The Kinetics of Reaction of 4-Nitrophenylnitromethane with N'-Propyl-N,Ndipropylbenzimidamide in Aprotic Solvents. A Steric Effect on Tunneling

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Thermodynamic and kinetic parameters have been established for the reaction between the carbon acid, 4-nitrophenylnitromethane, (4-NPNM), and the base N'-n-propyl-N,N-di-n-propylbenzimidamide, (N'PDPBA), in mesitylene and in chlorobenzene. In some cases deuteron transfer from $4-(D_2)NPNM$ to the base has also been studied. In addition, some results for the proton transfer reaction in tetrahydrofuran have been collected. Spectrophotometric methods have been employed to monitor the ion-pair product, which is solvatochromic. In general the solvent dependence of the parameters is as expected, but there is some indication of specific solvation. The kinetic isotope effects of 11 and 8 in mesitylene and chlorobenzene, respectively, are larger than those predicted classically. However, as is discussed the n-propyl group on the secondary nitrogen of the base may serve to reduce the extent of tunneling compared to that in an unsubstituted analogue by a steric effect.

KEY WORDS: Carbon acid-base reaction; kinetics; isotope effects; tunneling; steric effect.

1. INTRODUCTION

There have been many attempts to define the exact nature of those Cacids and their respective base proton acceptor partners which, in aprotic

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solvents, react to yield kinetic isotope effects (KIE, k^{H}/k^{D}), and other kinetic parameters indicative of proton tunneling;⁽¹⁻¹⁰⁾ however, the definition, and particularly as it refers to a steric influence on tunneling is far from complete. Controversy has arisen since early reports $^{(1,2)}$ of examples of proton tunneling, and of the solvent dependence of KIE, were said not to have taken into account the exchange process which could pertain when a deuteron transfers to a base containing a kinetically labile proton.⁽¹¹⁻¹⁶⁾ The solvent of focus was toluene. One effort to clarify the situation involved the measurement of tritium loss from tritiated 4-nitrophenylnitromethane (4-(T)NPNM) in the presence of 1,1,3,3-tetramethylguanidine (TMG).^(15,16) Extrapolation of the result from this experiment yielded a KIE which was much lower than the value originally reported,⁽²⁾ but still of a magnitude fitting a criterion for proton tunneling. The presence of extraneous water in solvents has been proposed as an explanation for discrepancies in results, particularly for reaction in toluene from which it is very difficult to remove water.⁽¹⁴⁾ Use of methyl substituted TMG, pentamethylguanidine, PMG, thus removing the potentially exchangeable hydrogen, yielded KIE values lower than were reported for TMG, which suggested⁽¹³⁾ that the extent of tunneling was reduced or the kinetic results obtained for deuteron transfer, using the unsubstituted guanidine, were not reliable. The bicyclic base DBU, (1,8-Diazabicyclo [5.4.0] undec-7-ene), has also been used⁽¹⁷⁾ to function as the proton (deuteron) acceptor, and has the merit of no exchangeable hydrogen; lower KIE values were observed, heightening the view that the earlier results using TMG as a base may not be dependable for calculation of tunneling corrections. Those studies employing PMG and DBU introduce possible steric constraints at the locus of transfer, and therefore the lower KIE values do not offer completely unequivocal proof that the original KIE values are not authentic.

One possible approach to resolution is a comparison of the KIE for reaction of a deuterated acid with deuterated base, the latter deuterated at the exchangeable site, and with undeuterated base. In a limited study using $4-(D_2)NPNM$ and deuterated dipropyl-benzimidamide, [(D)DPBA] in chlorobenzene, KIE values were very similar, barely outside of experimental error.⁽¹⁸⁾ However, it is conceivable that H/D exchange could occur at the deuterated site in (D)DPBA between the time of solution preparation and kinetic measurement rendering the close agreement of KIE perhaps fortuitous and of limited value. Considerable spurious H/D exchange by $4-(D_2)NPNM$ has been observed with anisole as solvent.⁽¹⁸⁾

Our interest in the kinetic and equilibrium properties of these systems has centered around solvent influences upon them and explanation of them.^(18–20) It was suggested in an early study⁽²⁾ that important differences in solvent effects on the KIE values for these systems, whereby an increase in solvent dielectric constant gave rise to a reduction in the KIE, arose because a more highly

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polar solvent effected an increase in the mass of the transferring proton (deuteron). Later work using toluene and dimethylsulfoxide⁽⁶⁾ has indicated that KIE values in some reactions are independent of dielectric constant, which led to the proposal of an uncoupled mechanism in which proton transfer precedes the solvent relaxation. Toluene^(2,9) and acetonitrile^(21,22) have been widely used, but evidence for some specific solvation effects is emerging from studies using other solvents.^(9,20) Several studies report that there is a steric effect upon tunneling, or potential tunneling reactions, sometimes apparently an enhancement, and in other cases a reduction.^(6–8,23–30) An examination of results obtained provides little scope for predicting the direction or magnitude of a steric effect. In the present paper the kinetics results for the reaction, [Eq. (1)], between



N'-propyl-N,N-dipropylbenzimidamide, (N'PDPPA), and 4-NPNM are reported as well as are the appropriate corresponding equilibrium parameters in mesitylene and in chlorobenzene. The purpose of obtaining these parameters is to improve our understanding of steric effects on this type of reaction, thereby on tunneling, and of variation of these effects with solvent. Some results are also reported for this reaction in tetrahydrofuran.

2. EXPERIMENTAL

2.1. Materials

4-NPNM was prepared and deuterated according to literature methods as reported previously.⁽²⁰⁾ N'PDPBA was prepared by a variation of the synthetic method of Weintraub.⁽³¹⁾ Direct application of the Weintraub method, *viz.* reacting N-propylbenzamide with triethyloxonium tetrafluoroborate in methylene chloride and reacting the precipitated salt, (by diethyl ether) with excess di-*n*-propylamine in absolute ethanol did not yield the desired product.

The procedure which was successful involved reacting the secondary amide, N,N-di-*n*-propylbenzamide, with triethyloxonium tetrafluoroborate in methylene chloride. Anhydrous diethyl ether was used to precipitate the intermediate tetrafluoroborate salt. Subsequently the salt, dissolved in absolute ethanol, was treated with an excess of n-propylamine, which resulted in the formation of crude N'PDPBA. Purification yielded a colorless oil, which was characterized by elemental analysis and standard spectroscopic methods. Elemental Analysis: percents, calculated for $C_{16}H_{26}N_2$: C 77.99; H 10.64; N 11.37; found, C 77.45; H 10.78; N 11.42.³

The solvents used in equilibrium and kinetics experiments, mesitylene, chlorobenzene, and tetrahydrofuran were the highest grade available (from Aldrich), and used as reported earlier.⁽²⁰⁾

2.2. Methods

Equilibrium measurements. The standard method which utilizes the Benesi-Hildebrand approach, was used to determine the equilibrium constants, $K^{(20)}$ Temperature was controlled in the range 15°C-40°C with circulating fluid from a Neslab Endocal RTE 8 thermostat bath. The observations were made at 435, 451, and 459 nm, respectively, in mesitylene, chlorobenzene, and tetrahydrofuran, on a Cary 219 spectrophotometer.

2.3. Kinetics

For the more rapid reactions kinetics were followed using a Nortech Laboratories (Hi-Tech) stopped-flow spectrophotometer, model SF-3L. The flow path is immersed in fluid which can be controlled to a given temperature, $\pm 0.1^{\circ}$ C. Data were acquired and treated using Hi-Tech supplied software by an Apple IIe computer, or reaction traces were recorded on a Tektronix oscilloscope as a trace of voltage *vs.* time and processed manually. Slower reactions (deuteron transfer) could be studied more conveniently using a Cary 219 spectrophotometer, with cuvettes regulated in temperature as already described. The Varian Advanced Kinetics Calculation program was used to process data. Wavelengths of observations for kinetics measurements were the same as those reported for equilibrium measurements.

In all cases solutions were made up immediately before use, with minimum exposure to the atmosphere. Kinetics experiments were run under pseudo first-order conditions, [N'PDPBA]>>[4-NPNM], so that data were collected with the assumption that they would be consistent with first order kinetics. The assumption was justified as excellent first-order plots were obtained, under all conditions reported. Concentrations and temperature ranges were selected to optimize the range of measurement and to avoid any potential problems of solute precipitation, while also avoiding approaching the time resolution limits of instruments.

Equilibrium parameters reported are an average of at least three individual experiments, and each observed rate constant k_{obs} used for the calculation of other kinetic parameters is an average of at least three, and usually five or six replicate measurements.

³Analysis performed at the University of New Hampshire by Deanna Cardin.

3. RESULTS AND DISCUSSION

3.1. Equilibrium

Equilibrium constants, ΔH° and ΔS° for the title reaction in mesitylene, chlorobenzene and THF are reported in Table I. Figure 1 is a typical plot of ln K vs. the reciprocal of the temperature, used to determine ΔH° . Clearly the solvent dependence of the magnitude of K is not consistent with a simple prediction based upon solvent polarity, viz. for a reaction in which ions are produced from neutral species, the product would be increasingly stabilized by increasingly polar solvents. The fact that K (89.5) in THF (dielectric constant $\epsilon = 7.25$) is less than is K (144) in mesitylene ($\epsilon = 2.28$) argues for either or both of favorable stabilization of reactants and relatively poor

 Table I.
 Equilibrium Constants and Thermodynamic Parameters for the Reaction of 4-NPNM and 4-(D₂)NPNM with N'PDPBA in Aprotic Solvents

°C	$10^{-2} K (mol - dm^{-3})$	$\Delta H^{\circ}(kJ-mol^{-1})$	$\Delta S^{\circ}(J-mol^{-1}-K^{-1})$
		Mesitylene ^a	
34.2	0.768 ± 0.05	-52.4 ± 0.7	-134 ± 3
29.2	1.11 ± 0.10		
25.4	1.44 ± 0.19		
20.2	2.15±0.07		
14.8	3.15 ± 0.03		
		Chlorobenzene ^b	
34.5	4.51 ± 0.02	-51.3 ± 0.9	-116±3
29.3	6.63 ± 0.05		
24.8	8.73±0.01		
24.6	9.01 ± 0.17		
19.7	12.8±0.3		
15.0	17.5±0.3		
	(Chlorobenzene ^{b,c}	
34.6	4.84±0.03	-52.4 ± 2.5	-119±9
29.2	6.69 ± 0.14		
24.7	8.73±0.01		
19.9	12.60±0.10		
15.2	19.4±0.3		
		THF ^d	
33.2	0.64 ± 0.02	-37.6 ± 3.0	-89 ± 11
25.2	0.895 ± 0.008		
15.8	1.56±0.02		

 $^{a}\epsilon = 2.28, \lambda = 414$ nm.

 ${}^{b}\varepsilon = 5.62, \lambda = 424$ nm.

^cDeuteron transfer.

 $d\epsilon = 7.28, \lambda = 437$ nm.



Fig. 1. Plot of ln K vs. 1/T for reaction of 4-NPNM with N'PDPBA in mesitylene.

solvation of product ion-pair in THF compared with mesitylene. Product solvation by chlorobenzene is very favorable (K = 872). Specific solvation which is dependent on solvent characteristics other than mirrored in the dielectric constant must be responsible. This feature of specific solvation with respect to chlorobenzene has been noted previously,⁽²⁰⁾ but less markedly so, for reaction between 4-NPNM and DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene). In this earlier work it appeared that, based upon the results for several solvents, a specific solvation effect of chlorobenzene rather than of THF as reflected in a larger ΔG° , caused the divergence from a straightforward dependence of K upon a measure of solvent polarity. The nature of this specific solvation is not obvious, whether one considers steric or unsaturated characteristics of the solvents. Other authors⁽⁹⁾ have also noted that kinetic parameters of this type of system do not always follow the simplest predicted trend with respect to solvent properties.

The formation of product is similarly exothermic in mesitylene and chlorobenzene and much less so in THF. This again may be a consequence of some particular functional difference in solvational ability of these solvents. If this suggestion is correct then it could be argued that the ether linkage of THF contributes to a lowered effectiveness of THF in stabilizing the ionpair product than the aromatic solvents, even though the dielectric constant of the former is higher. As expected, ΔS° values are negative as a reduction in species occurs upon product formation, and in addition because some solvent will be increasingly restricted by the charged nature of the product. Yet the trend in ΔS° is opposite from what might be expected. That ΔS° for the more polar THF is less negative (-89 J-mol⁻¹-K⁻¹) than it is for the nonpolar mesitylene (-134 J-mol⁻¹-K⁻¹) may indicate that the ion-pair product in mesitylene is a contact pair, in which there is some mutual charge neutralization, whereas in solvents of higher dielectric strength the solvent

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may be able to stabilize the product as relatively separate charges. However, based on the small data sample these arguments are quite speculative. Table I also illustrates that in chlorobenzene, the equilibrium constant, and associated thermodynamic parameters, are virtually identical for H^+ and D^+ transfer to form the product. Similar results have been found in other C-acid/base systems⁽²⁰⁾ indicating a lack of any significant acidity difference between the two hydrogen isotopes.

The maximum wavelengths of absorption of the ion-pair, [4-NPNM]⁻[NPDPBA]⁺, are 414nm, 424nm, and 437nm for mesitylene, chlorobenzene, and THF, respectively. Solvatochromism has been observed previously in other similar systems.^(2,18-20) Here the bathochromic shift increases with increasing solvent dielectric constant, which indicates increasing dipolar character of the excited state with respect to the ground state.⁽³²⁾ This could imply that the positive and negative centers of the cation and anion partners of the ion-pair become further separated, or charges are more delocalized, in the excited state as solvent polarity increases. The product species when solvents of higher dielectric constant are used are indeed free ions as judged by conductivity measurements.^(7,26)

3.2. Kinetics

The reaction rate is first order in the concentration of both the C-acid and the base. Kinetic measurements were made with the base in large excess so that the reaction rate is measured under pseudo first-order conditions. Table II provides a listing of the ranges of concentrations, the first order rate constants k_{obs} for reaction in each solvent, for proton transfers and deuteron transfers. In each case, at each temperature there is a reasonably linear correlation when k_{obs} is plotted against base concentration, allowing the second order rate constants (also listed in Table II) to be obtained from the slopes of such plots. The thermal activation parameters, ΔH^{\ddagger} and ΔS^{\ddagger} , were obtained by a standard method, and are presented in Table III. A puzzling aspect of this study is the unsatisfactory agreement between the equilibrium constants measured directly and those obtained from the ratio of forward rate constant to that obtained from the extrapolation to zero base concentration of the k_{obs} vs. base concentration plot. The latter is only feasible for the proton transfer reactions since the intercept is too small to obtain it reliably for the deuteron transfer. This lack of agreement, outside of experimental error, normally could be indicative of the formation of an intermediate species in the kinetic pathway. However, no other hint of the existence of such species arises from the equilibrium or kinetic observations, and there is no precedent for it in many comparable reaction systems in solvents of low dielectric constant such as used here. Therefore, this point remains unresolved at present.

°C	10 ³ [N'PDPBA] M	$10^2 k_{\rm obs} ({\rm s}^{-1})$	k (L-mol ⁻¹ s ⁻¹)
	М	esitylene ^{<i>a</i>,<i>b</i>}	
45.1	0.670-6.03	288-320	60.8 ± 3.3
40.0	0.890-6.23	174-206	58.3 ± 1.4
34.8	1.02-8.16	98.4-133	47.7±2.7
29.9	1.02-8.16	60.4-83.2	32.2 ± 0.8
25.0	0.503-10.1	36.7-64.6	29.5 ± 1.6
19.8	0.670-4.69	22.0-31.6	24.0 ± 4.5
	М	esitylene ^{c.d}	
38.3	0.795-1.58	0.427-0.883	5.79 ± 0.06
34.3	0.795-1.58	0.346-0.722	4.75 ± 0.04
29.1	0.907-1.80	0.335-0.649	3.50 ± 0.09
24.4	1.13-2.91	0.305-0.784	2.67 ± 0.09
19.6	0.795-1.38	0.189-0.315	2.19 ± 0.04
	Chl	orobenzene ^{a,e}	
39.5	1.22-6.10	202-297	202±13
35.0	1.00-5.00	121-181	152±9
29.9	1.10-5.50	75.6-125	112 ± 18
25.0	0.435-4.29	44.3-83.9	104 ± 5
20.0	1.04-5.20	34.0-61.7	67.9
15.6	1.00-6.00	27.3-48.7	42.9±0.7
	Chle	probenzene ^{c, f}	
34.5	0.216-0.859	0.491-1.94	22.6±0.2
28.8	0.216-0.859	0.388-1.43	16.3±0.1
24.8	0.270-0.752	0.414-1.05	13.2 ± 0.1
24.7	0.270-0.806	0.444-1.12	12.6 ± 1.0
19.8	0.270-1.34	0.357-1.49	10.9 ± 0.5
14.8	0.223-0.931	0.304-1.26	
		THF ^{a,g}	
25.0	0.45-2.30	53-116	247

Table II. Kinetic Data for the Reaction of 4-NPNM and $4-(D_2)NPNM$ with N'PDPDA in Aprotic Solvents

^aH⁺ transfer.

^b[4-NPNM] = $1.28 - 2.66 \times 10^{-5} M$. ^cD⁺ transfer. ^d[4-(D₂)NPNM] = $4.75 - 5.00 \times 10^{-5} M$. ^e[4-NPNM] = $1.91 - 4.25 \times 10^{-5} M$. ^f[4-(D₂)NPNM] = $1.48 - 1.63 \times 10^{-5} M$.

 $g[4-NPNM] = 2 \times 10^{-5} M.$

The second order rate constants for proton transfer follow an expected trend of increasing magnitude with increasing dielectric constant. Since only three points are available, attempts at quantitative correlations of the kinetic and solvent properties would not be meaningful. However, the feature of

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 Table III.
 Thermal Activation Parameters for the Reaction of 4-NPNM with N'PDPBA in Mesitylene and Chlorobenzene

Solvent	Transfer	ΔH^{\ddagger} kJ-mol ⁻¹	ΔS^{\ddagger} J-mol ⁻¹ - K^{-1a}
Mesitylene	H⁺	28.6±3.3	-121±11
Mesitylene	D+	37.9 ± 1.6	-109 ± 5
Chlorobenzene	H⁺	42.9±4.2	-64 ± 13
Chlorobenzene	D+	35.7 ± 3.5	-103 ± 12

^a Value at 25.0°C.

differing specific solvation effects invoked to explain some of the equilibrium quantities (vide supra), is absent or of smaller magnitude. That the transition state involves the partial movement of the proton from the methylene carbon of the acid to the receiving nitrogen of the imidamide, *i.e.*, the species are in close proximity in each solvent, supports the idea that the reason for the equilibrium properties not following a predictable trend is because the interaction of the solvent with the product can be either with a contact ionpair or with a solvent separated ion-pair. For proton transfer in mesitylene and chlorobenzene the enthalpy barrier to reaction, ΔH^{\ddagger} is 29 and 43 kJ mol^{-1} , respectively; values not necessarily consistent with expectation but possibly associated with different degrees of tunneling. The significantly negative entropies of activation, (see Table III), are consistent with increased molecular ordering within the activated complex, relative to the reactants. In addition although both solvents are of low polarity the developing charges within the activated complex could exert a restriction on them also contributing to the negative ΔS^{\dagger} . Deuteron transfer is markedly slower in both mesitylene and chlorobenzene, with KIE values at 25°C of 11 and 8, respectively. A tunneling component may be invoked to explain these values, but of smaller contribution as the solvent dielectric constant increases. Supporting experimental criteria such as the difference in enthalpies of activation and ratio of the preexponential (A) factors cannot be applied here as regrettably the activation parameters could not be obtained with sufficient precision. Indeed the enthalpies of activation for reaction in chlorobenzene are in reverse order from expectation if tunneling is significant. The KIE values are considerably smaller than those obtained in the same solvents with the unsubstituted imidamide, DPBA.⁽¹⁸⁾ If literature values of KIE values for the nonpropylated imidamide are authentic (reservations were noted in the Introduction), then this would indicate a significant steric effect, and a reduction of the extent of tunneling. Ideally a homologous series of substituents should be applied to the sp² nitrogen atom of DPBA and parallel thermodynamic and kinetic parameters acquired. However, while this course is being pursued, obtaining

such parameters with sufficient precision to render a systematic study of this potential steric effect meaningful may be a limiting practical factor.

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