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Pressure Effect on Rate Constants of Proton-transfer Reactions from 2,4,6-Trinitrotoluene to *N*,*N*,*N′*,*N′*-Tetramethylguanidine and 1,8-Diazabicyclo[5.4.0]undec-7-ene in Acetonitrile and Dichloromethane

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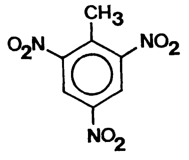
Influence of pressure on the rate constants of the proton-transfer reactions between title compounds was studied in acetonitrile and dichloromethane at 25 °C up to 1000 bar by means of a high-pressure stopped-flow method. In the reaction of 2,4,6-trinitrotoluene (TNT) with *N*,*N*,*N′*,*N′*-tetramethylguanidine, the volume of activation for the forward reaction $\Delta V_f^\ddagger$ is -12.7 ± 1.0 cm^3 mol^{-1} in acetonitrile and -19.0 ± 1.5 cm^3 mol^{-1} in dichloromethane. In the reaction of TNT with 1,8-diazabicyclo[5.4.0]undec-7-ene, $\Delta V_f^\ddagger$ is -9.0 ± 1.0 cm^3 mol^{-1} in acetonitrile and -10.8 ± 1.0 cm^3 mol^{-1} in dichloromethane. These results are discussed in comparison with other proton-transfer reactions.

Proton-transfer reaction in solution has been extensively studied from the theoretical and phenomenological viewpoints.[1–3] Some proton-transfer reactions also have attracted much interest because of occurrence of appreciable tunneling effect.[4] It is known that the proton-transfer reaction between 4-nitrophenylnitromethane (4NPNM) and a base such as amine[4,5] or alkoxide ion,[6] proceeds in a simple way.[7] In the case of the reaction of 2,4,6-trinitrotoluene (TNT) with ethoxide ion in ethanol, two colored compounds are formed.[8] At high concentrations of TNT($\approx10^{-3}$ M; 1 M$=$1 mol dm^{-3}) and ethoxide ion($\approx10^{-1}$ M) a brown species is formed, which is elucidated to be a type of Meisenheimer complex by Bernasconi.[9] On the other hand at low concentrations of TNT($\approx10^{-5}$ M) and ethoxide ion($\approx10^{-3}$ M), 2,4,6-trinitrobenzyl anion (TNT$^-$; $\lambda_{\max}=514$ nm) is mainly produced by a proton abstraction from the methyl group of TNT.[8,10] Since the reaction with a nonionic base is expected to shift in favor of the proton-transferred state compared with the case of an ionic base, Pruszynski *et al.*[11] have studied the reaction between TNT and *N*,*N*,*N′*,*N′*-tetramethylguanidine (TMG) in aprotic solvents, namely acetonitrile and benzonitrile. The reaction in both solvents produces a purple solution due to ion-pair which has the absorption maxima similar to those observed for the reaction of TNT with ethoxide ion in ethanol. Further, they have investigated this reaction in DMF solvent and discussed the relation between kinetic isotope effects and steric effects of solvent.[12]

If we can obtain some informations on the effective mass or volume change accompanied with the proton-transfer 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 or the energy of activation.[13] There are several works of high-pressure effects on the slow proton-transfer reactions.[14] However, as technical difficulty has restricted the high-pressure investigation on a reaction faster than several seconds, there are only a few reports on high-pressure effects on the fast proton-transfer reactions.[15,16] We reported previously[16] that the proton/deuteron-transfer reactions of 4NPNM+TMG in toluene and dichloromethane were accelerated at high pressure and the kinetic isotope rate ratio reduced from 11.9 at 1 bar to 9.3 at 1000 bar in toluene while it almost unchanged in dichloromethane(10.7±0.2).

In this paper we investigate the proton-transfer reactions between TNT(AH) and TMG(B) in acetonitrile and dichloromethane solvents by means of a high-pressure stopped-flow method up to 1000 bar at 25 °C. The reaction between TNT and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in both solvents is also studied. Such a base was chosen for the reasons that (a) the base nitrogen atom was not protonated in the free base,[7] (b) it was a strong base favorable to proton-transfer reaction, and (c) it was a cyclic amidine suitable for the study of the steric effect.

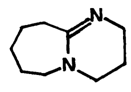
$$\mathrm{AH} + \mathrm{B} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [\mathrm{A}]^-[\mathrm{BH}]^+_{\text{ion pair}} \qquad (1)$$



TNT

$\mathrm{HN{=}C(NMe_2)_2}$

TMG



DBU

Experimental

Materials. 2,4,6-Trinitrotoluene (TNT) was purified by repeated crystallization from ethanol with charcoal; mp 81 °C. The purity of TNT was examined by NMR spectrum (methyl protons $\delta=2.75$, benzene ring protons $\delta=8.92$ in the ratio 3:2). *N*,*N*,*N′*,*N′*-Tetramethylguanidine (TMG, Nakarai Chemicals Co. Ltd.) was dried with potassium hydroxide and then distilled under a nitrogen atmosphere; bp 161 °C (lit, 161 °C). 1,8-Diazabicyclo[5.4.0]undec-7-ene(DBU, Nakarai Chemicals Co. Ltd., spectrograde reagent) was dried with potassium hydroxide and then distilled under reduced pressure. The pure DBU was identified by NMR spectrum. Acetonitrile was purified by the method of O'Donell[17] and then distilled over phosphorus pentaoxide; bp 82 °C. Dichloromethane was dried with calcium hydride and then distilled; bp 39.5—40 °C.

Apparatus and Procedure. Absorption spectra were determined by a Shimadzu UV-200S spectrophotometer. Kinetic measurements at 1 bar (1 bar$=10^5$ Pa) were carried out by a Union Giken RA-401 stopped-flow apparatus. In all measurements at 1 bar, the temperature was kept at 25.0±0.1 °C by circulating thermostated water. At

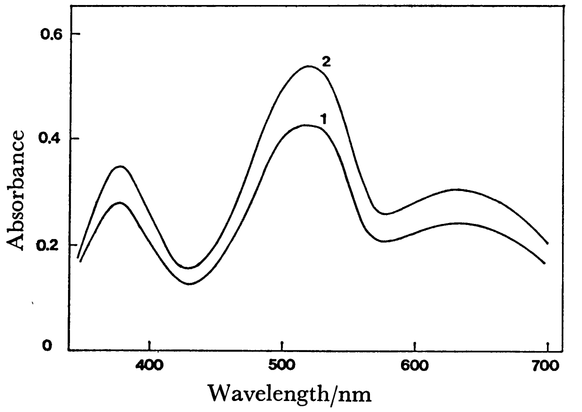


Fig. 1. Visible spectra of the product of the TNT+TMG reaction (1) and of the TNT+DBU reaction (2) in acetonitrile.

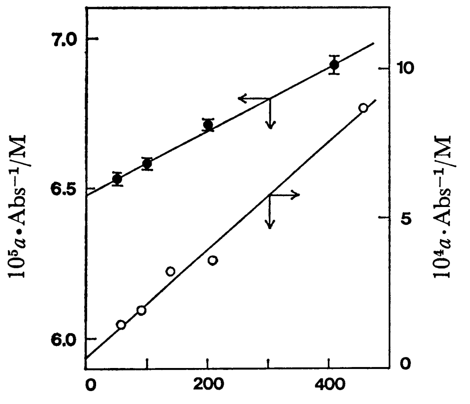


Fig. 2. Plots of a/Abs against reciprocal of DBU concentration in acetonitrile (open circles) and dichloromethane (closed circles) at 25 °C.

high pressure the reaction was followed by means of a high-pressure stopped-flow apparatus; the details were described elsewhere.[18)] In high-pressure measurements the temperature was kept at 25.0±0.5 °C by circulating thermostated fluid around the high-pressure vessels.

The following weighed-in concentrations of solutions at 1 bar were freshly prepared every day before use: TNT 0.02—0.03 mM, TMG 2—10 mM in acetonitrile and TNT 0.1—0.3 mM, TMG 5—100 mM in dichloromethane; TNT 0.02—0.06 mM, DBU 2—13 mM in acetonitrile and TNT 0.04—0.08 mM, DBU 3—18 mM in dichloromethane.

The rate of the proton-transfer reactions of TNT with TMG and DBU was determined by monitoring the change of the absorption with time at 520 nm in acetonitrile and at 530 nm in dichloromethane. The increase of the absorbance obeyed first-order kinetics when the base (TMG, DBU) existed in large excess over TNT. The observed rate constant k_{obsd} was determined by the least-squares fitting to the Guggenheim plot.

Results

The reactions of TNT with TMG and DBU within the range of present experimental concentrations give the purple anion. The possibility of reactions other than the proton-transfer was ruled out with reference to the careful examinations of Pruszynski *et al.*[11)] and Jarczewski *et al.*[12)] The absorption maxima for the ion-pair produced by a proton-transfer from the methyl group of TNT to TMG are around 375, 530, 635 nm in dichloromethane and identical to those observed in acetonitrile (378, 520, 635 nm). The reaction mixtures between TNT and DBU show the absorption maxima at around 375, 530, 635 nm in dichloromethane and 378, 520, 635 nm in acetonitrile; they are very similar to those observed in the reaction between TNT and TMG (Fig. 1), while each reactant is transparent in the visible region.

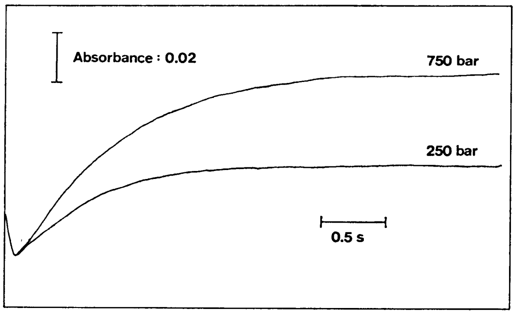


Fig. 3. Typical stopped-flow traces of the TNT+DBU reaction in dichloromethane at 25 °C. The absorbance change was monitored at 530 nm: [TNT]=3.4×10^{-5} M, [DBU]=2.40×10^{-3} M at 1 bar.

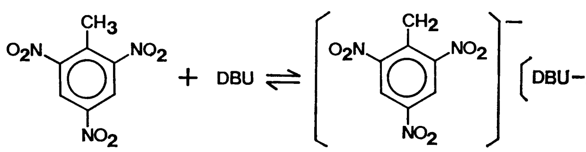
The equilibrium constant of the TNT+DBU reaction was determined at 25 °C and 1 bar according to the Benesi-Hildebrand equation (2).[19)] In this equation,

$$\frac{[\mathrm{a}]}{\mathrm{Abs}}=\frac{1}{K\varepsilon}\frac{1}{[\mathrm{b}]}+\frac{1}{\varepsilon} \tag{2}$$

[a] is the initial concentration of TNT, [b] that of the base, K the equilibrium constant, ε the molar absorption coefficient, Abs the absorbance at 520 nm in acetonitrile and 530 nm in dichloromethane at the equilibration. The fact that the plot of Eq. 2 gives a very good straight line as shown in Fig. 2 supports that the product is not separate ions but a contact one, namely ion-pair. Otherwise the plot would be significantly curved and the following would be valid:

$$\frac{[\mathrm{a}]}{\mathrm{Abs}}=\frac{1}{K\varepsilon^2}\frac{\mathrm{Abs}}{[\mathrm{b}]}+\frac{1}{\varepsilon}. \tag{3}$$

Therefore, it is concluded that the reaction path between TNT and DBU is simple and the same as that between TNT and TMG as described below.



(4)

In Fig. 3 are shown some representative traces of the increase of absorption with time. The stopped-flow trace at each pressure obeyed a first-order kinetic equation. The plot of k_{obsd} against TMG or DBU concentration [b] is of a straight line at each pressure (Figs. 4 and 5), in agreement with Eq. 5.

$$k_{\mathrm{obsd}}=k_{\mathrm{f}}[\mathrm{b}]+k_{\mathrm{b}} \tag{5}$$

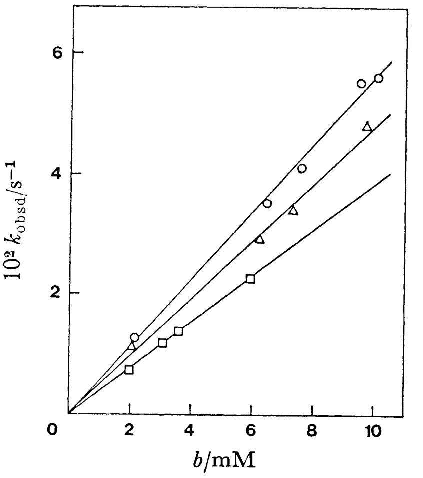


Fig. 4. Dependence of k_{obsd} on TMG concentration in acetonitrile at 25 °C.
□: 1 bar, △: 500 bar, ○: 1000 bar.

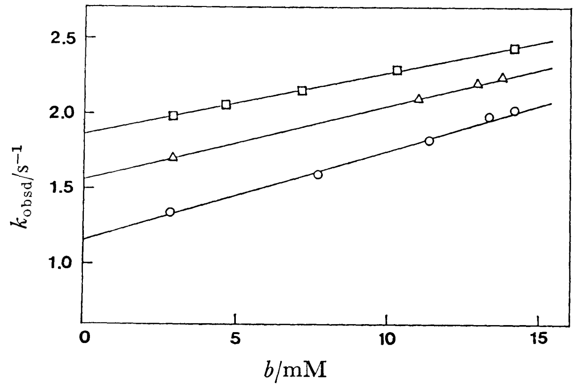


Fig. 5. Dependence of k_{obsd} on DBU concentration in dichloromethane at 25 °C.
□: 1 bar, △: 500 bar, ○: 1000 bar.

In the equation, k_f and k_b are the forward and backward rate constants of the proton-transfer reactions. Since molar concentration unit is convenient to compare the rate constants at various conditions, we corrected the weighed-in concentration at 1 bar for the compression of each solvent to know [b] of molar unit at high pressure. In the plots of Figs. 4 and 5, compression was taken into account on the basis of data of Srinivasan *et al.*[20] for acetonitrile and of Newitt *et al.*[21] for dichloromethane. Thus the values of k_f and k_b were determined from the dependence of k_{obsd} on TMG and DBU concentration by a least-squares method. The values of k_f are given in Table 1. The values of k_b in dichloromethane are given in Table 2, but in acetonitrile they are too small to be reliable and are not recorded. The equilibrium constants K are also evaluated and listed in Table 2.

Table 1. Rate constants k_f ($\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) at 25 °C

p/bar	(1)[a] AN[c]	(1)[a] DCM[d]	(2)[b] AN[c]	(2)[b] DCM[d]
1	3.84±0.05	3.13±0.07	204±4	41.8±0.8
250	4.17±0.08	3.71±0.10	220±4	46.9±1.0
500	4.73±0.09	4.58±0.10	230±4	49.2±0.8
750	5.34±0.10	5.19±0.12	238±5	52.4±1.2
1000	5.61±0.14	6.12±0.14	267±6	60.3±1.0

a) k_f of the TNT+TMG reaction. b) k_f of the TNT+DBU reaction. c) Acetonitrile solvent. d) Dichloromethane solvent.

Table 2. Rate constants k_b and equilibrium constants K in dichloromethane at 25 °C

p/bar	k_b/s^{-1} (1)[b]	k_b/s^{-1} (2)[c]	K[a] $(=k_f/k_b)/\mathrm{M}^{-1}$ (1)[b]	K[a] $(=k_f/k_b)/\mathrm{M}^{-1}$ (2)[c]
1	1.53±0.03	1.87±0.03	2.05 (2.0±0.6)[d]	22.4 (24±5)[d]
250	1.31±0.04	1.73±0.04	2.83	27.1
500	1.18±0.03	1.57±0.03	3.88	31.3
750	0.97±0.03	1.39±0.04	5.35	37.7
1000	0.76±0.03	1.15±0.03	8.05	52.4

a) K in acetonitrile at 1 bar and 25 °C is 4100 in the TNT+TMG reaction from Ref. 11 and 6070 in the TNT+DBU reaction from our result. b) The TNT+TMG reaction. c) The TNT+DBU reaction. d) From equilibrium measurement.

The volume of activation ΔV^* for either k_f or k_b was determined by

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = -\frac{\Delta V^*}{RT} + \Delta n^* \kappa, \qquad (6)$$

where, κ is the compressibility of the solvent, Δn^* the difference of the number of molecules from the initial to the transition state, T the absolute temperature, and R the gas constant. In the present reaction, the value of Δn^* is -1 for the forward reaction and zero for the backward one. The value of κ at 25 °C were calculated from the literatures.[20,21] The plots of $\ln k_f$ against pressure were almost linear for both systems and both solvents (Figs. 6 and 7). The values of ΔV_f^* are given in Table 3 together with ΔV_b^*.

Discussion

Equilibrium and Rate Constants at Atmospheric Pressure. In the reaction between TNT and ethoxide ion, Buncel *et al.*[10] found that when first-order rate constants k_{obsd} were plotted against ethoxide ion concentration it was slightly curved. The analysis of these results led them to the conclusion that the brown species other than TNT^- was formed. However, in the reaction between TNT and TMG, Pruszynski *et al.*[11] obtained a linear relation obeying Eq. 5 in both acetonitrile and benzonitrile. In our experiments also, the plots of k_{obsd} against TMG and DBU concentration [b] gave a straight line in acetonitrile and dichloromethane. The equilibrium constants obtained by rate constant ratio $K(=k_f/k_b)$ are well in accord with the direct determination after equilibration by Eq. 2 (Table 2), which strengthens the reliability of the determined rate constants.

The rate constant k_f of TNT+TMG reaction at 25 °C and 1 bar is 3.84±0.05 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ in acetonitrile, which is almost equal to Pruszynski's value (k_f=4.04±0.12 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$), and 3.13±0.07 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ in dichlo-

TABLE 3. VOLUMETRIC DATA AT 25 °C AND 1 bar

	(1)$^{a)}$		(2)$^{b)}$	
	AN$^{c)}$	DCM$^{d)}$	AN$^{c)}$	DCM$^{d)}$
$\Delta V_f^{\neq}$/cm^3 mol^{-1}	-12.7 ± 1.0	-19.0 ± 1.5	-9.0 ± 1.0	-10.8 ± 1.0
$\Delta V_b^{\neq}$/cm^3 mol^{-1}	—	$+17.1\pm1.7$	—	$+11.9\pm1.2$
ΔV°/cm^3 mol^{-1} $^{e)}$	—	-36.1 ± 3.2	—	-22.7 ± 2.2

a) The TNT+TMG reaction. b) The TNT+DBU reaction. c) Acetonitrile solvent. d) Dichloromethane solvent. e) $\Delta V^{\circ}=\Delta V_f^{\neq}-\Delta V_b^{\neq}$.

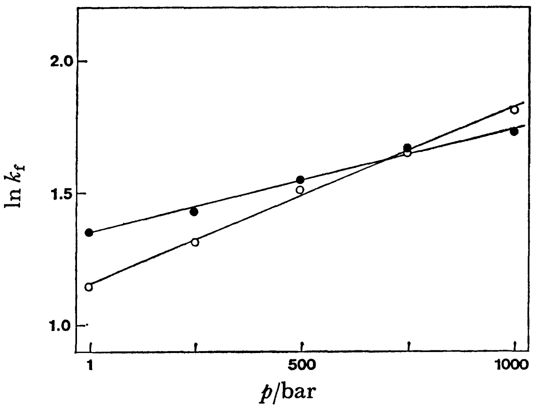


Fig. 6. Pressure dependence of ln k_f of the TNT+TMG reaction in acetonitrile (closed circles) and dichloromethane (open circles).

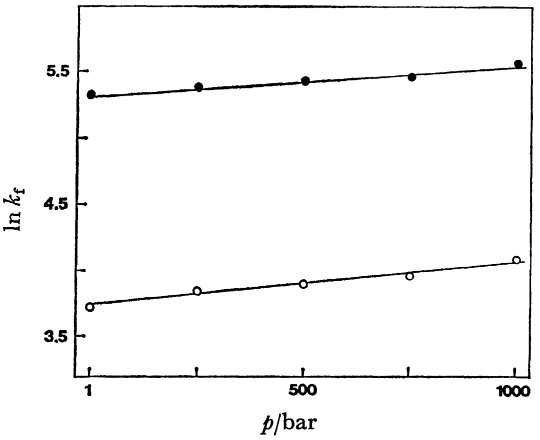


Fig. 7. Pressure dependence of ln k_f of the TNT+DBU reaction in acetonitrile (closed circles) and dichloromethane (open circles).

romethane. In the reaction between TNT and DBU, the value of k_f is 204±4 M^{-1} s^{-1} in acetonitrile and 41.8±0.8 M^{-1} s^{-1} in dichloromethane. In both reactions, the rate constants of the forward reaction in acetonitrile (dielectric constant; $\varepsilon=36$) are larger than those in dichloromethane ($\varepsilon=8.9$). These kinetic behaviors are in accord with the view that each reaction involves the formation of a polar transition state since the polar transition state is, in general, more stabilized in the higher polarity of solvent. Further, the kinetic results for TNT may be compared with those reported for the corresponding reaction of 4NPNM with TMG and DBU.[4,22] The forward rate constant k_f of the reaction of 4NPNM at 25 °C in toluene is larger for DBU ($k_f=2.7\times10^5$ M^{-1} s^{-1}) than for TMG ($k_f=2.29\times10^3$ M^{-1} s^{-1}) by a factor of about 120. While in our results k_f of the reaction of TNT is larger for DBU than for TMG by a factor of about 55 in acetonitrile and 15 in dichloromethane. Thus the explanation on the difference in solvent sensitivity between TMG and DBU is, even qualitatively controversial at present, but it is clear that 4NPNM releases the α-proton more easily than TNT irrespective of solvent or base.

Judging from the results of the reaction with 4NPNM,[22] DBU is a much stronger base: the equilibrium constant K at 25 °C is about 100 times larger than for *N,N*-diethylpentanamidine and about 70 times larger than for *N,N*-diethyldecanamidine. As found in Table 2, K between TNT and DBU is larger than between TNT and TMG: DBU is a much stronger base than TMG especially in less polar solvent. Between TNT and DBU, K at 25 °C and 1 bar is 6070±600 M^{-1} in acetonitrile and 24±5 M^{-1} in dichloromethane (from kinetic measurements, $K=k_f/k_b$ is 5200±400 and 22±4 M^{-1}, respectively). Therefore, the stability of the ion-pair in acetonitrile is higher than that in dichloromethane.

Pressure Effects on Reaction Rates. The volume of activation $\Delta V^{\neq}$ of chemical reactions in solution are recognized to give very important information about the reaction mechanism and the role of the solvent during activation.[23] $\Delta V^{\neq}$ mainly consists of two major contributions, one due to the structural change of activation ($\Delta V_{str}^{\neq}$), and the other due to the solvation change ($\Delta V_{solv}^{\neq}$) on going from the initial to the transition state.[24] In the case of the bond-forming process, $\Delta V_{str}^{\neq}$ would be negative. When electronic charge is generated during activation, $\Delta V_{solv}^{\neq}$ will also be negative. The proton-transfer reaction from TNT to TMG and DBU conforms to the above case; in fact, our data result is the negative values of the volume of activation. The volume of activation of the forward reaction $\Delta V_f^{\neq}$ of TNT+TMG reaction is -12.7 ± 1.0 cm^3 mol^{-1} in acetonitrile and -19.0 ± 1.0 cm^3 mol^{-1} in dichloromethane, and then $\Delta V_f^{\neq}$ of TNT+DBU reaction is -9.0 ± 1.0, -10.8 ± 1.0 cm^3 mol^{-1}, respectively. Absolute value of $\Delta V_f^{\neq}$ for TNT+TMG reaction in dichloromethane is a little larger than that of 4NPNM+TMG reaction (-15.3 ± 1.5 cm^3 mol^{-1})[16a] and that of 4NPNM+TMG-d_2 (-14.6 ± 1.7 cm^3 mol^{-1}).[16b]

On the basis of Kirkwood's theory,[25] Eqs. 7 and 8 hold for k and $\Delta V^{\neq}$, respectively;

$$\ln k = \ln k_0 + (N_0\Sigma\mu^2/a^3)q, \tag{7}$$

$$\Delta V^{\neq} = \Delta V_0^{\neq} - (N_0\Sigma\mu^2/a^3)(\partial q/\partial p)_T, \tag{8}$$

where $q=(\varepsilon-1)/(2\varepsilon+1)$, μ and a are dipole moment and radius, respectively, $\sum\mu^2/a^3$ the difference between the initial state and the transition state, and N_0 Avogadro's number. Since the reaction studied here proceeds through a highly polar transition state, the term $\sum\mu^2/a^3$ is expected to be positive. In many cases, though not generally, the larger the q value (the higher dielectric constant) the smaller the $(\partial q/\partial p)_T$ term. Thus, our results that the forward reaction proceeds faster and $\Delta V_f^\ddagger$ is less negative in the more polar solvent will be qualitatively explained by the above electrostatic solvation-model of an ionogenic reaction: similar tendency is found in many Menschutkin reactions.[26] Hence it is likely that even in the solvent of low polarity such as dichloromethane solvation in the proximity of reaction center, more or less, takes places.

Absolute values of $\Delta V_f^\ddagger$ for DBU are larger than those for TMG in both solvents. This may be attributed to the steric effect of DBU, that is, the nonplanar seven-membered ring of DBU will prevent solvation in the vicinity of reaction center. $\Delta V_f^\ddagger$ values in dichloromethane are considerably less negative compared with the volume change of reaction $\Delta V^\circ(=\Delta V_f^\ddagger-\Delta V_r^\ddagger)$ (Table 3). The transition state is therefore not as highly ionic as the ion-pair.

Further studies of the rate and its kinetic isotope effect in many solvents and other systems at high pressure will reveal the behavior of the solvent in the vicinity of reaction site.

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