Solvent, Pressure, and Deuterium Isotope Effects on Proton Tunnelling. The Reaction between 2,4,6-Trinitrotoluene and 1,8-Diazabicyclo[5.4.0]undec-7-ene in Aprotic Solvents

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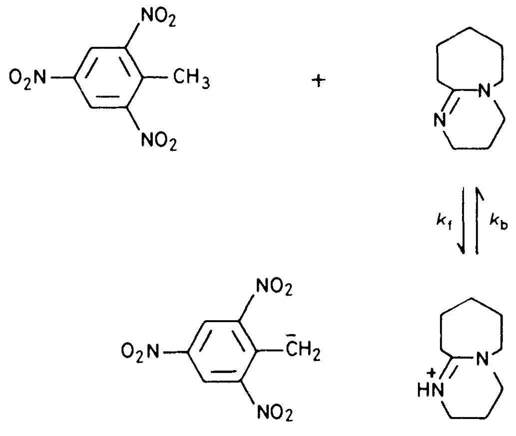
Proton tunnelling has been examined for the reaction between 2,4,6-trinitrotoluene and 1,8-diazabicyclo-[5.4.0]undec-7-ene in several aprotic solvents (acetonitrile, benzonitrile, 1,2-dichloroethane, and dichloromethane) in view of the solvent and pressure effects on the rate ratio k^H/k^D. The reaction rates have been measured in the range 1—1 000 bar at 25 °C by a high-pressure stopped-flow method. The reaction rate ratios k^H/k^D in all these solvents are greater than the semiclassical limit of the primary kinetic isotope effect and show a significant tunnelling contribution. Further, with increasing pressure from 1 to 1 000 bar, the ratio k^H/k^D at 25 °C diminishes from 19.1 to 16.9 in acetonitrile, from 15.9 to 15.0 in benzonitrile, and from 29.9 to 22.5 in 1,2-dichloroethane, respectively. However, the increases of the effective mass of the transferred particle with pressure are calculated to be about the same in all these solvents.

Proton transfer is one of the most fundamental and important of reactions, and kinetic isotope effects have been used as a means of investigating reaction mechanisms. The primary kinetic isotope effect of the proton-transfer reaction in solution has been studied in detail from both theoretical and phenomenological viewpoints,[1-3] especially from semiclassical theory.[4-8] A recent topic of interest is the quantum-mechanical tunnelling phenomenon associated with proton transfer.[9] The enormously large value of the kinetic isotope rate ratio has been almost satisfactorily explained on the basis of a tunnelling correction.[10-12] Proton transfer from a carbon acid such as 4-nitrophenylnitromethane (4NPNM) or 2,4,6-trinitrotoluene (TNT) to a nitrogen base such as guanidine is known to be subjected to tunnelling.[13-18] We have studied proton tunnelling between TNT and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[19]

The activation volume is well known to be a more easily interpretable quantity than the entropy or energy of activation.[20] If we can obtain information on the effective mass or volume change accompanying proton transfer, the behaviour of the solvent in the tunnelling phenomenon would be made clearer. There are several studies of pressure effects on slow proton- and hydride-transfer reactions in the absence [21] and presence [22,23] of tunnelling. Recent advances in high-pressure relaxation and stopped-flow methods have made it possible to investigate fast proton-transfer reactions.[24-26] By using a laser-photochemical relaxation technique, Caldin and his co-workers have examined the pressure effect on the fast proton transfer from 4NPNM to tetramethylguanidine (TMG), which is subject to remarkable tunnelling.[24] By means of a high-pressure stopped-flow method, we studied some proton- and deuteron-transfer reactions at high pressure [25,26] and reported that the kinetic isotope rate ratio of 4NPNM + TMG decreased with pressure and its decreasing rate depended on the solvent.[25] For the TNT + DBU reaction at 1 bar, it is known that the kinetic isotope rate ratio is remarkable even in a polar solvent like acetonitrile, perhaps because the size of the reactant molecules tends to favour the degree of tunelling.[19]

In this paper we deal with the kinetics of the proton–deuteron-transfer reaction of TNT ([$^2H_3$]TNT) with DBU in acetonitrile (AN), benzonitrile (PhCN), 1,2-dichloroethane (DCE), and dichloromethane (DCM) at high pressure and 25 °C for the following purposes. (1) We check the occurrence of tunnelling even when there exists a relatively strong interaction between moving particles and solvent molecules. (2) We confirm our view that not only the polarity but also the steric hindrance of the solvent molecule in the vicinity of the reaction site must affect tunnelling. (3) We examine how the variation of effective mass of transferred particles with pressure reflects that of kinetic isotope rate ratio.



Scheme.

Results

The reaction of [$^2H_3$]TNT, as well as TNT, with DBU over a range of concentrations gives a purple solution. The absorption maxima of the product as a result of proton–deuteron-transfer from the methyl group of TNT to DBU are *ca.* 380, 535, and 645 nm in PhCN, and almost identical with those observed in other solvents. The rate of the proton–deuteron-transfer reaction of TNT ([$^2H_3$]TNT) with DBU was determined by monitoring the change of absorbance with time at 520 nm in AN, 535 nm in PhCN, 532 nm in DCE, and 530 nm in DCM. The increase in the absorbance obeyed first-order kinetics when the base (DBU) was in large excess over TNT or [$^2H_3$]TNT. The observed first-order rate constant $k_{obs.}$ was determined by least-squares fitting to the Guggenheim plot. At each pressure the plots of $k_{obs.}$ against DBU concentration [B] are linear (Figures 1 and 2), in agreement with equations (1) and (2). In these equations, k_f^H, k_f^D, k_b^H, and k_b^D denote

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

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

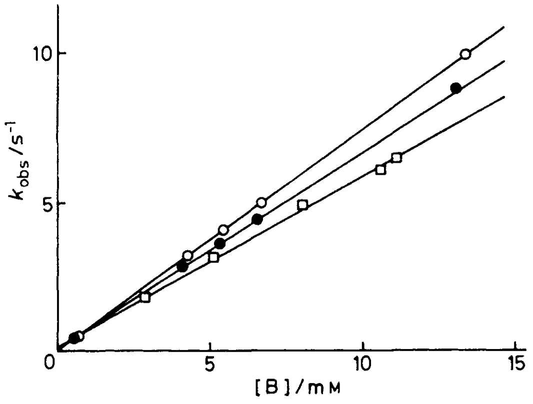


Figure 1. Dependence of $k_{obs.}$ on DBU concentration in the TNT + DBU reaction in 1,2-dichloroethane at 25 °C: □, 1 bar; ●, 500 bar; ○, 1 000 bar

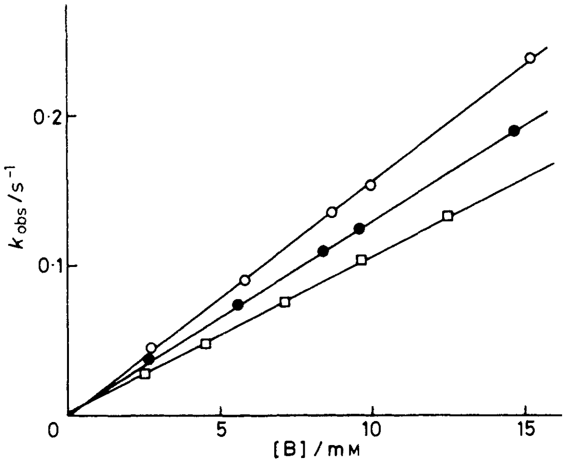


Figure 2. Dependence of $k_{obs.}$ on DBU concentration in the [$^2H_3$]-TNT + DBU reaction in acetonitrile at 25 °C: □, 1 bar; ●, 500 bar; ○, 1 000 bar

the forward and backward rate constants of the proton- and deuteron-transfer. In Figures 1 and 2, since the molar concentration unit was convenient to compare the rate constants at various conditions, we corrected the base concentration for compression by using data of Newitt *et al.*[27] for DCE and DCM, of Srinivasan *et al.*[28] for AN, and of Hilczer[29] for PhCN.* The values of k_f^H, k_f^D, and k_f^H/k_f^D at 25 °C are shown in Tables 1—3, respectively. However, the values of k_b^H and k_b^D in all these solvents and k_f^D in DCM are too small to be reliable and are not recorded. The activation volume $\Delta V^\ddagger$ for the forward reaction (Table 4) was determined by the linear plots of ln$k$ against p based on the transition state theory [equation (3), where κ is the compressibility of solvent, $\Delta n^\ddagger$ the difference

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

in the number of molecules between the initial and the transition state, T the absolute temperature, and R the gas constant]. $\Delta n^\ddagger$ is -1 for the present forward reaction and the values of κ at 25 °C were calculated from the literature.[27-29]

Table 1. Rate constants for the proton-transfer reaction at high pressure and 25 °C (k_f^H/l mol^{-1} s^{-1})

p/bar	CH_3CN [a]	C_6H_5CN	$C_2H_4Cl_2$	CH_2Cl_2 [a]
1	204 ± 4	310 ± 6	565 ± 10	41.8 ± 0.8
250	220 ± 4	320 ± 5	614 ± 10	46.9 ± 1.0
500	230 ± 4	328 ± 7	670 ± 11	49.2 ± 0.8
750	238 ± 5	334 ± 9	708 ± 12	52.4 ± 1.2
1 000	267 ± 6	338 ± 10	746 ± 14	60.3 ± 1.0

[a] Ref. 26.

Table 2. Rate constants for the deuteron-transfer reaction at high pressure and 25 °C (k^D/l mol^{-1} s^{-1})

p/bar	CH_3CN	C_6H_5CN	$C_2H_4Cl_2$
1	10.7 ± 0.2	19.5 ± 0.4	18.9 ± 0.4
250	11.9 ± 0.3	20.1 ± 0.4	22.1 ± 0.4
500	12.8 ± 0.3	20.8 ± 0.4	25.3 ± 0.4
750	14.0 ± 0.2	21.9 ± 0.4	27.9 ± 0.4
1 000	15.8 ± 0.2	22.5 ± 0.4	33.2 ± 0.4

Table 3. Kinetic isotope rate ratios k_f^H/k_f^D at high pressure and 25 °C

p/bar	CH_3CN (36.0) [a]	C_6H_5CN (25.2) [a]	$C_2H_4Cl_2$ (10.4) [a]
1	19.1 ± 0.6	15.9 ± 0.6	29.9 ± 1.2
250	18.5 ± 0.8	15.9 ± 0.6	27.8 ± 1.0
500	18.0 ± 0.7	15.7 ± 0.6	26.5 ± 0.8
750	17.0 ± 0.6	15.3 ± 0.7	25.4 ± 0.9
1 000	16.9 ± 0.6	15.0 ± 0.7	22.5 ± 0.6

[a] Dielectric constant.

Discussion

Tunnelling.—The kinetic isotope rate ratio of proton-deuteron transfer k^H/k^D should be at most 11 at 25 °C if we consider the reaction semiclassically. That is, this ' normal ' maximum is derived on the basis that the zero-point energy difference of a C–H and C–D vibration is lost in the transition state. An extraordinarily large value of k^H/k^D is usually understood to originate from quantum-mechanical tunnelling.[30] As found in Table 3, k_f^H/k_f^D at each pressure is larger than the semiclassical limit as described above. Even after correction for the secondary isotope effect which gives a rate change of only *ca.* 10% caused by the two deuterium atoms not transferred, these values must still be larger than semiclassical limits.† These facts suggest that tunnelling occurs in these aprotic solvents not only at atmospheric pressure but also at high pressure.

Activation Volumes.—The largely negative volumes of activation $\Delta V^\ddagger$(H) and $\Delta V^\ddagger$(D) indicate that the transition

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* In order only to determine the volume of activation, a correction for compression is unnecessary, because this correction term is cancelled out by the second term in equation (3); $(\partial \ln k_{f(\text{uncorrected})}/\partial p)_T = -\Delta V^\ddagger/RT$.

† For the reaction of [$^2H_3$]TNT with DBU, complications from isotope exchange due to the hydrogen of the base or by adventitious water in aprotic solvents must be excluded, because (1) the DBU molecule does not have an exchangeable hydrogen, (2) the deliberately added D_2O does not appreciably affect both k_f^D and k_b^D,[19] and (3) the very small amount of adventitious water (H_2O) in highly purified solvents does not make it difficult to determine k_f^H as well as k_f^D.

Table 4. Volumetric data, dielectric constants, and $(\partial q/\partial p)_T$ at 25 °C and 1 bar

Solvent	$\Delta V^\ddagger(\mathrm{H})$/ cm^3 mol^{-1}	$\Delta V^\ddagger(\mathrm{D})$/ cm^3 mol^{-1}	ε [a]	$10^5(\partial q/\partial p)_T$/ bar^{-1} [b]
C_6H_5CN	-7.4 ± 0.5	-8.0 ± 0.3	25.2	0.16
CH_3CN	-9.0 ± 1.0 [c]	-12.1 ± 0.8	36.0	0.23
$C_2H_4Cl_2$	-10.0 ± 0.8	-15.6 ± 0.9	10.4	0.99
CH_2Cl_2	-10.8 ± 1.0 [c]		8.9	1.15

[a] Dielectric constant. [b] Calculated from refs. 28 and 32. [c] Ref. 26.

state is solvated more strongly than the initial one. When proton transfer is subjected to tunnelling, the apparent activation volume in equation (3) does not represent entirely the volume change from reactants to transition state which has the maximum free energy along the reaction co-ordinate. For the 4NPNM + TMG reaction in which tunnelling was observed, Hubbard *et al.*[24] reported that $\Delta V^\ddagger$ was about equal for any solvent of low dielectric constant ($\varepsilon < 6$), and suggested that $\Delta V^\ddagger$ represented the structural volume contraction of the reacting acid–base pair alone without appreciable reorganization of the solvent molecules in the transition state.

We will consider the activation volume from a slightly different view. The rate constant k is expressed in terms of the classical rate constant k_s that is not associated with tunnelling and the tunnelling factor Q [equation (4)]. Differentiating the

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

logarithm of equation (4), we obtain the volumetric relation

$$\Delta V^\ddagger = \Delta V^\ddagger_s + \Delta V^\ddagger_t \tag{5}$$

(5) where equation (6) holds. The semiclassical activation

$$\Delta V^\ddagger_t = -RT(\partial \ln Q/\partial p)_T \tag{6}$$

volume $\Delta V^\ddagger_s$ consists of two major contributions, one due to structural change upon activation $\Delta V^\ddagger_{(str)}$ and the other due to the solvation change $\Delta V^\ddagger_{(solv)}$. The latter will include contributions from the electrostatic interaction $\Delta V^\ddagger_{(es)}$ and also from any specific interaction $\Delta V^\ddagger_{(spec)}$. Further, when we

$$\Delta V^\ddagger_s = \Delta V^\ddagger_{(str)} + \Delta V^\ddagger_{(es)} + \Delta V^\ddagger_{(spec)} \tag{7}$$

consider the continuum medium of dielectric constant ε, Kirkwood's model[31] gives equation (8) for the electrostatic

$$\Delta V^\ddagger_{(es)} = -A(\partial q/\partial p)_T \tag{8}$$

contribution, where $q = (\varepsilon - 1)/(2\varepsilon + 1)$, and A depends on the dipole moments and radii of the initial and transition states [$A = N_0\Sigma(\mu^2/a^3)$]. $\Delta V^\ddagger_{(str)}$ for general hydrogen-transfer forming a N–H bond is estimated to be *ca.* -12 cm^3 mol^{-1}.[32] Hubbard *et al.*[24] calculated $\Delta V^\ddagger_{(str)}$ to be *ca.* -10 cm^3 mol^{-1} for the 4NPNM + TMG system. The observed activation volumes $\Delta V^\ddagger(\mathrm{H})$, $\Delta V^\ddagger(\mathrm{D})$, and $(\partial q/\partial p)_T$[28,33] are given in Table 4. $\Delta V^\ddagger_s$ for an ionogenic reaction like proton transfer is negative and its magnitude is usually larger in less polar solvents of larger values of $(\partial q/\partial p)_T$. Since $\Delta V^\ddagger_{(str)}$ which is negative is reasonably taken as independent of the solvent, and any change of specific interaction from solvent to solvent is not recognized, the variation of $\Delta V^\ddagger_s$ with solvent may arise almost from the change of $\Delta V^\ddagger_{(es)}$. Thus the change of $\Delta V^\ddagger$ with solvent $\delta\Delta V^\ddagger$ may be represented by equation (9).

$$\delta\Delta V^\ddagger = \delta\Delta V^\ddagger_{(es)} + \delta\Delta V^\ddagger_t \tag{9}$$

The rough parallelism shown by the values of $\Delta V^\ddagger(\mathrm{H})$ or $\Delta V^\ddagger(\mathrm{D})$ in Table 4 and $(\partial q/\partial p)_T$ suggests that $\delta\Delta V^\ddagger$ is likely to reflect mainly the variation of $\Delta V^\ddagger_{(es)}$, though that of $\Delta V^\ddagger_t$ remains unsolved.

In this paper we do not consider $\Delta V^\ddagger_t$ itself but the change of effective mass of the proton transferred with pressure as described in the next section.

The variation of $\Delta V^\ddagger$ with solvent is also in accord with that of $\Delta S^\ddagger$ both for proton and deuteron transfer. A parallel change in $\Delta V^\ddagger$ and $\Delta S^\ddagger$ is often observed in other reactions in solution, and such a trend indicates coupling of the solvent molecules at the transition state.[34] In addition, the magnitude of $\Delta V^\ddagger(\mathrm{H})$ for DBU is smaller than that for TMG both in AN and DCM (-12.8 and -19.0 cm^3 mol^{-1}, respectively),[26] which suggests that the nonplanar seven-membered ring of DBU may hinder solvation in the vicinity of the reaction centre. The increase of $\Delta S^\ddagger(\mathrm{H})$ from -31.4 and -20.8 cal K^{-1} mol^{-1} for TMG[17] to -22.2 and -15.0 cal K^{-1} mol^{-1} for DBU in AN and PhCN, respectively, is consistent with an increase of $\Delta V^\ddagger(\mathrm{H})$.

Decrease of Kinetic Isotope Rate Ratio at High Pressure.— It is useful to know the pressure effect on the kinetic isotope rate ratio in solution because solvent participation in the reactive site is perturbed by the pressure.

Isaacs *et al.*[23] investigated the hydride-transfer reaction between Leuco-crystal Violet and chloranil which might have a significant tunnelling contribution, and proton transfer between benzoic acid and diazodiphenylmethane which had a normal kinetic isotope effect. The isotope rate ratio $k^{\mathrm{H}}/k^{\mathrm{D}}$ of the latter reaction was almost invariant with pressure ($k^{\mathrm{H}}/k^{\mathrm{D}}$ 4.5—4.7), while the rate ratio of the former decreased from 11 at 1 bar to 8 at 2 kbar. On the other hand, Palmer and Kelm[21] found that $k^{\mathrm{H}}/k^{\mathrm{D}}$ of the reaction between 2,6-di-t-butylphenol and 1,1-diphenyl-2-picrylhydrazyl (DPPH), though $k^{\mathrm{H}}/k^{\mathrm{D}}$ had a value as large as 18 at 1 bar, did not vary with pressure. We reported previously[25] that the proton–deuteron-transfer reactions of 4NPNM + TMG were accelerated at high pressure and $k^{\mathrm{H}}/k^{\mathrm{D}}$ reduced from 11.9 at 1 bar to 9.3 at 1 000 bar in toluene while it is almost unchanged in dichloromethane (10.7 ± 0.2).

As shown in Table 3, the kinetic isotope rate ratios of the TNT + DBU reaction decreased with increasing pressure in the solvents available and the decreasing rate of $k^{\mathrm{H}}_{\mathrm{f}}/k^{\mathrm{D}}_{\mathrm{f}}$ increased in the order PhCN < AN < DCE. These results also support our consideration that even in the proton-transfer reaction associated with tunnelling, solvent molecules are concerned partly with the transition state. Further, the fact that $k^{\mathrm{H}}_{\mathrm{f}}/k^{\mathrm{D}}_{\mathrm{f}}$ and its decreasing rate with pressure are not entirely related to solvent polarity suggests that tunnelling is also affected by the steric hindrance of the solvent molecule proximate to the reaction site. The steric effect of reactant molecules was pointed out previously[19] by comparing the TNT + DBU system with 4NPNM + TMG.

Isaacs *et al.*[23] pointed out that the reason why pressure reduced the degree of tunnelling might be that its effect was to force the solvent molecules into closer proximity with the reaction centre resulting in an increase in the effective mass of the moving proton. Thus the interaction of solute with solvent will be more affected by pressure in solvent of the lower solvating power; the increase of effective mass under pressure must be different from solvent to solvent.

We have calculated the increase of effective mass of proton under pressure in three solvents by assuming that the barrier dimensions (E and $2b$) at 1 bar[19] were invariant with pressure and the effective masses for proton- and deuteron-transfer differed by one atomic unit. We can express the semiclassical rate constant k_s by equation (10) in which E is the potential

Table 5. Relative variations of kinetic isotope rate ratio k^{H}/k^{D} and effective mass m^{H} with pressure

Solvent	p/bar	$(k^{H}/k^{D})_p/(k^{H}/k^{D})_1$	m_p^{H}/m_1^{H}
CH_3CN	1	1.00	1.00
	500	0.92 ± 0.02	1.05 ± 0.01
	1 000	0.88 ± 0.02	1.10 ± 0.01
C_6H_5CN	1	1.00	1.00
	500	0.98 ± 0.02	1.05 ± 0.01
	1 000	0.94 ± 0.02	1.10 ± 0.01
C_2H_4Cl	1	1.00	1.00
	500	0.89 ± 0.03	1.05 ± 0.01
	1 000	0.75 ± 0.04	1.11 ± 0.01

$$k_s = A_s \exp(-E/RT) \qquad (10)$$

barrier height for the reaction, and the tunnelling factor Q by

$$Q = 0.5u/\sin(0.5u) - \sum_{n=1}^{3} (-1)^n \exp[(u - 2n\pi)\alpha/u]/[(u - 2n\pi)/u] \qquad (11)$$

equation (11) using a parabolic potential and where $\alpha = E/\mathbf{k}T$, $u = h\nu/\mathbf{k}T$, and $\nu = \sqrt{(E/2m)}/\pi b$; $\mathbf{k}$ is Boltzmann's constant, h Planck's constant, E the height of barrier, b the half width of the barrier at base, m the mass of the transferred particle, ν the frequency of oscillation of a particle in parabolic potential, and Q the tunnelling factor.[13] The pre-exponential factor A_s is assumed to be the same for proton- and deuteron-transfer, and the kinetic isotope rate ratio can be written by equation (12).

$$k^{H}/k^{D} = (Q^{H}/Q^{D}) \exp[-(E^{H} - E^{D})/RT] \qquad (12)$$

We determined m^{H} ($m^{D} = m^{H} + 1$) by equations (11) and (12) so as to reproduce the experimental value of k_f^{H}/k_f^{D} at each pressure. The results showed that these increases in all these solvents were much the same, *i.e.*, in each solvent m^{H} increased by *ca.* 10% with increasing pressure from 1 to 1 000 bar (Table 5). It is remarkable that the increase of effective mass with pressure does not depend on solvent properties, while the kinetic isotope rate ratio and its pressure dependence change significantly with solvent. That is to say, even in the solvent which seems weakly coupled with the moving proton, the pressure does not promote the degree of coupling as expected from the greater pressure effect on k_f^{H}/k_f^{D}. The changing degree of k_f^{H}/k_f^{D} does not necessarily reflect the increasing degree of the effective mass which is brought about by forcing the solvent molecules into the proximity of the moving proton. Under a moderate pressure of a few kilobars, the main effect of pressure will be to reduce the free volume of solvent, and thus to increase the number of solvent molecules close enough to the reaction centre. So the change of effective mass may not appreciably depend on solvent polarity.

Experimental

Materials.—2,4,6-Trinitrotoluene (TNT), deuteriated 2,4,6-trinitrotoluene ([$^2H_3$]TNT), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were treated as described previously.[19] 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. Benzonitrile (PhCN) was purified by the molecular sieves (type 5A), dried with phosphorus pentaoxide, and then distilled several times. 1,2-Dichloroethane (DCE) and dichloromethane (DCM) were dried with calcium hydride and then distilled.

Apparatus and Procedures.—Absorption spectra were determined with a Shimadzu UV-200S spectrophotometer. Kinetic measurements at 1 bar were carried out by a Union Giken RA-401 stopped-flow apparatus. In all measurements at 1 bar the temperature was regulated to within ± 0.1 °C by circulating thermostatted water. At pressure intervals of 250 bar up to 1 000 bar, the reaction rates were followed by means of our high-pressure stopped-flow apparatus.[35] The temperature was kept at 25.0 ± 0.2 °C by circulating thermostatted fluid around the high-pressure vessels.

Solutions were freshly prepared each day before use and the following concentrations of solutions at 1 bar were used: TNT, [$^2H_3$]TNT, 0.02—0.08mM; DBU, 1.5—15mM in AN, 1.3—14mM in PhCN, 1—20mM in DCE, and 1.5—18mM in DCM.

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