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Solvent Effect under High Pressure. Participation of Solvent in the Activated Complex in the Menschutkin Reaction

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Rates of the reaction between 3,5-lutidine with ethyl iodide have been measured at 50 °C over the pressure range 1—1,940 kg/cm^2 in benzene-nitrobenzene mixtures. The solvation number and average pressure within the solvation-shell of activated complex have been estimated from the rates and the compression of solvent. The solvation number was almost independent of solvent composition, but not the average pressure within the solvation-shell. Estimation of the structural term of the activation volume $\Delta_1 V^{\ddagger}$ in the reaction has been discussed. The logarithms of the rate constants showed a linear relation with the E_T-values under atmospheric pressure.

The fundamental equation for the effect of pressure on the rate constant of a chemical reaction is

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\ddagger}}{RT} \qquad (1)$$

where $\Delta V^{\ddagger}$ is the activation volume of the reaction, *i.e.* the difference of the partial molar volumes of the reactants in the transition state and the initial state. The activation volume gives important information on the structure and properties of the transition state. The activation volume is of use for the mechanistic interpretation of chemical reactions since there is no method for investigating the detailed shape of activated complexes.

The reaction of alkylhalides with tertiary amines, known as the Menschutkin reaction, is a well-known heterolytic reaction under high pressure. The importance associated with the "ionic-solvation" component of $\Delta V^{\ddagger}$ implies that the magnitude of activation volume should depend on the nature o solvent. There are experimental evidences that $\Delta V^{\ddagger}$ is solvent-dependent. An extensive study of the influence of the solvent on the Menschutkin reaction under high pressure was made by Gonikberg and his collaborators.[1] The solvation number and the average pressure within the solvation-shell in the transition state for the Menschutkin reaction was estimated by Kondo *et al.*[2] Their investigation deals with the average values of various solvents. Actually, the values would change because of the variation of the influence of solvent on the activated complex if the nature of solvent

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[1] M. G. Gonikberg, "Khimicheskoe ravnovesie i skorost' reaktsii pri vysokikh davleniyakh," 3rd ed., Khimiya, Moscow (1969), p. 206, 278; Y. Ogo "Koatsu Kagaku" (Japanese Translation of Gonikberg's Book), Nikkan Kogyo Shinbunsha, Tokyo (1972), p. 180, 245.

[2] Y. Kondo, M. Uchida, and N. Tokura, This Bulletin, **41**, 992 (1968).

(solvent polarity) is altered.

Some attempts have been made to correlate the rate constants for the Menschutkin reactions with the polarity parameters of solvents representing various aspects of solvation. A solvent dielectric constant has been widely used as a measure of solvent polarity. However, it represents only a single macroscopic characteristic of solvent and cannot express adequately all the interactions between solute and solvent molecules. Thus empirical parameters of solvent polarity have been proposed for understanding the complexities of molecular interactions in solution. E_T-values are known as a solvent polarity scale which covers a greater range of solvents. The scale was obtained by determining the molar transition energy E_T for the solvatochromic band in the spectrum of a pyridinium *N*-phenolbetaine in various solvents.

This work deals with the scale as regards the reaction of 3,5-lutidine with ethyl iodide. The solvation number and average pressure within the solvation-shell in transition state for benzene-nitrobenzene mixtures were obtained by means of the compression of solvents. The relationships between the polarity of the solvent and the reaction rate were studied by the use of the E_T-value as an empirical parameter of solvent polarity.

Experimental

Materials. Commerical 3,5-lutidine was dried overnight with sodium hydroxide and distilled twice at reduced pressure; bp 59 °C/14 mmHg, n_D^{25} 1.5030. Commerical ethyl iodide of special grade was washed with dilute potassium hydroxide solution and water, dried with calcium chloride and filtered. After addition of sodium metal to the filtered substance, the solution was distilled at atmospheric pressure; bp 71.3 °C, n_D^{20} 1.5131.

Commercial benzene and nitrobenzene of special grade were purified according to method given in literature;[3] n_D^{20} (benzene) 1.5013, n_D^{20} (nitrobenzene) 1.5526.

N-(4-Hydroxy-3,5-diphenyl-phenyl)-2,4,6-triphenylpyridinium betaine, a color change indicator used for the measurement of the E_T-value, was synthesized as follows. 2,6-Diphenyl-4-aminophenol was prepared from dibenzyl ketone and sodium nitromalonaldehyde monohydrate synthesized from mucobromic acid. Betaine was obtained from the reaction between this substance and 2,4,6-triphenylpyrylium perchlorate synthesized from acetophenone and benzaldehyde.[4] The betaine was recrystallized in a methanol-water mixture (1 : 1); mp 207—280 °C. Found; C, 83.58; H, 5.26; N, 2.61%. Calcd for $C_{41}H_{33}O_3N$: C, 83.79; H, 5.66; N, 2.38%.

The E_T-values were determined for the solvatochromic band in the spectrum of a pyridinium betaine by using the following equation.

$$E_T = h\nu = 2.859\times10^5/\lambda_{\max} \text{ (in Å)} \quad \text{(kcal/mol)}$$

Procedures. Solutions of equimolar concentration (0.25 M) of 3,5-lutidine and ethyl iodide were introduced into a 5-ml reaction cell, and placed in a high pressure apparatus held at 50±0.12 °C during the reaction and quickly pressurized. After decompression the reaction cell was emptied into a flask containing 15-ml water. The reaction product was extracted by vigorous shaking with water. A portion of the aqueous layer was analyzed by titration with a silver nitrate solution.

E_T-values were measured with a Hitachi 139-type UV-VIS spectrophotometer.

Measurement of Compression. The compression, $K=(V_0-V_P)/V_0$, was determined by the measurement of the solvent volumes at atmospheric pressure V_0 and at P atom pressure V_P. The experiments for the benzene-nitrobenzene mixtures were carried out at 50 °C by means of Adams' method using a piezometer of about 11-ml capacity.[5] The pressure was measured by a Heise Bourdon-type gauge, the accuracy being checked with a pressure balance (free-piston pressure gauge). The rates of compression were in the order of 100 atm/min. The volume changes of Pyrex glass and mercury at high pressure was corrected with the values in literature.[6]

Results and Discussion

The rate constants of the reaction of 3,5-lutidine with ethyl iodide in benzene–nitrobenzene mixtures at 50 °C over the pressure range 1—1940 kg/cm² are summarized in Table 1. All the reaction rates followed second-order equation. The rate constants increased with an increase in pressure and concentration of nitrobenzene. The unexpected large rate constant at 0.8 mole fraction nitrobenzene and 1940 kg/cm² pressure suggests an unusual high concentration of reactants resulting from the freezing of solvent. The freezing temperatures of benzene and nitrobenzene under 2000 kg/cm² have been reported to be 58.0 and 49.5 °C, respectively.[7]

Estimation of Activation Volume. In order to evaluate $\Delta V^{\neq}$ it is necessary to confirm the functional dependence of rate constant upon pressure. Derivation of an analytical expression for the dependence has been discussed by various workers. Golinkin *et al.*[8] concluded that the quadratic function (3) provided the best representation of the dependence of logarithm of rate constant on pressure for some organic reactions. We checked the following three functions by the least-mean-squares method. It was concluded that a second-order polynomial (3) gives the best description of this system.

$$\ln k = A + BP \tag{2}$$

$$\ln k = A + BP + CP^2 \tag{3}$$

$$\ln (k/k_0)/P = A + BP^{0.523} \tag{4}$$

It is assumed in Eq. (2) that the dependence of the lograithm of the rate constant on pressure is linear. Eq. (4) is the Benson-Berson equation modified by means of the Tait equation.

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[3] J. A. Riddick and W. B. Bunger, "Organic Solvents," John Wiley & Sons, Inc., New York, N. Y. (1970), p. 796.

[4] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann. Chem.*, **661**, 1 (1963).

[5] L. H. Adams, *J. Amer. Chem. Soc.*, **53**, 3769 (1931).

[6] K. E. Bett, K. E. Weale, and D. M. Newitt, *Brit. J. Appl. Phys.*, **5**, 243 (1954); D. S. Tsiklis, "Handbook of Techniques in High Pressure Reaction and Engineering," Plenum Press, New York (1968), p. 24.

[7] "The International Critical Tables," Vol. 4, McGraw-Hill, New York (1933), p. 9.

[8] H. S. Golinkin, W. G. Laidlaw, and J. B. Hyne, *Can. J. Chem.*, **44**, 2193 (1966).

TABLE 1. RATE CONSTANTS AT 50°C, $k \times 10^4$(l mol^{-1} s^{-1})

Pressure (kg/cm^2)	Mole fraction of nitrobenzene					
	0	0.2	0.4	0.6	0.8	1.0
0	0.197	1.13	2.28	3.33	3.89	4.58
410	(0.460)	2.12	4.05	5.51	6.07	6.63
920	0.613	3.20	5.82	7.88	8.24	9.03
1430	0.963	4.47	8.42	10.5	11.8	10.9
1940	—	5.48	10.3	12.2	15.2	13.8

TABLE 2. FUNCTIONAL CONSTANTS OF Eq. (3) AND STANDARD DEVIATION

	Mole fraction of nitrobenzene					
	0	0.2	0.4	0.6	0.8	1.0
A	−10.84	−9.059	−8.7977	−7.977	−7.870	−7.648
$B\times 10^3$ (cm^2/kg)	1.464	1.416	1.301	1.171	0.9452	0.8058
$C\times 10^7$ (cm^4/kg^2)	−2.435	−3.239	−2.755	−2.688	−1.191	−1.378
$SD\times 10^2$	3.00	8.55	3.47	4.65	5.20	6.26

TABLE 3. ACTIVATION VOLUMES, MOLAR VOLUME OF SOLVENT, COMPRESSION AND AVERAGE PRESSURE WITHIN SOLVATION-SHELL$^{a)}$

	Mole fraction of nitrobenzene					
	0	0.2	0.4	0.6	0.8	1.0
$\Delta V^{\neq}$ (cm^3/mol)	−40.1	−38.8	−35.6	−32.0	−25.9	−22.1
$\Delta_2 V^{\neq}$ (cm^3/mol)	−22.1	−20.8	−17.6	−14.0	−7.9	−4.1
V_0 (cm^3/mol)	92.231	94.470	96.873	99.469	102.18	104.87
K	0.120	0.110	0.0908	0.0704	0.0387	0.0195
$\Delta P\times 10^{-3}$ (atm)	(2.0)	2.0	1.7	1.3	0.70	0.37

a) $n=2$, $\Delta_1 V^{\neq}=-18$ cm^3/mol

The functional constants of Eq. (3) and the standard deviation are given in Table 2.

Substituting Eq. (3) into Eq. (1) we obtain the following equation for the evaluation of $\Delta V^{\neq}$.

$$\Delta V^{\neq} = -RT(B+2CP) \qquad (5)$$

The activation volumes at atmospheric pressure calculated by this equation are listed in Table 3.

$\Delta V^{\neq}$ denotes the change of partial molar volumes which occurs when the transition state is formed from the initial species as given by Eq. (6). $\Delta V^{\neq}$ may be also expressed by Eq. (7) by considering the solvation term of the activated complex with partial electric charge. Eq. (8) is given in terms of compression.

$$\Delta V^{\neq} = \bar{V}^{\neq} - (\bar{V}_{\mathrm{L}}+\bar{V}_{\mathrm{E}}) \qquad (6)$$

$$= [\bar{V}^{\neq} - (\bar{V}_{\mathrm{L}}+\bar{V}_{\mathrm{E}})] - n(V_{\mathrm{o}}-V) \qquad (7)$$

$$= [\bar{V}^{\neq} - (\bar{V}_{\mathrm{L}}+\bar{V}_{\mathrm{E}})] - nKV_{\mathrm{o}} \qquad (8)$$

The bar represents a partial molar volume, L and E refer to 3,5-lutidine and ethyl iodide, respectively, n the number of solvent molecules incorporated into transition state (solvation number), V_0 molar volume of solvent, V molar volume of compressed solvent due to solvation, and K compression of the solvent.

By measurement of the partial molar volume of 3,5-lutidine and ethyl iodide, the partial molar volumes of both reagents were almost independent of solvent composition and were obtained as 116 and 84.3 cm^3 at 50 °C, respectively. Thus the partial molar volumes of the reactants seem to be equal to their molar volumes.

The $\Delta V^{\neq}$ value is the sum of $\Delta_1 V^{\neq}$ and $\Delta_2 V^{\neq}$, the former being the volume change of reacting particles themselves when they form the activated complex (structural effect), and the latter the corresponding volume change in the solvent (solvation effect). The value $\Delta_1 V^{\neq}$ corresponds to the first term and $\Delta_2 V^{\neq}$ to the second term on the right-hand side of Eqs. (7) and (8). Thus, the magnitude of K in Eq. (8) denotes the volume change due to the interaction of the surrounding solvent molecules with the activated complex, *i.e.* the compression of the solvent due to solvation. If Gonikberg's value[9] −18 cm^3/mol obtained from the reaction of pyridine with ethyl iodide can be used as the value $[\bar{V}^{\neq}-(\bar{V}_{\mathrm{L}}+\bar{V}_{\mathrm{E}})]$ in Eq. (8), the product of the solvation number and the compression, (nK), can be estimated from the observed values $\Delta V^{\neq}$ and V_0. Since the solvation number n can be evaluated we can estimate the average pressure within the solvation-shell of activated complex ΔP from the corresponding compression-pressure curve.

Estimation of Solvation Number and Average Pressure within Solvation-shell of Activated Complex. Eq. (9) is given by differentiation of Eq. (7) with respect to V_0 assuming that n and V are independent of external

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[9] M. G. Gonikberg and B. S. El'yanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1960**, 629.

pressure over the pressure range studied.

$$\frac{\partial \Delta V^{\ddagger}}{\partial V_0} = \frac{\partial}{\partial P}[V^{\ddagger}-(V_L+V_E)]\frac{\partial P}{\partial V_0} - n \qquad (9)$$

$$= -(\beta+n)$$

$$\beta = -\frac{\partial}{\partial P}[V^{\ddagger}-(V_L+V_E)]\frac{\partial P}{\partial V_0}$$

A similar equation was introduced by Gonikberg and El'yanov.[9]

If we assume that $\beta=0$, then we obtain the following expression for solvation number.

$$n = -\frac{\partial \Delta V^{\ddagger}}{\partial V_0} \qquad (10)$$

There is no evidence that β is zero. However, the partial molar volumes of 3,5-lutidine and ethyl iodide are nearly equal to their molar volumes. Therefore $[V^{\ddagger}-(V_L+V_E)]$ gives the structural effect of the activation volume $\Delta_1 V^{\ddagger}$. In a free-radical chain reaction without the participation of solvent, the activation volume is independent of the pressure over small pressure range. This suggests that the influence of β is negligible.

Figure 1 shows a plot of $\Delta V^{\ddagger}$ against V_0 under various pressures in nitrobenzene. We see that good linearity holds. The solvation number is evaluated to be 2 from the slope. Similar values have been estimated by the same plot for the other mixtures and benzene. The value K in Eq. (8) can be calculated by the use of these values. The results are listed in Table 3. Figure 2 shows the experimental results on the compression of the solvent at various pressures. The average pressures within the solvation-shell of activated complex ΔP were estimated from this graph (Table 3). The values of ΔP are not independent of solvent composition and show higher values for the solvents rich in benzene.

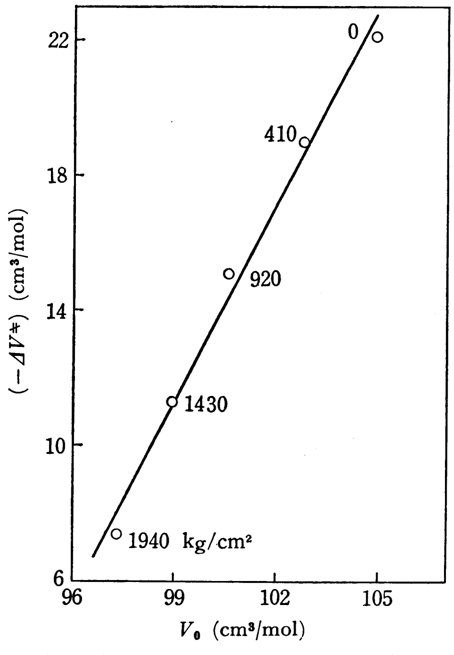

Fig. 1. Plots of activation volumes *vs.* molar volumes of solvent for the reaction of 3,5-lutidine with ethyl iodide at 50 °C in nitrobenzene.

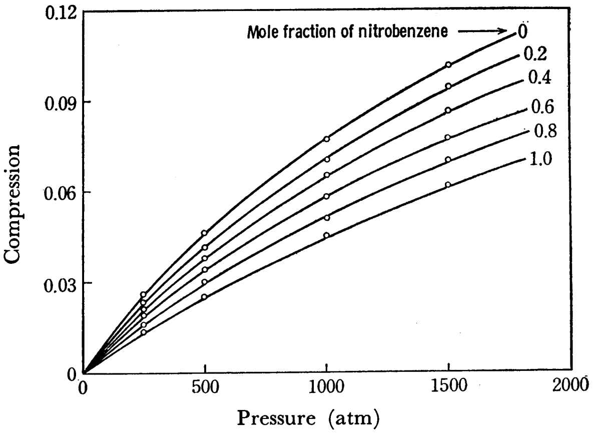

Fig. 2. Variation of the compression of solvent with pressure.

Gonikberg and El'yanov[9] tried to calculate $\Delta_1 V^{\ddagger}$ in the reaction of pyridine with ethyl iodide. They proposed three values of activation volume, −14, −18, and −22.5 cm³/mol, which were obtained by different analytical procedures. It seems reasonable to assume that −22.5 cm³/mol is too small since the over-all activation volume in nitrobenzene was observed to be −22.1 cm³/mol. The value −14 cm³/mol is also unfavorable since ΔP in benzene was calculated to be 2800 kg/cm², being extremely higher than the freezing pressure of benzene at 50 °C. It was concluded that the value −18 cm³/mol is reasonable. The data in Table 3 were calculated from $\Delta_1 V^{\ddagger}=-18$ cm³/mol. The ΔP of benzene was slightly higher than the value of freezing pressure. This was estimated by extrapolating the compression-pressure curve to freezing pressure. The unfavorable result might be due to the fact that inaccuracy of the starting data on the estimation of $\Delta V^{\ddagger}$ is large since the reaction in benzene takes place very slowly as compared with that in other solvents. Consequently, the value of ΔP of benzene is of low reliability.

The value ΔP can be evaluated also as follows. Isothermal compressibility is defined by $\kappa=-1/V(\partial V/$

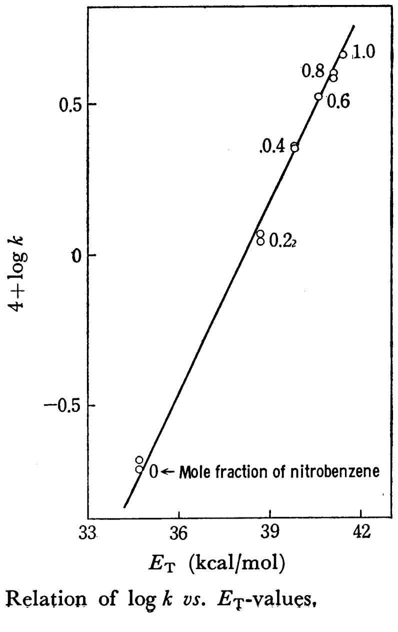

Fig. 3. Relation of log *k* *vs.* E_T-values.

$\partial P)_T$. We can write $\kappa'=(V_0-V_p)/V_0\cdot 1/\Delta P=K/\Delta P$ at certain pressure interval ΔP, and obtain an equation analogous to (8).

$$\Delta V^{\ddagger} = [V^{\ddagger}-(V_L+V_E)] - n\kappa' V_0 \Delta P \qquad (11)$$

However, κ' at pressure interval of ΔP cnanot be obtained experimentally, and κ at atmospheric pressure is generally used as κ' for the estimation of the ΔP in Eq. (11). Thus the procedure by means of the direct measurement of K is more accurate than that with the use of Eq. (11).

E_T-value. The E_T-values and the λ_{max} of benzene–nitrobenzene mixtures at 25 °C are shown in Table 4. Figure 3 gives a plot of the E_T-values against logarithms of the rate constants under atmospheric pressure. It seems that the E_T-value is an available empirical parameter of the solvent polarity for the present reaction because of the linearity. Gonikberg and El'yanov[10] reported that the volume contraction due to solvation in the transition state is 1/6—1/14 of that in the final state in the Menschutkin reaction. It is suggested that the E_T-values are useful parameters in this type of reaction. The activation volumes and E_T-values at atmospheric pressure became greater with an increase in the quantity of nitrobenzene, but no particular correlation has yet been established between them. In order to correlate the E_T-values to the activation volumes, it is necessary to observe the pressure dependence of the E_T-values, since the pressure dependence of the rate constant is required for the calculation of activation volume.

TABLE 4. λ_{max} AND E_T-VALUES FOR BENZENE-NITROBENZENE MIXTURES AT 25°C

	Mole fraction of nitrobenzene					
	0	0.2	0.4	0.6	0.8	1.0
λ_{max} (nm)	824	739	718	704	695	690
E_T (kcal/mol)	34.7	38.7	39.8	40.6	41.1	41.4

The authors are indebted to Dr. Takashi Moriyoshi for the measurement of the compression.

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[10] M. G. Gonikberg and B. S. El'yanov, *Dokl. Akad. Nauk SSSR,* **130,** 545 (1960).