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TABLE II: Value of  $k_1$  at 296 K near 1-atm N<sub>2</sub> Pressure

method <sup><i>a</i></sup>	$10^{12}k_1,$ cm <sup>3</sup> s <sup>-1</sup>	ref
FP-UV of Cl <sub>2</sub> -O <sub>2</sub> -CH <sub>2</sub> OH	$2.5 \pm 0.2$	this work
PR-UV of H,-O,	4.0	5
MM-UV of Cl,-O,-H,	2.5	3
PHg-UV of $H_2$ -O <sub>2</sub>	4.7	15
SSP of $H_2 - O_2 - O_3$	$3.3^{b}$	8
SSP of $H_2 - O_2 - O_3$	8.7 <sup>b</sup>	16
SSP of HO, NO,	$3.8^{c}$	17
MM UV of O <sub>3</sub> -H <sub>2</sub> O <sub>2</sub> -He	3.6	14
FP-UV of Cl <sub>2</sub> -O <sub>2</sub> -CH <sub>3</sub> OH	$3.0 \pm 0.2$	10

<sup>*a*</sup> FP-UV, flash photolysis, ultraviolet absorption; MM-UV, molecular modulation, ultraviolet absorption; PHg-UV, pulsed Hg sensitization, ultraviolet absorption; SSP, steady-state photolysis. <sup>*b*</sup> Based on the reference reaction  $HO_2 + O_3 \rightarrow OH + 2O_2$  for which  $k = 2.0 \times 10^{-15}$  cm<sup>3</sup> s<sup>-1</sup> at 296 K.<sup>18</sup> <sup>*c*</sup> Based on the reference reaction  $HO_2 + NO_2$  $(+M) \rightarrow HO_2NO_2$  (+M); the uncertainty in  $k_1$  is a factor of 2.

Thrush and Wilkinson<sup>4</sup> using a flow discharge tube with LMR detection at low pressures (2–4 torr, He). Our value at 1 atm of N<sub>2</sub> agrees with the value of  $2.5 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> recommended by NASA,<sup>2</sup> but other studies at higher pressures, which are summarized in Table II, support a higher value.

Our data clearly indicate a low-pressure limiting rate coefficient in agreement with the extrapolation of Sander et al.<sup>10</sup> but in complete disagreement with others<sup>3-5</sup> who

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investigated the reaction at low pressures.

In order to account for the pressure and negative temperature dependence, Cox and Burrows and Thrush and Wilkinson proposed that the disproportionation reaction 1 actually proceeds through a stabilized  $H_2O_4$  molecule

$$HO_2 + HO_2 (+M) \rightleftharpoons H_2O_4 (+M)$$
 (a,b)

$$H_2O_4 \rightarrow H_2O_2 + O_2 \tag{c}$$

$$HO_2 + HO_2 (+M) \rightarrow H_2O_2 + O_2 (+M)$$
 (1a)

A steady-state analysis of this mechanism gives

$$k_{1a} = k_a k_c [M] / (k_b [M] + k_c)$$
 (II)

To account for the low-pressure limiting value observed by us, it is necessary to include a two-body abstraction reaction, i.e., in addition to reaction 1a, reaction 1b is also

$$2\mathrm{HO}_2 \to \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 \tag{1b}$$

important. This would imply that as  $[\mathbf{M}] \rightarrow 0$ ,  $k_1 \rightarrow k_{1b}$ . From our data, the value of  $k_{1b}$  would be  $\simeq 1.4 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>. This value might be slightly high because of potential wall removal of HO<sub>2</sub>. Using the methods outlined by Heicklen,<sup>19</sup> we find that at 5 torr the wall reaction could account for up to 75% of the total reaction if every collision of HO<sub>2</sub> with the wall is effective. However, since there is no significant pressure dependence between 5 and 123 torr, wall reaction is unlikely to be important.

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# Kinetics and Tunneling in the Proton- and Deuteron-Transfer Reaction between 2,4,6-Trinitrotoluene and 1,8-Diazabicyclo[5.4.0]undec-7-ene in Some Aprotic Solvents

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The proton/deuteron-transfer reactions of 2,4,6-trinitrotoluene with 1,8-diazabicyclo[5.4.0]undec-7-ene in acetonitrile, 1,2-dichloroethane, and dichloromethane have been found to produce an ion pair. The reaction rates at 5–35 °C of the proton- and deuteron-transfer reactions have been followed by a stopped-flow method. The reaction rate ratio  $k^{\rm H}/k^{\rm D}$  diminishes from 24.0 at 10 °C to 18.3 at 30 °C in acetonitrile and from 35.0 at 15 °C to 27.1 at 30 °C in 1,2-dichloroethane. The difference in the activation energies  $E_{\rm a}^{\rm D} - E_{\rm a}^{\rm H}$  is 2.3 and 2.1 kcal mol<sup>-1</sup> in acetonitrile and 1,2-dichloroethane, respectively. The ratio of Arrhenius preexponential factors is 2.5 in acetonitrile and 2.0 in 1,2-dichloroethane. All these values are greater than the semiclassical limits which can be predicted since the primary kinetic isotope effect is brought about by loss of the zero-point energy difference between C-H and C-D bond at the transition state. This remarkable isotope effect, when fitted to Bell's equation, indicates that there is a considerable contribution from proton tunneling. These results are discussed in comparison with those of other proton/deuteron-transfer reactions.

## Introduction

The proton-transfer reaction has gained considerable attention in physical chemistry, since it is one of the most fundamental reactions and occasionally is subject to tunneling. Recently, the primary kinetic isotope effect of the proton-transfer reaction in solution has been extensively studied from theoretical and phenomenological viewpoints.<sup>1,2</sup> Many models have been proposed in order to explain the numerical values of the primary kinetic isotope effect.<sup>3-8</sup> Westheimer<sup>4</sup> has predicted that the kinetic

<sup>(19)</sup> J. Heicklen, "Colloid Formation and Growth: A Chemical Kinetics Approach", Academic Press, New York, 1976, p 8-13.

<sup>(1)</sup> E. F. Caldin, Chem. Rev., 69, 135 (1969), and references cited therein.

<sup>(2)</sup> E. F. Caldin and V. Gold, "Proton-Transfer Reaction", Chapman and Hall, London, 1975.

isotope rate ratio  $k^{\rm H}/k^{\rm D}$  should be a maximum in the symmetrical transition state if tunneling is not taken into account. A number of investigators<sup>9</sup> have presented discussions along these lines, though the explanation of such a maximum only by his treatment has been questioned.<sup>10</sup> There is another theoretical treatment based on tunneling.<sup>11</sup> The enormously large value of the kinetic isotope rate ratio has been often explained on the basis of a tunneling correction.<sup>12-14</sup>

In particular, several investigations of the following proton/deuteron-transfer reactions have attracted much interest because of the appreciable tunneling effect: the reaction of 4-nitrophenylnitromethane (4NPNM) with tetramethylguanidine (TMG) from the viewpoints of solvent effect<sup>15-17</sup> and pressure effect,<sup>18</sup> the reaction of 4NPNM with pentamethylguanidine (PMG),<sup>19</sup> and the reaction of 2,4,6-trinitrotoluene (TNT) with TMG.<sup>20,21</sup> However, the evidence supporting tunneling has been occasionally equivocal or not enough for the intermolecular proton-transfer reactions in solution.<sup>16,22,23</sup>

In this paper we have investigated the kinetics of the proton/deuteron-transfer reaction of TNT (AH) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, B) in acetonitrile, 1,2-dichloroethane, and dichloromethane solvents by means of a stopped-flow method.



A base such as DBU was chosen because (1) the base nitrogen atom was not protonated in the free base,<sup>16</sup> (2) it

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**Figure 1.** Plots of [AH]/a against reciprocal of DBU concentrations in 1,2-dichloroethane: TNT + DBU (O), TNT- $d_3$  + DBU ( $\oplus$ ).

was a strong base favorable to proton-transfer reactions, and (3) it was a cyclic amidine suitable for the study of the steric effect.

### **Experimental Section**

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 its NMR spectrum (methyl protons,  $\delta$  2.75, benzene ring protons,  $\delta$  8.92, in the ratio 3:2). Deuterated 2,4,6-trinitrotoluene  $(TNT-d_3)$  was obtained by addition of 1 mL of 1 M NaOD in  $D_2O$  to 4 g of TNT dissolved in a  $D_2O$ -DMF mixture (10:90 v/v, 100 mL).<sup>20</sup> Neutralization with a few drops of concentrated DCl in D<sub>2</sub>O was effected after 4 h within which the proton-deuteron exchange was complete at room temperature.<sup>24</sup> The solution was poured into an excess of  $D_2O$ , a yellow substance being precipitated. These procedures were repeated three more times. The product was then recrystallized from carbon tetrachloride with charcoal and evaporated to dryness under vacuum; pale yellow needles were obtained (mp 80.5-81 °C). The NMR spectrum of TNT- $d_3$  showed an isotopic purity of better than 98% deuterium in the methyl group of TNT. TNT and TNT- $d_3$  thus obtained were kept separately in vacuum desiccators.

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. No impurity of DBU was detected in the NMR spectrum. The distillation was repeated periodically and the distillate stored under an atmosphere of dry oxygenfree nitrogen.

Solvents were purified by standard methods and the distillation was repeated at frequent intervals. Acetonitrile (AN) was dried with calcium hydride and then distilled over phosphorus pentaoxide. 1,2-Dichloroethane (DCE) and dichloromethane (DCM) were dried with calcium hydride and then distilled.

Apparatus and Procedure. 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  $\pm 0.1$  °C by circulating thermostated water. Solutions were freshly prepared every day before use and the following concentrations of solutions were used: TNT, TNT- $d_3$ , 0.02–0.08 mM; DBU, 1.5–15 mM in AN, 1–20 mM in DCE, and 1.5–18 mM in DCM.

The rate of the proton/deuteron-transfer reactions of TNT and TNT- $d_3$  with DBU was determined by monitoring the change of the absorbance with time at 520 nm in AN, 532 nm in DCE, and 530 nm in DCM. The increase

<sup>(3)</sup> L. Melander, "Isotope Effects on Reaction Rates", Ronald Press, New York, 1960, and literatures cited therein.

<sup>(24)</sup> E. Buncel, A. R. Norris, K. E. Russell, and R. Tucker, J. Am. Chem. Soc., 94, 1646 (1972).



**Figure 2.** Dependence of  $k_{obsd}$  on DBU concentration of the TNT + DBU reaction in 1,2-dichloroethane:  $T = 30 \ ^{\circ}C$  (O), 25  $^{\circ}C$  ( $\bigoplus$ ), 20  $^{\circ}C$  ( $\Delta$ ), 15  $^{\circ}C$  ( $\bigoplus$ ), 10  $^{\circ}C$  ( $\square$ ).

of the absorbance obeyed first-order kinetics when the base (DBU) existed in large excess over TNT or TNT- $d_3$ . The observed first-order rate constant  $k_{obsd}$  was determined by least-squares fitting to the Guggenheim plot.

#### Results

The reaction of  $TNT-d_3$ , as well as TNT, with DBU within the range of present experimental concentrations gives a purple solution. The possibility of reactions other than proton/deuteron-transfer was ruled out by reference to a previous paper.<sup>25</sup> The absorption maxima of the product as a result of proton/deuteron-transfer from the methyl group of TNT to DBU are around 378, 532, and 635 nm in DCE and almost identical with those observed in other solvents (378, 520, and 635 nm in AN, and 375, 530, and 635 nm in DCM); they are very similar to those observed in the reactions of TNT and  $TNT-d_3$  with TMG,<sup>20,21,25</sup> while each reactant is transparent in the visible region. The rates of change of absorbance increments with reaction time are identical with each other at these three maximum wavelengths; this proves that these three absorption maxima are due to one species.

The equilibrium constant of the TNT + DBU reaction in DCE as well as in AN and DCM<sup>25</sup> was determined at 25 °C according to the Benesi-Hildebrand equation.<sup>26</sup>

$$[AH]/a = 1/K\epsilon[B] + 1/\epsilon$$
(1)

In this equation, [AH] is the initial concentration of TNT, [B] that of DBU, K the equilibrium constant,  $\epsilon$  the molar absorptin coefficient, and a the absorbance at 532 nm in DCE after equilibration. The fact that the plot of eq 1 gives a very good straight lines as shown in Figure 1 supports the idea that the product is not separate ions but an



**Figure 3.** Dependence of  $k_{obsd}$  on DBU concentration of the TNT- $d_3$  + DBU reaction in acetonitrile: T = 30 °C (O), 25 °C ( $\oplus$ ), 20 °C ( $\Delta$ ), 15 °C ( $\Delta$ ), 10 °C ( $\square$ ).

TABLE I: Rate Constants for the Proton-Transfer Reaction  $k_f^H$  (M<sup>-1</sup> s<sup>-1</sup>)

 n °a	A NTC	DOD	DOM
 r, °C	AN"	DCE	DCM <sup>e</sup>
30	$271 \pm 2$	635 ± 11	
25	$204 \pm 4$	$565 \pm 10$	$41.8 \pm 1.5$
20	$171 \pm 4$	$465 \pm 6$	$36.8 \pm 1.4$
15	$131 \pm 2$	$413 \pm 6$	$29.2 \pm 1.2$
10	$101 \pm 2$	$319 \pm 6$	$24.0 \pm 1.0$
5			$17.7 \pm 0.7$

 $^{a}$  Acetonitrile.  $^{b}$  1,2-Dichloroethane.  $^{c}$  Dichloromethane.

TABLE II: Rate Constants for the Deuteron-Transfer Reaction  $k_f^D~(M^{-1}~s^{-1})$  and Kinetic Isotope Rate Ratios  $k_f^{\rm H}/k_f^{\rm D}$ 

T	$T$ $k_{f}^{D}$		$k_{\rm f}^{\rm H}/k_{\rm f}^{\rm D}$	
°Ĉ	AN <sup>a</sup>	DCE <sup>b</sup>	AN <sup>a</sup>	$DCE^b$
35		$29.2 \pm 0.5$		
30	$14.8 \pm 0.2$	$23.4 \pm 0.5$	$18.3 \pm 0.5$	$27.1 \pm 0.8$
25	$10.7 \pm 0.2$	$18.9 \pm 0.4$	$19.1 \pm 0.6$	$29.9 \pm 0.9$
20	$8.5 \pm 0.2$	$15.2 \pm 0.4$	$20.1 \pm 0.6$	$30.6 \pm 0.9$
15	$6.0 \pm 0.2$	$11.8 \pm 0.3$	$21.8 \pm 0.6$	$35.0 \pm 1.1$
10	$4.2 \pm 0.1$		$24.0 \pm 0.7$	

<sup>a</sup> Acetonitrile. <sup>b</sup> 1,2-Dichloroethane.

ion pair. Otherwise the plot would be significantly curves and eq 2 would be valid. Therefore, it is concluded that

$$[AH]/a = a/K\epsilon^{2}[B] + 1/\epsilon$$
(2)

the reaction between TNT and DBU in DCE produced simply an ion pair as well as those in AN and DCM.

In kinetic measurement the stopped-flow trace obeys a first-order kinetic equation at each temperature when the base concentration is in large excess over the TNT or TNT- $d_3$  concentration. The plots of  $k_{obsd}$  against DBU

<sup>(25)</sup> N. Sugimoto, M. Sasaki, and J. Osugi, Bull. Chem. Soc. Jpn., 54, 2598 (1981).

<sup>(26)</sup> H. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., 71, 2703 (1949).

TABLE III: Equilibrium Constants K (M<sup>-1</sup>) and Backward Rate Constants  $k_b$  (s<sup>-1</sup>) for the Proton-Transfer Reaction at 25 °C

solvent	K	k <sub>b</sub>
${ m AN}^a { m DCE}^b$	$\begin{array}{r} 6070 \pm 700^d \\ 1230 \pm 100^d \\ 1300 \pm 150^e \end{array}$	$\begin{array}{c} 0.03^{f} (0.04^{h}) \\ 0.46^{f} (0.39^{h}) \\ 0.01^{g} (0.004^{h}) \end{array}$
$DCM^{c}$	$24 \pm 5^{d}$	$1.74^{f} (1.87^{h})$

<sup>a</sup> Acetonitrile. <sup>b</sup> 1,2-Dichloroethane. <sup>c</sup> Dichloromethane. <sup>d</sup> From equilibrium measurements for H<sup>+</sup> transfer. <sup>e</sup> From equilibrium measurements for D<sup>+</sup> transfer. <sup>f</sup>  $k_b^{H} = k_f^{H}/K^{H}$ . <sup>g</sup>  $k_b^{D} = k_f^{D}/K^{D}$ . <sup>h</sup> From kinetic measurements.

concentration [B] are linear (Figures 2 and 3), in agreement with eq 3 and 4. In these equations,  $k_{\rm f}^{\rm H}, k_{\rm f}^{\rm D}, k_{\rm b}^{\rm H}$ , and  $k_{\rm b}^{\rm D}$ 

$$k_{\text{obsd}} = k_{\text{f}}^{\text{H}}[\text{B}] + k_{\text{b}}^{\text{H}}$$
(3)

$$k_{\text{obsd}} = k_{\text{f}}^{\text{D}}[\text{B}] + k_{\text{b}}^{\text{D}} \tag{4}$$

denote the forward and backward rate constants of the proton- and deuteron-transfer reactions. These were determined from the dependence of  $k_{obsd}$  on DBU concentration by a least-squares method, and the values of  $k_{\rm f}^{\rm H}$ ,  $k_{\rm f}^{\rm D}$ , and  $k_{\rm f}^{\rm H}/k_{\rm f}^{\rm D}$  are given in Tables I and II. However, the value of  $k_{\rm f}^{\rm D}$  in DCM is too small to be reliable and is not recorded. The equilibrium constants K of the protonand deuteron-transfer reactions at 25 °C are listed in Table III. The backward rate constants  $k_{\rm b}$  could be determined either by  $k_{\rm f}$  and K owing to the relationship  $k_{\rm b} = k_{\rm f}/K$  or by direct kinetic experiment owing to eq 3 and 4. As seen in Table III, the agreement between these values obtained by the different procedures is satisfactory in all these cases, but in the case of deuteron transfer in DCE it is not enough because of the very small value of  $k_b^{D}$ . To investigate the effect of small amounts of  $D_2O$  in the case of deuteron transfer, the rate of deuteron transfer from  $\text{TNT-}d_3$  to DBU was measured in  $D_2$ O-saturated DCE.<sup>27</sup> The results are given in Figure 4. The apparent value for  $k_b^D$  obtained in  $D_2O$ -saturated DCE is also small and the value for  $k_f^{D}$ is not affected by the presence of  $D_2O$ . In DCE with deliberately added  $H_2O$  the curves of absorbance change with time deviated considerably from the truly exponential ones which were observed in the case of highly purified DCE. In our case we need not apprehend the possibility that the reaction rate is made complex due to the isotopic exchange catalyzed by the small amount of water which exists inevitably. From the temperature dependence of the second-order rate constants  $(k_{\rm f}^{\rm H} \text{ and } k_{\rm f}^{\rm D})$ , the activation parameters  $\Delta H_{\rm f}^{*}$ ,  $\Delta S_{\rm f}^{*}$ ,  $\Delta G_{\rm f}^{*}$ , and Arrhenius preexponential factors (A factors) were computed by a least-squares method (Table IV).

#### Discussion

Mechanism of Reaction. In the case of the reaction of TNT with ethoxide ion in ethanol, two colored compounds are formed.<sup>28</sup> At high concentrations of TNT ( $\sim 10^{-3}$  M) and ethoxide ion ( $\sim 10^{-1}$  M) a brown species is formed, which is elucidated to be a type of Meisenheimer complex by Bernasconi.<sup>29</sup> On the other hand, at low concentrations of TNT ( $\sim 10^{-5}$  M) and ethoxide ion ( $\sim 10^{-3}$  M), the 2,4,6-trinitrobenzyl anion (TNT<sup>-</sup>;  $\lambda_{max} = 514$  nm) is mainly produced by proton abstraction from the methyl group of TNT.<sup>24,28</sup> The reaction of TNT with TMG in some aprotic solvents<sup>20,21</sup> also results in a purple solution due to an ion



**Figure 4.** Plots of  $k_{obsd}$  against DBU concentration for the TNT- $d_3$  + DBU reaction at 25 °C in highly purified DCE (O) and in D<sub>2</sub>O-saturated DCE ( $\oplus$ ).

pair having absorption maxima similar to those of the reaction solution containing TNT<sup>-</sup>.

The reaction of TNT with DBU in some aprotic solvents is similar to that with TMG.<sup>20,21,25</sup> The visible absorption spectra of the reaction product, TNT<sup>-</sup>, is identical for the two bases and in our study there is no indication that the dimer of the base has participated in the carbanion formation reaction, which was reported to be significant at high concentrations.<sup>30</sup> Therefore, the reaction of TNT with a nonionic base causes only a proton transfer.

The equilibrium constants were determined by assuming that the product existed as an ion pair. The possibility of the complex formation with more than a 1:1 ratio of TNT to base<sup>31</sup> was not studied, since, even if the complex was formed, such a reaction would be a slow one preceded by fast proton-transfer on which the present work was focused. As a matter of fact, the spectrum of a solution immediately after mixing persisted for more than 10 min.

Kinetics and Equilibrium. In the reaction between TNT and ethoxide ion, Buncel et al.<sup>24</sup> found that the plots of the observed first-order rate constant  $k_{obsd}$  vs. ethoxide ion concentration were slightly curved. The analysis of these results led them to conclude that a brown species other than TNT<sup>-</sup> was formed. In the reaction between TNT and TMG, however, Pruszynski et al.20 obtained a linear relation obeying eq 3 and 4 in both acetonitrile and benzonitrile. In our experiments plots of  $k_{obsd}$  against DBU concentration also give straight lines in AN, DCE, and DCM. Furthermore, the following facts indicate that the reaction of TNT with DBU is a simple 1:1 reaction forming the proton-transferred ion pair: (1) The equilibrium constant K is almost unchanged for deuterated TNT in DCE though  $k_{\rm f}$  and  $k_{\rm h}$  are remarkably dependent isotopically. (2) The rate constant  $k_b$  determined by kinetic measurement is in good accord with that obtained by  $k_f/K$ as shown in Table III.

The equilibrium constant between TNT and DBU is larger than that between TNT and TMG ( $K = 4100 \text{ M}^{-1}$  in AN<sup>20</sup> and 2 M<sup>-1</sup> in DCM<sup>25</sup>); DBU is a much stronger

<sup>(27)</sup> We acknowledge the reviewer who suggested the experiment in DCE with deliberately added  $D_2O$ .

<sup>(28)</sup> E. F. Caldin and G. Long, Proc. R. Soc. London, Ser. A, 226, 263 (1955).

<sup>(29)</sup> C. F. Bernasconi, J. Org. Chem., 36, 167 (1971).

<sup>(30)</sup> J. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc., 91, 2875 (1969).

<sup>(31)</sup> E. Buncel and B. Menon, J. Org. Chem., 44, 317 (1979).

TABLE IV: Activation Parameters of the Proton- and Deuteron-Transfer Reactions at 25 °C

		DCE <sup>b</sup>	DCM <sup>c</sup>	
$\Delta H_{\mathbf{f}}^{+}(\mathbf{H})$ , kcal mol <sup>-1</sup> $\Delta S_{\mathbf{f}}^{+}(\mathbf{H})$ , cal mol <sup>-1</sup> $\mathbf{F}$ $\Delta G_{\mathbf{f}}^{+}(\mathbf{H})$ , kcal mol <sup>-1</sup> $\log A^{\mathbf{H}}$	$\begin{array}{ccc} 7.7 \pm 0.2 \\ -22.2 \pm 0.7 \\ 14.3 \pm 0.4 \\ 8.4 \pm 0.1 \end{array}$	$5.2 \pm 0.2 \\ -28.6 \pm 0.9 \\ 13.7 \pm 0.5 \\ 6.9 \pm 0.1$	$\begin{array}{c} 6.5 \pm 0.3 \\ -29.2 \pm 0.9 \\ 15.2 \pm 0.6 \\ 6.8 \pm 0.1 \end{array}$	
$\Delta H_{\mathbf{f}}^{+}(\mathbf{D})$ , kcal mol <sup>-1</sup> $\Delta S_{\mathbf{f}}^{+}(\mathbf{D})$ , cal mol <sup>-1</sup> k $\Delta G_{\mathbf{f}}^{+}(\mathbf{D})$ , kcal mol <sup>-1</sup> $\log A^{\mathbf{D}}$	$\begin{array}{cccc} 10.0 \pm 0.3 \\ -20.3 \pm 0.8 \\ 16.0 \pm 0.4 \\ 8.8 \pm 0.1 \end{array}$	$\begin{array}{r} 7.3 \pm 0.3 \\ -28.1 \pm 0.8 \\ 15.7 \pm 0.6 \\ 7.2 \pm 0.1 \end{array}$		

<sup>a</sup> Acetonitrile. <sup>b</sup> 1,2-Dichloroethane. <sup>c</sup> Dichloromethane.

base than TMG. In the reaction of TNT with DBU both K and  $k_{\rm f}^{\rm H}$  are very small in comparison with those of the reaction between 4NPNM and DBU even in toluene<sup>32</sup> (K=  $1.8 \times 10^4$  M<sup>-1</sup> and  $k_f^{\rm H} = 2.7 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup> at 25 °C); TNT may be a much weaker carbon acid than 4NPNM, that is, 4NPNM releases the  $\alpha$  proton more easily than TNT. The results in Table III that K increases with increasing polarity of the solvent suggest qualitatively that the ion pair is mainly stabilized by electrostatic interaction with the surrounding solvent molecules. The rate constant  $k_{\rm f}^{\rm H}$  at 25 °C in DCE is greater than those observed in AN and DCM by factors of about 3 and 13, respectively. The rate difference results mostly from the activation enthalpy differences as shown in Table IV.

The largely negative entropies of activation  $\Delta S_f^*(\mathbf{H})$  and  $\Delta S_f^*(D)$  indicate that the transition state is solvated more strongly than the initial state. We have reported<sup>25</sup> that the activation volume  $\Delta V_{\rm f}^{*}({\rm H})$  of the reaction between TNT and DBU was less negative in AN (-9.0 cm<sup>3</sup> mol<sup>-1</sup>) than in DCM  $(-10.8 \text{ cm}^3 \text{ mol}^{-1})$ , which was qualitatively explained by the electrostatic solvation model of an ionogenic reaction. As found in Table IV, the tendency of the variation of  $\Delta S_f^*(\mathbf{H})$  with solvent is consistent with that of  $\Delta V_{\rm f}^{*}({\rm H})$ . The parallel changes of  $\Delta V^{*}$  and  $\Delta S^{*}$  are often observed in other reactions in solution, and such a tendency indicates the coupling of the solvent molecule at the transition state.<sup>33</sup> It was also found<sup>25</sup> that the magnitude of  $\Delta V_f^*(H)$  for DBU was smaller than that for TMG both in AN and DCM (-12.8 and -19.0 cm<sup>3</sup> mol<sup>-1</sup>, respectively), which would suggest reasonably that the nonplanar seven-membered ring of DBU prevented solvation in the vicinity of the reaction center. The increase of  $\Delta S_f^*(H)$ from -31.4 cal K<sup>-1</sup> mol<sup>-1</sup> for TMG<sup>20</sup> to -22.2 cal K<sup>-1</sup> mol<sup>-1</sup> for DBU in AN is well consistent with the increase of  $\Delta V_{f}^{*}(\mathbf{H})$ . Therefore, these present results lead us to support our previous consideration on the volume of activation: These proton-transfer reactions, though being subjected to the tunneling effect as described later, pass through a transition state in which solvent molecules are not completely excluded from the vicinity of the reacting molecules but concerned partly with reactants through electrostatic interaction.

Kinetic Isotope Effect and Tunneling. Recent studies of kinetic hydrogen isotope effects have shown the occurrence of tunneling.<sup>1,2</sup> A proton/deuteron abstraction being associated with tunneling exhibits the following characteristic features:<sup>1,2,34-36</sup> a kinetic isotope rate ratio  $k^{\rm H}/k^{\rm D} > 10$  at 25 °C, an activation energy difference  $E_{\rm a}^{\rm D}$ 

TABLE V: Characteristic Observations of Tunneling for the TNT + DBU Reaction

	AN <sup>a</sup>	$DCE^{b}$	
$k_{f}^{H}/k_{f}^{D}$ at 25 °C	$19.1 \pm 0.6$	$29.9 \pm 0.9$	>10
$\Delta H_{\mathbf{f}}^{+}(\mathbf{D}) - \Delta H_{\mathbf{f}}^{+}(\mathbf{H}),$ kcal mol <sup>-1</sup>	$2.3 \pm 0.2$	$2.1 \pm 0.2$	>1.35
$A^{\mathbf{D}}/A^{\mathbf{H}}$	$2.5~\pm~0.3$	$2.0~\pm~0.2$	>1.4
<sup>a</sup> Acetonitrile <sup>b</sup> 1 2-	Dichloroetha	ne.	

 $-E_{a}^{H} > 1.35$  kcal mol<sup>-1</sup>, and a ratio of the Arrhenius preexponential factors of  $A^{\rm D}/A^{\rm H} > 1.4$ . These quantities should be all greater than those calculated on the basis that the zero-point energies of a C-H and a C-D stretching vibration are lost in the transition state. It is also known that tunneling leads to a curved Arrhenius plot at extremely low temperature.<sup>15</sup>

Caldin and Mateo's study<sup>15</sup> of the reaction between 4NPNM and TMG in some aprotic solvents is one of the most typical and detailed investigations for tunneling. They have found very interesting results of the variations of  $k^{\rm H}/k^{\rm D}$  with solvents at 25 °C: Unusually large kinetic isotope rate ratios  $(k^{\rm H}/k^{\rm D} = 40-50)$  were found in nonpolar solvents such as toluene, while in the more polar solvents such as acetonitrile the rate ratios were much smaller  $(k^{\rm H}/k^{\rm D} = 10-13)$ . These results were explained in terms of tunneling and it was suggested that the magnitude of the tunneling was dependent strongly on the polarity of solvent. Rogne et al.,<sup>11,19</sup> however, presented evidence that the deuteron-transfer reaction of 4NPNM- $d_2$  with TMG in toluene was complicated by isotopic exchange due to the hydrogen of undeuterated TMG and that  $k^{\rm H}/k^{\rm D}$  was considerably smaller than reported, probably only about 11. From these results they suggested that there was perhaps no significant effect of the polarity of solvent on the kinetic isotope rate ratio and tunneling. Kresge et al.<sup>37</sup> measured the rates of loss of tritium in this system using 4NPNM-1-t and also reported that the value of  $k^{\rm H}/k^{\rm D}$  $(=(k^{\rm H}/k^{\rm T})^{1/1.442})$  was about 14. However, on reinvestigating the deuteron-transfer reaction, Caldin et al.<sup>17</sup> found nearly the same high value of  $k^{\rm H}/k^{\rm D}$  as before, and also found that deuterated TMG gave the same value. Thus this problem is very complicated and debatable yet.

For the reaction of  $\text{TNT-}d_3$  with DBU in this paper, the complication that appeared in the above reaction must be excluded, because (1) the DBU molecule does not have exchangeable hydrogen, (2) the deliberately added  $D_2O$ does not affect appreciably both  $k_{\rm f}^{\rm D}$  and  $k_{\rm b}^{\rm D}$  (Figure 4), and (3) the very small amount of adventitious water  $(H_2O)$ in highly purified solvents does not make it unceratin to determine  $k_{\rm f}^{\rm H}$  as well as  $k_{\rm f}^{\rm D}$ . Therefore, the large kinetic isotope effects detected in this reaction are attributable to the tunneling phenomenon. The results obtained in our experiments are listed in Table V. As found in Table V,

<sup>(32)</sup> E. F. Caldin and O. Rogne, J. Chem. Soc., Faraday Trans. 1, 74, 2605 (1978).

<sup>(33)</sup> M. Sasaki, N. Takisawa, F. Amita, and J. Osugi, J. Am. Chem. Soc., 102, 7268 (1980). (34) R. P. Bell, Trans. Faraday Soc., 55, 1 (1959).

<sup>(35)</sup> L. Melander and W. H. Saunders, Jr., "Reaction Rates of Isotopic Molecules", 2nd ed, Wiley, New York, 1980. (36) R. P. Bell, "The Tunneling Effect in Chemistry", Chapman and

Hall, London, 1980.

<sup>(37)</sup> A. J. Kresge and M. F. Powell, J. Am. Chem. Soc., 103, 201 (1981).

 $k_{\rm f}^{\rm H}/k_{\rm f}^{\rm D}$  at 25 °C,  $\Delta H_{\rm f}^{*}({\rm D}) - \Delta H_{\rm f}^{*}({\rm H})$ , and  $A^{\rm D}/A^{\rm H}$  are all larger than the semiclassical limits as described above. These isotope effects actually contain not only primary but also secondary isotope effects caused by the influence of two deuterium atoms which are not transferred. However, since this type of secondary isotope effect usually gives a rate change of only about 10–15%, these values for the primary kinetic isotope effect in this reaction must still be larger than the semiclassical limits even after correction for the secondary effect. Consequently, it can be concluded that tunneling occurs in the proton-transfer reaction between TNT and DBU in both AN and DCE.

Not only do these results give supporting evidence for a significant tunneling contribution to the reaction but it seems probable that the transition state is linear and approximately symmetric on the assumption that all or most of the zero-point energies would be lost in this state.<sup>3,4</sup> In addition, the values of isotope effects in the reaction of TNT with DBU in AN are larger than those with TMG<sup>20</sup>  $(k^{\rm H}/k^{\rm D} = 17.3 \text{ at } 30 \,^{\circ}\text{C}$ , 18.5 at 25 °C, 19.2 at 20 °C, and  $\Delta H^*(\text{D}) - \Delta H^*(\text{H}) = 1.6 \text{ kcal mol}^{-1}$ ). This fact may support the idea that tunneling is increased by a bulky substance, because such material excludes solvent molecules from the reaction site and the motions of solvent molecules are unlikely to be coupled with those of the proton. The difference in  $\Delta S_f^*(\text{H})$  between DBU (-22 cal K<sup>-1</sup> mol<sup>-1</sup>) and TMG (-32 cal K<sup>-1</sup> mol<sup>-1</sup>)<sup>20</sup> also agrees with this concept.

We have calculated the tunneling correction factor Q to manifest the contribution of tunneling. The tunneling correction factor Q is defined as the ratio of the actual rate constant k to the semiclassical rate constant  $k_s$ :

$$Q = k/k_{\rm s} \tag{5}$$

Bell used a symmetrical parabolic barrier to give an expression for  $Q^{34}$ 

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

where  $\alpha = E/kT$ ,  $u = h\nu/kT$ , and  $\nu = (E/2m)^{1/2}/\pi b$ ; k is Boltzmann's constant, h Plank's constant, E the height of barrier, b the half-width of barrier at the base, m the mass of the particle transferred, and  $\nu$  the frequency of oscillation of a particle in parabolic potential well having the same curvature as the parabolic potential. In general, Q increases with increasing u and  $\alpha$ , but Q is insensitive to  $\alpha$  if u is not too large.<sup>35</sup> Thus Q increases with decreasing temperature. An increase of m decreases u and hence Q.

The tunneling correction at a given temperature depends on the term  $2E/b^2$  composed of the barrier dimensions and hence  $\nu$ . Assuming that the preexponential factor A is the same for H and D in the absence of tunneling, we obtain the isotope ratio of the tunneling correction  $Q^{\rm H}/Q^{\rm D}$  from eq 5:

$$Q^{\rm H}/Q^{\rm D} = (k^{\rm H}/k^{\rm D}) \exp[-(E^{\rm D} - E^{\rm H})/RT]$$
 (7)

TABLE VI:Tunneling and Barrier Parameters in theTNT + DBU Reaction

	AN <sup>a</sup>	$DCE^{b}$
$E_a^{H}$ , kcal mol <sup>-1</sup>	8.3 ± 0.2	5.8 ± 0.2
$E_a^{-D}$ kcal mol <sup>-1</sup>	$10.6 \pm 0.3$	$7.9 \pm 0.3$
$E^{\mathrm{H}}$ , kcal mol <sup>-1</sup>	$9.3 \pm 0.05$	$10.3 \pm 0.05$
$E^{\mathbf{D}}$ , kcal mol <sup>-1</sup>	$10.7 \pm 0.05$	$11.7 \pm 0.05$
$E_{a}^{H}/E^{H}$	0.89	0.56
2 <i>b</i> , A	$0.962 \pm 0.002$	$0.880 \pm 0.002$
$v_{\rm H},  {\rm cm}^{-1}$	970	1116
$Q^{\rm H}(25~^{\circ}{\rm C})$	$3.19 \pm 0.06$	$5.95 \pm 0.20$
$\tilde{Q}^{\mathbf{D}}(25 ^{\circ}\mathrm{C})$	$1.79 \pm 0.03$	$2.23 \pm 0.10$
$(k^{\rm H}/k^{\rm D})_{\rm calcd} (25 ^{\circ}{\rm C})$	18.8	28.6
$(k^{\rm H}/k^{\rm D})_{\rm Arrh} (25 ^{\circ}{\rm C})$	19.1	29.2

<sup>a</sup> Acetonitrile. <sup>b</sup> 1,2-Dichloroethane.  $E_a$ , activation energy; E, height of the barrier; 2b width of the barrier at base; v, wave number along the reaction path; Q tunneling correction factor.

On the basis of the reasonable restriction,  $E^{\rm D} - E^{\rm H} \leq 1.4$  kcal mol<sup>-1</sup>, we can estimate  $Q^{\rm H}/Q^{\rm D}$  to be larger than 1.7 in AN and 2.6 in DCE, using the experimentally determined  $k^{\rm H}/k^{\rm D}$  and eq 7.

We first assumed that only the proton or deuteron moved, so that  $m_{\rm H} = 1$  and  $m_{\rm D} = 2$  amu, and used the first four terms of eq 6. Calculations of Q were done by computer and in these calculations we used two assumptions: (1) the width 2b of the barrier at base was the same for H and D, and (2)  $E^{\rm D} - E^{\rm H} \leq 1.4$  kcal mol<sup>-1</sup>. The values of  $E^{\rm H}, E^{\rm D}$ , and of the width 2b of the barrier were adjusted by trial and error until we obtained the values of  $(k^{\rm H}/k^{\rm D})_{\rm calcd}$  which reproduced the experimental values of  $(k^{\rm H}/k^{\rm D})_{\rm Arrh}$  taken from the Arrhenius plots over the whole range of experimental temperature. These calculations fix the values of  $E^{\rm H}$  and  $E^{\rm D}$  within ±0.05 kcal mol<sup>-1</sup> and that of 2b within ±0.002 Å. The results are given in Table VI.

As seen in Table VI,  $Q^{H}$  at 25 °C both in AN and DCE is larger than unity which is expected in the case of no tunneling contribution. In addition, the value of  $v_{\rm H}$  in both solvents is significantly larger than the value  $(345 \text{ cm}^{-1})$ found for the reaction of 4NPNM with 1,8-bis(dimethyl)aminonaphthalene in t-BuOH which is not associated with tunneling effect.<sup>21</sup> The change of  $Q^{H}$  and  $Q^{D}$ with solvent can be explained well in terms of the relative magnitude of the barrier height  $(E^{\rm H}, E^{\rm D})$  and the barrier width (2b). It is reasonable that  $E^{H}$  decreases with increasing solvent polarity (AN,  $\epsilon = 37$ ; DCE,  $\epsilon = 10.4$ ;  $\epsilon$  is the dielectric constant). On the contrary,  $E_a^{H}$  is larger in AN than in DCE. This result can be understood on the basis of tunneling correction. The fact that Q values are larger in DCE than in AN results in the smaller ratio of  $E_a^{\text{H}}/E^{\text{H}}$  in DCE. That is, since the large contribution of tunneling lowers the activation energy enough below the barrier height,  $E_a^{H}$  can become smaller in DCE than in AN even if the barrier is higher in DCE.

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