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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 amine[3] 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.

$$O_2NC_6H_4CH_2NO_2 + HN{=}C(NMe_2)_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [O_2NC_6H_4CHNO_2]^-[H_2N{=}C(NMe_2)_2]^+ \qquad (1)$$

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

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

		p/bar				
	solvent	1	250	500	750	1000
$10^{-3}k_f$/ $M^{-1}s^{-1}$	toluene	1.72±0.03	1.94±0.02	2.46±0.02	2.77±0.01	3.30±0.02
	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
	dichloromethane	1.48±0.40	1.13±0.35	0.86±0.50	1.05±0.43	1.21±0.35

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).

$$k_{obs} = k_f b + k_b \qquad (2)$$

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

Then, the volume of activation $\Delta V^{\ddagger}$ for either k_f or k_b was determined by equation(3).

$$RT\left(\frac{\partial \ln k}{\partial p}\right)_T = -\Delta V^{\ddagger} + RT\Delta n^{\ddagger}\kappa \qquad (3)$$

In this equation, κ is the compressibility of the solvent, $\Delta n^{\ddagger}$ 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 $\Delta n^{\ddagger}$ is -1 for the forward reaction and zero for the backward one. The term $RT\kappa$ at 25°C was calculated from the literatures[8,9] to be 2.3 cm^3mol^{-1} for toluene and 2.4 cm^3mol^{-1} for dichloromethane. The plots of $RT\ln k_f$ against pressure were almost linear for both solvents(Fig. 2). In toluene the plot of $RT\ln k_b$ *vs.* pressure also gave a straight line, but in dichloromethane no systematic pressure-dependence of $RT\ln k_b$ was found. The numerical values of $\Delta V_f^{\ddagger}$ and $\Delta V_b^{\ddagger}$ 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.

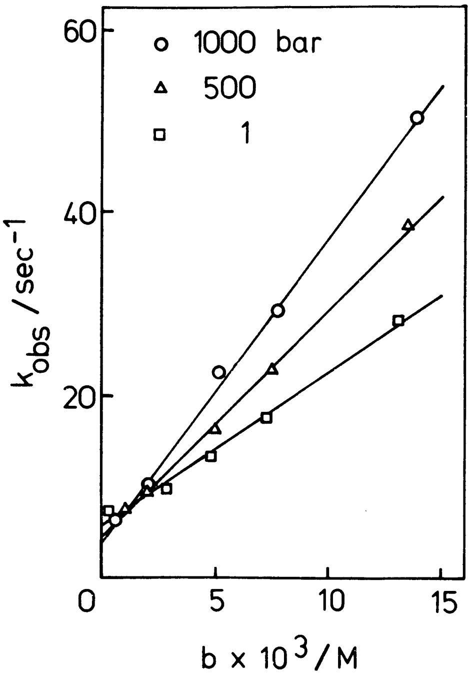

Fig. 1. Dependence of k_{obs} on TMG concentration in toluene at 25°C.

Value of $\Delta V_f^{\ddagger}$ may be considered as made up of two major contribution, one due to the structural change of activation $\Delta V_{f(str)}^{\ddagger}$, and the other due to the solvation term $\Delta V_{f(solv)}^{\ddagger}$. Caldin *et al.* emphasized their interpretation by another result[7]

Table 2. Volumetric data and physical properties of solvents

	toluene	*o*-xylene	dichloromethane	chlorobenzene
$\Delta V^{\ddagger}_{f}/\mathrm{cm^3 mol^{-1}}$	-18.8 ± 1.9^{a}	-16.6 ± 0.4^{b}	-15.3 ± 1.5^{a}	-14.9 ± 1.4^{b}
$\Delta V^{\ddagger}_{b}/\mathrm{cm^3 mol^{-1}}$	$+6.8\pm1.0^{a}$		0^{a}	
$\Delta V^{\circ}/\mathrm{cm^3 mol^{-1}}$	-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
$10^5(\frac{\partial q}{\partial p})_T/\mathrm{bar^{-1}}$	1.58^{c}		1.15^{c}	0.87^{c}
	0.71^{d}	0.56^{d}	0.44^{e}	$0.38^{d,e}$

[a] Present work. [b] Ref. 7. Corrected for the solvent compression. In toluene, $\Delta V^{\ddagger}_{f}=-20.9\ \mathrm{cm^3mol^{-1}}$ and $\Delta V^{\circ}=-27.8\ \mathrm{cm^3mol^{-1}}$. [c] Ref. 10. [d] Ref. 11. [e] Ref. 12.

that volumes of activation in several low-polarity solvents were all nearly equal to $\Delta V^{\ddagger}_{f(str)}$ 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(ε>6) might be more negative because the solvation term $\Delta V^{\ddagger}_{f(solv)}$ 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).

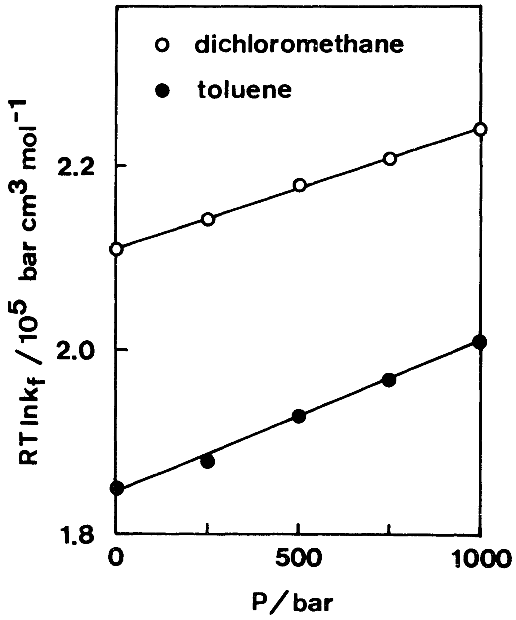

Fig. 2. Pressure dependence of k_f.

$$\Delta V^{\ddagger}_{f} = \Delta V^{\ddagger}_{f(str)} - N_0\Sigma\frac{\mu^2}{a^3}\left(\frac{\partial q}{\partial p}\right)_T \qquad (4a)$$

$$\Delta V^{\ddagger}_{f(solv)} = - N_0\Sigma\frac{\mu^2}{a^3}\left(\frac{\partial q}{\partial p}\right)_T \qquad (4b)$$

In equation (4), $q=(\varepsilon-1)/(2\varepsilon+1)$, 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 N_0 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 $\Delta V^{\ddagger}_{f}$ 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 $\Delta V^{\ddagger}_{f}$ becomes more negative with the increase of $(\partial q/\partial p)_T$ in accordance with equation(4a). A plot of $\Delta V^{\ddagger}_{f}$ against $(\partial q/\partial p)_T$ shows a roughly straight line, and extrapolation to $(\partial q/\partial p)_T \to 0$ gives -10~-11 $\mathrm{cm^3mol^{-1}}$ of $\Delta V^{\ddagger}_{f(str)}$ which is in agreement with the calculated value[7] 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 $\Delta V°(=\Delta V_f^{\ddagger}-\Delta V_b^{\ddagger})$ for toluene than for dichloromethane is also accounted for mainly by the electrostatic model for an ionogenic reaction. The variation of $\Delta V°$ is compatible with the variation of $\Delta S°$ from toluene(-25±4 cal $mol^{-1}K^{-1}$) to dichloromethane(-11.4±1.0 cal $mol^{-1}K^{-1}$).$^{3)}$

The work on the isotope rate ratio k_H/k_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.

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