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Kinetic Study of Proton Tunneling in the Reaction between 2,4,6-Trinitrotoluene and 1,8-Diazabicyclo[5.4.0]-undec-7-ene in Benzonitrile

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The proton tunneling has been examined for the reaction between 2,4,6-trinitrotoluene and 1,8-diazabicyclo[5.4.0]undec-7-ene in benzonitrile in view of the solvent effect on the rate ratio k^H/k^D as well as on the various activation parameters. The reaction rate ratio k^H/k^D diminishes from 18.3 at 15 °C to 14.5 at 35 °C. The difference in the activation energies $E_a^D - E_a^H$ is 8.8 kJ mol^{-1} and the ratio of Arrhenius preexponential factors is 2.5. All these values are greater than the semiclassical limits of the primary kinetic isotope effects. According to Bell's equation the remarkable isotope effect is due to considerable contribution from tunneling in benzonitrile. The present results, being compared with those in other aprotic solvents, are discussed in relation with the effects of solvent polarity, specific acid-solvent interaction, and geometrical bulkiness in the vicinity of the reaction site.

Recently the primary kinetic isotope effect of the proton-transfer reaction in solution has been studied in detail from theoretical and phenomenological viewpoints.[1,2] The semiclassical theory of kinetic isotope effects, especially as applied to hydrogen and proton transfers, is well developed.[3–8] One of the recent topics is the quantum-mechanical tunneling phenomenon associated with a proton-transfer reaction.[9] The enormously large value of the kinetic isotope rate ratio has been almost explained on the basis of a tunneling contribution.[10–12]

In particular, the following proton/deuteron-transfers have attracted much interest because the experimental results of kinetic parameters and isotope effects are explained evidently by taking account of the appreciable tunneling effect; the reactions of (4-nitrophenyl)nitromethane (4NPNM) with tetramethylguanidine (TMG),[13–16] and pentamethylguanidine (PMG),[17] and the reactions of 2,4,6-trinitrotoluene (TNT) with TMG,[18–20] and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[21]

In the results of the reaction between 4NPNM and TMG[13] there appeared a sharp difference in the degree of kinetic isotope rate ratio k^H/k^D between the polar and nonpolar solvents: The larger was the dielectric constant, the smaller was the rate ratio. However, in the reaction of TNT with TMG,[18] a reverse tendency was found that k^H/k^D was 20.4 in acetonitrile (dielectric constant, $\varepsilon = 36$) and 13.7 in benzonitrile ($\varepsilon = 25.2$). It seems likely that a solvent character other than polarity also affects the degree of tunneling.

We reported previously proton tunneling of the reaction between TNT and DBU in acetonitrile (MeCN) and 1,2-dichloroethane (DCE).[21] In this paper we deal with the kinetics of the proton/deuteron-transfer reactions of the same system in benzonitrile (PhCN) for the purpose of investigating the steric effect of the medium. Benzonitrile is chosen as solvent because it is more bulky and less polar molecule than acetonitrile and so it might allow a greater contribution from tunneling.

Experimental

Materials. 2,4,6-Trinitrotoluene (TNT), 2,4,6-trinitrotoluene-α,α,α-d_3 (TNT-d_3), and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) were treated as described previously.[21] Benzonitrile (PhCN) was purified by the molecular sieves (type 5A), dried with phosphorus pentaoxide, then distilled several times. This treatment was repeated at frequent intervals.

Apparatus and Procedures. Absorption spectra were determined with a Shimadzu UV-200S spectrophotometer. Kinetic measurements were carried out with a Union Giken RA-401 stopped-flow apparatus. In all measurements the temperature was regulated within ±0.1 °C by circulating thermostated water. Solutions were freshly prepared before use and the following concentration of solutions were used: TNT, TNT-d_3, 0.02—0.08 mM; DBU, 1.3—14 mM. The apparent reaction rate was determined according to the same procedure as before.[21]

Results and Discussion

The reaction of TNT-d_3, as well as TNT, with DBU in PhCN gives a purple solution due to an ion pair. The absorption maxima of the product as a result of proton/deuteron-transfer from the methyl group of TNT to DBU are around 380, 535, and 645 nm in PhCN, and almost identical with those observed in other solvents.[21] The equilibrium constants K^H, K^D of the TNT, TNT-d_3+DBU reactions in PhCN were determined at 25 °C according to the Benesi-Hildebrand equation[22] (Fig. 1).

$$[\mathrm{AH}]/a = 1/K\varepsilon[\mathrm{B}] + 1/\varepsilon. \qquad (1)$$

In this equation, [AH] is the initial concentration of TNT, [B] that of DBU, K the equilibrium constant, ε the molar absorption coefficient, and a the absorbance at 535 nm after equilibration. In kinetic measurement the stopped-flow trace fitted a first-order kinetic equation very well at each temperature when DBU existed in large excess over TNT or TNT-d_3. The plots of the observed first-order rate constant k_{obsd} against DBU concentration [B] are linear in agreement with Eqs. 2 and 3 (Figs. 2 and 3).

$$k_{\mathrm{obsd}} = k_{\mathrm{f}}^{\mathrm{H}}[\mathrm{B}] + k_{\mathrm{b}}^{\mathrm{H}}, \tag{2}$$

$$k_{\mathrm{obsd}} = k_{\mathrm{f}}^{\mathrm{D}}[\mathrm{B}] + k_{\mathrm{b}}^{\mathrm{D}}. \tag{3}$$

In these equations, $k_{\mathrm{f}}^{\mathrm{H}}$, $k_{\mathrm{f}}^{\mathrm{D}}$, $k_{\mathrm{b}}^{\mathrm{H}}$, and $k_{\mathrm{b}}^{\mathrm{D}}$ denote the forward and backward rate constants of the proton- and deuteron-transfer reactions. The values of $k_{\mathrm{f}}^{\mathrm{H}}$, $k_{\mathrm{f}}^{\mathrm{D}}$, and $k_{\mathrm{f}}^{\mathrm{H}}/k_{\mathrm{f}}^{\mathrm{D}}$ at each temperature are given in Table 1 together with those of K^{H} and K^{D} determined by equilibrium measurements at 25 °C. However, the values $k_{\mathrm{b}}^{\mathrm{H}}$ and $k_{\mathrm{b}}^{\mathrm{D}}$ are too small to be reliable and are not recorded. From the temperature dependence of the second-order rate constants ($k_{\mathrm{f}}^{\mathrm{H}}$ and $k_{\mathrm{f}}^{\mathrm{D}}$), the activation parameters E_{a}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$, and Arrhenius preexponential factors (A factors) were computed by a least-squares method (Table 2).

The result in Table 1 that K^{H} increases with solvent polarity suggests qualitatively that the ion pair is mainly stabilized by electrostatic interaction with the surrounding solvent molecules. On the other hand, increase of the activation energy $E_{\mathrm{a}}^{\mathrm{H}}$ as well as the rate constant $k_{\mathrm{f}}^{\mathrm{H}}$ is out of accord with increasing solvent polarity. $E_{\mathrm{a}}^{\mathrm{H}}$ in PhCN is greater than those observed in MeCN and DCE by 8.0 and 18.4 kJ mol^{-1}, respectively, although solvent polarity increases in the order MeCN>PhCN>DCE. Contrary to ordinary cases, increasing solvent polarity tends to decrease $k_{\mathrm{f}}^{\mathrm{H}}$. These apparent differences in activation energy and rate constant between solvents originate from tunneling effect as described later.

The largely negative entropies of activation $\Delta S^{\neq}$

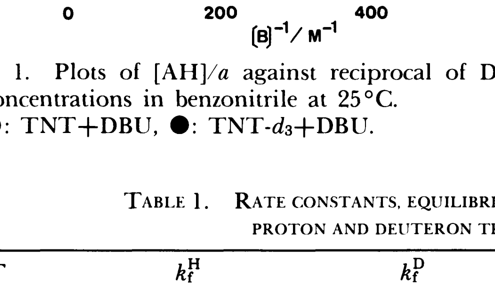

Fig. 1. Plots of [AH]/a against reciprocal of DBU concentrations in benzonitrile at 25 °C.
○: TNT+DBU, ●: TNT-d_3+DBU.

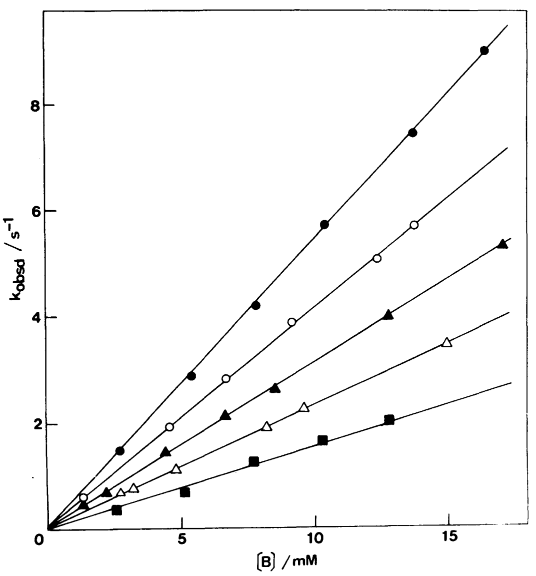

Fig. 2. Dependence of k_{obsd} on DBU concentration of the TNT+DBU reaction in benzonitrile.
●: 35 °C, ○: 30 °C, ▲: 25 °C, △: 20 °C, ■: 15 °C.

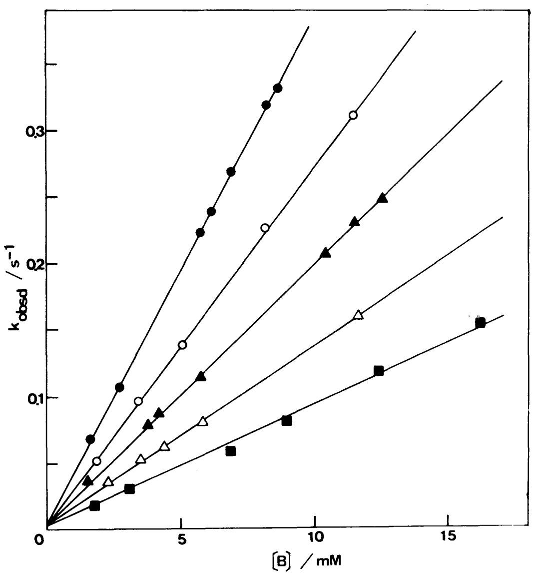

Fig. 3. Dependence of k_{obsd} on DBU concentration of the TNT-d_3+DBU reaction in benzonitrile.
●: 35 °C, ○: 30 °C, ▲: 25 °C, △: 20 °C, ■: 15 °C.

Table 1. Rate constants, equilibrium constants, and kinetic isotope rate ratios of the proton and deuteron transfer reactions in benzonitrile (ε=25.2)[a]

T / °C	$k_{\mathrm{f}}^{\mathrm{H}}$ / M^{-1} s^{-1}	$k_{\mathrm{f}}^{\mathrm{D}}$ / M^{-1} s^{-1}	$k_{\mathrm{f}}^{\mathrm{H}}/k_{\mathrm{f}}^{\mathrm{D}}$	K^{H} / M^{-1}	K^{D} / M^{-1}
35	554±10	38.3±0.8	14.5±0.5		
30	410±8	27.4±0.5	15.0±0.6		
25	310±6	19.5±0.4	15.9±0.6	5700±400	5500±350
	(204±4)[b]		(19.1±0.6)[b]	(6070±700)[b]	
	(565±10)[c]		(29.9±0.9)[c]	(1230±150)[c]	
20	233±5	13.5±0.3	17.3±0.8		
15	174±5	9.5±0.2	18.3±0.8		

a) Dielectric constant (ε) is 36.0 for acetonitrile and 10.4 for 1,2-dichloroethane. b) In acetonitrile (Ref. 21). c) In 1,2-dichloroethane (Ref. 21).

TABLE 2. ACTIVATION PARAMETERS OF THE PROTON AND DEUTERON TRANSFER REACTIONS IN BENZONITRILE AT 25 °C

	H^+-Transfer	D^+-Transfer
E_a/kJ mol^{-1}	42.7±0.8 (34.7±0.8)$^{a)}$ (24.3±0.7)$^{b)}$	51.5±0.8
$\Delta H^{\ddagger}$/kJ mol^{-1}	40.2±0.8	49.0±0.8
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	−62.8±2.5 (−92.9±2.9)$^{a)}$ (−119.7±3.8)$^{b)}$	−55.2±2.9
$\Delta G^{\ddagger}$/kJ mol^{-1}	58.6±1.7	65.7±1.7
log A	9.9±0.1	10.3±0.1
$E_a^D - E_a^H$/kJ mol^{-1}	8.8±1.6	
A^D/A^H	2.5±1.5	

a) In acetonitrile (Ref. 21). b) In 1,2-dichloroethane (Ref. 21).

TABLE 3. TUNNELING PARAMETERS FOR THE TNF+DBU REACTION IN VARIOUS SOLVENTS$^{a)}$

	$CH_3CN^{b)}$	C_6H_5CN	$C_2H_4Cl_2{}^{b)}$
E^H/kJ mol^{-1}	38.9±0.2	43.9±0.2	43.1±0.2
E^D/kJ mol^{-1}	44.8±0.2	49.8±0.2	49.0±0.2
$2b$/A	0.962±0.002	1.148±0.002	0.880±0.002
$2E^H/b^2$	20.1	15.9	26.6
E_a^H/E^H	0.89	0.97	0.56
ν^H/cm^{-1}	970	866	1116
Q^H (25 °C)	3.19±0.06	2.37±0.02	5.95±0.20
Q^D (25 °C)	1.79±0.03	1.56±0.02	2.23±0.10
$(k^H/k^D)_{calcd}$ (25 °C)	18.8±0.3	16.1±0.3	28.6±0.8
$(k^H/k^D)_{Arrh}$ (25 °C)	19.1±0.5	16.1±0.4	29.2±0.8

a) E_a: Activation energy; E: height of the barrier; $2b$: width of the barrier at base; ν: wave number along the reaction path; Q: tunneling factor. b) Ref. 21.

indicate that the transition state is solvated more strongly than the initial one. For the TNT+DBU reaction, $-\Delta S^{\ddagger}$ (H) in PhCN is smaller by about 30 J K^{-1} mol^{-1} in comparison with that in MeCN. Such a tendency, which is also found in the 4NPNM+TMG[13] and TNT+TMG reactions,[18] will suggest that the initial state in PhCN is more strongly solvated than that in MeCN. The stronger solvation in PhCN seems to be a result of the interaction of π electrons of PhCN with TNT rings.[18]

Tunneling in a proton/deuteron-transfer reaction is revealed by the following characteristic features;[1,2,9] a kinetic isotope rate ratio $k^H/k^D > 11$ at 25 °C, an activation energy difference $E_a^D - E_a^H > 5.8$ kJ mol^{-1}, and a ratio of the Arrhenius preexponential factors $A^D/A^H > 1.4$. As found in Tables 1 and 2, the present results conform to the above mentioned features of tunneling. We have evaluated quantitatively the tunneling correction factor Q to manifest tunneling contribution according to the procedure described previously.[21] The tunneling factor Q is, in general, defined as the ratio of the actual rate constant k to the semiclassical rate constant k_s:

$$Q = k/k_s. \tag{4}$$

Assuming that the preexponential factor A is the same for H and D in the absence of tunneling, we obtain Eq 5:

$$Q^H/Q^D = (k^H/k^D)\exp[-(E^D - E^H)/RT]. \tag{5}$$

Further, Q is expressed by assuming a symmetrical parabolic potential barrier:

$$Q = 0.5u/\sin(0.5u) - \sum_{n=1}^{\infty}(-1)^n \exp[(u-2n\pi)\alpha/u]/[(u-2n\pi)/u], \tag{6}$$

where $\alpha = E/kT$, $u = h\nu/kT$, and $\nu = (E/2m)^{1/2}/\pi b$; k is Boltzmann's constant, h Planck's constant, E the height of barrier, b the half width of the barrier at the base, m the mass of the particle transferred, and ν the frequency of oscillation of a particle in parabolic potential. We calculated Q^H and Q^D under the same conditions described previously.[21] The values of E^H, E^D, and $2b$ were adjusted in Eqs. 5 and 6 by trial and error until the calculated rate ratios $(k^H/k^D)_{calcd}$ reproduced the experimental ones of $(k^H/k^D)_{Arrh}$ taken from the Arrhenius plots over the whole range of experimental temperature. These calculations fix the values of E^H and E^D within ±0.2 kJ mol^{-1} and those of $2b$ within ±0.002 A. The results in PhCN are given in Table 3 together with those in MeCN and DCE.[21] As seen in Table 3, Q^H at 25 °C in all these solvents is larger than unity, that is, the reaction is subjected to tunneling.

Tunneling factor Q is closely related with the curvature at the top of the potential barrier, $2E/b^2$, and so it also gives a criterion of tunneling. If we take $m^H = 1$ and $m^D = 2$ amu in continuum medium irrespective of solvent, E will decrease with increasing solvent polarity, and so Q^H will be smaller in more polar solvent. The comparison between DCE and MeCN will conform to this case. The barrier width $2b$ is a little longer in MeCN perhaps because of the partial specific interaction of CN group with TNT. But the difference of tunneling factors is mainly due to that of E. Besides electrostatic or specific interaction, the solvent environment in the vicinity of reaction site must affect the degree of tunneling. When geometrical bulkiness of a solvent molecule is significant, we have to consider two effects: One is the steric hindrance which will work so as to separate the acid-base distance, and the other is to form a solvent cage in which reaction takes place under much less electrostatic effect of solvent. The former case will depress the tunneling degree, while the latter will enhance. The present results in PhCN suggest that the solvent PhCN molecule works so as not to form a cage-like environment around the reactive site but to separate the barrier width $2b$. For the case of PhCN the interposition of solvent molecule enlarges the distance between proton donor and acceptor, and brings about the smaller degree of tunneling, because there may be the stronger solvation due to π electron interaction between PhCN and TNT ring.

In this study we could not unfortunately discriminate the purely steric effect of solvent molecule. For that purpose an experiment in a bulky and nonpolar solvent is required, but within the preliminary experiments in various solvents we could not find any solvent in which the reaction took place effectively.

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