HIGH-PRESSURE STOPPED-FLOW KINETICS OF PROTON-TRANSFER REACTION BETWEEN 4-NITROPHENYLNITROMETHANE AND 1,1',3,3'-TETRAMETHYLGUANIDINE IN APROTIC SOLVENTS

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The proton-transfer reaction between title compounds was kinetically studied in toluene and dichloromethane at 25°C up to 1000bar by the use of a high-pressure stopped-flow method. The volumes of activation were explainable on the basis of Kirkwood's electrostatic model.

Proton-transfer reaction in solution has been extensively studied from the theoretical and phenomenological viewpoints.^{1,2)} It is known that the proton-transfer reaction between 4-nitrophenylnitromethane(4-NPNM) and a base such as amine³⁾ or alkoxide ion,⁴⁾ proceeds in a simple way. And this reaction has attracted much interest since it shows an appreciable tunnelling effect in many solvents.^{1,3)} If we can obtain some informations on the effective mass or volume change accompanied with the reaction, the behavior of the solvent in the vicinity of the reactive site will be made clear. The volume of activation is well known to be a more easily interpretable quantity than the entropy of activation or the energy of activation.⁵⁾ However, technical difficulty has restricted the high-pressure study on a reaction faster than a few seconds. There are only a few works on a high-pressure stopped-flow method.⁶⁾

The present work was carried out to investigate proton-transfer reaction by the use of a high-pressure stopped-flow method^{6b)} up to 1000bar at 25.0±0.5°C. We chose, at first, the 4-NPNM + TMG(1,1',3,3'-tetramethylguanidine) system in toluene and dichloromethane. Although Caldin *et al.*⁷⁾ reported the pressure effect on this system in aromatic hydrocarbon solvents by a laser temperature-jump method, we will give here a little different explanation.

The proton-transfer reaction between 4-NPNM and TMG in aprotic solvents (toluene and dichloromethane) produces a yellow solution due to an ion pair with λ_{max} around 440nm.

$$O_2 NC_6 H_4 CH_2 NO_2 + HN = C (NMe_2)_2 \xrightarrow{k_f} [O_2 NC_6 H_4 CHNO_2] [H_2 N = C (NMe_2)_2]^+ (1)$$

The rate of the proton-transfer reaction, which was followed spectrophotometrically at 440nm, obeys first-order kinetics very well when the base existed in large excess over 4-NPNM. The observed rate constant k_{obs} was determined by

		p/bar					
	solvent	1	250	500	750	1000	
$10^{-3} k_{f}/$	toluene	1.72±0.03	1.94±0.02	2.46±0.02	2.77±0.01	3.30±0.02	
M-1s-1	dichloromethane	4.97±0.04	5.62±0.04	6.68±0.04	7.38±0.06	8.31±0.05	
k _b /s ⁻¹	toluene	5.57±0.20	5.43±0.20	4.72±0.15	4.40±0.10	4.38±0.20	
U	dichloromethane	1.48 ± 0.40	1.13±0.35	0.86±0.50	1.05±0.43	1.21±0.35	

(2)

Table 1. Rate constants, k_f and k_h at 25°C

Guggenheim's plot. A plot of k_{obs} against base concentration(b) gave a straight line at each pressure(Fig. 1), in agreement with equation(2).

 $k_{obs} = k_f b + k_b$

Thus the values of k_f and k_b were determined from the dependence of k_{obs} on b by a leastsquares method. The values of k_f and k_b are given in Table 1.

Then, the volume of activation ΔV^{\ddagger} for either k_{f} or k_{b} was determined by equation(3).

 $RT\left(\frac{\partial lnk}{\partial p}\right)_{T} = -\Delta V^{\ddagger} + RT\Delta n^{\ddagger}\kappa \qquad (3)$

In this equation, κ is the compressibility of the solvent, Δn^{\ddagger} the difference of the number of molecules between the initial state and the transition state, T the absolute temperature, and R the gas constant. In the present reaction, the value of Δn^{\ddagger} is -1 for the forward reaction and zero for the backward one. The term RTK at 25°C was calculated from the literatures^{8,9}) to be 2.3 cm³mol⁻¹ for toluene and 2.4 cm³mol⁻¹ for dichloromethane. The plots of RTInk_f against pressure were almost





linear for both solvents (Fig. 2). In toluene the plot of RT1nk vs. pressure also gave a straight line, but in dichloromethane no systematic pressure-dependence of RT1nk was found. The numerical values of ΔV_f^{\ddagger} and ΔV_b^{\ddagger} are given in Table 2. Caldin *et al.*³⁾ found that there appeared a sharp difference in the degree of tunnelling effect from the less polar solvent (dielectric constant; $\varepsilon < 6$) to the more polar solvent ($\varepsilon > 6$). They interpreted that solvent molecules were coupled with the moving proton in the more polar solvent, and the effective mass became greater than unity (1.17-1.27 a.m.u.), while in the less polar solvent the absence of such a coupling resulted in the effective mass of unity and so the remarkable tunnelling effect.

Value of ΔV_{f}^{\dagger} may be considered as made up of two major contribution, one due to the structural change of activation $\Delta V_{f}^{\dagger}(str)$, and the other due to the solvation term $\Delta V_{f(solv)}^{\dagger}$. Caldin *et al.* emphasized their interpretation by another result⁷

	toluene	<i>o</i> -xylene	dichloromethane	chlorobenzene
$\Delta V_f^{+}/cm^{3}mol^{-1}$	-18.8±1.9 ^a	-16,6±0,4 ^b	-15,3±1.5 ^a	-14.9±1.4 ^b
$\Delta V_{b}^{\frac{1}{4}}/cm^{3}mol^{-1}$	+6.8±1.0 ^a		0 ^a	
$\Delta V^{\circ}/cm^{3}mol^{-1}$	-25.6±2.9 ^a	-23.3 ± 0.3^{b}	-15,3 ^a	-23.8 ± 3.5^{b}
ε (25°C)	2.38	2.57	8.64	5.62
$10^{5} \left(\frac{\partial q}{\partial p}\right)_{T} / bar^{-1}$	1.58 ^c		1.15 ^c	0,87 [°]
	0.71 ^d	0.56 ^d	0.44 ^e	0,38 ^d ,e

Table 2. Volumetric data and physical properties of solvents

^aPresent work. ^bRef. 7. Corrected for the solvent compression. In toluene, ΔV_{f}^{\ddagger} -20.9 cm³mol⁻¹ and ΔV° =-27.8 cm³mol⁻¹. ^cRef. 10. ^dRef. 11. ^eRef. 12.

that volumes of activation in several lowpolarity solvents were all nearly equal to $\Delta V_{f(str)}^{\ddagger}$ and independent of the solvents. However, to our understanding, their interpretation would lead to the result that the volume of activation in the more polar solvent($\varepsilon > 6$) might be more negative because the solvation term $\Delta V_{f(solv)}^{\ddagger}$ must be taken into account which is expected to be negative. As seen in Table 2, such an expectation is not the case. The present result seems to point to an electrostatic model which Caldin *et al*. rule out. A calculation based on the Kirkwood equation gives equations (4a) and (4b).

$$\Delta V_{f}^{\ddagger} = \Delta V_{f(str)}^{\ddagger} - N_{0} \Sigma \frac{\mu^{2}}{a^{3}} \left(\frac{\partial q}{\partial p}\right)_{T} \qquad (4a)$$
$$\Delta V_{f(solv)}^{\ddagger} = -N_{0} \Sigma \frac{\mu^{2}}{a^{3}} \left(\frac{\partial q}{\partial p}\right)_{T} \qquad (4b)$$



Fig. 2. Pressure dependence of k_f.

In equation (4), $q=(\epsilon-1)/(2\epsilon+1)$, μ and *a* are dipole moment and radius, respectively, $\Sigma \mu^2 / a^3$ the difference between the initial state and the transition state, and N₀ Avogadro's number. As the reaction proceeds through a highly polar transition state, the term $\Sigma \mu^2 / a^3$ is expected to be positive. We have corrected the Caldin's values of ΔV_f^{\pm} for solvent compression, and the values of $(\partial q / \partial p)_T$ were cited from more reliable literatures(Table 2). As found in Table 2, the magnitude of $(\partial q / \partial p)_T$ of a solvent considerably differs among literatures but the sequence of its variation from solvent to solvent is alike in spite of different literatures. There exists a rough tendency that ΔV_f^{\pm} becomes more negative with the increase of $(\partial q / \partial p)_T$ in accordance with equation(4a). A plot of ΔV_f^{\pm} against $(\partial q / \partial p)_T$ shows a roughly straight line, and extrapolation to $(\partial q / \partial p)_T \rightarrow 0$ gives $-10 \sim -11$ cm³mol⁻¹ of $\Delta V_f^{\pm}(\text{str})$ which is in agreement with the calculated value⁷ based on collinear approach of C, H, and N atoms until the CH---N hydrogen bonding distance at the transition state.

Much more negative value of $\Delta V^{\circ} (=\Delta V_{f}^{\pm} - \Delta V_{b}^{\pm})$ for toluene than for dichloromethane is also accounted for mainly by the electrostatic model for an ionogenic reaction. The variation of ΔV° is compatible with the variation of ΔS° from toluene(-25±4 cal mol⁻¹K⁻¹) to dichloromethane(-11.4±1.0 cal mol⁻¹K⁻¹).³

The work on the isotope rate ratio $k_{\rm H}^{\prime}/k_{\rm D}$ is going on, and the pressure-effect on the tunnelling factor will reveal how the effective mass changes in response to the enhanced solvating-power with a fixed solvent molecular structure.

The authors are grateful to Mr. F. Amita for maintenance of the high-pressure stopped-flow apparatus. The present work was supported by the Research Grant-in-Aid from the Ministry of Education (No. 454123).

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(Received May 20, 1980)

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