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EFFECT OF SOLVENT ON PROTON TUNNELING IN THE REACTIONS OF 4-NITROPHENYLNITROMETHANE WITH 1-ETHYLPYPERIDINE AND 1,8-DIAZABICYCLO[5.4.0]UNDEC-7-ENE

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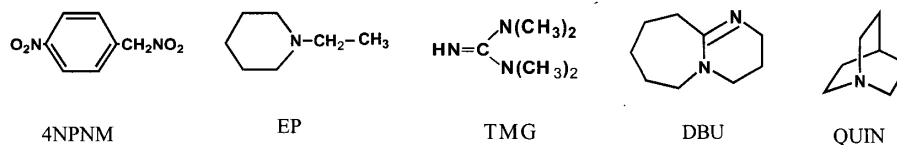
Abstract

A kinetic study has been carried out on the proton-transfer reactions from 4-nitrophenylnitromethane(4NPNM) to 1-ethylpiperidine (EP) and to 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile and dichloromethane by means of a stopped-flow method, the attention being focused to solvent effect on kinetic isotope effect (k_f^H/k_f^D) and degree of tunneling. For the 4NPNM-EP system, k_f^H/k_f^D at 25°C was 17.2 and the activation energy difference, $E_{af}^D - E_{af}^H$, was as large as 10.8 kJmol⁻¹, which suggested that the degree of proton-tunneling was significant. On the contrary, for the 4NPNM-DBU system the degree of proton-tunneling in both acetonitrile and dichloromethane was not so significant as 4NPNM-EP reaction. The semi-empirical analysis on the basis of the Bell's treatment showed that the barrier width for 4NPNM-EP was larger and barrier height became much higher in comparison to the reaction of 4NPNM with the bases such as DBU or tetramethylguanidine(TM_G). Those results were considered from the viewpoints of solvation effect on the transition state.

Introduction

Proton-transfer is one of the most fundamental reaction in solution, and has been extensively studied from the theoretical and phenomenological viewpoints¹⁻³. For chemical reactions associated with movement of light particles such as protons or electrons, sometimes tunneling may not be negligible. So, the important is not whether tunneling occurs, but whether it is detectable experimentally⁴.

We have done kinetic studies on proton tunneling for several reactions, between some carbon acids such as 4-nitrophenylnitromethane (4NPNM) or 2,4,6-trinitrotoluene(TNT) and bases such as tetramethylguanidine (TM_G)^{5,6}, 1,8-diazabicyclo[5.4.0]undec-7-ene



(DBU)⁷⁻¹⁰, or quinuclidine(QUIN)¹¹, and elucidated the environmental effect just in the vicinity of the reaction site. It has been recognized that geometrical factors around reaction site affect importantly the degree of tunneling^{5,6,12}. We should consider two kinds of effects concerning the substituents near the reactive site and the effect of solvent. One is the effect of forming a cage-like structure in which the proton-transfer process is much less coupled with solvent motion, and the other is the increasing acid-base distance. The effect of solvent is associated with the degree of solvation, and so reflected on the potential energy barrier. A large tunneling contribution was observed for TNT-DBU reaction⁷, in which the reactive site is partly concealed by the adjacent NO₂ groups. This factor was considered in terms of the former influence. On the other hand, for TNT and 1-substituted piperidine systems in acetonitrile¹³, the bulkiness of 1-substituent operated so as to make the acid-base reactive site distant, leading to smaller tunneling contribution. This factor was considered in terms of the latter influence. However, since the latter factor is associated also with prevention of solvent approach to reaction site, the relative degree of tunneling contribution will be solvent dependent.

In the present paper, we have dealt with proton-and deuteron-transfer reaction of 4NPNM with 1-ethylpiperidine(EP) and with DBU in acetonitrile and dichloromethane as solvent. Particular interest has been paid to a problem how the two factors described above is reflected upon the tunneling degree.

Experiments

Materials. Synthesis of 4-nitrophenylnitromethane and its deuteration were described previously¹¹. Commercially obtained 1-ethylpiperidine(Wako Pure Chemical Industries Ltd.) was dried with potassium hydroxide and then distilled. 1,8-Diazabicyclo[5.4.0]undec-7-ene (Wako Pure Chemical Industries Ltd.) was dried with potassium hydroxide and then distilled under reduced pressure, and the distillate was stored under an atmosphere of dry oxygen-free nitrogen. Acetonitrile was dried with calcium hydride, being distilled over diphosphorus pentoxide, and then it was refluxed for 1h over calcium hydride and distilled again. Dichloromethane was dried with calcium chloride, being distilled over diphosphorus pentoxide.

Every equilibrium and kinetic measurement was done with fresh solutions which were prepared in a glove box under nitrogen atmosphere immediately after solvent purification, and the following concentrations were used: 4NPNM, 4NPNM-d₂, 0.02-0.06 mM; EP, 3-16 mM; and DBU, 0.4-10 mM.

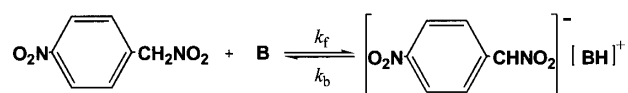
UV Spectra and Kinetic Measurements. UV spectra were recorded by a Hitachi U-2000 spectrophotometer. Kinetic measurement was carried out with a RA 2000 stopped-flow apparatus(Otsuka electronics) in which each reaction solution was driven directly by nitrogen pressure into a mixing chamber, and so the reaction solution was in contact with dry nitrogen during every kinetic measurement. The temperature range was 5.0-30°C.

Results and Discussions

The visible absorption spectrum of the mixture of 4NPNM and EP showed a single broad peak around 425nm in dichloromethane, and 488nm in acetonitrile. For the deuterated acid, the spectrum did not differ from the non-deuterated one. Similar spectra were observed for 4NPNM-DBU mixtures, 448nm in dichloromethane and 462 nm in acetonitrile. Moreover, the rate of absorption increment with time was almost the same with each other at the different wavelengths: this proved that the absorption in the visible region was due to one species.

Equilibrium and Kinetics of 4NPNM- EP systems. The equilibrium constant of 4NPNM-EP reaction was determined at 25°C according to the Benesi-Hildebrand equation¹⁴⁾ as given by eq (1) on the basis of Scheme 1, in which B denoted EP or DBU.

Scheme 1



$$\frac{a}{Abs} = \frac{1}{K\varepsilon} \times \frac{1}{[B]} + \frac{1}{\varepsilon} \quad (1)$$

In eq (1), a is the initial concentration of the acid, $[B]$ the initial concentration of the base where $[B] \gg a$, Abs the absorbance, ε the molar absorbance, and K is equilibrium constant($=k_f/k_b$). The molar absorbance ε determined by the plot of Fig. 1 was $2.4 \times 10^4 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$, which agreed well with $2.9 \times 10^4 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$ of 4NPNM-QUIN¹¹⁾ and $3.0 \times 10^4 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$ of 4NPNM-TMG systems¹⁵⁾. So the reaction 4NPNM-EP produced simply an ion pair. The temperature dependence of K gave the thermodynamic parameters, ΔH^0 and ΔS^0 as listed in Table 1.

The stopped-flow traces at the absorption peak wavelength, obeyed a first-order kinetics when EP existed in large excess over 4NPNM. The fitting was done to a single exponential function. It is known that presence of water in aprotic solvent causes often an artifact in analyzing kinetic curves, however, the correlation factor for a single exponential function was better than 0.999 over three or four half-lives. So, in the present reactions, we need not apprehend the possibility that the reaction rate is made complex

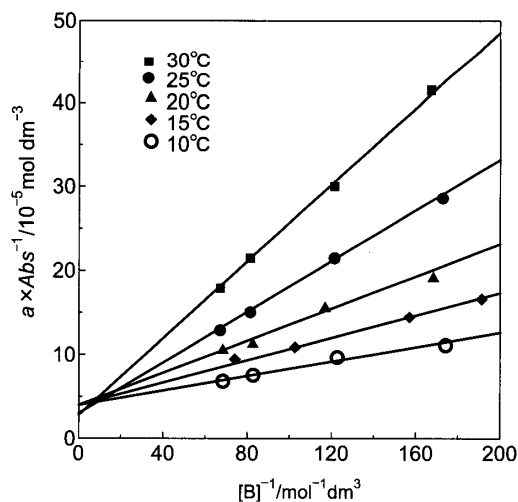


Fig. 1 Benesi-Hildebrand plots for 4NPNM-EP reaction in dichloromethane.

Table 1. Equilibrium constants and thermodynamic parameters for 4NPNM-EP reactions in dichloromethane.

$T/^\circ\text{C}$	$K^{\text{H}}/\text{dm}^3\text{mol}^{-1}$	$\Delta H^0(\text{H})/\text{kJmol}^{-1}$	$\Delta S^0(\text{H})/\text{JK}^{-1}\text{mol}^{-1}$
30	15.5	-60.2	-175
25	24.1		
20	34.6		
15	53.7		
10	83.0		

due to the isotopic exchange catalyzed by the small amount of water which may exist inevitably even in purified solvent¹⁶⁾. Moreover, it is known that the isotopic exchange of -CH₂- proton of 4NPNM is not so rapid¹⁷⁾ as the reaction of Scheme 1 when the OH⁻ concentration is of the order of 10⁻⁴ M. As expected, the plot of k_{obsd} against EP concentration gave a good straight line at each temperature as shown Fig. 2, in agreement with eq(2).

$$k_{\text{obsd}} = k_f [\text{B}] + k_b \quad (2)$$

In this equation k_f and k_b denote the forward and reverse rate constants, respectively. As found in Fig. 2, since the slope corresponding to k_f couldn't be determined accurately, k_f was calculated as $k_f = K \times k_b$ where K was that determined by equilibrium measurement (Table 1). Showing proton or deuteron transfer by the superscript H or D, respectively, the corresponding values thus determined are listed in Table 2. Table 4 lists the kinetic

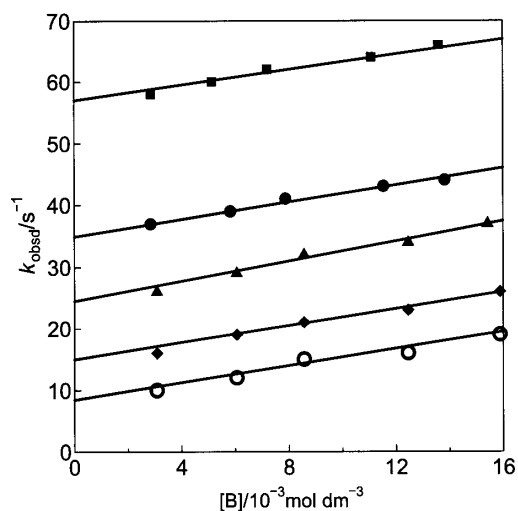


Fig. 2 Dependence of k_{obsd} on EP concentration for 4NPNM-EP reaction in dichloromethane. The symbols are the same as those in Fig. 1.

Table 2. Rate constants and kinetic isotope effects for 4NPNM-EP reactions in dichloromethane.

$T/^{\circ}\text{C}$	$k_f^{\text{H}}/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$	$k_b^{\text{H}}/\text{s}^{-1}$	$k_f^{\text{D}}/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$	$k_f^{\text{H}}/k_f^{\text{D}}$
30	911	58.6	64.9	14.0
25	836	34.7	48.5	17.2
20	778	22.5	38.1	20.4
15	714	13.3	28.5	25.0
10	655	7.89	21.3	30.8

Table 3. Rate constants and kinetic isotope effects for 4NPNM-DBU reactions in acetonitrile(AN) and dichloromethane(DM).

$T/^{\circ}\text{C}$	$k_f^{\text{H}}/10^5\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$		$k_f^{\text{D}}/10^4\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$		$k_f^{\text{H}}/k_f^{\text{D}}$	
	AN	DM	AN	DM	AN	DM
30		3.96		3.82		10.4
25	2.59	3.60	2.62	3.23	9.90	11.1
20	2.32	3.34	2.25	2.92	10.3	11.4
15	2.08	3.02	1.92	2.45	10.8	12.3
10	1.85	2.71	1.63	2.06	11.3	13.2
5.0	1.64		1.37		12.0	

Table 4. Kinetic isotope effect and activation parameters for and 4NPNM-DBU reactions in acetonitrile(AN)^{a)} and dichloromethane(DM)^{a)} at 25°C.

	4NPNM-EP		4NPNM-DBU	
	AN	DM	AN	DM
$k_f^H/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$	1.14×10^3	8.36×10^2	2.59×10^5	3.60×10^5
$k_f^D/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$		48.5	2.62×10^4	3.23×10^4
k_f^H/k_f^D		17.2	9.9	11.0
$E_{af}^H/\text{kJmol}^{-1}$	28.2	21.8	15.7	13.2
$E_{af}^D/\text{kJmol}^{-1}$		32.6	22.2	22.2
$E_{af}^D - E_{af}^H/\text{kJmol}^{-1}$		10.8	6.5	9.0
$\Delta S_f^\ddagger(\text{H})/\text{JK}^{-1}\text{mol}^{-1}$	-100	-105	-96.9	-103
$\Delta S_f^\ddagger(\text{D})/\text{JK}^{-1}\text{mol}^{-1}$		-85.8	-94.2	-92.6
A_f^D/A_f^H ^{b)}		4.0	1.5	3.4
$K^H/\text{dm}^3\text{mol}^{-1}$		24.0		
$\Delta H^0(\text{H})/\text{kJmol}^{-1}$		-60.2		
$\Delta S^0(\text{H})/\text{JK}^{-1}\text{mol}^{-1}$		-175		

^{a)} dielectric constant $\epsilon=37.5$ for AN, 9.1 for DM.

^{b)} Arrhenius pre-exponential factor ratio.

and activation parameters determined by the temperature dependence of rate constants. At 25°C k_f is larger in polar solvent(acetonitrile) than less polar one(dichloromethane). However, the activation energy is much less in dichloromethane than acetonitrile. The entropy of activation $\Delta S_f^\ddagger(\text{H})$ is less negative in acetonitrile, which indicates that the transition state is looser in acetonitrile than dichloromethane. That seems to be opposed to the classical understanding on solvation effect on reaction rate. And that behavior will be discussed later from the vierpoints of tunneling.

Equilibrium and Kinetics of 4NPNM- DBU systems. For the 4NPNM-DBU system, equilibrium constant couldn't be determined because the product ion pair was not so stable.

The stopped-flow traces fitted to single exponential function, the rate obeying a pseudo first-order rate law when DBU existed in large excess over acid concentration. Since a plot similar to Fig. 2, however, didn't show a meaningful intercept which was very close to zero, the reverse rate constant k_b could not be determined. Rate constant and kinetic isotope rate ratio are listed in Table 3, and Table 4 lists the kinetic and activation parameters together with the 4NPNM-EP reaction. For 4NPNM-DBU reaction also, as similar to the 4NPNM-EP, E_{af}^H and $\Delta S_f^\ddagger(\text{H})$ are both larger in acetonitrile than dichloromethane, but the difference between solvents is much smaller than the case of the 4NPNM-EP. For the deuteron-transfer the difference due to solvent almost disappears.

The Kinetic Isotope Effect and Tunneling. A proton/deuteron transfer from a carbon acid associated with tunneling is known to exhibit the following features^{1,18,19}): kinetic isotope rate ratio $k^H/k^D > 11$ at 25°C, activation energy difference $E_a^D - E_a^H > 4.8 \text{ kJmol}^{-1}$, ratio of the Arrhenius pre-exponential factor $A^D/A^H > 1.4$, and the Arrhenius plot curves at low temperature. On the basis of the above features the kinetic isotope rate ratios given in Table 2 show that the appreciable tunneling is associated with the 4NPNM-EP reaction in dichloromethane. As found in Table 3, even with 4NPNM-DBU reaction tunneling may be associated, though the degree will be less than 4NPNM-EP.

The tunneling correction factor Q was calculated according to the Bell's treatment by using a parabolic potential^{1,18}),

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

where $u = h\nu/kT$, and $\nu = (E/2m)^{1/2}/b$; k is Boltzmann's constant, h Planck's constant, E the height of barrier, $2b$ the width of barrier at the base, m the effective mass of the transferring particle, and ν the frequency of oscillation of a particle in a parabolic potential or curvature of the potential curve at the top. If the tunneling degree is not so high, we can approximate eq (2) by the first term¹⁸).

$$Q = \frac{0.5u}{\sin(0.5u)} \quad (3)$$

We have tried to calculate the tunneling factors of 4NPNM-EP and 4NPNM-DBU systems on the basis of eq(3). Under the assumption that $m^H = (1/2)m^D = 1 \text{ amu}$ and $E^D - E^H \leq 4.8 \text{ kJ mol}^{-1}$, the values of E_f^H , E_f^D and $2b$ were adjusted by trial and error until we could reproduce the experimental values of $(k_f^H/k_f^D)_{\text{Arrh}}$ taken from the Arrhenius plots over the whole range of experimental temperature. These tunneling parameters are given in Table 5 together with the reactions of 4NPNM with TMG for comparison.

The value of (k_f^H/k_f^D) of EP is larger than that of DBU(Table 4). That result is opposite to the reactions of TNT with amidine bases in acetonitrile¹³), in which (k_f^H/k_f^D) is 16.2 for TNT-EP, 19.1 for TNT-DBU, and 18.5 for TNT-TMG. Table 5 shows that the barrier width $2b$ is nearly equal each other for DBU and TMG, and longer for EP. Since the base such as TMG accepts and stabilizes the proton during the amidine structure, the closest approach distance at the transition state is apparently shorter than the actual distance. In EP, on the other hand, a proton must be accepted by only one lone pair orbital, which extends to a greater distance than sp^2 hybridization: the more extended sp^3 orbital on N atom can also explain the larger barrier width for EP than amidine bases^{20,21}). Such an increase of barrier width should reduce the tunneling degree. So the enhanced kinetic isotope effect as observed and the enhanced tunneling degree as calculated for EP

Table 5. Proton tunneling parameters for reactions of 4NPNM with some bases in dichloromethane at 25°C.

	base		
	EP ^{a)}	DBU ^{a)}	TMG ^{b)}
$Q^H(\text{at } 25^\circ\text{C})$	8.61	3.01	2.86
ν^H/cm^{-1}	991	905	936
E^H/kJmol^{-1}	35.2	18.5	20.2
E_{af}^H/E^H	0.62	0.71	0.84
$2b/\text{Å}$	1.40	0.86	0.95

a) present work. b) ref. 15

compared to amidine bases have to come from higher barrier height E and larger difference of $E_{\text{af}}^D - E_{\text{af}}^H$, that is, activation energy for H^+ -transfer of EP is really much less than the barrier height.

Then what does make the barrier height higher for proton transfer of 4NPNM-EP in dichloromethane? With regard to the effect of bulkiness near the reaction site on tunneling we have to consider another interaction different from increased distance between acid and base molecules as described above. Bulkiness of a base molecule may exclude solvent molecules from the reaction site and reduce their motion coupled with the transferring proton. The ethyl substituent of EP will operate to do so. Then EP, compared to amidine bases, will make the effective mass of the transferring proton to decrease or the barrier height to increase, working so as to increase tunneling contribution. As a result of the sum of these two opposing contributions to tunneling, increasing barrier width and increasing barrier height, the curvature ν becomes larger in EP than DBU or TMG. However, an opposing result was obtained for the case of TNT-substituted piperidine systems in acetonitrile, where substituted piperidines made smaller contribution to tunneling compared to amidine bases, and the increasing bulkiness of the substituent operated to reduce the tunneling¹³⁾. Such a significant difference can be attributed to the difference of degree of solvation at the transition state depending on solvent polarity. Because D^+ -transfer is much less associated with tunneling, $\Delta S_f^\ddagger(D)$ can partly reflect behavior of the semi-classical transition state. As found in Table 4 EP has less negative entropy of activation $\Delta S_f^\ddagger(D)$ than amidine bases in dichloromethane. That behavior is consistently understood as follows; dichloromethane is participated in the transition state of 4NPNM-EP reaction in less extent than the 4NPNM-amidines, perhaps because the bulky substituent weakens the approach of solvent molecules as well as an acid. On the contrary, since acetonitrile is more strongly solvated at the transition state, the difference of extent of solvation between EP and amidine bases is obscure and the effect of increasing barrier width appears remarkably.

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