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Solvent Effect under High Pressure. A Novel Procedure for the Estimation of the Activation Volume and an Abnormal Acceleration of Reaction under High Pressure

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In order to examine the relation between the effects of solvents and the effects of pressure on reaction rates, an apparatus for kinetic runs under pressure was constructed and the rates of the Menschutkin reaction were measured in various solvents under pressure. A graphical method for the calculation of an activation volume from experimental results was then developed and applied to these data. Experimental results in acetonitrile, methanol, and nitromethane showed a linear relation between $\log(k_p/k_1)/P$ *vs.* P, but in the case of benzene and nitrobenzene large deviations from the line, that is, abnormal accelerations due to pressure, were observed at 1200 and 1500 ($\mathrm{kg\cdot cm^{-2}}$). Analyzing these data, it was concluded that this abnormal acceleration was due to a freezing of the solvent with the increase in pressure.

Reactions of alkylhalides with tertiary amines are generally called Menschutkin reactions, and since the first kinetic study by Menschutkin⁽¹⁾ appeared, the effect of solvents on this reaction has been extensively studied previously and summarized in many reviews.⁽²⁾

The present authors previously treated this reaction in liquid sulfur dioxide and, by the use of the results obtained in various solvents, discussed the effect of solvation on the rate of reaction in the liquid phase.⁽³⁾ Further, in order to obtain information about the interactions between a solvent and a solute molecule, the volume change which accompanies the dissolution of solutes was measured by the present authors in liquid sulfur dioxide.⁽⁴⁾

Recently an investigation into the rates of solution reactions at various hydrostatic pressures has been undertaken in order to determine a useful method for the study of reaction mechanisms.

In this experiment, with the aim of examining the relation between the rate of reaction in solution and the nature of the solvent, Menschutkin reactions between triethylamine and ethyliodide were carried out in various solvents over a wide range of pressures.

Experimental

Materials. Ethyliodide was washed with a dilute sodium thiosulfate solution, water, a sodium carbonate solution, and again water successively, dried, and then distilled; bp 72.5°C. Triethylamine was distilled from aceticanhydride, dried with activated alumina, and

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1) N. Menschutkin, *Z. Physik. Chem.*, **6**, 41 (1890).

2) a) E. A. Moelwyn-Hughes, "Kinetics of Reaction in Solution," Sec. Ed., Oxford Univ. Press, London (1947), p. 207; b) E. L. Eliel, "Steric Effects in Organic Chemistry," ed. by M. S. Newmann, John Wiley & Sons, New York (1956), Chap. 2; c). C. Kimura, *Yuki Gosei Kagaku Kyokaishi,* **22**, 261 (1964).

3) N. Tokura and Y. Kondo, This Bulletin, **36**, 200 (1963); N. Tokura and Y. Kondo, *ibid.*, **37**, 133 (1964).

4) Y. Kondo, T. Goto, I. Suo and N. Tokura, *ibid.*, **36**, 1230 (1966).

distilled; bp 89.5°C. The solvents used in this experiment were purified by known methods.[5]

Analysis. The iodide ion produced was titrated with a silver nitrate solution potentiometrically, as has been described earlier.[3]

Apparatus. The pressure equipment used is shown in Fig. 1. The reactor is a sawn-off 30 ml enemasyringe (A) and plunger that are inside a pressure vessel (E) made of Ni-Cr-Mo steel. The vessel was filled with oil, and the reactor was connected to the head of the vessel by means of polyethylene packing (B).

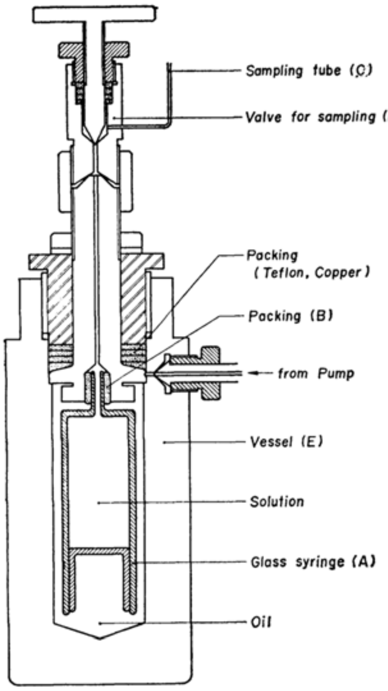

Fig. 1. Apparatus for kinetic runs under pressure.

The oil pressure was generated by means of a plunger pump and was adjusted to the required value by means of a high-pressure screw pump. The pressure in the vessel was measured by means of a Bourdon gauge arranged in the midway position between the vessel (E) and the screw pump. The pressure vessel (E) was immersed in a thermostat bath held at 25±0.1°C during the reaction.

Kinetic Procedure. The reaction mixture, kept at the reaction temperature, was injected into the reactor through a sampling tube (C); then the head of the apparatus was quickely attached to the vessel, which had previously been adjusted to the reaction temperature, and the vessel was brought up to the required pressure. Samples for analysis were taken from the reactor by opening the valve for sampling (D), and oil was pumped into the vessel (E) up to the required pressure after sampling.

The reaction rates in such solvents as benzene and nitrobenzene in which the product, tetraethylammoniumiodide, was insoluble, were obtained as follows.

Solutions of equimolar concentrations of ethyliodide and triethylamine were prepared, and equal volumes of them were mixed in small polyethylene ampoules; these ampoules were sealed quickly and, after vigorous shaking, were immersed into the pressure vessel (E). They were withdrawn periodically and analyzed by the method described earlier.[3]

Typical run in an acetonitrile solvent are given in Table 1.

TABLE 1. A TYPICAL RUN FOR THE REACTION OF EtI WITH $(Et)_3N$ IN ACETONITRILE AT 25°C

P kg·cm^{-2}	k_p l·mol^{-1}·sec^{-1}	k_p/k_1	$\log(k_p/k_1)/P\times 10^4$ kg^{-1}·cm^2
1	2.14×10^{-4}	1	
300	3.02×10^{-4}	1.43	5.18
300	3.06×10^{-4}	1.45	5.38
600	4.14×10^{-4}	1.96	4.87
900	5.17×10^{-4}	2.45	4.32
900	5.69×10^{-4}	2.69	4.77
1200	7.17×10^{-4}	3.39	4.42
1500	8.93×10^{-4}	4.22	4.17
1500	9.94×10^{-4}	4.70	4.48

Results and Discussion

Estimations of Activation Volumes. The fundamental equation for the effect of the pressure on the rate constant, k, of a one-step chemical reaction is, according to the transition state theory;

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

where $\Delta V^{\neq}$ is the volume of the activation of the reaction.[6]

Although the volume of activation has been calculated graphically from the slope of the curve of $\ln k$ against the pressure, it has recently been pointed out that $\Delta V^{\neq}$ is generally dependent on the pressure[7]; therefore, the value at zero external pressure should be used in determining reaction mechanisms. Various methods of estimating $\Delta V^{\neq}$ at zero external pressure have since been developed.

Bonson *et al.* derived a theoretical expression for the estimation of $\Delta V^{\neq}$ at atmospheric pressure ($\Delta V_0^{\neq}$) by treating a transition complex as having the compressibility properties of ordinary molecules and by then applying the Tait equation to the expression of its compressibility.[8] On the basis of a consideration of volume-energy relations along the reaction coordinate, Walling and Tanner have, however proved that the applicability of

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[5] "Technique of Organic Chemistry, VII, Organic Solvent," ed. by A. Weissberger, Interscience Publisher, New York (1955).

[6] S. Glasstone *et al.* "The Theory of Rate Processes," McGraw-Hill Book Company Inc., New York (1941), Chap. 8.

[7] S. D. Hamann "Physico-Chemical Effects of Pressure," Butterworths Scientific Publications, London (1957), Chap. 9.

[8] S. W. Benson and J. A. Berson, *J. Am. Chem. Soc.*, **84**, 152 (1962).

Benson-Berson's model is at best restricted to small groups of nonionic reactions.[9]

Another method of estimating $\Delta V_0^{\neq}$ accurately is to connect any point on the $\ln k$ *vs.* p curve with the origin with a straight line and to then extrapolate the slope to zero external pressures.[10]

In contrast to these methods however, a power-series treatment of experimental data such as Eq. (1), where $A' = (-\Delta V_0^{\neq})$, B' is the coefficient of the initial compressibility of $\Delta V^{\neq}$, seems to be the simplest and most precise approach.[9,11] Because the plots of $\log(k_p/k_1)/P$ *vs.* P showed linearity, as is shown in Fig. 2, the experimental data were treated by Eq. (2) in this experiment; then, by extrapolating to zero external pressure, A could be obtained from the ordinate and B, from the slope.

$$\boldsymbol{R}T \ln k_p = \boldsymbol{R}T \ln k_1 + A'P + B'P^2 + C'P^3 \quad (1)$$

$$\log (k_p/k_1)/P = A + BP \quad (2)$$

It is characteristic of a graphical method that it is easy to extrapolate to zero external pressure and that with it it is possible to eliminate at once isolated points which are obviously in error. One example of this plot is shown in Fig. 2, while the results obtained in these experiments are collected in Table 2.

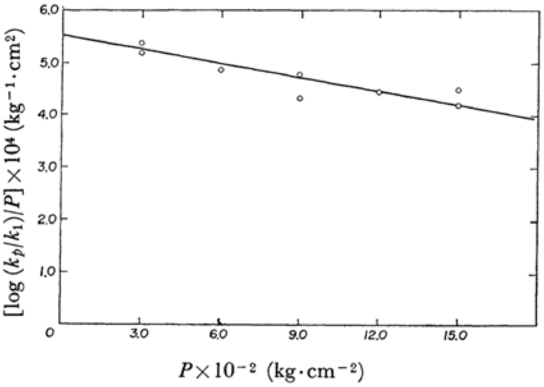

Fig. 2. Plot of $\log (k_p/k_1)/P$ *vs.* P for the reaction of ethyliodide with triethylamine in acetonitrile at 25°C.

TABLE 2. RESULTS OF THE MENSCHUTKIN REACTION BETWEEN TRIETHYLAMINE AND ETHYLIODIDE UNDER PRESSURE

Solvent	$A \times 10^{+4}$ kg^{-1}·cm^2	$B \times 10^8$ kg^{-2}·cm^4	$-\Delta V_0^{\neq}$ ml·mol^{-1}
Acetonitrile	5.52	−8.67	32.1
MeOH	5.50	−10.7	32.0
Nitromethane	5.81	−12.6	33.8
Benzene*	7.47	−15.5	43.5
Nitrobenzene*	5.16	−13.5	30.0

* In the calculation the data below 900 kg·cm^{-2} were used.

As the rate constant, k, is based on the molar concentration scales, small correction terms involving the compressibility of the solvent should be introduced into the estimation of $\Delta V^{\neq}$; as a rule, however these have been ignored.[7]

While the authors were carrying out this experiment, Hartmann and his collaborators[10] reported their findings on the effect of the pressure on the rates of the Menschutkin reaction between pyridine and methyliodide. In Table 3, these results are listed; the following two points may be concluded from a comparison of the data.

1) The $[-\Delta V_0^{\neq}]$ value for the reaction of triethylamine with ethyliodide is greater by about 10 ml·mol^{-1} than that for the reaction of pyridine with methyliodide; this difference holds constant for the three solvents listed above.

TABLE 3. COMPARISON OF $[-\Delta V_0^{\neq}]$ VALUES IN SOLVENTS

Reaction	Nitrobenzene	MeOH	Benzene
Pyridine + MeI[10]	19.7	22.6	31.9
Et_3N + EtI	30.0	32.0	43.5

2) The order of the increase of $[-\Delta V_0^{\neq}]$ is as follows:

$$\text{Nitrobenzene} < \text{MeOH} < \text{Benzene}$$

The differences in $[\Delta V_0^{\neq}]$ values among them are similar:

$$\Delta\Delta V_0^{\neq} \approx 2 \text{ } (ml\cdot\text{mol}^{-1}) \text{ for nitrobenzene-MeOH}$$

$$\Delta\Delta V_0^{\neq} \approx 10 \text{ } (ml\cdot\text{mol}^{-1}) \text{ for MeOH-benzene}$$

It has been suggested[7] that the activation volume, $\Delta V_0^{\neq}$, of the reactions in a solution is made up of two terms: $\Delta V_1^{\neq}$, which represents the change in volume of the molecules themselves when they form the transition state; and $\Delta V_2^{\neq}$, which is the corresponding change in the volume of the surrounding solvent caused by the rearrangement of its molecules.

Since the effects of solvents on the rate of the reaction in a solution are closely related to the solvation of a solute molecule, comparisons of the activation volume in various solvents would give information about the interactions between a solvent and a solute molecule.

The total volume, V_t, of a solution composed of N mol of the solvent and n mol of the solute would be given by:

$$V_t = (N - nZ)V^{\circ} + nV_s + nZV \quad (3)$$

where V°, V_s, V, and Z are the molar volumes of a pure solvent, of a solute and of a solvated

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[9] C. Walling and D. D. Tanner, *ibid.*, **85**, 612 (1963).

[10] H. Hartmann, H. Kelm and G. Rinck, *Z. Physik. Chem. N. F.*, **44**, 335 (1965).

[11] E. Whalley "Advances in Phys. Org. Chem.," Vol. 2, ed. by V. Gold Academic Press, New York (1964), p. 93.

TABLE 4

Solvent	Benzene	Methanol	Nitrobenzene
$(-\Delta V_0^{\neq})[ml\cdot mol^{-1}]$	43.5	32.0	30.0
$K\times 10^{11}[cm^2\cdot dyn^{-1}]$ [14]	9.67	12.77*	5.03
$KV^\circ\times 10^9[cm^5\cdot dyn^{-1}\cdot mol^{-1}]$	8.65	5.20	5.17

* The data at 27.6°C

solvent, and the solvation number of the solute, respectively.

Therefore the partial molar volume of the solute, V_s°, is given by:

$$\overline{V}_s^\circ = \left(\frac{\partial V}{\partial P}\right)_N = V_s + Z(V - V^\circ) \tag{4}$$

Since the compressibility, K, is defined by:

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{5}$$

the volume change of a solvation, ΔV, may be approximately expressed as follows:

$$\Delta V = (V - V^\circ) = (-1)KV^\circ\Delta P \tag{6}$$

The substitution of Eq. (6) into Eq. (4) yields:

$$\overline{V}_s^\circ = V_s - ZKV^\circ\Delta P \tag{7}$$

From Eq. (7) it may be concluded that the partial molar volume of a solute may be expressed as a function of a solvation number, the compressibility, and the molar volume of a pure solvent, and the average pressure within the cosphere of a solute, ΔP.

If we assume that, since in the Menschutkin reaction the reactant molecules are electrically neutral, the partial molar volumes of the reactants, $\overline{V}_A^\circ$, $\overline{V}_B^\circ$, are nearly constant throughout the solvents, then the activation volume is given by:

$$\begin{aligned}\Delta V_0^{\neq} &= \overline{V}^0_{\neq} - (\overline{V}_A^\circ + \overline{V}_B^\circ)\\ &= \{V_{\neq} - (\overline{V}_A^\circ + \overline{V}_B^\circ)\} - ZKV^\circ\Delta P\end{aligned} \tag{8}$$

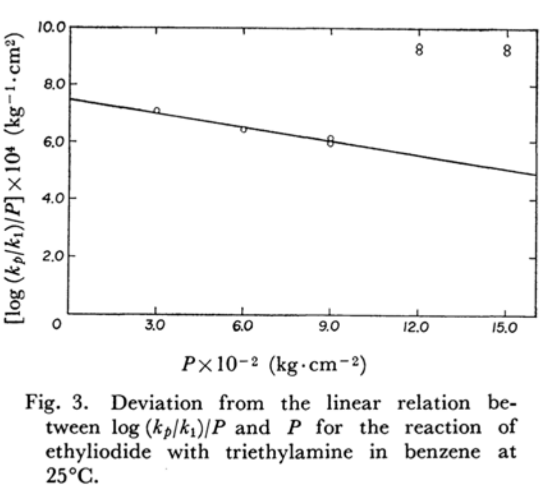

Fig. 3. Deviation from the linear relation between $\log(k_p/k_1)/P$ and P for the reaction of ethyliodide with triethylamine in benzene at 25°C.

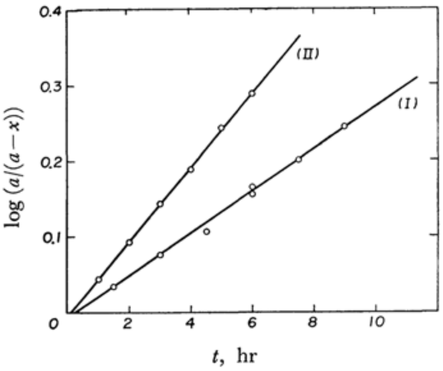

Fig. 4. First order plot for the reaction of ethyliodide with triethylamine under high pressure at 25°C.
Curve 1, at 1200 $(kg\cdot cm^{-2})$;
2, at 1500 $(kg\cdot cm^{-2})$

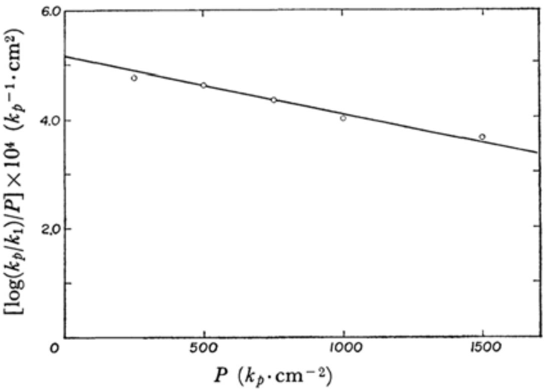

Fig. 5. Plot of $\log(k_p/k_1)/P$ *vs.* P calculated from the data of Hartmann *et al.*[10] for the reaction of methyliodide with pyridine in benzene at 50°C.

The solvent effects on the activation volume would be due to the existence of the second term on the right-hand side of Eq. (8). The values for $\Delta V_0^{\neq}$, K and KV° at 25°C are presented in Table 4.

If the values for $(Z\Delta P)$ are nearly constant throughout the solvents, a linear relation should exist between the activation volume and the value for KV°.

The activation volumes in Table 4 appear to be correlated with the value for KV° rather than with

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[14] C. D. Hodgman "Handbook of Chemistry and Physics," 44th Ed., The Chemical Rubber Publishing Co., Cleveland (1962), pp. 2212—2218.

the compressibility. However, further experimental results are necessary to confirm the above relation.

An Abnormal Acceleration of the Reaction Rate under Pressure. For the runs in acetonitrile, methanol, and nitromethane, the plot of log $(k_p/k_1)/P$ *vs.* P gave a good straight line, as is shown in Fig. 2, but in the case of the benzene and nitrobenzene solvents, a large deviation from linearity, that is, a greater acceleration effect of the pressure than that expected from the power-series treatment, was observed at the pressures of 1200 and 1500 (kg·cm^{-2}) [see Fig. 3].

Recently Pincock and his collaborator[12] found, from a study of the reaction of methyliodide with triethylamine in frozen solutions, that the reaction rates were moderately accelerated by the freezing of the solvent molecules and that the reaction followed first-order kinetics in frozen solutions, in contrast to the second-order kinetics holding in normal (*i. e.*, unfrozen solution) reactions.

It is clear that this reaction in frozen solutions occurs in highly concentrated liquid regions; these regions disappear during a run as soluble reactants are converted to the insoluble product.

The relation between the melting temperature of a substance and the external pressure is described thermodynamically in Eq. (3); under the conditions of $\Delta H_f > 0$ and $(V_l - V_s) > 0$, the melting temperature rises with an increase in the external pressure:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right) = \frac{\Delta H_f}{T(V_l - V_s)} \tag{3}$$

where ΔH_f and $(V_l - V_s)$ are the heat of fusion and the volume change of fusion respectively.

TABLE 5. MELTING POINTS AT HIGH PRESSURE[13]

P, atm	Nitrobenzene	Benzene
1	5.6°C	5.4°C
1000	27.9°C	33.3°C
2000	49.5°C	58.0°C

Judging from the data of Table 5, it may be assumed that moderate portions of solvent molecules were frozen over the ranges of pressure where the abnormal acceleration of reaction rate was observed.

Experimental results at pressures of 1200 and 1500 kg cm^{-2} in a benzene solution follow first-order kinetics, as has been indicated by Pincock *et al.* in frozen benzene solutions[12] (see Fig. 4). Moreover, if this abnormal acceleration occurs on the freezing of solvent molecules, the plot of log $(k_p/k_1)/P$ *vs.* P should give a straight line at temperatures higher than the melting points of solvent molecules under increased external pressure. Experimental results[10] at 50°C, where the solution was not frozen even at 1500 kg·cm^{-2}, gave a good straight line, as is shown in Fig. 5.

From the fact presented above, it may be understood that this acceleration effect is due to the result of the freezing of solutions; the frozen portion in the solution being composed of a pure solvent component, the reaction proceeds exclusively in highly-concentrated liquid regions. This graphical method is very useful for detecting abnormal effects such as those shown above as well as for calculating the $\Delta V_0^{\ne}$ value and the initial compressibility of the activation volume.

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[12] R. E. Pincock and T. E. Kiovsky, *J. Am. Chem. Soc.*, **88**, 51 (1966).

[13] N. R. C. of U. S. A., "The International Critical Tables," Vol. 4, McGraw-Hill, New York (1933), p. 9.