and *p*-chlorotoluenes, *p*-methoxytoluene, ethylbenzene, and cumene were distilled prior to use. Chlorinated compounds that were not available commercially were prepared by using *tert*-butyl hypochlorite;[24] epoxides were prepared according to the procedure of Lewis.[25] The commercial bleach used was Chlorox, which was found by iodometric titration[26] to be 0.55 M in hypochlorite, 1.2 M chloride, 0.01 M chlorite, and 0.3 M chlorate. Chloride-free hypochlorite was prepared by distillation of commercial bleach at pH 6 under vacuum at 43 °C.

General Methods. Mass spectra were obtained on a Finnigan 3200 mass spectrometer coupled to a Finnigan 9500 gas chromatograph by a glass column (6 ft × $^{1}/_{8}$ in) containing 20% polypropylene glycol (PPG) on Chromosorb W. Reaction products were quantitated by GLC on a Perkin-Elmer Series 881 gas chromatograph equipped with dual flame-ionization detectors. The columns used for analysis were (a) 20% PPG on Chromosorb W (12 ft × $^{1}/_{8}$ in.), (b) 20% Carbowax 20 M on Chromosorb W (8 ft × $^{1}/_{8}$ in.), and (c) 20% silicon gum rubber, SE-30, on Chromosorb W (12 ft × $^{1}/_{8}$ in.). Most of the products were identified by comparing their GLC retention times and mass spectra with those of authentic samples. Yields were determined by using internal standards; at least three analyses were run on each sample, and only those that agreed within ±4% were averaged.

Reaction of Toluene. In a typical reaction, 10 mmol of toluene dissolved in 25 mL of methylene chloride was added to 100 mL (55 mmol) of commercial bleach, the pH of which had been adjusted to between 8 and 9 with concentrated HCl. Tetrabutylammonium hydrogen sulfate (2 mmol) was added and the mixture was stirred at room temperature under nitrogen until GLC indicated that over 90% of initial toluene had reacted (4 h). The layers were then separated and the organic layer was washed with cold water (2 times), dried ($MgSO_4$), and filtered, *o*-dichlorobenzene added as the internal standard, and the mixture diluted to a known volume with methylene chloride.

The amounts of products and unreacted toluene were determined by GLC on column a using a temperature program from 80 to 135 °C at 6 °/min. Products were eluted in 31 min in the order of *o*-chlorotoluene, *m*- and *p*-chlorotoluenes (elute together), benzaldehyde, benzyl chloride, benzal chloride, benzyl alcohol, and cresols. Benzoic acid was isolated from a scaled-up reaction mixture by using the usual extraction techniques and quantitated by weight following crystallization from aqueous ethanol.

Relative Reactivities of Arenes and Alkanes. These were determined by competitive techniques at 22 °C, the reaction taking place in vigorously shaken ampules sealed under N_2. With arenes as reactants, a reaction mixture consisting of 1 mmol of each of the two arenes, 0.5 mmol of *o*-chlorobenzene as an internal standard, 10 mmol of distilled aqueous hypochlorite (5 mL, pH 9), 25 mmol of sodium chloride, 0.4 mmol of tetrabutylammonium hydrogen sulfate, and 3 mL of CH_2Cl_2 was allowed to react until ca. 50% of the most reactive arene had reacted. Workup was performed as described earlier and the mixtures were analyzed with column c. The relative reactivities were calculated by eq 8

$$\frac{k_A}{k_B} = \frac{\log (A_i/A_f)}{\log (B_i/B_f)} \qquad (8)$$

where k_A/k_B is the relative reactivity of compound A to compound B and the subscripts i and f refer to the initial and final peak areas of the two arenes relative to the internal standard.

The relative reactivities of primary, secondary, and tertiary hydrogens were determined from the isomer distribution of chloroalkanes found after the reaction of *n*-butane and 2,3-dimethylbutane. In a typical experiment an excess (10 mmol) of the alkane in 3 mL of CH_2Cl_2 was shaken under N_2 in a sealed ampule for 1 h at 22 °C with a pH 8.5 aqueous solution (4 mL) containing 2 mmol of distilled sodium hypochlorite, 5 mmol of sodium chloride, and 0.1 mmol of tetrabutylammonium hydrogen sulfate. Products from the chlorination of *n*-butane and 2,3-dimethylbutane were analyzed with column c at 45 and 90 °C, respectively.

Reaction with Anisole. The procedure employed was similar to that used with toluene. Commercial bleach (50 mL, 28 mmol OCl^-) at pH 8–9 containing 2 mmol of tetrabutylammonium hydrogen sulfate was stirred for 2 h at room temperature under N_2 with a solution of 10 mmol of anisole in 25 mL of CH_2Cl_2. The reaction mixture was analyzed with column b at 135 °C.

Reaction with Alkenes. For the reaction of cyclohexene the procedure was similar to that used with anisole except that tetra-*n*-butylammonium hydroxide was used as the PTC and the reaction was allowed to proceed for 5 h. The reaction mixture was analyzed by GLC with column a and an inlet temperature of 100 °C to avoid decomposition of the chlorocyclohexenes. The monochlorides and epoxide eluted in 14 min at 85 °C, after which the temperature was programmed to 140 °C at 8 °C/min to elute the other products. In two separate experiments 10 mmol of *trans*- or *cis*-3-hexene in 3 mL of CH_2Cl_2 were reacted for 1 h at room temperature with 5 mL of commercial bleach (2.8 mmol OCl^-) adjusted to pH 9. The products were analyzed by using column a at 105 °C.

Registry No. Anisole, 100-66-3; cyclohexene, 110-83-8; *trans*-3-hexene, 13269-52-8; *cis*-3-hexene, 7642-09-3; *p*-methoxytoluene, 104-93-8; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; toluene, 108-88-3; *p*-chlorotoluene, 106-43-4; *m*-chlorotoluene, 108-41-8; ethylbenzene, 100-41-4; cumene, 98-82-8; deuterium, 7782-39-0; *n*-butane, 106-97-8; 2,3-dimethylbutane, 79-29-8; nitrobenzene, 98-95-3; benzene, 71-43-2; hypochlorite, 14380-61-1; dichlorine monoxide, 7791-21-1; monooxygenase, 9038-14-6.

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Pressure Effect on Tunneling of the Proton- and Deuteron-Transfer Reaction of 2,4,6-Trinitrotoluene with 1,8-Diazabicyclo[5.4.0]undec-7-ene in Acetonitrile

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Abstract: The reaction rates of the proton-/deuteron-transfer reaction of 2,4,6-trinitrotoluene with 1,8-diazabicyclo[5.4.0]-undec-7-ene in acetonitrile at the temperature range 10–40 °C and the pressure range 1–1000 bar have been obtained by means of a high-pressure stopped-flow method. With increasing pressure from 1 to 1000 bar, the rate ratio k^H/k^D at 25 °C changes from 19.1 to 16.9, the activation energy difference $E_a^D - E_a^H$ from 2.3 to 2.0 kcal mol^{-1}, and the ratio of Arrhenius preexponential factor A^D/A^H from 2.5 to 1.6, respectively. All these values signify that tunneling occurs even at high pressure. The analysis based on the parabolic potential results in the following: (1) The decrease of k^H/k^D is not due to the change of semiclassical rate ratio k_s^H/k_s^D but to the decrease of the ratio of tunneling factor Q^H/Q^D. (2) The height of potential barrier E and tunneling factor Q decrease and the activation energy E_a increases with pressure.

The correction of tunneling effect associated with the proton-transfer reaction, that is, the so-called proton tunneling has been theoretically elucidated since the 1930's. The first estimate of tunneling correction was that of Wigner[1] and his equation is still

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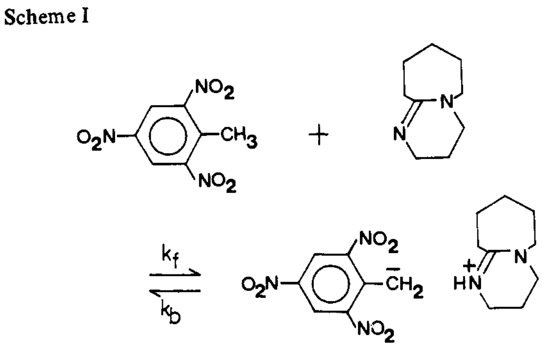
Scheme I



useful when the correction is small. With regard to larger tunneling correction, the first approach was made by Bell[2] who approximated the potential energy barrier by a symmetric and inverted parabola. His theory activated extensively experimental studies of tunneling in chemistry. One of the noteworthy experimental works was on the proton tunneling of (4-nitrophenyl)nitromethane (4NPNM) and tetramethylguanidine (TMG) reaction by Caldin and Mateo.[3] They found very interesting and anomalous results that the kinetic isotope rate ratio k^{H}/k^{D} varied with solvent at 25 °C from 10 to 50: The larger was the dielectric constant and the smaller was the rate ratio. The results suggested that tunneling occurred more easily in nonpolar solvents. Since then have appeared many experimental investigations,[4-6] and the above results are debatable yet.[7-9] Saunders et al. developed, though on the basis of the same potential, an alternative procedure in tunneling correction and applied it to the kinetic isotope effects in eliminations from 2-phenylethyl derivatives.[10]

The study of pressure effect on chemical reactions in solution are well recognized to give enormous and important information about the role of solvent in activation and the reaction dynamism.[11] Recently there have appeared several papers[12-16] of pressure effect on the kinetic isotope rate ratios and tunneling. Isaacs et al.[13] found that for the proton transfer between diphenyldiazomethane and benzoic acid not associated with tunneling the kinetic isotope rate ratio k^{H}/k^{D} was almost unchanged with pressure (4.5–4.7), while for the hydride transfer between leucocrystal violet and chloranil k^{H}/k^{D} decreased from 11 at 1 bar to 8 at 2 kbar. They thought that the increased effective mass of the transferred particle with pressure diminished the extent of tunneling and so proposed that the pressure dependence of k^{H}/k^{D} would become a criterion for the identification of tunneling. We reported previously[15] that the proton-/deuteron-transfer reactions of 4NPNM with 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 is almost unchanged in dichloromethane (10.7 ± 0.2).

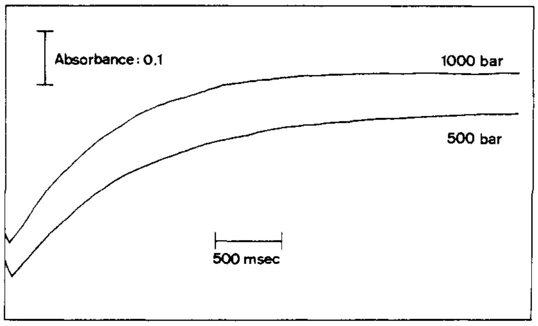


Figure 1. Typical stopped-flow traces of the TNT + DBU reaction in acetonitrile at 10 °C. The absorbance change was monitored at 520 nm: [TNT] = 2.0×10^{-5} M, [DBU] = 1.15×10^{-2} M at 1 bar.

Table I. Rate Constants for the Proton-Transfer Reaction k_f^{H} (M^{-1} s^{-1}) at Various Pressures and Temperatures

	T, °C			
p, bar	10	20	25	40
1	101 ± 2	171 ± 4	204 ± 4	427 ± 10
250	107 ± 2	188 ± 4	220 ± 4	479 ± 13
500	112 ± 2	192 ± 4	230 ± 4	500 ± 12
750	115 ± 2	196 ± 3	238 ± 5	565 ± 14
1000	118 ± 3	205 ± 4	267 ± 6	580 ± 10

Table II. Rate Constants for the Deuteron-Transfer Reaction k_f^{D} (M^{-1} s^{-1}) at Various Pressures and Temperatures

	T, °C			
p, bar	10	25	30	40
1	4.2 ± 0.1	10.7 ± 0.2	14.8 ± 0.2	27.2 ± 0.4
250	5.1 ± 0.1	11.9 ± 0.3		30.7 ± 0.5
500	5.4 ± 0.1	12.8 ± 0.3	18.2 ± 0.3	34.0 ± 0.6
750	5.6 ± 0.2	14.0 ± 0.2		39.7 ± 0.5
1000	6.1 ± 0.2	15.8 ± 0.2	22.1 ± 0.4	42.4 ± 0.5

Table III. Kinetic Isotope Rate Ratios k_f^{H}/k_f^{D} at Various Pressures and Temperatures

	T, °C		
p, bar	10	25	40
1	24.0 ± 0.8	19.1 ± 0.6	15.7 ± 0.5
250	21.0 ± 0.6	18.5 ± 0.5	15.6 ± 0.5
500	20.7 ± 0.5	18.0 ± 0.4	14.7 ± 0.4
750	20.5 ± 0.5	17.0 ± 0.3	14.2 ± 0.4
1000	19.3 ± 0.4	16.9 ± 0.3	13.7 ± 0.3
$\Delta V^{\ddagger}$(H), $cm^3\ mol^{-1}$	−5.7 ± 0.4	−9.0 ± 1.0	−13.0 ± 1.0
$\Delta V^{\ddagger}$(D), $cm^3\ mol^{-1}$	−11.3 ± 0.7	−12.1 ± 0.8	−14.4 ± 1.0

In this paper we have investigated the kinetic isotope rate ratios and the differences of activation parameters of the proton-/deuteron-transfer reaction of TNT with DBU in acetonitrile (Scheme I) at various temperatures and pressures to examine the following problems: (1) What does the decrease of k^{H}/k^{D} with pressure mainly depend on? (2) How does the "classical" activation volume change under the influence of tunneling? (3) How do the tunneling parameters vary with increasing pressure?

Experimental Section

Materials. 2,4,6-Trinitrotoluene (TNT), deuterated 2,4,6-trinitrotoluene (TNT-d_3), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were treated as described previously.[5,16] Acetonitrile (AN) used as solvent was dried with molecular sieves and then with calcium hydride until hydrogen gas was not evolved and finally distilled over phosphorus pentoxide.

Apparatus and Procedures. Absorption spectra were determined with 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. At the pressure interval of 250 up to 1000 bar, the

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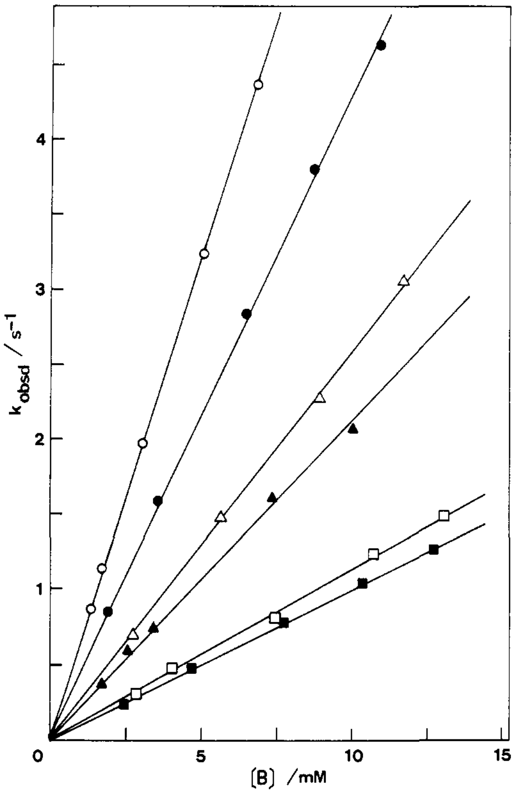

Figure 2. Dependence of k_{obsd} on DBU concentration of the TNT + DBU reaction in acetonitrile: 1 bar, 10 °C (■); 1000 bar, 10 °C (□); 1 bar, 25 °C (▲); 1000 bar, 25 °C (△); 1 bar, 40 °C (●); 1000 bar, 40 °C (○).

reaction rates were followed by means of our high-pressure stopped-flow apparatus.[17] Both at 1 bar and high pressure, the temperature range was from 10 to 40 °C and regulated within ±0.1 °C by circulating thermostated fluid.

Solutions were freshly prepared every day before use and following concentrations of solutions at 1 bar were used: TNT, TNT-d_3, 0.02–0.08 mM; DBU 1.5–15 mM. The apparent reaction rate was determined according to the same procedure as before.[5]

Results

In kinetic measurement the stopped-flow trace fits a first-order kinetic equation very well at each temperature and pressure when the base concentration is in large excess over the TNT or TNT-d_3 concentration (Figure 1). The plots of the observed first-order rate constant k_{obsd} against DBU concentration [B] are linear in agreement with eq 1 and 2 (Figures 2 and 3). Here, k_f^H, k_f^D,

$$k_{obsd} = k_f^H[B] + k_b^H \qquad (1)$$

$$k_{obsd} = k_f^D[B] + k_b^D \qquad (2)$$

k_b^H, and k_b^D are the forward and backward rate constants of the proton- and deuteron-transfer reactions.

The base concentration at each pressure is of molarity unit corrected for the compression of solvent.[18] The values of k_f^H, k_f^D, and k_f^H/k_f^D at each temperature and pressure are given in Tables I, II, and III, respectively. However, the value of k_b is too small to be reliable and is not recorded.

The activation volume $\Delta V^{\ddagger}$ at each temperature for the forward reaction was determined by

$$(\partial \ln k_f/\partial p)_T = -\Delta V^{\ddagger}/RT + \Delta n^{\ddagger}\kappa \qquad (3)$$

where, κ is the compressibility of solvent being calculated from literature,[18] and $\Delta n^{\ddagger}$ is the difference of the number of molecules between the initial and transition state ($\Delta n^{\ddagger} = -1$ for the forward reaction). The values of $\Delta V^{\ddagger}$(H) and $\Delta V^{\ddagger}$(D) for the proton- and deuteron-transfer reactions, respectively, are shown in Table III. From the temperature dependence of the second-order rate constants (k_f^H and k_f^D), the activation parameters at 1, 500, and 1000 bar were computed by a least-squares method (Table IV).

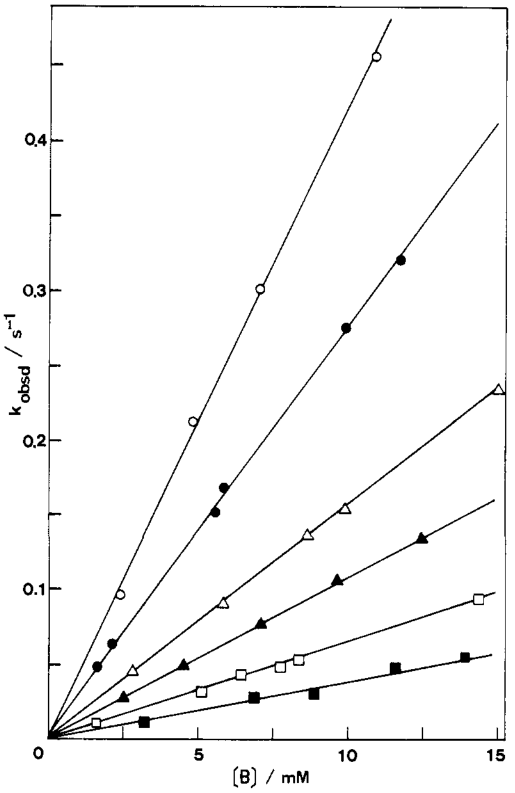

Figure 3. Dependence of k_{obsd} on DBU concentration of the TNT-d_3 + DBU reaction in acetonitrile: 1 bar, 10 °C (■); 1000 bar, 10 °C (□); 1 bar, 25 °C (▲); 1000 bar, 25 °C (△); 1 bar, 40 °C (●); 1000 bar, 40 °C (○).

Table IV. Activation Parameters of the Proton- and Deuteron-Transfer Reactions at Various Pressures[a]

	p, bar		
	1	500	1000
E_a^H, kcal mol^{-1}	8.3 ± 0.2	8.7 ± 0.2	9.3 ± 0.2
$\Delta H^{\ddagger}$(H), kcal mol^{-1}	7.7 ± 0.2	8.1 ± 0.2	8.7 ± 0.2
$\Delta S^{\ddagger}$(H), cal K^{-1} mol^{-1}	−22.2 ± 0.7	−20.3 ± 0.7	−18.0 ± 0.5
$\Delta G^{\ddagger}$(H), kcal mol^{-1}	14.3 ± 0.4	14.2 ± 0.4	14.1 ± 0.3
$\log A^H$	8.4 ± 0.1	8.7 ± 0.1	9.3 ± 0.1
E_a^D, kcal mol^{-1}	10.6 ± 0.3	10.8 ± 0.3	11.3 ± 0.2
$\Delta H^{\ddagger}$(D), kcal mol^{-1}	10.0 ± 0.3	10.2 ± 0.3	10.7 ± 0.2
$\Delta S^{\ddagger}$(D), cal K^{-1} mol^{-1}	−20.3 ± 0.8	−19.2 ± 0.7	−16.9 ± 0.6
$\Delta G^{\ddagger}$(D), kcal mol^{-1}	16.0 ± 0.5	15.9 ± 0.5	15.8 ± 0.4
$\log A^D$	8.8 ± 0.1	9.0 ± 0.1	9.5 ± 0.1
k_f^H/k_f^D	19.1 ± 0.6	18.0 ± 0.4	16.9 ± 0.3
$E_a^D - E_a^H$, kcal mol^{-1}	2.3 ± 0.5	2.1 ± 0.5	2.0 ± 0.4
A^D/A^H	2.5 ± 1.5	2.0 ± 1.4	1.6 ± 1.3

[a] At 25 °C. Uncertainty is calculated as standard deviation.

Discussion

Tunneling Phenomena. Tunneling on a proton-/deuteron-transfer reaction is revealed by the following characteristics:[4,19–21] a kinetic isotope rate ratio $k^H/k^D > 11$ at 25 °C, an activation energy difference $E_a^D - E_a^H > 1.4$ kcal mol^{-1}, and a ratio of the Arrhenius preexponential factors $A^D/A^H > 1.4$. Although these criteria provide a clear indication of tunneling, all of the char-

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Table V. Variation of Q^H/Q^D and k_s^H/k_s^D with Pressure[a]

	p, bar		
	1	500	1000
$(k^H/k^D)_{Arrh}$	19.1 ± 0.6	17.7 ± 0.4	16.5 ± 0.4
Q^H/Q^D	1.70 ± 0.23	1.51 ± 0.20	1.43 ± 0.31
k_s^H/k_s^D	11.3 ± 1.9	11.7 ± 1.8	11.5 ± 2.7

[a] At 25 °C.

acteristics are not always observed experimentally. Even the lower value of k^H/k^D is sometimes subjected to tunneling.[10]

The smaller the effective mass of the species in motion is the more favored tunneling will be. Also it will be favored for sharper curvature of the potential energy surface at the transition state. Therefore, we must consider two interactions at transition state; one is the interaction between proton donor and acceptor, and the other is the interaction between the transferred particle and solvent molecules. First, repulsive steric interactions between the donor and acceptor may steepen potential energy curves near the point of intersection and hence increase permeability. Second, if the particle being transferred is strongly coupled with solvent molecules on proceeding through the transition state, the probability of tunneling will be diminished because the effective mass of the proton and deuteron increases. This may explain why tunneling has taken place more often in gas phase or nonpolar media,[22] while it can not be observed so frequently in solution, especially in polar solvents. So if tunneling is evidenced in a reaction system even in polar solvent, that system will be very appropriate to study the influence of solvent coupling with the transferred proton. In the reaction between TNT and DBU in AN, TNT and DBU possess steric hindrance toward each other while AN is polar and must be coupled more or less with the transferred particle. Therefore, the present reaction serves as a good example for the study of tunneling in solution. As found in Table IV, k_f^H/k_f^D at 25 °C, $E_a^D - E_a^H$, and A^D/A^H at these pressures are all larger than the semiclassical limits as described above. Even after correction for the secondary isotope effect, which gives a rate change of only about 10% caused by two deuterium atoms not transferred, these values must still be larger than semiclassical limits. Therefore, these facts lead us to the conclusion that tunneling occurs in the proton-transfer reaction between TNT and DBU in AN not only at atmospheric pressure but at high pressure.

In addition, the value of kinetic isotope rate ratio (k^H/k^D = 19.1 at 1 bar and 25 °C) of the reaction of TNT with DBU in AN is larger than that of TNT + TMG (18.5)[23] or 4NPNM + DBU (13.3)[24] in the same solvent. This fact may support the idea that tunneling is increased by a bulky substance, because the motion of the transferring proton becomes difficult to be coupled with the solvent molecule.

Decrease of Tunneling at High Pressure. Table III shows that the kinetic isotope rate ratio k^H/k^D of the TNT + DBU reaction in AN decreases with increasing pressure, and the magnitude of decreasing k^H/k^D increases as temperature lowers. It is important to examine what the decrease of k^H/k^D with increasing pressure depends on. Generally, the tunneling factor Q is defined as the ratio of the actual rate constant k to the semiclassical one k_s:

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

Consequently, we can divide the overall isotope effect k^H/k^D into the tunnel correction Q^H/Q^D and the semiclassical isotope effect k_s^H/k_s^D.

$$k^H/k^D = (Q^H/Q^D)(k_s^H/k_s^D) \tag{5}$$

We must examine separately the pressure dependency of Q^H/Q^D and k_s^H/k_s^D. The actual rate constant k and the semiclassical rate constant k_s are represented by eq 6 and 7, respectively. In

$$k = A\exp(-E_a/RT) \tag{6}$$

$$k_s = A_s\exp(-E/RT) \tag{7}$$

these equations E_a and E are the apparent activation energy and classical barrier height, and A and A_s are the Arrhenius preexponential factors that would be found in the presence and absence of tunneling, respectively. From eq 4, 6, and 7 one obtains eq 8 and 9. By assuming a symmetrical parabolic potential barrier,[5]

$$E_a - E = RT^2(\partial \ln Q/\partial T), \tag{8}$$

$$\ln(A/A_s) = \ln Q + T(\partial \ln Q/\partial T) \tag{9}$$

the tunneling factor Q can be written in terms of u and α.

$$Q = 0.5u/\sin(0.5u) - \sum_{n=1}^{\infty}(-1)^n\exp[(u - 2n\pi)\alpha/u]/[(u - 2n\pi)/u] \tag{10}$$

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 barrier at the base, m the mass of the transferred particle, and ν the frequency of oscillation of a particle in a parabolic potential. In order to estimate k_s^H/k_s^D and Q^H/Q^D, we first approximate eq 10 by the first term, which is adequate when $u<2\pi$.

$$Q = 0.5u/\sin(0.5u) \tag{10$'$}$$

Further, assuming $A_s^H = A_s^D$, one gets eq 11 from eq 9 and 10′.[10]

$$\ln(A^H/A^D) = \ln[u^H\sin(0.5u^D)] + 0.5u^H\cot(0.5u^H) - \ln[u^D\sin(0.5u^H)] - 0.5u^D\cot(0.5u^D) \tag{11}$$

Determining u^H and u^D from eq 11 at each pressure, we can obtain the variation of Q^H/Q^D with pressure from eq 10′ and hence that k_s^H/k_s^D from eq 5. By use of the reasonable relation $u^D = u^H/2^{1/2}$, which is equivalent to assuming $m^H = 1$ and $m^D = 2$ amu and $E^{1/2}/b$ are the same for proton and deuteron,[10] u^H are varied until eq 11 reproduced the most probable value of ln (A^H/A^D) obtained experimentally at each pressure. The calculated results at 1, 500, and 1000 bar were shown in table V together with the most probable experimental values of $(k^H/k^D)_{Arrh}$. Q^H/Q^D decreases with increasing pressure while k_s^H/k_s^D does not change even at 1000 bar. Therefore, although A factors contain considerable experimental errors and the estimation of Q from eq 10′ is not so exact, it is surely concluded that the decrease of k^H/k^D with increasing pressure arises mainly not from k_s^H/k_s^D but from Q^H/Q^D. The result supports quantitatively the supposition[13-15] that the zero-point energies and vibrational frequencies of the reactant molecules would not be significantly affected by moderate pressures, and "normal" kinetic isotope effects would be independent of pressure while kinetic isotope effects deriving in part from tunneling would be pressure dependent.

Activation Volume Affected by Tunneling. The activation volume $\Delta V^{\ddagger}$ of chemical reaction in solution consists mainly of two major contributions; one due to the structural change of activation $\Delta V^{\ddagger}_{str}$, and the other due to the solvation change $\Delta V^{\ddagger}_{solv}$ on going from the initial to the transition state.[25] In the case of the bond-forming process, $\Delta V^{\ddagger}_{str}$ would be negative. When electronic charge is generated upon activation, $\Delta V^{\ddagger}_{solv}$ will also be negative. The activation process of proton-/deuteron-transfer reaction between TNT and DBU confirms the above case; in fact, our data result in the negative values of activation volume.

However, if the reaction is subjected to tunneling, it is not necessarily the case explained by the above consideration. The apparent volume of activation $\Delta V^{\ddagger}$ consists of the semiclassical activation volume $\Delta V^{\ddagger}_s$ and the term of "tunneling volume" $\Delta V^{\ddagger}_t$,

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_s + \Delta V^{\ddagger}_t \tag{12}$$

where

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$$\Delta V^{\ddagger}_{s} = -RT(\partial \ln k_s/\partial p)_T;\ \Delta V^{\ddagger}_{t} = -RT(\partial \ln Q/\partial p)_T \qquad (13)$$

Since k_s^H at each pressure can be obtained from k^H and Q^H and k_s^D can be obtained in the same way, $\Delta V^{\ddagger}_s$(H) and $\Delta V^{\ddagger}_s$(D) at 25 °C and 1 bar are evaluated: The results show $\Delta V^{\ddagger}_s(\mathrm{H}) = -16.4$ and $\Delta V^{\ddagger}_s(\mathrm{D}) = -15.5$ cm^3 mol^{-1}. These values of the semiclassical activation volume $\Delta V^{\ddagger}_s$ are similar to those of the proton- and deuteron-transfer reactions not affected by tunneling.[12] Ewald[26] estimated $\Delta V^{\ddagger}_{str}$ of the general hydrogen-transfer reaction on the basis of the formation of a bond between hydrogen and nitrogen, and $\Delta V^{\ddagger}_{str}$ would amount to about -12 cm^3 mol^{-1}. Hubbard et al.[27] calculated $\Delta V^{\ddagger}_{str}$ (-10 cm^3 mol^{-1}) of the 4NPNM + TMG reaction based on collinear approach of C, H, and N atoms until the CH- - -N hydrogen-bonding distance at the transition state. Now the magnitude of $\Delta V^{\ddagger}_s$ of the TNT + DBU reaction is slightly larger than these values of $\Delta V^{\ddagger}_{str}$. This fact that $\Delta V^{\ddagger}_{solv}$ is negative also supports our previous consideration: The proton-transfer reactions, though being subjected to tunneling, pass through a transition state in which solvent molecules are partly participated through electrostatic interaction.

As far as we treat $\Delta V^{\ddagger}_t$, the meaning of tunneling volume will be understood only as a indication of pressure effect on Q in usual way (eq 13). The tunneling volume $\Delta V^{\ddagger}_t$ at 25 °C and 1 bar is obtained from $\Delta V^{\ddagger}$ and $\Delta V^{\ddagger}_s$: $\Delta V^{\ddagger}_t(\mathrm{H}) = +7.4$ and $\Delta V^{\ddagger}_t(\mathrm{D}) = +3.4$ cm^3 mol^{-1}. Although $\Delta V^{\ddagger}_t$ is zero in the absence of tunneling, these values of the present reaction affected by tunneling are positive, and also $\Delta V^{\ddagger}_t$(H) is much larger than $\Delta V^{\ddagger}_t$(D).

Barrier Dimension at High Pressure. We have calculated the tunneling factor Q at high pressure to manifest more clearly the contribution of tunneling. There are two typical procedures to assess the tunneling effect and the barrier dimensions. One is the evaluation by Saunders, Jr., et al.[10] We used this method in the previous section in order to estimate k_s and Q at several pressures. The other is the procedure by Caldin and Mateo,[3] in which the first four terms in eq 10 are taken into account. It is assumed that the barrier width b is the same for H and D transfer, and $E^D - E^H \leq 1.4$ kcal mol^{-1}. Further, provided $A_s^H = A_s^D$, eq 14 is obtained from eq 5. We adjust the values of E^H, E^D, and b

$$k^H/k^D = (Q^H/Q^D)\exp[-(E^H - E^D)/(RT)] \qquad (14)$$

by trial and error until k^H/k^D from eq 10 and 14 reproduce the experimental values over the whole range of experimental temperature. We reported already the solvent effect on the same reaction[5] in which the tunneling correction was analyzed according to the latter calculation method. Since the purpose of the discussion in this section is to find the relative change of the potential barrier with external pressure, we try to analyze the data along the latter method.

We assumed $m^H = 1$ and $m^D = 2$ amu even at high pressure in eq 10, while the barrier dimensions (E and $2b$) were varied with pressure. This assumption means that change of solvent coupling with the moving proton influences the barrier dimensions without varing the mass of proton. We made a further assumption: $E^D - E^H = 1.4$ kcal mol^{-1} not only at 1 bar[5] but at high pressure because k_s^H/k_s^D did not depend on pressure. By the same procedure,[5] the values of E and $2b$ under pressure were adjusted in eq 10 and 14.[28] The results are given in Table VI.

Table VI. Tunneling and Barrier Parameters at High Pressure[a]

	p, bar		
	1	500	1000
E_a^H, kcal mol^{-1}	8.3 ± 0.2	8.7 ± 0.2	9.3 ± 0.2
E^H, kcal mol^{-1}	9.3 ± 0.3	9.0 ± 0.3	8.6 ± 0.3
$2b$, A	0.962 ± 0.020	0.982 ± 0.020	1.008 ± 0.030
$2E^H/b^2$	20.1	18.7	16.9
ν_H, cm^{-1}	970 ± 35	935 ± 34	890 ± 31
ν_D, cm^{-1}	734 ± 25	709 ± 24	678 ± 29
Q^H (25 °C)	3.19 ± 0.33	2.86 ± 0.26	2.53 ± 0.25
Q^D (25 °C)	1.79 ± 0.08	1.72 ± 0.07	1.63 ± 0.08
$(k^H/k^D)_{calcd}$ (25 °C)	18.8 ± 1.1	17.7 ± 1.0	16.5 ± 0.9
$(k^H/k^D)_{Arrh}$ (25 °C)	19.1 ± 0.6	17.7 ± 0.4	16.5 ± 0.4

[a] E_a, activation energy; E, height of the barrier; $2b$, width of the barrier at base; ν, wavenumber along the reaction path; Q, tunneling factor.

The curvature at the top of the barrier corresponds to a negative force constant, $-2E/b^2$, and its absolute value also gives a criterion of tunneling. The value of $2E/b^2$ in Table VI decreases with increasing pressure; that is to say, the top of the barrier becomes much rounder with increasing pressure. Furthermore, it is noteworthy that the height of the potential energy barrier E^H decreases and the activation energy E_a^H increases with pressure. The result can be considered as follows: Since pressure forces the solvent molecules to approach to the vicinity of reactive site and enhances electrostatic interactions, E^H is lowered, and hence Q^H decreases while E_a^H increases with pressure. As also found in Table VI, Q^H decreases more than 20% while Q^D decreases less than 10% with increasing pressure from 1 to 1000 bar. By taking the first term in eq 10 when $u < 2\pi$ and expanding cot $(0.5u)$, we can approximate the pressure dependence of Q as follows,

$$(\partial \ln Q/\partial p)_T = (u^2/12 + u^4/720 + ...)(\partial \ln u/\partial p)_T \qquad (15)$$

Then

$$(\partial \ln Q/\partial p)_T = \mathrm{f}(\nu)(\partial \ln u/\partial p)_T \qquad (16)$$

where $\mathrm{f}(\nu) = u^2/12 + u^4/720 + ...\ (>0)$. Since the value of $(\partial \ln \nu/\partial p)_T$ and hence of $(\partial \ln u/\partial p)_T$ is about the same for H and D, the large difference of $(\partial \ln Q/\partial p)_T$ for H and D depends mainly on that of $\mathrm{f}(\nu)$ and hence of ν. Additionally, it would be concluded from these results that the larger Q is the larger is the amount of variation of Q with pressure. The pressure dependence of the kinetic isotope rate ratio changes with temperature in such fashion that the larger k^H/k^D is the more significantly it changes with pressure.

Registry No. 2,4,6-Trinitrotoluene, 118-96-7; 1,8-diazabicyclo-[5.4.0]undec-7-ene, 6674-22-2; deuterium, 7782-39-0.

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(28) It is almost impossible to fix three or more parameters so as to give the best fit to the observed rate constant ratio involving experimental uncertainty over the temperature range of the experiment. Only by taking the most probable value of $(k^H/k^D)_{Arrh}$, these calculations can fix the values of E within ±0.05 kcal mol^{-1} and those of $2b$ within ±0.005 Å.