Kinetics, Isotope Effects, and Mechanism of the Reaction of 1-Nitro-1-(4-nitrophenyl)alkanes with DBU in Acetonitrile

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The kinetics of the reaction of $O_2NC_6H_4C(L)(R)NO_2$ (R = Me, Et, Pr^i, NNPE, NNPP, or MNNPP, respectively; L = H, D) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile (MeCN) are reported. The nature of the product indicates that substantial dissociation into free ions occurs. The usefulness of Benesi–Hildebrand relationship for distinguishing between ion pairs and ions of the product is discussed in detail.

The reaction shows low activation enthalpy value $\Delta H^\ddagger$ = 15.4, 17.8, and 19.9 kJ mol^{-1} and large negative entropies of activation $\Delta S^\ddagger$ = −131, −134, and −147 J mol^{-1} K^{-1} for NNPE, NNPP, and MNNPP respectively.

The kinetic isotope effects k_H/k_D (12.5, 12.4, and 12.3) are large, showing no variation, the more sterically hindered the substrate. The values of the isotope effects exerted on the activation parameters indicate the contribution of a tunnelling effect Q_H/Q_D = 1.35 at 25 °C.

The influence of water on the kinetics is also examined and discussed with respect to reliability of kinetic measurements of such reactions systems.

The reactions of *C*-acids with cyclic bases have been examined kinetically.[1–4] The evaluation of factors influencing the mechanism of reaction and the primary deuterium kinetic isotope effects were the main purpose of these studies. In our previous studies[5–8] we found that, even in polar solvents, it is possible to observe large kinetic deuterium isotope effects and a significant contribution from proton-tunnelling. We observed k_H/k_D = 10.7, 20.0, and 20.9 for the reaction between cyano(4-nitrophenyl)phenylmethane (CNPPM) with 1,1′,3,3′-tetramethylguanidine (TMG)[6] and the more hindered bases tetramethyl-2-phenylguanidine (TMPhG)[5] and 1,8-bis-(dimethylamino)naphthalene (DMAN)[8] all in acetonitrile.

Moderate values of kinetic isotope effects were found for the reaction of 4-nitrobenzyl cyanide (NBC) with TMG.[8] These indicate the predominant influence of steric factors of the bases used. However comparing the reaction between CNPPM and TMPhG[5] with that between NBC and TMG[8] both in MeCN, it is evident that despite the greater crowding in the former reaction and comparable values of ΔpK_a, the reactions have similar rates and enthalpies of activation, which suggests an 'additional' acceleration by tunnelling of the transferred proton of the former reaction system. The rate constants and enthalpies of activation were almost equal for both systems[5,8] in reactions involving protons and substantially different for the deuteron-transfer reactions.

The data obtained showed no appreciable tunnelling effects and the dramatic decrease in the observed kinetic isotope effects (k_H/k_D) for the less sterically hindered reaction between NBC and TMG compared with that between CNPPM and TMPhG (both carried out in MeCN).[5,8]

The situation seems to be clear enough, taking into account the reaction of CNPPM with DMAN;[6] the difference in the rate constants is evidently due to steric factors, but enthalpies of activation are the same for the reactions of the *C*-acid for TMPhG and DMAN ($\Delta H^\ddagger$ = 26.2[5] and 26.0[8] kJ mol^{-1}), respectively. The steric demands are thus reflected in the different Arrhenius pre-exponential factors ($A = 2.1 \times 10^8$ and 8.5×10^5 dm^3 mol^{-1} s^{-1}, respectively).

Although the kinetic isotope effects and tunnelling corrections are attributed entirely to steric hindrance, though it is not quite certain whether steric hindrance of both the *C*-acid and the base make the same contribution to the overall steric effect of the proton-transfer reaction. Therefore, the purpose of the present paper is to show the influence of different types of steric hindrance brought by treating *C*-acids of varying structure with the same strong base (DBU) on the kinetic isotope effect.

The nature of the reaction product and the equilibrium constants of the proton-transfer reactions were commonly determined by carrying out of a series of absorbance measurements at constant *C*-acid concentration and varying base concentration.[1–3,5,9,10]

Taking into account the Benesi–Hildebrand[11] relationship, the plot of [AH]/OD against 1/[B]/([AH] = concentration of *C*-acid, [B] = concentration of base, OD = optical density), should be a straight line of intercept $1/\varepsilon_{IP}$ and slope $1/K\varepsilon_{IP}$ (ε = molar extinction coefficient, K = equilibrium constant) in the case of ion pairs. The assumption that the product consists of separate ions leads to a straight line for the plot of [AH]/OD against OD/[B].[9]

In our previous papers we found that the equation derived from the assumption of the ion-pair product is valid.[1–9,12] However, we also found that the reaction between CNPPM and DMAN in acetonitrile solvent shows detectable dissociation of the ion-pair product. In this case neither of the two equations is valid.[8] Therefore it was only possible to make an approximate estimate of the equilibrium constant K and the molar extinction coefficient ε for this system of reaction.

For most proton-transfer reactions between nitroalkanes and amines, carried out in aprotic solvents including acetonitrile, the Benesi–Hildebrand relationship is valid which indicates that the product is in the form of ion pairs.[1–9,12] This opinion has been confirmed even for low concentrations of nitroalkanes and this aroused our suspicions regarding the nature of the product and hence the correctness of further manipulation of the kinetic data and equilibrium measurements. This promoted us to examine and discuss the usefulness and reliability of Benesi–Hildebrand method in these systems.

The proton-transfer reactions are commonly carried out in reaction systems containing low, but definite, amounts of water. The traces of water originate from the solvent and also the reacting base. The amount of water in carefully dried solvent and base seems to be large enough to influence the reaction mechanism. Some aspects of this have been already discussed,[6,13–15] however the problem is far from resolved. In view of

Table 1. N.m.r. spectroscopic data of nitroalkanes.

Nitroalkane	δ_H(90 MHz; $CDCl_3$; internal $SiMe_4$)[a]
1-Nitro-1-(4-nitrophenyl)ethane (NNPE)	1.95 (3 H, d, CH_3) 5.73 (1 H, q, J 6.95 Hz, $CHNO_2$) 7.65 (2 H, m, *ortho* protons) 8.28 (2 H, m, *meta* protons)
1-Nitro-1-(4-nitrophenyl)propane (NNPP)	1.02 (3 H, t, CH_3) 1.90–2.82 (2 H, m, CH_2) 5.49 (1 H, m, $CHNO_2$) 7.66 (2 H, m, *ortho* protons) 8.27 (2 H, m, *meta* protons)
2-Methyl-1-nitro-1-(4-nitrophenyl)propane (MNNPP)	0.78 (3 H, d, CH_3) 1.56 (3 H, d, CH_3) 2.56–2.98 (1 H, m, CH) 5.18 (1 H, d, J 10.94 Hz, $CHNO_2$) 7.71 (2 H, m, *ortho* protons) 8.28 (2 H, m, *meta* protons)

[a] The ^1H n.m.r. spectra were recorded on a JEOL FX 90 Q spectrometer.

Table 2. Mass spectra[a] and melting points of NNPE, NNPP, and MNNPP.

	M.p./°C	m/z (rel. intensity)
NNPE	68–69	151 (9.6), 150 (100.0), 120 (10.3), 104 (40.9), 103 (30.5), 92 (27.8), 91 (23.0), 78 (25.2), 77 (23.8), 76 (6.3), 63 (10.0), 51 (17.7), 50 (12.5), 39 (11.6), 31 (21.3)
NNPP	69–70	165 (9.2), 164 (100.0), 137 (8.0), 136 (93.5), 118 (16.6), 117 (25.6), 115 (18.3), 106 (22.6), 103 (7.5), 91 (21.8), 90 (20.1), 89 (10.8), 78 (23.8), 77 (16.2), 63 (10.8), 51 (13.3), 50 (7.8), 47 (30.8), 46 (8.9), 42 (14.2), 40 (15.5), 32 (24.4), 31 (37.4), 28 (19.6), 27 (14.4)
MNNPP	75–76	179 (11.8), 178 (100.0), 150 (15.2), 136 (69.0), 132 (41.0), 117 (52.6), 116 (17.6), 115 (41.6), 106 (35.2), 103 (11.5), 91 (31.7), 90 (25.1), 89 (19.0), 78 (45.3), 77 (22.2), 65 (12.1), 63 (22.2), 55 (22.5), 51 (21.6), 50 (12.7), 41 (19.6), 39 (34.3), 31 (60.6), 29 (17.9), 28 (15.0), 27 (20.8)

[a] The mass spectra were measured with JEOL D-100.

this we wish to report further results obtained concerning the influence of water on the kinetics and kinetic isotope effects of the proton transfer reactions.

Experimental

Pure 1-nitro-1-(*p*-nitrophenyl)alkanes were prepared by a modified Emmons and Pagano method,[16] by the oxidation of the appropriate oxime of *p*-nitrophenyl alkyl ketones with trifluoroperacetic acid.

Trifluoroperacetic acid was prepared from hydrogen peroxide (90%; 0.1 mol), trifluoroacetic anhydride (0.11 mol), and acetonitrile (25 cm^3). This was added dropwise over 1 h to a well stirred mixture of the appropriate oxime (0.02 mol), Na_2HPO_4 (0.24 mol), urea (0.02 mol) and dry acetonitrile (20 cm^3). The mixture was heated under gentle reflux throughout the addition. The heating was continued for 15 min after which time the addition was complete. The progress of the oxidation was monitored by thin layer chromatography. The reaction mixture was then cooled and water (300 cm^3) was added. The resulting mixture was extracted with three portions of methylene chloride (3 × 50 cm^3). The combined extracts were washed with two portions of water (2 × 50 cm^3) and then dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was obtained in 90% yield. This was crystallized from ethanol to give white–yellow needles of the appropriate 1-nitro-1-(*p*-nitrophenyl) alkanes.

The ^1H n.m.r. spectra of the substituted nitroalkanes are given in Table 1.

The pattern of resonances due to ring protons approximates to an AA′XX′ spectrum; the coupling constants (assumed positive) are $J_{2,3} = J_{5,6} = 8.49$ Hz, $J_{2,5} = J_{3,6} = 0.40$ Hz, $J_{3,5} + J_{2,6} = 4.44$ Hz.

Mass spectroscopic data and m.p.s are given in Table 2.

Oximes of p-*Nitrophenyl Alkyl Ketones.*—A mixture of the appropriate ketone (5 g), hydroxylamine hydrochloride (5 g) methanol (50 cm^3) and pyridine (5 cm^3) was heated under reflux for 30 min. The addition of water precipitated the oximes quantitatively. The oximes were then recrystallized from cyclohexane. The melting points of oximes are 172–173, 143–145, and 159–160 °C for R = Me, Et, and Pr^i, respectively.

p-*Nitroacetophenone.*—This was commercial product purchased from Aldrich.

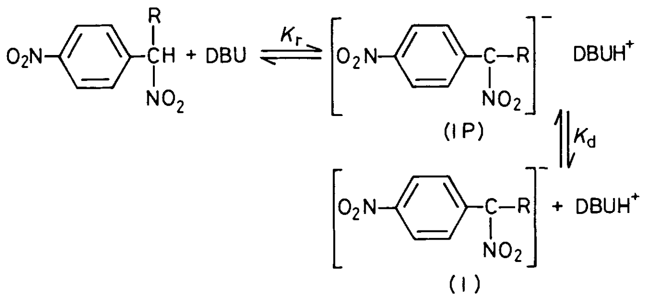
p-*Nitropropiophenone.*—This was prepared according to the method of Puterbaugh.[17] Crystals were obtained, m.p. 85–86 °C (from ethanol then cyclohexane).

p-*Nitroisobutyrophenone.*—This was prepared by oxidation of 2-methyl-1-(p-nitrophenyl)propan-1-ol with chromic acid at 60 °C. M.p. 49–50 °C (from methanol) δ($CDCl_3$; internal $SiMe_4$; 60 MHz) 1.2 (6 H, d, CH_3), 3.6 (1 H, septet, CH), and 8.0–8.4 (4 H, m, ring protons).

2-*Methyl*-1-(4-*nitrophenyl*)*propan*-1-*ol.*—This was obtained according to the Ford–Moore method[18] originally applied to the preparation of 1-(p-nitrophenyl)ethanol. The resulting mixture of *ortho* and *para* isomers was fractionally distilled through a short Vigreaux column, under reduced pressure.

The fraction collected at 183–195 °C and 6 mmHg contained almost pure *p*-isomer. This was purified by column chromatography through silica and eluting with diethyl ether–hexane (1:6). M.p. 46–48 °C. δ($CDCl_3$; internal $SiMe_4$; 60 MHz) 0.8 (3 H, d, CH_3), 1.0 (3 H, d, CH_3), 1.6–2.2 (1 H, m, Me_2CH), 3.4 (1 H, s, OH), 4.5 (1 H, d, C*H*OH, 7.4 (2 H, m, *ortho* protons), and 8.1 (2 H, m, *meta* protons).

2-*Methyl*-1-*phenylpropan*-1-*ol.*—This was obtained by reduction of isobutyrophenone (0.3 mol) with $NaBH_4$ (1.35 mol) in 75% methanol (1 dm^3). After the addition of isobutyrophenone the reaction mixture was heated under reflux for 15 min, and then dilute HCl (1:1; 200 cm^3) was added. The methanol was evaporated under reduced pressure and a white precipitate appeared. This was filtered off and washed with diethyl ether. The filtrate was extracted with three portions of ether (50 cm^3). The combined extracts were washed with water and dried over (Na_2SO_4). After the ether had been evaporated, the crude product (43 g, 94%), free from starting material, was obtained. This product was used for next step of the synthesis without further purification.



Scheme.

Acetonitrile.—The commercial product purchased from BDH was purified by the O'Donnell method[14] with a final distillation over P_2O_5.[5] Distillation and storage was maintained under positive pressure of argon.

1,8-Diazabicyclo[5.4.0]*undec-7-ene* (DBU).—The commercial product purchased from Aldrich was dried over potassium hydroxide pellets and then fractionally distilled under reduced pressure. The middle fraction was collected and used. The base was protected against moisture and CO_2 with argon.

Equilibrium and Kinetic Measurements.—The optical-density measurements were made on Specord M-40 spectrophotometer fitted with a constant-temperature bath to control the temperature of the cell block to within 0.1 °C. The solvent was always freshly distilled and the stock solutions of both normal and deuteriated *C*-acids and DBU were freshly prepared.

The pseudo-first-order kinetics were performed using 2×10^{-5} mol dm^{-3} concentration of the *C*-acid and a varying concentration of DBU (1.01×10^{-3}–5.05×10^{-3}, 0.944×10^{-3}–4.72×10^{-3}, and 2.0×10^{-2}–1.0×10^{-1} mol dm^{-3} for NNPE, NNPP, and MNNPP respectively), DBU was always in at least a 45-fold excess.

The kinetic measurements for both normal and deuteriated *C*-acids were completed using a stopped-flow spectrophotometer. From the kinetic curves the pseudo-first-order rate constants k_{obs} were calculated using Guggenheim plots. The observed rate constants were a function of base concentration according to following function where k_f is the rate of the forward reaction, c_B is the concentration of the base used.

$$k_{obs} = k_f c_B$$

The second-order rate constants were calculated slopes of plots of the pseudo-first-order rate constants k_{obs} *versus* base concentration. The second-order rate constants were obtained by a linear least-squares calculation. The activation parameters were evaluated from these by means of the method of least-squares fit to the transition state theory equation.

The equilibrium measurements of the reactions of NNPE and NNPP with DBU were carried out with equimolar additions of L-ascorbic acid to prevent slow, but visible oxidation of their anions with time. Degassing and subsequent saturation of the solvent with argon was not satisfactory. The kinetic runs carried out in a stopped flow spectrophotometer were performed without L-ascorbic acid, since the oxidation of the anion product was slow compared with proton/deuteron transfer. A blank test performed with an equimolar amount of L-ascorbic acid showed no difference in ordinary runs, assuring us that no influence due to oxidation on the kinetic runs occurred.

Conductivity measurements were carried out using a 'Tesla' BM 484 conductivity bridge operating at 1 592 Hz with a conventional, calibrated cell with platinum electrodes. The cell constant was 0.6116, determined with 10^{-2} mol dm^{-3} aqueous potassium chloride in the normal way. The cell was sealed to exclude atmospheric moisture and gases. The temperature was maintained at 25 °C.

Results and Discussion

The reaction of 1-nitro-1-(4-nitrophenyl)alkanes (NNPE, NNPP, MNNPP) with DBU base in MeCN gives the coloured product of λ_{max} 500 nm. The reaction is a proton transfer as indicated by disappearance of the ^{1}H n.m.r. peak at δ *ca.* 5.5, characteristic for methine protons. The reaction mechanism is given in the Scheme.

The ion-pair product (IP) in the high-polarity solvent MeCN dissociates to free ions (I). In previous papers[1,2,5,9] the nature of the product was defined spectrophotometrically from equilibrium measurements using the Benesi–Hildebrand relationship.[11] The equilibrium constant K_r is given by

$$\underset{\text{acid}}{AH} + \underset{\text{base}}{B} \overset{K_r}{\rightleftharpoons} \underset{\substack{\text{ion pair}\\(\text{IP})}}{A^-\,BH^+} \overset{K_d}{\rightleftharpoons} \underset{\substack{\text{free ions}\\(\text{I})}}{A^- + BH^+} \qquad (1)$$

equation (2), when $c_B \gg c_{AH}$

$$K_r = \frac{[\text{IP}]}{(c_{AH} - [\text{IP}])c_B} \qquad (2)$$

then

$$\frac{c_{AH}}{\text{OD}} = \frac{1}{\varepsilon} + \frac{1}{K_r\varepsilon} \cdot \frac{1}{c_B} \qquad (3)$$

where OD is the optical density and ε is the molar extinction coefficient of the product.

If the product is an ion pair, a plot of c_{AH}/OD *versus* $1/c_B$ will be a straight line of intercept $1/\varepsilon$; and slope $1/K_r\varepsilon$. A similar treatment for ion products leads to equation (4)

$$\frac{c_{AH}}{\text{OD}} = \frac{1}{\varepsilon} + \frac{1}{K\varepsilon^2}\frac{\text{OD}}{c_B} \qquad (4)$$

where $K = K_r K_d$.

If the product consists of separate ions then equation (4) is fulfilled and a plot of the Benesi–Hildebrand[11] relation (3) should be curved.

A review of literature show that most authors are convinced of the negligible dissociation of the ion-pair product[1,2,5,8,9,10,12] of the reaction between nitroalkanes and amines in acetonitrile. This opinion was deduced from the better linearity of the graph of c_{AH}/OD *vs.* $1/c_B$ compared with c_{AH}/OD *vs.* OD/c_B obtained for the assumption of ion pairs and ions, respectively.

Taking into account that several salts in the concentration range 1×10^{-5}–1×10^{-4} mol dm^{-3} dissociate fairly well in MeCN,[19,20] the product of nitroalkanes and amines, which consists of large ions of delocalized charge, seems to be dissociated in MeCN much more than is stated for these ordinary salts (Me_4NBr, Me_4NCl,[19] $LiNO_2$, Et_4NHSO_4.[20]) Therefore we performed conductivity measurements of the reaction of 2-methyl-1-nitro-1-(4-nitrophenyl)propane (MNNPP) and 1-nitro-1-(4-nitrophenyl)methane (NNPM) with DBU and TMG in MeCN, in order to verify previous spectrophotometric results.[1,2,5,8–10,12] We chose these two *C*-acids because of their high resistance to oxidation of their anions.

Taking into account equation (1) the following equilibria can be derived:

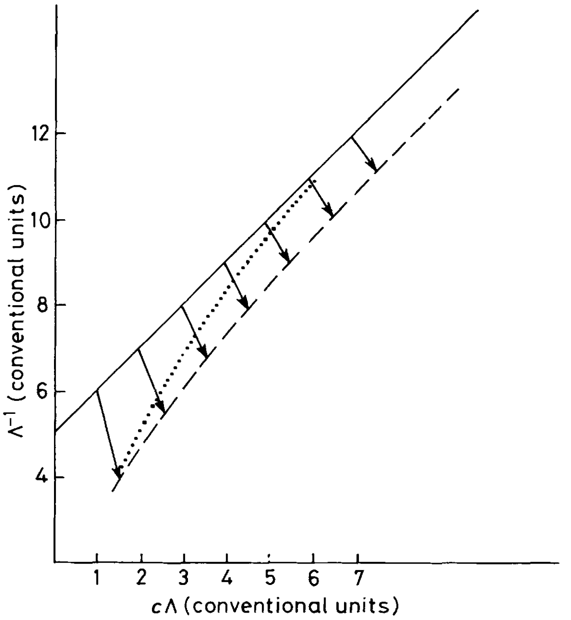


Figure 1. The calculated Kraus–Bray plots demonstrating the deviations caused by conductivity of ionic contaminant of the system: (——), the regular KB plot not perturbed; (— — —), KB plot perturbed by constant conductivity value of the contaminant. The regular KB plot is shifted by 1 000 κ_0 in the direction of $c\Lambda$, where κ_0 = conductivity caused by contaminant = 5×10^{-3} conv. units; (. . . .), the perturbed KB plot in the case of a conductivity decrease of the contaminant along with increase in $c\Lambda$ (the linear decrease of κ_0 with increased $c\Lambda$ of the graph is assumed).

$$K_r = \frac{[\mathrm{IP}]}{[\mathrm{AH}][\mathrm{B}]} \tag{5}$$

$$K_d = \frac{[\mathrm{I}]^2}{[\mathrm{IP}]}, \text{ where } [\mathrm{I}] = [\mathrm{A}^-] = [\mathrm{BH}^+] \tag{6}$$

Hence

$$K = K_r K_d = \frac{[\mathrm{I}]^2}{[\mathrm{AH}][\mathrm{B}]} \tag{7}$$

so

$$K = \frac{[\mathrm{I}]^2}{\{c_{\mathrm{AH}} - [\mathrm{I}] - [\mathrm{IP}]\}\{c_{\mathrm{B}} - [\mathrm{I}] - [\mathrm{IP}]\}} \tag{8}$$

When $c_B \gg c_{AH}$ then the equation (8) can be written

$$K = \frac{[\mathrm{I}]^2}{\{c_{\mathrm{AH}} - [\mathrm{I}] - [\mathrm{I}]^2/K_d\}c_{\mathrm{B}}} \tag{9}$$

Equation (9) can be used to derive the relationship (10) similar to Kraus–Bray relation:

$$1/\Lambda = 1/\Lambda_0 + \left(\frac{1}{K_r K_d c_B} + \frac{1}{K_d}\right) c\Lambda/\Lambda_0^2 \tag{10}$$

where Λ is the equivalent conductivity and Λ_0 is the equivalent conductivity at infinite dilution.

The effective equilibrium constant K_{ef} can be deduced from the Kraus–Bray relation. When $K_r c_B \gg 1$ then $K_{ef} = K_d$, and approaches $K_r K_d c_B$ when $K_r c_B \ll 1$.

$$\frac{1}{K_{ef}} = \frac{1}{K_d K_r c_B} + \frac{1}{K_d} \tag{11}$$

From equation (11) the K_d and K_r values can be estimated using relation $1/K_e$ *vs.* $1/c_B$. Since in our case the K_{ef} values are sensitive to impurities in the reactants we used the inequalities (12) and (13) derived from equation (11) to estimate the lower

$$K_d > K_{ef} \tag{12}$$

$$K_r K_r c_B > K_{ef} \tag{13}$$

limit of K_d. The small amounts of impurities which probably have the same cation as the electrolyte under investigation, enhance the conductance, and increase the slope of the Kraus–Bray plot. Therefore the K_{ef} values obtained from the Kraus–Bray formalism [plot of $1/\Lambda$ *vs.* $c\Lambda$ – (Figure 1)] constructed from uncorrected conductance values are low and represent the lower limit of the true value. The K_{ef} values are large so Shedlovsky[21] treatment should be applied. However we found that our K_{ef} values obtained by the Kraus–Bray method differ by only *ca.* 20% from those calculated using the Shedlovsky relation. Since our consideration requires only approximate and lower-limit K_d values, the exact values were not necessary.

In Table 3 are given the conductivity parameters for the products of reaction of 1-nitro-1-(4-nitrophenyl)alkanes with amidines in MeCN at 298.15 K. The dissociation constants K_{ef} of the product of the reaction between 1-nitro-1-(4-nitrophenyl)-alkanes with amidines (TMG, DBU) in MeCN at 298.15 K are presented in Table 4.

The K_{ef} values presented in Table 4 were computed from the relation $1/\Lambda$ *vs.* $c\Lambda$ [equation (10)] using the values given in Table 3(*a*)–(*c*). As we have already mentioned, these values determine the lower limit of the dissociation constants of the ion pairs. Of particular interest was the kinetic region of c_{AH} [(1–5) $\times 10^{-5}$ mol dm^{-3}]. Taking into account the K_{ef} values collected in Table 4 we find that in the kinetic region of the substrate concentration, the products of reaction undergo at least 97% dissociation, for free ions. In view of the fact that the K_{ef} values for the reaction of MNNPP with DBU increase with increased concentration of DBU, we propose that the degree of dissociation of the ion pairs is also equal to 97%, which still is rather underestimated. The dependence of K_{ef} on DBU concentration shows that this value corresponds to $K_r K_d c_B$ rather than K_d, then by virtue of relation (11) the values of K_d and K_r can be roughly calculated. Their values depend on the amount of impurities present in the system, but despite this we estimated the dissociation constant K_d of the ion-pair product of MNNPP$^-$, DBUH$^+$ to be larger than 1×10^{-2} mol dm^{-3}.

The calculated values of $K_r K_d$ oscillate between 1.4×10^{-2} and 3.3×10^{-2} what is in good agreement with the value of 1.96×10^{-2} obtained by spectrophotometric method using equation (4).

Likewise, a number of conductivity experiments were carried out for less stable products of the NNPE, and NNPP reaction with DBU. These show that their equivalent conductivity is very similar to the values found for the reaction of NNPM and MNNPP with amidines. However these reactions of NNPE and NNPP were not examined in detail owing to the high susceptibility to oxidation of their ionic products.

Spectrophotometric Examination of the Equilibria of the Reaction of C-acids with DBU.—The spectrophotometric examination of the equilibria of the reaction between *C*-acids and DBU were carried out at constant *C*-acids concentration and varying DBU concentration. The concentration of the base was

Table 3. Conductivity values of the products of the reaction between nitro-(4-nitrophenyl)alkanes with amidines (TMG, DBU) in MeCN at 298.15 K.

System	c_{AH}/ 10^{-3} mol dm^{-3}	Λ/ cm^2 mol^{-1} Ω^{-1}
NNPM–TMG[a]	0.2	211.5
$c_{TMG} = 4.15 \times 10^{-2}$ mol dm^{-3}	0.4	175.5
	0.6	165.0
	0.8	155.3
	1.0	147.5
	1.2	142.9
	1.4	137.7
	1.6	134.7
	1.8	131.3
	2.0	128.4
NNPM–DBU[b]	0.4286	137.0
$c_{DBU} = 3.23 \times 10^{-2}$ mol dm^{-3}	0.800	126.7
	1.125	118.4
	1.412	115.1
MNNPP–DBU[c]	0.4286	97.1
$c_{DBU} = 3.23 \times 10^{-2}$ mol dm^{-3}	0.8571	77.9
	1.286	67.6
	1.714	61.2
	2.143	55.8
	2.571	52.0
$c_{DBU} = 6.24 \times 10^{-2}$ mol dm^{-3}	0.4138	110.5
	0.8276	91.2
	1.241	81.0
	1.655	74.1
	2.069	68.5
	2.485	65.2
$c_{DBU} = 9.05 \times 10^{-2}$ mol dm^{-3}	0.4	117.4
	0.8	98.4
	1.2	88.2
	1.6	81.5
	2.0	76.0
	2.4	72.4
$c_{DBU} = 0.141$ mol dm^{-3}	0.375	126.7
	0.750	106.4
	1.125	96.5
	1.500	90.2
	1.875	84.9
	2.250	81.4

κ_0 = [a] 1.018. [b] 0.830. [c] 0.830, 0.967, 1.086, 1.234.

always in large excess compared with the *C*-acid, enabling the use of equations (3) and (4) for the calculation of the equilibrium constant of the ion pairs or free ions. Since the anions of NNPE and NNPP were susceptible to oxidation, which could not be eliminated by evacuating the oxygen from the system, the equilibrium measurements were carried out in the presence of L-ascorbic acid. The anion of the reaction of MNNPP with DBU was stable enough to enable direct spectrophotometric measurements to be made without any precautions.

The *C*-acids NNPE, NNPP ($c_{AH} = 2 \times 10^{-5}$ mol dm^{-3}) react with DBU ($c_B = 7.1 \times 10^{-4}$–1.04×10^{-2} mol dm^{-3}) to give only small changes in the absorbance values (less than 3%) showing the 97% conversion that renders both equations (3) and (4) unreliable as indicators of the nature of the product. A significant difference took place with MNNPP where equation (4) fits better, indicating free ions, in accordance with conductivity measurements (see the correlation coefficients in Table 5).

In Table 6 are given the values of equilibrium constants K_rK_d together with the equilibrium constants K_{BH} calculated from the Benesi–Hildebrand equation (3), in which the false assumption that the product is an ion pair was taken, in order to compare them with the values of the equilibrium constants formerly reported.[1] The equilibrium constants calculated from equation (3) are very large $(K_{BH})_{25}$ = 48 000 ± 8 000, 35 000 ± 3 000, and 900 ± 40 for NNPE, NNPP, and MNNPP, respectively (Table 6). These last values have no physical sense but they are quoted here for consistency with previous common practice. The true values of the equilibrium constants K_rK_d for these systems of reactions were 0.92, 0.67, and 0.0196 for NNPE, NNPP and MNNPP, respectively (Table 6).

Taking into account the minimum value of $K_d = 1.87 \times 10^{-3}$ mol dm^{-3} for MNNPP (Table 4) the appropriate maximum value of K_r can be estimated using equation (14). As we can see

$$K_r(\text{max.}) = \frac{K_rK_d}{K_d(\text{min.})} = 10.5 \text{ dm}^3 \text{ mol}^{-1} \qquad (14)$$

this is much smaller than the effective equilibrium constant K_{BH} = 900 dm^3 mol^{-1} (Table 5) calculated from equation (3). The difference between K_{BH} and the real K_r equilibrium constants is a manifestation of the dissociating properties of MeCN. Thus the extent of conversion for the Scheme would be much smaller in case if the product existed mainly as the ion pairs.

The equilibria measure at six different temperatures in the range 10–35 °C for the reaction between MNNPP and DBU made possible the computation of thermodynamic parameters (Table 5). The entropy of reaction $\Delta S^{\circ}_{BH} = 3 \pm 3$ J mol^{-1} K^{-1} is similar to that (6.7 J mol^{-1} K^{-1}) previously reported by Caldin[14] for the reaction of NNPM with TMG in MeCN, and is

Table 4. The estimation of the effective dissociation constants K_{ef} of the products of the reaction between 1-nitro-1-(4-nitrophenyl)alkanes and amidines in MeCN at 298.15 K.

System	$c_B/10^{-2}$ mol dm^{-3}	$K_{ef} = K_d$(min.)/ mol dm^{-3}	Λ_0(max.)[a]	Λ_0(min.)[b]
NNPM–TMG	4.15	2.20×10^{-3}	200	161
NNPM–DBU	3.23	3.00×10^{-3}	154	118
MNNPP–DBU	3.23	4.40×10^{-4}	154	78
	6.24	9.80×10^{-4}	140	87
	9.05	1.33×10^{-3}	139	90
	14.14	1.87×10^{-3}	138	94

[a] K_{ef} and Λ_0(max.) are estimated from the Kraus–Bray equation or values given in Table 3. [b] Λ_0(min.) = maximum value of Λ, $= \dfrac{1\,000(\kappa - \kappa_0)}{c_{AH}}$ calculated from the values in Table 1. The true value of Λ_0 is larger than the Λ_0(min.).

Table 5. Equilibrium constants, molar extinction coefficients, and thermodynamic parameters of the reaction of MNNPP with DBU calculated from equations (3) and (4).[a]

T/°C	K_{BH}/mol dm^{-3}	ε_{515}/dm^3 mol^{-1} cm^{-1}	r
Equation (3)			
10	1 200 ± 80	17 000 ± 300	0.980
15	1 070 ± 60	17 000 ± 300	0.995
20	950 ± 50	17 000 ± 300	0.989
25	900 ± 40	16 800 ± 200	0.994
30	780 ± 30	16 600 ± 200	0.994
35	680 ± 20	16 400 ± 200	0.994
	$\Delta H° = -16.1 \pm 0.8$ kJ mol^{-1}	$\Delta S° = 3 \pm 3$ J mol^{-1} K^{-1}	
Equation (4)	$K_rK_d/10^{-2}$		
10	2.88 ± 0.13	17 600 ± 200	0.993
15	2.58 ± 0.11	17 600 ± 200	0.994
20	2.14 ± 0.06	17 700 ± 100	0.997
25	1.96 ± 0.04	17 600 ± 100	0.999
30	1.56 ± 0.03	17 700 ± 100	0.999
35	1.21 ± 0.02	17 800 ± 100	0.999
	$\Delta H° = -24 \pm 2$ kJ mol^{-1}	$\Delta S° = -115 \pm 8$ J mol^{-1} K^{-1}	

[a] c_{DBU} in the range 1.67×10^{-3} to 5×10^{-2} mol dm^{-3}. r = correlation coefficient.

Table 6. Equilibrium constants[a] and molar extinction coefficients for the products of the reaction of 1-nitro-1-(4-nitrophenyl)alkanes with DBU in MeCN at 25 °C.

R	$\lambda_{max.}$/nm	$10^2\ K_r\ K_d$ (ε/dm^3 mol^{-1} cm^{-1})	K_{BH}/dm^3 mol^{-1} (ε_{BH}/dm^3 mol^{-1} cm^{-1})
H	491	— (28 500)	—
Me	508	92 ± 15 (24 200 ± 100)	48 000 ± 8 000 (24 200 ± 100)
Et	514	67 ± 6 (25 900 ± 100)	35 000 ± 3 000 (25 900 ± 100)
Pr^i	515	1.96 ± 0.04 (17 600 ± 100)	900 ± 40 (16 800 ± 200)

[a] K_{BH} = the equilibrium constant calculated from Benesi–Hildebrand relation. K_rK_d = equilibrium constants calculated from equation (4).

considerably bigger than those values found in less polar solvents.[22] These reaction entropy values (3.0 and 6.7 J mol^{-1} K^{-1}) are too large to be accounted for by the ionogenic reaction, and those for polar solvents are curious. Assuming that the ion-pair product dissociates into free ions, the calculated $\Delta S°$ value becomes -115 ± 8 J mol^{-1} K^{-1}, which is very close to the entropy of the reaction carried out in chlorobenzene.[22]

The Possible Factors Influencing the Validity of the Benesi–Hildebrand Equation for Dissociated Systems.—There are three things that could influence the spectrophotometric measurements in the direction of the Benesi–Hildebrand equation. The first factor is the possible oxidation of the anionic product already mentioned. We found, for the reactions examined, that destruction of the product is faster for lower concentrations of the amine base. This causes the deviation towards the fulfilment of Benesi–Hildebrand equation. The other possibility is a formation of the triple ions. In this case the number of moles of product would be half that of the substrate, causing artificial fulfilment of equation (3). Under these circumstances the system should demonstrate considerable conductance. By virtue of the limiting equivalent conductivity of the reaction products (Table 4) this possibility for our systems was excluded. Assuming that the total amount of the product exists as the triple ions then the stoichiometric concentration of c_{AH} should be divided by two to give incredibly large Λ_0 values, particularly for NNPM.

Finally the third factor that might influence the equilibrium of the dissociated system could be the concentration of BH^+ ions resulting from side reactions produced by acidic contaminants reacting with DBU. In the extreme case of the BH^+-ion concentration being larger than the concentration of the reacting C-acid and independent of base concentration c_B then the Benesi–Hildebrand relationship could erroneously be fulfilled, equation (15).

$$K_rK_d/c_{BH^+} = \frac{[A^-]}{[AH]c_B},\ c_{BH^+} = \text{const.} \gg c_{AH} \qquad (15)$$

If c_{BH^+} increases proportionally to $c_B^{\frac{1}{2}}$, then equation (4) is approximately fulfilled, finally if c_{BH^+} changes more slowly than $c_B^{\frac{1}{2}}$ then we will have deviations from equation (4) directing towards the fulfilment of the Benesi–Hildebrand equation. We presume that the first condition (c_{BH^+} = const. $\gg c_{AH}$) favouring the Benesi–Hildebrand equation is valid for the reaction of the amidine base with trace of contamination of the solvent, excluding water, which is visible from the small equilibrium constants for the reaction between the base and H_2O (Table 9, see later).

Possible traces of acetic acid in the MeCN (up to 1×10^{-4} mol dm^{-3}) can render[22] c_{DBUH^+} larger than c_{AH} used in spectrophotometric measurements. Our calculations showed that if the amidine used does not introduce the ionic contaminants, then equation (3) fits better than equation (4) even if the concentration of acetic acid in MeCN is equal to the concentration of C-acid.

In our systems the conductivity measurements suggest that c_{DBUH^+} is comparable to c_{AH} used for spectrophotometric examinations, but increases almost proportionally to $c_{DBU}^{\frac{1}{2}}$. Hence we conclude that the possible contaminations of the system should not cause the deviation from equation (4), which is in accord to our observations. In conclusion, we propose that the Benesi–Hildebrand relationship can be used for the estimation of equilibrium constants only when conductivity examination indicates no appreciable dissociation of the product.

Kinetic Measurements.—The Guggenheim plots and the plots of $k_{obs.}$ *versus* base concentration were all good straight lines for

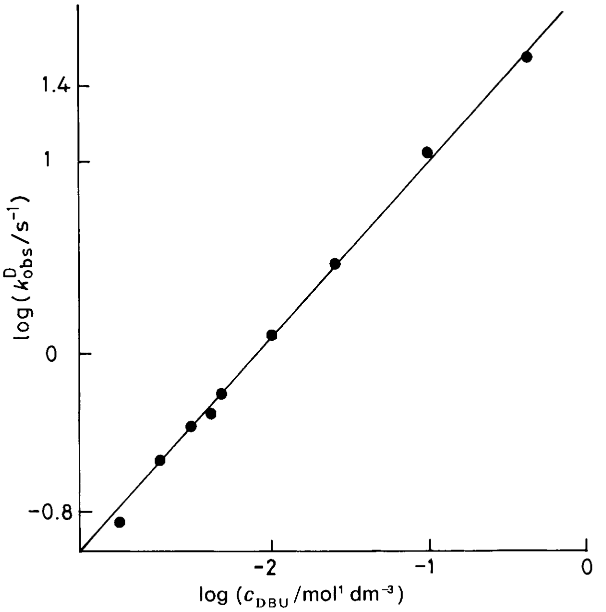


Figure 2. Plot of $\log k_{obs.}$ *vs.* $\log c_{DBU}$ for the reaction of [^{2}H]NNPE with DBU in MeCN at 20 °C. c_{DBU} = 0.001–0.5 mol dm^{-3}.

the concentration of DBU in the range 1×10^{-3}–5×10^{-1} mol dm^{-3} (Figure 2). The rate constants and kinetic isotope effects are collected in Table 7. The range of the base concentration was chosen to minimize the contribution of the reverse reaction to the observed rate constants $k_{obs.}$ so the plots of $k_{obs.}$ *versus* c_{DBU} cross through the origin within the standard deviation. The second-order rate constants for the forward reaction k_f for protonated and deuteriated compounds are given in column 4 of the Table 7. These decrease by *ca.* one order of magnitude (k_f = 1 820, 489, and 43.2 dm^3 mol^{-1} s^{-1} for NNPE, NNPP, and MNNPP respectively) with increased steric hindrance of the reacting *C*-acid. These different steric demands of R substituents of the substrate do not influence the primary deuterium kinetic isotope effects k_H/k_D which are large, but almost invariable, at *ca.* 12.5 at 25 °C.

The *C*-acids for the systems examined were designed such that the influence of steric hindrance on the primary kinetic isotope effects (KIE) could be observed. In previous papers the increase in steric hindrance enhanced considerably the values of KIE.[2,3,5,23] We therefore expected a similar effect for our system. Recently Sugimoto *et al.*[24] found that the reaction of 2,4,6-trinitrotoluene with piperidine and 1-methyl-, 1-ethyl- and 1-phenylethyl-piperidine in MeCN unexpectedly showed a decrease in the KIE values as the bulk of the substituents increased, so their results together with ours cast doubt upon the hitherto accepted views concerning the role of steric hindrance.

The activation parameters collected in Table 8 are the large negative activation entropies $\Delta S^{\ddagger}$ and the moderate activation enthalpies $\Delta H^{\ddagger}$, characteristic of bimolecular ionogenic proton-transfer reactions. The large, negative $\Delta S^{\ddagger}$ values (−135 J mol^{-1} K^{-1}) indicate considerable ordering of the transition state. The contemporaneous increase of enthalpy of activation $\Delta H^{\ddagger}$ and negative values of entropy of activation along with increasing steric hindrance of the reacting molecules cause a rise in free enthalpy of activation $\Delta G^{\ddagger}$ of *ca.* 10 kJ mol^{-1}. Therefore the absence of a compensating effect implies that the direction of the $\Delta S^{\ddagger}$ changes is determined by restriction of the free motion within the active complex rather than desolvation of the transition state. The changes in free enthalpy of activation $\Delta G^{\ddagger}$ produced by differences in steric hindrance of alkyl groups of the *C*-acid are the same order of magnitude as previously found by other authors for the introduction of crowding into the reaction centre by the reacting base.[23,25,26] Therefore, in addition to solvation effects, the steric effects contribute considerably to the overall value of the entropy of activation $\Delta S^{\ddagger}$.

In the case of the free enthalpy of reaction calculated by taking into account the formation of free ions the reaction of MNNPP falls into slightly endoergic region, ΔG° = 9.7 kJ mol^{-1} while the two others ΔG° = 0.2 and 0.99 kJ mol^{-1} for NNPE and NNPP, respectively, correspond to an expected maximum in the KIE *vs.* ΔG° relationship at ΔG° = 0.[27]

The dissociation process does not contribute to the symmetry of the transition state, so ion-pair formation should be the sole factor. In view of the fact that the dissociation constants K_d are 10^{-3}–10^{-2} we propose that these reaction systems are slightly exoergic with the reaction of MNNPP placed exactly at the maximum. According to Bell,[27] such systems have symmetrical transition states and are predicted to be subject to the maximum proton tunnelling and KIE. Thus relatively small changes in the ΔG° values near the maximum make these systems favourable for the examination of the influence of steric, tunnelling, and kinetic deuterium isotope effects.

The entropy of activation $\Delta S^{\ddagger}$ = −135 J mol^{-1} K^{-1} (Table 8) is very similar to the entropy of reaction (ΔS° = −115 J mol^{-1} K^{-1} yet this is not an indication of the charge separation in the transition state as is the case with the product.[28] This is not contrary to the values of ΔG° discussed previously by Bernasconi[29] who stated that the entropy change related to the restricted motion of the solvent molecules does not depend on the quantity of the solvated charge.

In the previously examined reactions between TMG and 4-nitrophenylcyanomethane (NPCM) and cyano-(4-nitrophenyl)-phenylmethane (CNPPM) carried out in MeCN[5,8] we found small, but observable increases in the $\Delta S^{\ddagger}$ values with increased steric hindrance ($\Delta\Delta S^{\ddagger}_{H}$ = 4, $\Delta\Delta S^{\ddagger}_{D}$ = 23 J mol^{-1} K^{-1}). This change is even more distinct, neglecting small differences in symmetry of the transition state, for the more hindered reactions between CNPPM with TMG and phenyltetramethylguanidine (PhTMG) in MeCN.[5,6]

In case of highly hindered strong amine bases it seems to be that the access of the solvent molecules to the developing positive charge of the transition state will be strongly reduced, in contrast with the poor solvation of the negative charge by aprotic solvents, as is the case when modifying the steric hindrance brought by reacting *C*-acids of different bulky R-substituents. The phenyl group of PhTMG does not influence the distance between this base and CNPPM in the previously studied reaction,[5] but certainly obstructs the solvation process.

The kinetic isotope effects on the activation parameters (Table 8) show that they are subject to small changes with the steric hindrance of reacting *C*-acid, in contrast with the considerable increase found for enhanced steric hindrance of the reacting base.[1,5,6,8,23] On the other hand, the results obtained for the reaction of two different acids nitro(4-nitrophenyl)-methane (NNPM) and NNPE with DMAN in MeCN[30] show no similarity in the activation parameters although the values of k_H/k_D were not very different. Leffek *et al.*[30] attempted to explain this by two different mechanisms for the proton transfer operating there: a bimolecular reaction for the less-hindered *C*-acid and a two-step process in which the step involving the base is not rate-determining.

The low sensitivity of kinetic isotope to the steric effects of the reacting *C*-acid, in general, and particularly in the reaction examined suggests the uncoupled mechanism[31] in which the solvent reorganization precedes the proton transfer. Therefore

Table 7. Observed and second-order rate constants for proton- and deuteron-transfer reactions between 1-nitro-1-(4-nitrophenyl)alkanes (O_2N-$C_6H_4C(L)NO_2Me$; L = H, D) and DBU in acetonitrile solvent.

T/°C	$c_{DBU}/10^{-3}$ mol dm^{-3}	$k_{obs}/10^{-2}$ s^{-1}	k_f/dm^3 mol^{-1} s^{-1}	k_H/k_D
NNPE				
5	1.01–5.05	113–567	1 140 ± 20	
10	1.01–5.05	130–654	1 280 ± 40	
15	1.01–5.05	141–726	1 430 ± 20	
20	1.01–5.05	166–822	1 630 ± 30	
25	1.01–5.05	193–928	1 820 ± 10	
30	1.01–5.05	222–1 089	2 150 ± 10	
35	1.01–5.05	247–1 205	2 390 ± 50	
[^{2}H]NNPE				
5	1.01–5.05	6.8–37.3	75.2 ± 0.7	15.2 ± 0.3
10	1.01–5.05	9.0–43.4	85 ± 1	15.0 ± 0.5
15	1.01–5.05	10.8–52.6	103 ± 1	13.9 ± 0.2
20	1.01–5.05	12.6–63.8	127 ± 1	12.8 ± 0.2
25	1.01–5.05	16.5–76.6	150 ± 3	12.1 ± 0.2
30	1.01–5.05	19.7–91.6	177 ± 2	12.1 ± 0.2
35	1.01–5.05	23.4–108.8	207 ± 6	11.5 ± 0.4
NNPP				
5	0.944–4.72	23.3–129	279 ± 6	
10	0.944–4.72	28.7–144	308 ± 8	
15	0.944–4.72	32.5–177	383 ± 6	
20	0.944–4.72	39.6–204	431 ± 11	
25	0.944–4.72	44.2–231	496 ± 6	
30	0.944–4.72	51.4–264	555 ± 11	
35	0.944–4.72	62.3–309	651 ± 6	
[^{2}H]NNPP				
5	0.984–4.92	1.55–8.69	18.3 ± 0.2	15.2 ± 0.4
10	0.984–4.92	2.17–10.7	21.9 ± 0.3	14.1 ± 0.4
15	0.984–4.92	2.72–13.4	27.2 ± 0.2	14.1 ± 0.2
20	0.984–4.92	3.45–16.2	32.2 ± 0.2	13.4 ± 0.4
25	0.984–4.92	4.58–19.9	39.2 ± 0.7	12.6 ± 0.3
30	0.984–4.92	5.65–24.3	48.2 ± 1.2	11.5 ± 0.4
35	0.984–4.92	7.46–30.0	58.4 ± 2.5	11.1 ± 0.5
MNNPP				
5	20–100	45–218	22.0 ± 0.6	
10	20–100	57–261	26.1 ± 1.1	
15	20–100	66–323	32.0 ± 0.5	
20	20–100	79–372	36.8 ± 0.4	
25	20–100	94–442	43.2 ± 0.7	
30	20–100	110–499	48.7 ± 0.4	
35	20–100	132–584	56.7 ± 1.0	
[^{2}H]MNNPP				
5	20–100	2.94–14.2	1.40 ± 0.03	15.7 ± 0.5
10	20–100	3.48–17.3	1.75 ± 0.04	14.9 ± 0.7
15	20–100	4.36–21.8	2.20 ± 0.02	14.5 ± 0.3
20	20–100	5.40–27.3	2.68 ± 0.07	13.7 ± 0.4
25	20–100	6.58–33.0	3.31 ± 0.03	13.0 ± 0.2
30	20–100	8.44–40.7	4.06 ± 0.04	12.0 ± 0.2
35	20–100	10.2–50.1	4.94 ± 0.09	11.5 ± 0.3

Table 8. Activation parameters, tunnelling corrections, and kinetic isotope effects for the reaction of 1-nitro-1-(4-nitrophenyl)alkanes $O_2NC_6H_4$-$C(L)NO_2R$ with DBU in MeCN.

R	$\Delta H^‡_H$/ kJ mol^{-1}	$\Delta S^‡_H$/ J K^{-1} mol^{-1}	$\Delta H^‡_D$/ kJ mol^{-1}	$\Delta S^‡_D$/ J K^{-1} mol^{-1}	$10^{-5}A_H$	A_H/A_D	$(\Delta H^‡_D - \Delta H^‡_H)$/ kJ mol^{-1}	$(Q_H/Q_D)_{25}$	$(k_H/k_D)_{25}$ (calc.)
Me	15.4 ± 0.6	−131 ± 2	22.4 ± 0.6	−128 ± 2	24 ± 6	0.7 ± 0.2	7.0 ± 0.8	1.26 ± 0.08	12.5 ± 0.1
Et	17.8 ± 0.7	−134 ± 2	25.2 ± 0.5	−130 ± 2	18 ± 5	0.6 ± 0.2	7.4 ± 0.9	1.35 ± 0.10	12.4 ± 0.1
Pr^i	19.9 ± 0.5	−147 ± 2	27.5 ± 0.2	−142.8 ± 0.5	3.5 ± 0.7	0.6 ± 0.1	7.6 ± 0.5	1.38 ± 0.07	12.8 ± 0.1

most kinetic isotope effects for similar reactions fluctuate around k_H/k_D = 11–20, which indicates the total loss of zero-point energy differences for stretching, or even both stretching and bending, vibrations of the C–L bond in the transition state, found for the polar aprotic solvents.[5,8]

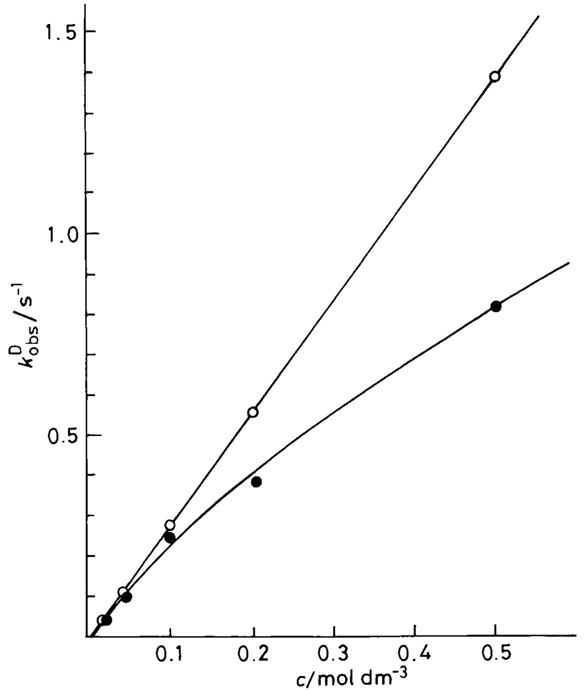


Figure 3. The influence of added water on the kinetics of the reaction of [^{2}H]MNNPP with DBU in MeCN at 20 °C: ○, c_{DBU}; ●, $c_{DBU} = c_{H_2O}$.

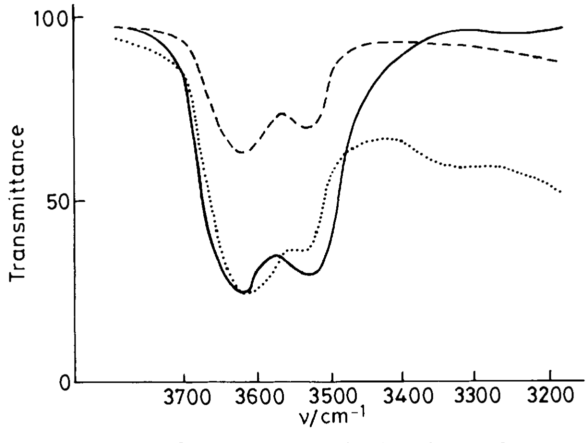


Figure 4. I.r. spectra of water and an equimolar mixture of DBU–H_2O in MeCN: (——), 0.3 mol dm^{-3} H_2O; (– – –), 0.0968 mol dm^{-3} DBU–H_2O; (. . . .) 0.375 mol dm^{-3} DBU–H_2O.

The values of the activation parameters (Table 8) and large values of kinetic isotope effects $k_H/k_D = 12.5$ (Tables 7 and 8) suggest that the symmetrical transition state must come early along the reaction co-ordinate before advanced rehybridization takes place.

The data collected in Table 8 show the small contributions of the tunnelling effect of the transferred proton to the overall reaction rate. This is indicated by the ratio of $A_H/A_D < 1$ and $\Delta H^{\ddagger}_{D} - \Delta H^{\ddagger}_{H} > 4.6$ kJ mol^{-1}. Hence the tunnelling correction factors calculated according to the program derived by Saunders,[32] $Q_H/Q_D = 1.3$, proves our earlier findings that the tunnelling effect appears to be present in the proton-transfer reactions despite the high polarity of the solvents used.[5,8]

The Influence of Water on the Kinetics of Proton-transfer Reactions.—The influence of traces of water contained in the solvent and the base on the kinetics of the reaction of nitro(nitrophenyl)alkanes has already been considered,[5,9,13,15] with reference to the formation of the hydroxy anions or the ion pairs of type BH^+ OH^-,[5,9,13] which could trigger side reactions which generally cause the acceleration of proton- and, in particular, deuteron-transfer reactions, in turn causing considerable reduction in the KIE. Knowing that the careful purification of DBU leads to the reagent containing less than 0.4% water (as judged from i.r. spectra) and also that carefully purified acetonitrile, (see the Experimental) still contained *ca.* 0.001% water, we attempted to elucidate the influence of water on the kinetics and mechanism of the proton-transfer reaction under investigation.

Table 9. Conductivity of the DBU–H_2O system in MeCN.

c_{DBU}/mol dm^{-3}	κ/10^{-5} cm^{-1} Ω^{-1}	κ′^{a}/10^{-5} cm^{-1} Ω^{-1}
0.2	1.422	1.952
0.1	1.030	—
0.05	0.8983	1.543
0.02	0.6018	0.9229
0.005	0.3647	0.6716
0.0005	0.1583	0.1943

[a] DBU:H_2O = 1:1.

The mixture DBU–H_2O, $c_{DBU} = c_{H_2O}$ was used to perform kinetic measurements with deuteriated MNNPP. The plots in Figure 3 demonstrate the dependence of $k_{obs.}$ on the DBU concentration with and without the addition of water.

For low concentrations of DBU–H_2O (1:1) the discrepancy between the rate constants is meaningless, while for large concentration of DBU–H_2O it becomes significant, causing large decreases in the reaction rate. Taking into account that the plot of $k_{obs.}$ *vs.* c_{DBU} in the absence of water is a good straight line for the whole DBU concentration range, the negative curvature of the graph for $c_{DBU} = c_{H_2O}$ (Figure 3) could be interpreted in terms of the decreased reactivity of the $DBUH^+$ OH^- ion-pairs compared with free DBU base. However, the conductivity measurements (Table 9) show that the formation of $DBUH^+$ OH^- and its further dissociation in MeCN is not very advanced. The data in Table 9 show that the addition of water to DBU does not increase the conductivity of the system to any extent. There is a slight possibility that the concentration of free $DBUH^+$ and OH^- ions would be extremely small (*i.e.* assuming $\Lambda_0(DBUH^+\ OH^-) = 100$, the concentration of free ions would be at most 1.95×10^{-4} mol dm^{-3} at $c_{DBU} = c_{H_2O} = 0.2$ mol dm^{-3}.

In the DBU–H_2O concentration range in which rates are considerably suppressed, the i.r. spectrum (Figure 4) shows changes indicating the appearance of new species. These could be the ion pairs ($DBUH^+$ OH^-) or hydrogen-bonded complexes DBU ··· HOH. Taking into account the low conductivity of the DBU–HOH system and considerable dissociation of electrolytes in MeCN[19,20] it seems to be unlikely that ion pairs are predominantly formed. This is also supported by Taft's ^{19}F n.m.r. studies of *p*-fluorophenol–amine systems in CCl_4. He found that the strong amines and *p*-fluorophenol (which is much more acidic than water) formed hydrogen-bonded complexes rather than ion pairs.[33] Hence the conclusion is that, in our case, competitive hydrogen bonding of the water molecule by the DBU and acetonitrile exists.

In low concentrations of DBU–H_2O the water molecule is bonded to MeCN rather than to DBU. The fact that non-hydrogen bonded DBU is more reactive, towards *C*-acids may account for the considerable reduction of the reaction rate with increased concentration of DBU–H_2O.

Since the reagents and solvents for the kinetic measurements were carefully dried, and since the dependence of the rate upon water concentration is weak, no significant change caused by residual water should be expected for proton-transfer reactions carried out under these conditions.

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