Kinetics of Proton and Deuteron Transfer from α,4-Dinitrotoluene to 1,8-Bis(dimethylamino)naphthalene in Alcoholic Solvents

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Evidence is presented to show that the reaction between α,4-dinitrotoluene and 1,8-bis(dimethylamino)naphthalene, in either propan-2-ol or t-butyl alcohol as solvent, is a proton transfer from the carbon acid to the nitrogen base to give an ion pair. The second-order rate constants for the proton and deuteron transfer reactions have been determined over the temperature range 10—45 °C in the two solvents. The reactions are relatively slow and are characterized by enthalpies of activation of 10—14 kcal mol^{-1} (42—58 kJ mol^{-1}) and entropies of activation of —17 to —31 cal mol^{-1} K^{-1} (—71 to —130 J mol^{-1} K^{-1}). The isotopic rate ratios are small ($k_H/k_D < 3$), although $\Delta H_D{}^{\ddagger} - \Delta H_H{}^{\ddagger}$ is normal (ca. 1 kcal mol^{-1}), with compensation by positive values for $\Delta S_D{}^{\ddagger} - \Delta S_H{}^{\ddagger}$.

THE kinetics and isotope effects of proton transfer from α,4-dinitrotoluene (1) have been studied for a number of bases and solvent systems.[1-4] This work is of particular interest because of the large isotope effects found by Caldin and Mateo [2,3] with the strong base tetramethylguanidine in non-polar solvents. The remarkable basicity of 1,8-bis(dimethylamino)naphthalene (2) (pK_a 12.34 in water[5]) provides an interesting reaction for

kinetic measurements of primary deuterium isotope effects and activation parameters in proton transfer reactions, since this diamine is a strained molecule in which strain is effectively relieved by protonation.[5] The high basicity of the compound is attributed to relief of steric strain upon protonation[5] and the strong interaction between the two nitrogen lone pairs.[6] In addition to the presence of steric strain in the initial state of the base, which would lead to steric acceleration of the

[1] E. F. Caldin, A. Jarczewski, and K. T. Leffek, Trans. Faraday Soc., 1971, 67, 110.

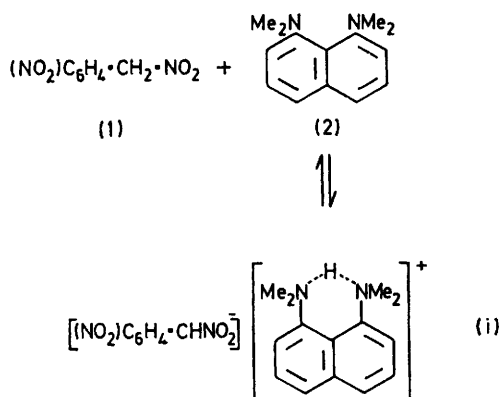[2] E. F. Caldin and S. Mateo, J.C.S. Chem. Comm., 1973, 854.

[3] E. F. Caldin and S. Mateo, J.C.S. Faraday I, 1975, 1876.

[4] E. F. Caldin and S. Mateo, J.C.S. Faraday I, 1976, 112.

[5] R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, Chem. Comm., 1968, 723.

[6] F. Gerson, E. Haselbach, and G. Plattner, Chem. Phys. Letters, 1971, 12, 316.

reaction, there is also the possibility of steric hindrance to proton transfer from α,4-dinitrotoluene to the bulky base [equation (i)].

$$(NO_2)C_6H_4 \cdot CH_2 \cdot NO_2 \; + \; \text{(2)}$$

(1)   (2)

$$[(NO_2)C_6H_4 \cdot CHNO_2]^- \quad [\text{structure}]^+ \qquad (i)$$

The reaction is indeed much slower than the other proton transfer reactions of α,4-dinitrotoluene. The second-order rate constants were similar to those for the reaction of bis-(4-nitrophenyl)methane with alkoxides in alcoholic solvents. In that reaction, abnormal entropy isotope effects were observed,[7,8] i.e. $\Delta S_D^{\ddagger} - \Delta S_H^{\ddagger}$ values were negative; this was attributed to a time lag for solvent reorganization relative to proton transfer.[8]

The reaction of the diamine (2) with α,4-dinitrotoluene in alcoholic solvents was studied in an attempt to gain further insight into the dependence of primary isotope effects on steric hindrance factors in these solvents and, in particular, into isotope effects on the entropy of activation.

EXPERIMENTAL

Materials.—α,4-Dinitrotoluene was prepared by the method of Cooke and MacBeth,[9] and the deuteriated analogue was prepared from this by exchange with sodium methoxide–methan[2H]ol.[1] The exchange process was carried out four times and yielded material 99% isotopically pure according to the n.m.r. spectrum.

Reagent grade propan-2-ol was passed through a column of molecular sieves (3 Å) and then fractionally distilled under dry, oxygen-free nitrogen at 82.4 °C. Reagent grade t-butyl alcohol was dried over calcium oxide, distilled from sodium metal, and then fractionally distilled at 82.4 °C. Both alcohols were protected from moisture and carbon dioxide by storage under dry, oxygen-free nitrogen. 1,8-Bis(dimethylamino)naphthalene (Aldrich) had m.p. 49—50 °C.

Kinetic Measurements.—Stock solutions were made up by dissolving weighed samples of the carbon acid and the base in the appropriate alcohol. Solutions were brought to the desired temperature and combined to yield the reaction mixture in a volumetric flask, the ' dead ' volume of which was filled with dry, oxygen-free nitrogen. The reaction was followed by using a Specord UV-Vis spectrophotometer (Carl-Zeiss Jena) scanning at a fixed wavelength in the region of λ_{max} 429 nm in propan-2-ol and 443 nm in t-butyl

[7] J.-H. Kim and K. T. Leffek, *Canad. J. Chem.*, 1974, **52**, 592.
[8] A. Jarczewski, P. Pruszynski, and K. T. Leffek, *Canad. J. Chem.*, 1975, **53**, 1176.
[9] R. G. Cooke and A. K. MacBeth, *J. Chem. Soc.*, 1938, 1024.

alcohol. The optical cells were maintained at constant temperature ±0.1 °C.

The first-order rate constants were calculated from absorbance values read from the reaction trace, by the Guggenheim method.[10] The second-order rate constants were calculated from the plots of the first-order rate constants vs. base concentration by the method of least squares (ODRA 204 computer). A linear least-squares fit was also applied to the variation of the second-order rate constants vs. $1/T$ in order to obtain the activation parameters.

RESULTS AND DISCUSSION

The proton transfer shown in equation (i), in which the product is an ion pair, is believed to take place in the two solvents used in this study, propan-2-ol and t-butyl alcohol. The absorption maxima for the dinitrotoluene–diamine mixtures were 429 and 443 nm in propan-2-ol and t-butyl alcohol, respectively, but 500—505 nm in acetonitrile. This solvent shift is qualitatively similar to, but smaller than that for the anion of bis-(4-nitrophenyl)methane in ethanol–acetonitrile.[11] Similar solvent shifts have been found for carbanions by other workers.[12,13] The λ_{max} value in acetonitrile is slightly greater than that in the same solvent for the ion-pair products from α,4-dinitrotoluene and tetramethylguanidine (493 nm)[3] and triethylamine (490 nm).[1]

Since the reaction was slower than expected, the possibility was investigated that the diamine (2) was not
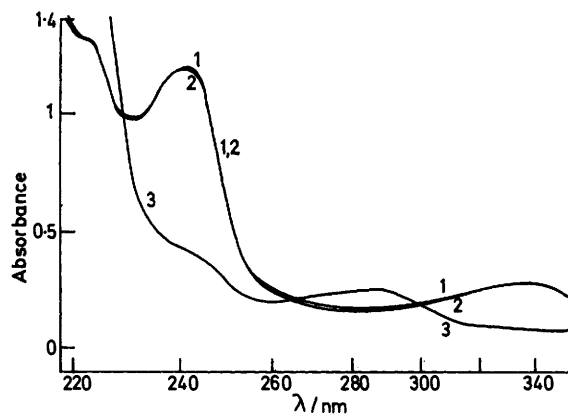

FIGURE 1   U.v. absorption spectrum for 1,8-bis(dimethylamino)-naphthalene; concentration 1×10^{-6}M in (1) acetonitrile, (2) acetonitrile–propan-2-ol (50% v/v), and (3) acetonitrile–methanol (50% v/v)

reacting at all with the carbon acid but was abstracting a proton from the solvent, giving rise to alkoxide ion in low concentration which then reacted with the dinitrotoluene, giving an apparent small second-order rate constant when calculated with respect to the base concentration. The u.v. absorption peak at 242 nm of the diamine (2) in acetonitrile is unchanged by the addition of 50% (v/v) of propan-2-ol or t-butyl alcohol, as shown in Figure 1, whereas the same amount of methanol

[10] E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.
[11] J.-H. Kim and K. T. Leffek, *Canad. J. Chem.*, 1973, **51**, 2805.
[12] K. Bowden and R. Stewart, *Tetrahedron*, 1965, **21**, 261.
[13] K. T. Leffek and P. H. Tremaine, *Canad. J. Chem.*, 1971, **49**, 1979.

removes this peak. However, added bis-(4-nitrophenyl)-methane, which reacts readily with alkoxide ions to yield a violet-coloured anion,[14] did not indicate the presence of methoxide ions even when the concentration of the diamine (2) was 0.2M. The interaction between the diamine (2) and solvent alcohol, therefore, does take place with methanol, although no methoxide ion is detectable within the limits of the above test. There appears to be no proton abstraction or any other specific interaction between the diamine (2) and propan-2-ol or t-butyl alcohol.

The reaction, therefore, appears to be a proton transfer from the dinitrotoluene (1) to the diamine (2) with the alcohols acting only as solvents. If the product is an ion pair as shown in equation (i), the expression relating the optical density (o.d.) of the equilibrium mixture, the
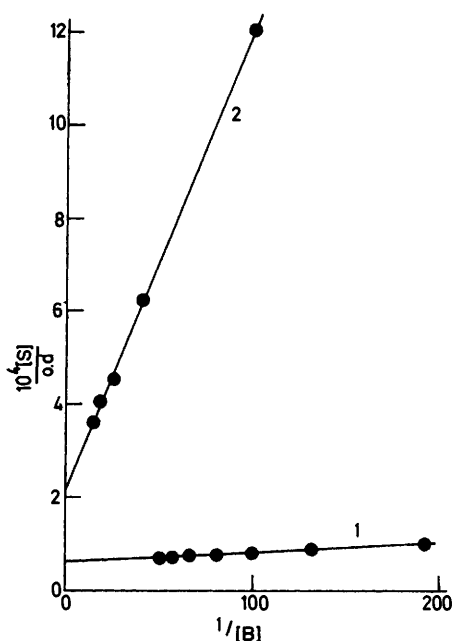

FIGURE 2 Plots of 1/[B] vs. [S]/o.d. for the reaction of α,4-dinitrotoluene with 1,8-bis(dimethylamino)naphthalene in (1) propan-2-ol at 25 °C and (2) t-butyl alcohol at 30 °C

molar absorptivity (ε) of the ion pair product, and the equilibrium constant K for the process with the initial concentrations of the substrate [S] and base [B] is equation (ii).

$$[S]/\text{o.d.} = 1/K[B]\varepsilon + 1/\varepsilon \qquad (ii)$$

The reaction in both solvents fitted this equation, as shown in Figure 2. The intercepts and slopes yield ε = 16 500 ± 150 l mol⁻¹ cm⁻¹, K = 270 ± 10 l mol⁻¹ in propan-2-ol at 25 °C, and ε = 4 800 ± 300 l mol⁻¹ cm⁻¹, K = 21 ± 2 l mol⁻¹ in t-butyl alcohol at 30 °C. These values of ε and K are lower than the corresponding ones observed by Caldin and Mateo [3] for the ion pair formed from the same substrate and tetramethylguanidine in for example, acetonitrile, but they follow the same trend observed for the reaction of bis-(4-nitrophenyl)methane with ethoxide ion in ethanol–acetonitrile.[11] In that

case, both K and ε decreased with increasing amounts of ethanol in the solvent.

First-order rate constants for the reaction of the normal and the deuteriated compound were obtained by a procedure similar to that described previously.[8] The initial substrate concentration was 1 × 10⁻⁴M and the base concentration between 5 × 10⁻³ and 3.5 × 10⁻²M. The second-order rate constants derived from these measurements (i.e. the slopes of the k_1 vs. base concen-

TABLE 1

Second-order rate constants for proton and deuteron transfer from α,4-dinitrotoluene to 1,8-bis(dimethylamino)naphthalene [a]

Temp. (°C)	$10^3 k_{2H}$	$10^3 k_{2D}$	k_{2H}/k_{2D}
(a) Propan-2-ol solvent			
10	8.6 ± 0.6	5.4 ± 0.04	1.6 ± 0.1
15	12.9 ± 0.3	7.3 ± 1.5	1.8 ± 0.3
20	17.9 ± 0.6	10.8 ± 0.2	1.6₅ ± 0.1
25	26.4 ± 2.7	15.2 ± 0.3	1.7 ± 0.2
30	30.8 ± 3.1	19.1 ± 0.6	1.6 ± 0.2
35	37.2 ± 3.4	28.0 ± 1.4	1.3 ± 0.2
40	55.2 ± 1.4	35.7 ± 0.1	1.5₅ ± 0.1
45	73.1 ± 2.9	48.1 ± 0.1	1.5 ± 0.2

Temp. (°C)	$10^2 k_{2H}$	$10^2 k_{2D}$	k_{2H}/k_{2D}
(b) t-Butyl alcohol solvent			
30	29.1 ± 0.7	9.8 ± 0.4	3.0 ± 0.1
32.5	34.8 ± 0.9	12.0 ± 0.3	2.9 ± 0.1
35	39.9 ± 0.9	14.6 ± 0.2	2.7 ± 0.1
37.5	47.4 ± 1.1	17.5 ± 1.2	2.7 ± 0.2
40	58.5 ± 1.4	20.4 ± 0.8	2.9 ± 0.2

[a] Initial concentration of substrate 1 × 10⁻⁴M; k_{2H} and k_{2D} units are 1 mol⁻¹ s⁻¹ and refer to 4-(NO₂)C₆H₄·CH₂·NO₂ and 4-NO₂·C₆H₄·CD₂·NO₂, respectively; the limits quoted are standard deviations.

tration plots) are shown in Table 1, together with the isotopic rate ratios. The activation parameters calculated from the second-order rate constants are listed in Table 2.

TABLE 2

Activation parameters for the reactions of normal and deuteriated α,4-dinitrotoluene with 1,8-bis(dimethylamino)naphthalene

Parameter	Propan-2-ol	t-Butyl alcohol
$\Delta H_H^{\ddagger}$/kcal mol⁻¹	10.5 ± 0.4	12.9 ± 0.6
$\Delta H_D^{\ddagger}$/kcal mol⁻¹	11.3 ± 0.4	14.0 ± 0.4
$\Delta S_H^{\ddagger}$/cal mol⁻¹ K⁻¹	−30.8 ± 1.4	−18.5 ± 1.9
$\Delta S_D^{\ddagger}$/cal mol⁻¹ K⁻¹	−29.0 ± 1.2	−16.9 ± 1.3
$\Delta H_D^{\ddagger} - \Delta H_H^{\ddagger}$	0.8 ± 0.5	1.1 ± 0.7
$\Delta S_D^{\ddagger} - \Delta S_H^{\ddagger}$	1.8 ± 1.8	1.5 ± 2.3
log (A_D/A_H)	0.39 ± 0.36	0.34 ± 0.4
A_D/A_H	2.5	2.2

Reaction Rates and Activation Parameters.—Despite the fact that 1,8-bis(dimethylamino)naphthalene (2) is a stronger base than normal aliphatic amines,[5] its reaction with α,4-dinitrotoluene is relatively slow. Semiquantitative experiments showed that the reaction had a second-order rate constant ca. 25 times smaller than that of triethylamine and 15 times smaller than that of tri-n-butylamine in acetonitrile at 30 °C; thus there seems to

14 A. Jarczewski and K. T. Leffek, Canad. J. Chem., 1972, 50, 24.

be some steric hindrance in the rate of proton transfer to the diamine (2). No reaction was detected after 3 days in toluene as solvent; however this is probably due mainly to a very small equilibrium constant for the proton transfer in toluene.

The enthalpies of activation in Table 2 cover the range 10.5—14 kcal mol^{-1}, similar to the range for proton transfer from several different carbon acids to alkoxide bases in alcoholic solvents,[11,13,15-18] which have been interpreted as arising mainly from the desolvation of the base in the initial state. The reactions in t-butyl alcohol have a slightly higher enthalpy of activation, with a considerably less negative entropy of activation, than those in propan-2-ol, a compensation effect characteristic of reactions in which solvation changes are kinetically important.[18] This difference in activation parameters may be explained in terms of solvation, on the premises that the transition state is more strongly solvated than the initial state by both alcohols, because of the charge development in the transition state, and that the transition state is more strongly solvated by propan-2-ol than by t-butyl alcohol. The bulky uncharged initial state, on the other hand, will be better solvated by the t-butyl alcohol. Thus, if desolvation of the base is the dominant factor in determining the enthalpy of activation, this parameter will be greater in t-butyl alcohol. Also, on the basis of the above two premises, the entropy of the initial state is more negative in t-butyl alcohol, whereas the entropy of the transition state is less negative in t-butyl alcohol than in propan-2-ol, leading to a smaller negative entropy of activation in t-butyl alcohol.

Isotope Effects.—The isotopic rate ratios (Table 1) are small, indicating that there is probably no contribution from proton tunnelling. This is confirmed by the data in Table 1 which show that the isotopic differences in the enthalpies of activation are as predicted for the loss of zero-point energy from one carbon–hydrogen stretching

vibration. The fact that a difference in enthalpies of 1 kcal mol^{-1} is observed indicates that the desolvation effects discussed above, although they may make up the major part of $\Delta H^{\ddagger}$, are not the only rate-determining factors. Desolvation must take place before proton transfer can occur, but the proton transfer is part of the rate-controlling step of the reaction.

The isotopic differences in the entropies of activation are normal, *i.e.* $\Delta S_D^{\ddagger} - \Delta S_H^{\ddagger}$ values are positive, which compenstates for the 1 kcal mol^{-1} difference in enthalpies and yields the small rate constant ratios. Thus, we do not find the abnormal negative values of $\Delta S_D^{\ddagger} - \Delta S_H^{\ddagger}$ observed in other proton transfer reactions,[7,8,19] which can be attributed to solvent lag during the proton transfer.[3,8,20] The absence of this effect and the absence of abnormally large isotope rate ratios lead to the conclusion that the proton transfer to the diamine (2) in these alcoholic solvents is governed to a major extent by reorganization of the initial state solvation shell, and that the motion of the solvent molecules is coupled with the proton transfer. Although this mechanism is not proved, it offers the most satisfactory rationalization of the activation parameters and isotope effects consistent with earlier interpretations of activation parameter measurements. The isotope effects themselves show only that a C–H stretching vibration is lost in the transition state and that the barrier width is large. This wide barrier is postulated to arise from the coupled motion of the solvent molecules but it could also be due to steric hindrance. The conclusion of coupled solvent motion with proton transfer differs from that of Kurz and Kurz,[21] who considered that proton transfers to large bases would proceed *via* a three-step mechanism in which the first and third steps involve only solvent reorganization and the second step only an uncoupled proton transfer.

[15] E. F. Caldin and J. C. Trickett, *Trans. Faraday Soc.*, 1953, **49**, 772.

[16] E. F. Caldin, *J. Chem. Soc.*, 1959, 3345.

[17] E. F. Caldin, M. Kasparian, and G. Tomalin, *Trans. Faraday Soc.*, 1968, **64**, 2802.

[18] E. F. Caldin, E. Dawson, R. M. Hyde, and A. Queen, *J.C.S. Faraday I*, 1975, 528.

[19] P. W. K. Flanagan, Ph.D. Thesis, Ohio State University, 1957 (*Diss. Abs.*, 1958, **18**, 1980).

[20] E. F. Caldin in ' Reaction Transition States,' ed. J. E. Dubois, Gordon and Breach, London, 1972, p. 247.

[21] J. L. Kurz and L. C. Kurz, *J. Amer. Chem. Soc.*, 1972, **94**, 4451.