J. Chem. Soc., Faraday Trans. 1, 1982, **78**, 3619-3627

Effect of Solvent on the Kinetics of the Reaction between Dialkylbenzimidamides and 4-Nitrophenylnitromethane

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Received 2nd April, 1982

Rate constants have been determined for the proton-transfer reaction of 4-nitrophenylnitromethane, $NO_2C_6H_4CH_2NO_2$, with two *NN*-dialkylbenzimidamides, $HN{=}C(C_6H_5)NR_2$, where R = 1-butyl, or 1-propyl, in the temperature range 273-303 K in some aprotic solvents of low polarity. In the concentration ranges used the reaction to form an ion-pair product is first-order in acid and first-order in benzimidamide. The reactions were monitored spectrophotometrically employing the stopped-flow method. An examination of the relationships of the forward proton-transfer rate constants at 298 K, in six solvents, for the dibutyl compound to a solvent permittivity function and to the solvent polarity parameter (E_T) shows that a polar activated complex develops; this is compatible with reaction in which ions are produced. The corresponding kinetic parameters for the dipropyl analogue in three solvents are consistent with this pattern. There is no significant effect upon the kinetic parameters of variation of the alkyl group in the benzimidamide. The energies of activation for forward proton transfer are small, in the range 10-23 kJ mol^{-1}, while in the reverse direction the energies of activation range is 65-114 kJ mol^{-1}. A Brønsted-type plot using the forward rate constants and the derived equilibrium constants at 298 K yields a coefficient which is indicative of a significant degree of proton transfer in the transition state. However, the highly exothermic nature of the reaction and the low energies of activation in the forward direction suggest a reactant-like activated complex. Provisional results (forward rate constants and energies of activation) for deuteron transfer from the deuterated acid to both benzimidamides in di-1-butyl ether and in chlorobenzene are reported. The hydrogen-ion transfer results are compared with those reported for reaction of the title acid with 1,1,3,3-tetramethylguanidine.

The kinetics of the reaction between 4-nitrophenylnitromethane (4-NPNM) and 1,1,3,3-tetramethylguanidine (TMG) have been studied in several aprotic solvents by Caldin and Mateo.[1] They observed large kinetic isotope effects and anomalous Arrhenius parameters and concluded that the carbon acid releases a proton to the base by a pathway which involves quantum-mechanical tunnelling.[2-6] The variations of the kinetic and activation parameters with solvent were interpreted as indicating that the transfer of the proton is coupled to motions of solvent molecules for the reaction in polar solvents such as acetonitrile, but not in non-polar solvents such as toluene. Studies by Caldin and coworkers using other bases, notably quinuclidine, triethylamine and tributylamine, in both toluene and other solvents (anisole and chlorobenzene) yielded results which were consistent with the solvent dependence noted earlier. The kinetic isotope effect, which was reported to be 45 at 298.0 K for TMG and 4-NPNM in toluene, took a much smaller value for the reactions with tertiary bases,[7-10] although still larger than could be attributed to zero-point energy differences only. This suggested that the barrier width for a given height may be less for the imine bases. The virtually constant value of the volume of activation, ΔV^*, for the reaction of TMG and 4-NPNM in five solvents of low polarity was also interpreted[11] as support for the earlier analysis of solvent influence upon kinetic isotope effects. The kinetic isotope effects and activation parameters for the reactions of 4-NPNM with two alkylimidamides,[10] a cyclic imidamide[12] and pentamethylguanidine[13] were of magnitudes which were also consistent with the need for a tunnelling correction. Subsequently the reaction of TMG was further investigated, and the consequences of exchangeable hydrogen in TMG were examined.[14-16] If the assumed mechanism of deuteron transfer was modified to incorporate the assumption of rapid exchange between the two forms of hydrogen on the imine nitrogen of the ion pair, then the kinetic isotope effect derived for the reaction in toluene was much lower (*ca.* 11 at 298.0 K).[15, 16] Concern has been raised[12] over the consequences of the presence of extraneous water, which is very difficult to remove from TMG, upon the kinetics. Residual water does not significantly affect the proton transfer to TMG, but the apparent rate of the deuteron transfer may be affected.[17] Extraneous water does not appear to affect formation of the ion pair formed by pentamethylguanidine or its deuterated analogue in toluene and acetonitrile[18] or the loss of tritium from tritiated 4-NPNM reacting with TMG in toluene.[19]

Before the appearance of these latest publications we undertook a study of the reaction of 4-NPNM with two benzimidamide bases, *NN*-di-1-propylbenzimidamide and *NN*-di-1-butylbenzimidamide,† in various solvents with a view to determining the relationships of kinetic parameters with solvent.[20] On the basis of results subsequently reported for the reaction of pentamethylguanidine and 4-NPNM in two solvents it has been suggested[19] that the interpretation of the dependence of the kinetic parameters upon solvent proposed earlier is not correct. This report is concerned primarily with the effect of solvent upon the kinetics of the proton-transfer reaction, but we report also some preliminary results on the deuteron-transfer reaction.

EXPERIMENTAL

MATERIALS

4-NPNM was synthesized by a literature method[21] and stored in a darkened desiccator. [^{2}H]4-NPNM was supplied by Dr C. J. Wilson. DPBA and DBBA were synthesized according to a literature method.[22] (The latter imidamide has not been reported previously.) Deuterated DPBA, [^{2}H]DPBA, was prepared by shaking a ten-fold excess of D_2O with a sample of DPBA and then removing the solvent using a rotary evaporator. Following a repetition of this process the product was purified by vacuum distillation.

Characterization of bases was by elemental analysis and proton n.m.r. spectroscopy. Bases were stored in darkened desiccators over dry nitrogen.

Solvents used were purified from reagent-grade commercial products by standard methods using extra precautions to exclude atmospheric moisture. Purified solvents were kept in dark containers with, when appropriate, drying agents within the solvent. An atmosphere of dry nitrogen was maintained over the solvent, the containers of which were stored in sealed vessels over dehydrating agents. In experiments with carbon tetrachloride as solvent it was found that kinetic data for the reaction of DBBA with 4-NPNM were unchanged within experimental variation when Aldrich Gold Label spectroscopic grade solvent was used in place of solvent samples purified in our laboratory.

METHODS

Solution spectra, equilibrium measurements and some deuteron-transfer kinetics were recorded using a Cary 14 spectrophotometer. A wavelength of 450 nm was used for monitoring purposes. The temperature of solutions was controlled by using a Lauda K-2/R thermostatting system.

Most kinetic studies were carried out using a Durrum–Gibson stopped-flow spectrophotometer

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† *NN*-di-1-propylbenzimidamide and *NN*-di-1-butylbenzimidamide are abbreviated to DPBA and DBBA, respectively.

with a 2 cm cuvette and a Kel-F flow system. Oscilloscope photographic records of the reactions monitored at 450 nm were analysed to determine the rate constants by a method previously reported.[23] All data recorded yielded first-order kinetic plots linear for at least three half-lives, except in some cases at low base concentrations when the formation of product is not favoured and the signal amplitudes are very small, or when a mixture of 4-NPNM and [^{2}H]4-NPNM was deliberately used. The values reported for rate constants are averages of usually four to seven replicate determinations. The temperature was maintained constant throughout a given kinetic run by a circulating fluid whose temperature was controlled by a Neslab RTE-8 bath. The accuracy with which the temperature of solutions is known is reduced the further that is from the ambient temperature in the type of stopped-flow instrument used.

RESULTS

PROTON TRANSFER

The kinetic data for reaction (1),

$$\text{4-NPNM} + \text{DBBA} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (\text{4-NPNM})^- (\text{DBBA})^+ \ldots \qquad (1)$$

the ion-pair product of which has an intense yellow colour, are consistent with eqn (2):

$$k_{obs} = k_f[\text{DBBA}] + k_b. \qquad (2)$$

Here k_{obs} is the first-order rate constant obtained from reaction traces under the condition of base concentration in large excess over acid concentration. (Parallel equations may be written for reaction of DPBA.) Plots of k_{obs} against total base concentration are linear over the range of base concentration studied, yielding the second-order forward and first-order reverse rate constants (k_f and k_b) from the slope and intercept, respectively. The kinetic data and the concentration conditions for reaction (1) are reported in table 1. A summary of kinetic results and derived activation parameters together with the standard deviations for these is presented in table 2. The excess of base was typically five to ten fold, usually in the region 1-10 mmol dm^{-3}. The particular concentration range that can be used for a given reaction depends on the reaction rate, the need for sufficient base excess and the position of equilibrium for the temperature and solvent employed. Over the ranges studied the plots reveal no systematic deviation from linearity.

Given that it is difficult to remove water from TMG then it seems unlikely that benzimidamide bases are readily rendered anhydrous. Although normal precautions to exclude water were taken during the preparation and purification of reagents, the purification of solvents and the preparation of solutions and during kinetic experiments, undoubtedly trace amounts are present. The interpretation of results, however, is based on the assumption that extraneous water has no significant effect upon the proton-transfer reactions studied since no effect is detected. In one reaction, that between DPBA and 4-NPNM in carbon tetrachloride, solvent for the base was saturated with water. At 293 K k_f^H, the forward rate constant (48 mol^{-1} dm^3 s^{-1}), is within experimental error of the value for the dry solvent, and the reverse rate constant is changed from *ca.* 2.5 to 2.0 s^{-1}, but this change is almost within the range of experimental error. Other studies of the effect of added water upon the kinetics of carbon acid–base reactions have shown a similar result to that reported here; *viz.* the rate of proton transfer from 4-NPNM to 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene in chlorobenzene is unaffected when the solvent is saturated with water but the reverse rate is lowered by about one-half.[24]

A comparison with some proton-transfer rates to a benzimidamide in anisole is possible. In an earlier study, k_f^H (for *NN*-diethylbenzimidamide) was reported as

TABLE 1.—RATE CONSTANTS FOR REACTIONS OF 4-NITROPHENYLNITROMETHANE WITH DBBA AND DPBA IN VARIOUS SOLVENTS

solvent	temp/K	[DBBA]/10^{-3} mol dm$^{-3a,b}$	av. k_{obs}^{H}/s^{-1}	k_f^H/mol^{-1} dm^3 s^{-1c}	k_b^H/s^{-1}
carbon tetrachloride	283	5.0-25.0	0.61-1.42	43.2±4.3	0.37±0.072
	288	7.0-27.0	1.33-1.97	33.0±2.1	1.07±0.039
	293	7.0-27.0	1.95-2.83	40.8±3.9	1.70±0.072
	298	10.0-33.0	2.35-4.27	83.9±25.0	1.14±0.060
di-1-butyl ether	281	3.0-30.0	1.57-4.58	111.9±2.3	1.27±0.04
	284.6	7.0-30.0	3.13-5.73	119.5±7.4	2.30±0.14
	288.4	3.0-30.0	3.32-7.01	141±9.9	3.06±0.18
	293.9	3.0-30.0	5.76-9.91	138±18	5.92±0.33
anisole	280.7	3.0-24.0	2.02-7.36	208±8.30	1.63±1.24
	284.9	2.0-26.0	3.27-7.15	141±25	2.87±0.35
	289.0	3.0-12.0	4.56-6.65	226±87	3.68±0.74
	290.9	2.93-24.4	5.01-10.4	238±13	4.36±0.20
	293	3.0-24.7	6.92-10.9	183±11	6.54±0.17
	298	1.82-24.4	9.60-14.9	228±30	8.82±0.40
	303	2.93-18.6	12.6-16.8	245±27	12.1±0.3
chlorobenzene	280.5	3.86-8.69	2.46-3.64	242±16	1.55±0.10
	285.4	2.90-19.3	3.80-7.56	229±1.1	3.14±0.01
	291.4	2.90-17.4	5.21-9.20	271±8.0	4.47±0.09
	298	1.93-17.4	9.45-13.7	265±43	9.24±0.45
	304	4.83-21.2	17.5-22.4	320±59	16.1±0.8
tetrahydrofuran	275.8	0.43-2.68	0.508-0.963	211±33	0.446±0.058
	278.6	0.43-3.42	0.646-1.39	259±33	0.533±0.065
	291.3	3.35-21.4	3.69-8.67	275±5.2	2.76±0.07
	298	8.43-20.1	6.51-10.4	329±43	3.90±0.64
	303	3.35-21.4	7.67-15.0	421±47	6.32±0.63
dichloromethane	278.3	2.30-9.20	1.50-3.69	339±25	0.610±0.164
	290.6	4.90-24.5	5.02-14.3	484±116	4.10±1.80
	295.5	2.4-12.0	6.27-10.2	451±87	5.33±0.66
	298.5	2.3-9.2	5.34-9.14	530±27	4.28±0.17

solvent	temp/K	[DPBA]/10^{-3} mol dm$^{-3a,b}$	av. k_{obs}^{H}/s^{-1}	K_f^H/mol^{-1} dm^3 s^{-1c}	k_b^H/s^{-1}
carbon tetrachloride	293	10-25	3.1-4.0	62±10	2.54±0.18
di-1-butyl ether	281	5.0-30	1.49-4.55	112±8	1.10±0.14
	284.6	3.0-30	1.80-5.67	130±19	1.55±0.39
	293.9	10-30	7.62-10.4	148±18	6.14±0.39
chlorobenzene	279.9	4.0-20	2.20-6.72	292±22	0.96±0.30
	283.8	4.0-20	2.69-8.74	393±34	1.25±0.44
	288.1	2.5-20	3.16-11.2	434±34	2.46±0.40
	294.6	6.0-20	9.26-15.6	463±59	5.97±0.82
	299.1	4.0-20	13.0-20.6	442±109	12.8±1.4
	300.0	3.0-25	16.9-27.9	533±67	13.5±1.1

[a] The ranges of initial concentrations of the two benzimidamides used are given. [b] The initial concentration of 4-NPNM was 5.0×10^{-5} mol dm^{-3} except in a few cases where an initial concentration of 1.0×10^{-4} mol dm^{-3} was used. The value of k_{obs} was independent of initial acid concentration within experimental error. [c] Values of k_f^H and k_b were obtained from plots of k_{obs} against base concentrations according to eqn (2). Uncertainties are standard deviations.

283±7 mol^{-1} dm^3 s^{-1} at 298 K,[10] while in the present study a value of k_f^H of 228±30 mol^{-1} dm^3 s^{-1} has been determined for the dibutyl analogue at the same temperature. This supports the present kinetic data, particularly at temperatures close to ambient where temperature control is satisfactory.

TABLE 2.—SUMMARY OF KINETIC AND ACTIVATION PARAMETERS FOR REACTIONS OF DBBA AND DPBA WITH 4-NPNM AT 298 K (EXCEPT AS NOTED)

solvent	$k_f^H/10^{-2}$ mol^{-1} dm^3 s^{-1}	K_b^H/s^{-1}	E_{af}^H/kJ mol^{-1}	E_{ab}^H/kJ mol^{-1}	K^H(k)	K^H(sp)
		DBBA				
CCl_4	0.84±0.25	1.14±0.59	—	—	—	
DBE	1.48±0.19	7.51±0.42	12.3±4.6	79.5±5.3	19.7	
$C_6H_5OCH_3$	2.28±0.30	8.82±0.40	9±7	63±4	25.9	
CB	2.65±0.43	9.24±0.45	11.2±3.5	65.2±5.8	28.7	
THF	3.29±0.43	3.90±0.64	14.3±3.2	69.8±4.5	84.4[a]	71.9[b] (297.6)
CH_2Cl_2	5.24±0.26	4.15±0.17	23.2±7.3	114±26	126	
		DPBA				
CCl_4	0.62±0.10 (293)	2.54±0.18 (293)	—	—	—	
DBE	1.61±0.20	8.12±0.52	13.8±3.9	94.0±8.8	19.8	
CB	4.18±0.79	13.4±1.1	15.1±4.1	96.9±4.9	31.2	

[a] K^H(k), (range 276-303 K) $\Delta H^\ominus = -55.3 \pm 6.6$ kJ mol^{-1}; b K^H(sp), (range 279-303 K) $\Delta H^\ominus = -58.1 \pm 3.4$ kJ mol^{-1}.

DEUTERON TRANSFER

It has been noted earlier that extraneous water affects the deuteron-transfer reaction more than the proton ionisation for the TMG system in toluene.[17] Therefore the limited data reported below for the deuteron-transfer reaction, for the benzimidamides with 4-NPNM in chlorobenzene and in di-l-butyl ether and for DBBA in anisole, are probably more subject to the effect of the presence of water, even though such an effect is not readily apparent, and are to be treated as provisional. For the reaction in anisole there is a further reason for caution. After being allowed to stand in anisole for a few hours a sample of [^{2}H]4-NPNM loses a significant fraction of initial deuterium. This is shown by the appearance of two steps widely separated in time in the stopped-flow spectrophotometer. The first step corresponds to the proton-transfer reaction (in the tenths of a second range), and the second stage occurs over several seconds, which corresponds to the loss of a deuteron from the acid. The results reported are from experiments conducted within about an hour of making the anisole solution of [^{2}H]4-NPNM, before the hydrogen exchange on the acid has reached a very significant proportion. This rapid exchange process did not occur with other solvents, in which the deuterated acid appears to be stable virtually indefinitely. It is not known what component of the solvent or impurity facilitates this rapid exchange in anisole. The effect of this spurious exchange upon the exclusive proton-transfer reaction (k_f^H) would be negligible.

At 298 K apparent values of k_f^D are 5.32±0.04 and 4.82±0.40 mol^{-1} dm^3 s^{-1} in di-l-butyl ether and 14.1±1.0 and 12.5±0.3 mol^{-1} dm^3 s^{-1} in chlorobenzene for reactions of DBBA and DPBA, respectively. These are extrapolated from results at other temperatures. In anisole the value of k_f^D, measured at 298 K for the reaction of DBBA, is 7.98±0.17 mol^{-1} dm^3 s^{-1}. The range of excess base and concentrations of acid and base are similar to those used in the proton-transfer studies.

For deuteron transfer to deuterated DPBA in chlorobenzene apparent values of k_f^D are 15.8±0.6 mol^{-1} dm^3 s^{-1} at 294.9 K and 12.9±1.0 mol^{-1} dm^{-3} s^{-1} at 297.5 K for two independent determinations. When eqn (2) is used for deuteron-transfer reactions it is not possible to determine k_b^D reliably because the intercept seems to be anomalously low, a situation noted by others for similar systems.†

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† For example ref. (1).

ACTIVATION PARAMETERS AND EQUILIBRIUM CONSTANTS

The Arrhenius activation parameters, where determined, are subject to a higher probable error than those determined for the TMG system. This arises because standard deviations in k_f and k_b are generally larger than those reported earlier; in turn this can be attributed in part to the less favourable equilibrium position (the benzimidamides are weaker bases than TMG) yielding smaller signal amplitude changes and in part to the less satisfactory temperature control of the reactant and product solutions with the available instrument. The relatively small possible temperature range that can be employed also contributes to the magnitude of error in the activation parameters. Despite these difficulties the ranges of activation energy are clear (table 2). For forward transfer of the proton the range is E^H_{af} = 10-23 kJ mol^{-1} and for the reverse reaction the activation energy E^H_{ab} is 65-114 kJ mol^{-1} for DBBA in five solvents. For reactions of DPBA in di-1-butyl ether and chlorobenzene, E^H_{af} is 14-15 kJ mol^{-1} while E^H_{ab} is 94-97 kJ mol^{-1}.

Provisional values (all in kJ mol^{-1}) of the activation energies for the deuteron-transfer reactions are for reaction of DBBA: $E^D_{af} = 37 \pm 4$ (six temperatures, 272-300.2 K) in di-1-butyl ether, $E^D_{af} = 22 \pm 3$ (three temperatures, 277.6-298 K) in anisole, and $E^D_{af} = 33.4 \pm 7.5$ (four temperatures, 277.6-293 K) in chlorobenzene; and for reaction of DPBA, $E^D_{af} = 39 \pm 5$ (five temperatures, 280.5-299.8 K) in di-l-butyl ether, $E^D_{af} = 42.5 \pm 1.3$ (four temperatures, 273.4-300.3 K) in chlorobenzene.

A series of determinations at four temperatures using deuterated DPBA in chlorobenzene, over the range 281.6-297.5 K, yields a provisional value of $E^D_{af} = 42 \pm 8.8$ kJ mol^{-1}. No determinations of E^D_{ab} are possible since k^D_b is not calculated, as indicated above.

Values of the equilibrium constant for the formation of the protonated base, derived from the ratio of the forward and reverse rate constants, range from 20-30 mol^{-1} dm^3 in very low-polarity solvents such as di-1-butyl ether ($D = 3.06$) and carbon tetrachloride ($D = 2.28$) to *ca.* 130 mol^{-1} dm^3 in the relatively high-polarity solvent dichloromethane ($D = 9.08$). The values of K^H (table 1) are subject to a significant error (not reported) as a derived value, but a general trend of increasing strength of the acid–base reaction with increase in dielectric constant is observed. In one solvent, tetrahydrofuran, the equilibrium constant has been measured spectrophotometrically, and the value obtained, 72 mol^{-1} dm^3 at 298 K, is reasonably consistent with the kinetically derived value (84 mol^{-1} dm^3). In this solvent the reaction enthalpy change, $\Delta H^{\ominus}$, is determined as -58.1 ± 3.4 and -55.3 ± 6.6 kJ mol^{-1} by the equilibrium and kinetic methods, respectively, in satisfactory agreement.

Considering the error associated with the determination of k^D_b, calculation of K^D is not warranted. If K^D has a similar magnitude to K^H, as would be expected, then the intercept of the plot of k_{obs} against benzimidamide concentration, although small, would be detectable. However, it is very small and not distinguishable from zero. There are several possible reasons for the observation being at variance with the prediction, but because of the provisional status of the deuteron-transfer results these will not be described. Use of deuterated *NN*-di-1-propylbenzimidamide in an effort to eliminate isotopic exchange yields results which also give rise to low intercepts on the k_{obs} axis. This, however, is an ambiguous result since traces of water present could facilitate the dedeuteration of the base.

DISCUSSION

The forward proton-transfer reaction is characterized by rate constants in six solvents which range from 84 $dm^3\ mol^{-1}\ s^{-1}$ in carbon tetrachloride to 524 $dm^3\ mol^{-1}\ s^{-1}$ in dichloromethane, for DBBA at 298 K. The dipropylbenzimidamide reaction with 4-NPNM has rate constants similar to those for DBBA in the three solvents in which it has been studied. The results are consistent with a pattern of partial transfer of charge in the activated complex, and parallel those of Caldin and Mateo[1] for the reaction of TMG with 4-NPNM. In the latter reaction with the stronger base, a greater range of solvent dielectric was used but the magnitude of solvent dielectric influence on rate was smaller.

In di-l-butyl ether and in chlorobenzene, at 298 K, k_f^H and k_b^H values vary little with varying alkyl group on the base, indicating that the bulkiness of these offer similar hindrance or no hindrance to the acceptance of the proton. This pattern is repeated in comparing the values of k_f^H in anisole for DBBA and the diethyl analogue,[10] and is sustained in consideration of the deuteron-transfer reactions to both DBBA and DPBA in di-1-butyl ether and in chlorobenzene. The equilibrium constants, reflecting the completed acid–base reaction, increase with increase in solvent polarity, are in agreement with prediction and mirror the results for the substituted guanidine reaction.

Energies of activation for the forward proton-transfer reaction are very small (10-23 $kJ\ mol^{-1}$) and imply that the entropies of activation are large and negative. For the reaction with DBBA a plot of the logarithm of k_f^H against the solvent permittivity function $(D-1)/(2D+1)$ (employing the relationship derived by Kirkwood[25]) is reasonably linear (fig. 1) with a positive slope, indicating the development of a polar activated complex and supporting the model of solvent dielectric effects upon the kinetics of reaction of neutral molecules where non-electrostatic influences of solvent upon the activated complex are similar to those upon the reactants.[25] The range of values of E_T, the empirical solvent polarity parameter, for the solvents used[26] is limited, but the plot is consistent with a linear dependence of log k_f^H on E_T (fig 2), as expected for a reaction producing ions. Both plots are reasonably similar to those found for the corresponding reaction with TMG. Results for proton and deuteron transfer in toluene from 4-NPNM to various bases, where isotope exchange on the base has been incorporated in the kinetic scheme and where extraneous water is considered to have a negligible effect, have been plotted by Rogne *et al.*[14] in the form of a Brønsted-type plot (log k_f^H and log k_f^D against log K^H). The results reported here for k_f^H and K^H in di-1-butyl ether and in anisole (which have dielectric constants fairly close to that of toluene) fit well to the lower of the two lines described. The slope gives a Brønsted coefficient of *ca.* 0.9, indicative of a high degree of transfer of the proton in the transition state. This is difficult to reconcile with the very low energy barrier and the highly exothermic nature of the reaction in the forward direction, which would give rise to the prediction of a reactant-like configuration in the transition state.

It appears that the proton transfer is anomalous in that the energies of activation (10-23 $kJ\ mol^{-1}$) are barely greater than that characteristic of diffusion control, yet the rate constants are seven or eight orders of magnitude lower than typical values for diffusion control at 298 K. In contrast the provisional values of E_{af}^D are 30-40 $kJ\ mol^{-1}$. The isotope effect (k_f^H/k_f^D) based on provisional values of k_f^D is in the range 20-30 at 298 K. Both of these results, *viz.* $\Delta E_a = E_{af}^D - E_{af}^H > 4\text{-}5\ kJ\ mol^{-1}$ and $k_f^H/k_f^D > 7$, are thought† to be criteria for tunnelling, and lead to the requirement of a tunnelling correction for the reaction rate. Hence these results would imply that

† For example chap. 4 of ref. (5).

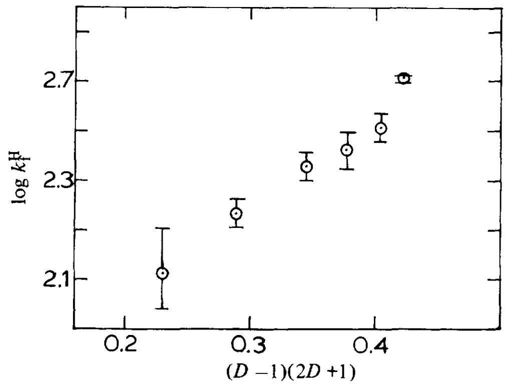

FIG. 1.—Plot of log k_f^H for proton transfer from 4-NPNM to DBBA against the solvent permittivity function, $(D-1)/(2D+1)$, in various solvents at 298 K. See text for the basis of this plot. The points in order of increasing value along the abscissa are for the reaction in carbon tetrachloride, di-1-butyl ether, anisole, chlorobenzene, tetrahydrofuran and dichloromethane.

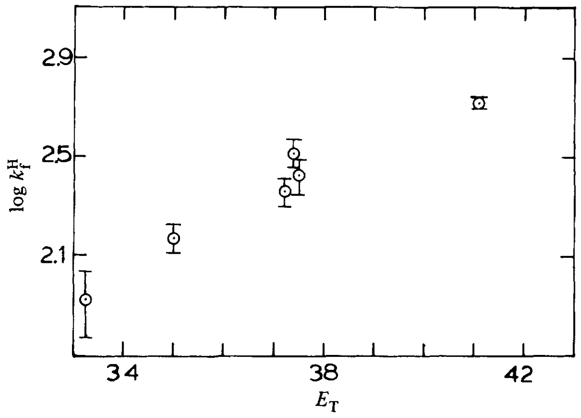

FIG. 2.—Plot of log k_f^H for proton transfer from 4-NPNM to DBBA against the empirical solvent polarity parameter, E_T, in various solvents at 298 K. The points in order of increasing value along the abscissa are for the reaction in carbon tetrachloride, di-1-butyl ether, anisole, tetrahydrofuran, chlorobenzene and dichloromethane.

tunnelling may occur in the transfer of a proton from 4-NPNM to benzimidamides. Since, however, the deuteron results are as yet only provisional, a conclusion regarding tunnelling is not justified at present.

We have considered the application to the present work of the two principal criticisms levelled at earlier work in this area where tunnelling has been invoked. The influence of extraneous water upon the reactions reported here can be predicted to be insignificant for proton transfer but may not necessarily be disregarded for deuteron transfer. The effect of rapid hydrogen exchange upon the imine nitrogen of the base acceptor has been fully discussed.[15, 19] For the benzimidamide systems, rapid isotopic exchange would have even greater consequences for producing an apparent rate constant which does not truly represent k_f^D, since the ratio of k_b^D to k_f^D is much higher than it would be in the guanidine system. Prevention of isotopic mixing can be achieved by deuterating the amine nitrogen before reaction occurs. Our limited data for the reactions of deuterated base with deuterated 4-NPNM are compatible with a scheme in which isotopic exchange is not rapid. However, it is conceivable that reactions of both deuterated and non-deuterated base could be affected by extraneous water. We hope to report later the results of further measurements made with special precautions to exclude water.

The authors are indebted to Dr C. J. Wilson for discussions prior to this work and to Prof. E. F. Caldin for sharing results prior to their publication. C.D.H. also acknowledges with gratitude extensive personal discussion and correspondence with Prof. Caldin. Neil Linsky and Elizabeth Corless are thanked for their assistance with preliminary experimental work, and Philip Duce is thanked for help with some calculations. This research was supported in part by the Central University Research Fund of the University of New Hampshire, Graduate School and Research Office.

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