92.0 ± 6.4	775	42.1 ± 0.8
122.6	104 ± 8	776	41.5 ± 1.0
	2,6-dibromonitrosobenzene		
0.1	2.40 ± 0.10	765	39.5 ± 0.1
24.5	3.01 ± 0.08	765	40.2 ± 0.1
49.0	3.41 ± 0.12	767	40.3 ± 0.1
73.5	4.00 ± 0.20	768	40.6 ± 0.2
98.1	5.02 ± 0.12	769	41.1 ± 0.1
122.6	5.91 ± 0.17	770	41.3 ± 0.2
	2,6-dimethylnitrosobenzene		
0.1	101 ± 1	810	48.7 ± 0.2
24.5	130 ± 1	810	49.7 ± 0.2
49.0	176 ± 3	810	51.9 ± 0.3
73.5	200 ± 7	810	50.9 ± 0.7
98.1	236 ± 6	810	50.6 ± 0.5
122.6	274 ± 17	810	50.2 ± 2.2

where ΔV is the volume change at infinite dilution, ΔV^{conf} is the configurational part of ΔV [3, 13] and equal to the second term in Eq. (4), T is the temperature, κ_T is the isothermal compressibility of the solvent, R the gas constant; here we consider the volume change for one mol of the extent of reaction. As well-known [14], it is somewhat difficult to accurately determine the slope of the plot of ln K vs. P around 0 MPa because the equilibrium constant is usually unavailable below 0.1 MPa (at negative pressures). To make trustworthy our comparative study of theory and experiment, we evaluate the volume change not at 0.1 MPa but at 61.3 MPa (the middle pressure between the lowest and the highest). The values of log K which depend on pressure as shown in Fig.2 are fitted by the least-squares method to the function of the form

$$\log K = a_0 + a_1 P + a_2 P^2 \qquad (6)$$

which leads to the evaluation of the configurational volume changes as summarized in Table 2.

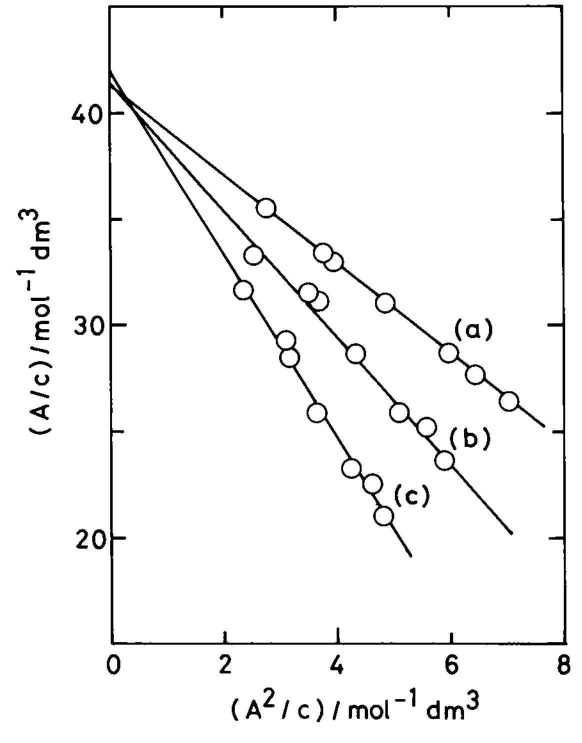


Fig. 1
Plots of A/c against A^2/c for 2,6-dichloronitrosobenzene (DCNB) in carbon tetrachloride at 25°C and high pressures.
(a) 0.1 MPa; (b) 49.0 MPa; (c) 98.1 MPa

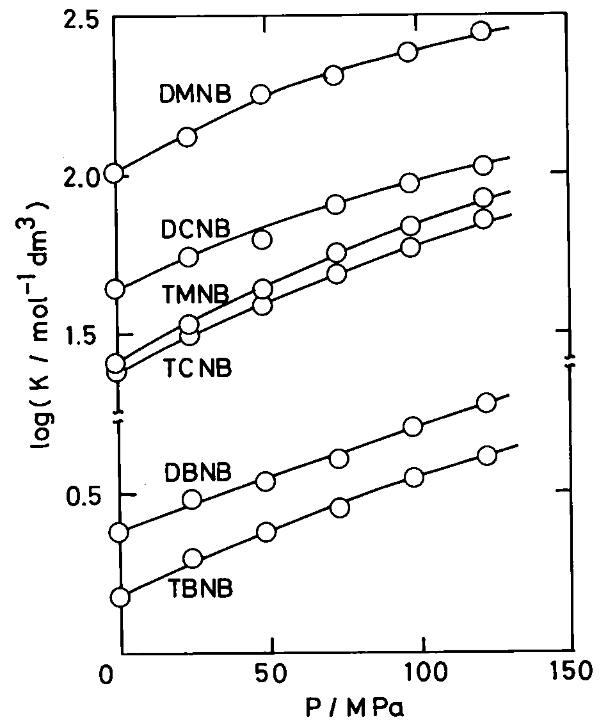


Fig. 2
Pressure dependence of the equilibrium constants for dimerization of the substituted nitrosobenzenes in carbon tetrachloride at 25°C. DMNB, 2,6-dimethylnitrosobenzene; DCNB, 2,6-dichloronitrosobenzene; TMNB, 2,4,6-trimethylnitrosobenzene; TCNB, 2,4,6-trichloronitrosobenzene; DBNB, 2,6-dibromonitrosobenzene; TBNB, 2,4,6-tribromonitrosobenzene

Table 2
Configurational volume changes (cm^3 mol^{-1}) accompanying the dimerization reaction of the nitrosobenzenes in carbon tetrachloride at 25°C and 61.3 MPa

	Experimental	Theoretical	
	$\Delta V^{\mathrm{conf}\ a)}$	$\Delta V_{\mathrm{ref}}^{\mathrm{conf}\ b)}$	$\Delta V_{\mathrm{per}}^{\mathrm{conf}\ c)}$
TCNB	$-20.7 \pm 0.6\ (-24)$	-24	4
TBNB	$-18.9 \pm 0.8\ (-24)$	-25	3
TMNB	$-22.7 \pm 0.8\ (-28)$	-26	4
DCNB	$-16.9 \pm 0.8\ (-20)$	-24	9
DBNB	$-17.2 \pm 0.7\ (-17)$	-25	9
DMNB	$-20.0 \pm 1.6\ (-30)$	-26	7

[a] The values in the parentheses are those at 0.1 MPa.
[b] The values at 0.1 MPa are 10% larger in magnitude.
[c] At 0.1 MPa, the values increase by 75%.

The configurational volume changes are in the range of -17 to -23 cm^3 mol^{-1} at 61.3 MPa and somewhat more negative at 0.1 MPa. The volume changes are in the sequence of the substituents Me < Cl ≃ Br and slightly dependent on the number of polar substituents; the trisubstituted nitrosobenzenes give a more negative volume change than the corresponding disubstituted nitrosobenzenes in the case of chloro- and bromonitrosobenzenes. The volume changes obtained in the present study are comparable with the volume change accompanying the dimerization of nitrogen dioxide [10].

4. Discussion

4.1. Reference Volume Change

When the intermolecular potentials are assumed to be pairwise additive, the configurational volume change accompanying the dimerization reaction is expressed in terms of the cavity distribution function $y(l)$ between the reacting molecules as [14]

$$\Delta V^{\mathrm{conf}} = -RT\frac{\partial \ln y(l)}{\partial P} \tag{7}$$

where l is the bond length in the product dimer. This is the key equation which connects the configurational volume change with the present-day liquid theory. The traditional picture of the volume change expressed by Eq. (1) is equivalent to the following equation:

$$y(l) = y_{\mathrm{ref}}(l) \cdot X_{\mathrm{per}}(l) \tag{8}$$

where $X_{\mathrm{per}}(l)$ is unity when the perturbation is absent. According to the van der Waals picture, the liquid structure is determined mainly by the repulsive intermolecular interactions which are regarded as hard core repulsions in many cases [6]. Hence we take the cavity distribution function of the hard sphere system as the reference; this molecular approach has been successfully applied to the studies on the volume change accompanying the contact-complex formation reaction [3] and the packing efficiencies of methylene and methyl groups in n-alkane liquids [5].

Let us evaluate the reference volume change for the dimerization reaction of our interest. The nitrosobenzene molecule is considered here to be composed of the reaction part A and the residual part B. Furthermore, we assume that part A is approximately described as a sphere of radius

r_A, and that part B does not affect the volume change accompanying the dimerization reaction. The latter assumption corresponds to the postulate of the independent volume change for unit reactions [5].

Since it is very difficult to accurately calculate the effective radius of the reaction site A composed of several atoms, we estimate its approximate value on the assumption that the core volume of the reaction part A is equal to the sum of the core volumes of the constituent atoms; an upper limit is set by the neglect of the overlapping of the atomic volumes. These approximations lead to the following simple relation:

$$r_A^3 = r_N^3 + r_O^3 + r_S^3 \tag{9}$$

where r_N, r_O, and r_S are the van der Waals radii of the nitrogen atom, oxygen atom, and the o-substituent, respectively; in the case of the methyl substituent, $r_S^3 = r_C^3 + 3r_H^3$. The reaction part is considered to be composed of the nitroso group and one of the o-substituents because the other o-substituent does not come into contact with another nitrosobenzene molecule in the trans dimer. Inserting the van der Waals radii of the relevant atoms [15] into Eq. (9), we obtain r_A as 0.24 nm for TCNB and DCNB, 0.25 nm for TBNB amd DBNB, and 0.26 nm for TMNB and DMNB.

The extent to which the reacting sites penetrate into each other from the contact position in forming the dimer is taken to be 0.19 nm; this is the difference between the contact distance (0.32 nm) of the N atoms [15] and the N – N bond length (0.13 nm) in the resulting dimer N,N′-dioxyazobenzene [16].

The remaining problem of how to evaluate the size of the carbon tetrachloride molecule has been discussed in a previous paper [3]; the effective radius is evaluated as 0.268 nm. When we use this value for the size the packing fractions of carbon tetrachloride are 0.500 and 0.526 at 0.1 and 61.3 MPa, respectively.

Applying the above parametric values to the analytical expression for the cavity distribution function and following the procedure described elsewhere in detail [5], we obtain the configurational volume changes; they are in the range of −24 to −26 cm^3 mol^{-1} at 61.3 MPa as summarized in the third column of Table 2 [17]. The calculated reference volume changes are in reasonable agreement with the experimental ones despite the incorporation of rather crude approximations. The satisfactory agreement indicates the validity of the van der Waals picture of liquid also for the case of the volume change accompanying the chemical reaction in the liquid phase.

Although the reference volume changes calculated above are rather close to the observed volume changes, the former are more negative by a few cm^3 mol^{-1}. This discrepancy may be related to the overestimate of r_A due to Eq. (9). In a reverse manner, we can obtain such a value of r_A that may reproduce the whole experimental value of the volume change: such values of r_A are 2.05 ± 0.06, 1.85 ± 0.08, 2.27 ± 0.09, 1.64 ± 0.09, 1.67 ± 0.07, and 1.98 ± 0.17 Å for TCNB, TBNB, TMNB, DCNB, DBNB, and DMNB, respectively. Although in fact, these smaller values of r_A make the agreement perfect, the r_A values obtained in the reverse manner bring anout another serious problem of the inequality of r_A for the di- and trisubstituted nitrosobenzenes except for the methyl substitution; because of the absence of the effect of the para substitution, both should have the same value of r_A if the perturbation volume change can be ignored. In consequence, we have to consider the contribution of the second term in Eq. (1).

At the end of this section, it is noteworthy that the calculated reference volume change is not so much dependent on the effective radius of the reaction site r_A which is the most uncertain factor in the above discussion. When the penetration length is kept constant the configurational volume change ΔV^{conf} at 61 MPa varies only to the following extent: the decrease in r_A from 0.25 to 0.15 nm causes the increase in ΔV^{conf} from −25 to −16 cm^3 mol^{-1}, though the core volume ($4\pi r_A^3/3$) itself decreases by a factor of 4.6.

4.2. Perturbation Volume Change

When the polarity of organic molecules is assumed to be given by the vector sum of the bond dipole moments, the nitrosobenzenes of our interest have a certain dipole moment but the resulting dimers do not. The Kirkwood [18] electrostatic theory of solvation for a dipole in continuum dielectrics enables us to evaluate the perturbation volume change in Eq. (1) in the following way:

$$\Delta V_{\mathrm{per}}^{\mathrm{conf}} = -2N \cdot 3(\mu^2/a^3)(\partial\varepsilon/\partial P)/(2\varepsilon + 1)^2 \tag{10}$$

where N is the Avogadro number, ε is the dielectric constant of the solvent, P is the pressure, and μ and a are the dipole moment and the effective radius of the monomer molecule, respectively.

To apply the simple electrostriction theory given by Eq. (10), we should reduce the shape of the molecule where a point dipole is embedded to a sphere of radius a. We assume that the radius a is given in terms of the core volume of the nitrosobenzene molecule V_C as

$$V_C = \frac{4}{3}\pi a^3 . \tag{11}$$

The core volumes of the nitrosobenzene molecules are evaluated by summing up the increments of the constituent groups as proposed by Kitaigorodsky [15]. The obtained core volumes are in the range of 0.13 to 0.16 nm^3 providing the radius a in the range of 0.31 to 0.34 nm.

According to the sum of the dipole moments [19], the molecular dipole moments are estimated as $3.2\,D$ ($1\,D = 3.34 \cdot 10^{-30}$ Cm) for TCNB, TBNB, TMNB, and DMNB, $4.8\,D$ for DCNB, and $4.9\,D$ for DBNB; the trisubstituted nitrosobenzenes have the same dipole moment due to the symmetry. The value of the dielectric constant of carbon tetrachloride and its pressure derivative are available in Ref. [12].

Using the above values of the parameters involved in Eq. (10), we obtain the perturbation volume changes summarized in the last column of Table 2. When the reference and perturbation volume changes are added together, the resultant theoretical volume changes agree well with the observed ones; although it appears that the agreement is perfect, it would be somewhat accidental in view of the crude approximations for the size of the reaction site. At any rate, the volume change for the prototype dimerization reaction can be understood satisfactorily by the application of the perturbation theory of liquid.

The difference in the volume change between tri- and disubstituted nitrosobenzenes is not quantitatively explained by the electrostatic theory. The shortcoming of this type may well be expected owing to the reduction of the molecular shape to a sphere and the limitation of the multipole expansion in a short range. A new idea will be required for constructing a reliable framework for understanding the perturbation volume change where the molecular shape and charge distribution are considered in an explicit manner.

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Activation Volume for Dimerization Reaction of 2,4,6-Trimethylnitrosobenzene in Solution

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Chemical Kinetics / High Pressure / Liquids / Solutions / Statistical Mechanics

The effect of pressure on the rate and equilibrium constants for the dimerization reaction of 2,4,6-trimethylnitrosobenzene in acetonitrile was studied up to 196 MPa at 25°C in order to examine whether the dynamical effect on the reaction process in solution can be neglected as assumed in the transition state theory. All the rate constants relevant to the dimerization were determined by the pressure relaxation method. The configurational reaction volume for the dimerization and the activation volume for the dissociation were -17.4 ± 0.7 and $+5.1 \pm 0.3\ \mathrm{cm^3\ mol^{-1}}$ at 98 MPa, respectively. The experimental results were in reasonable agreement with the theoretical ones that were calculated for the model system composed of hard spheres according to the liquid theory and the transition state theory. The dynamical effect on the activation volume was not detected in the present reaction system.

1. Introduction

The activation volume data have so far been accumulated for various organic, biological, and inorganic reactions in solution as a result of the recent advance in the experimental technique of the high-pressure kinetic study [1, 2]. However, the theoretical foundation of their interpretation is not well developed. At present, we need to understand the static and dynamic roles of solvent in determining the volumetric feature of the chemical reaction in solution.

In contrast to the prevailing feeling, activation volume is not a simple function of structural changes in reacting molecules in the activation step even if we can neglect the solvent dynamical effect; although bond formation or breakage initiates a volume change and may determine the sign, the

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