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Equilibrium and kinetic study of the proton transfer reactions between nitroalkanes and strong organic bases - phosphazenes in tetrahydrofuran solvent

Research Article

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Abstract: Proton transfer reactions rates between carbon acids 1-nitro-1-(4-nitrophenyl)ethane (NPNE), 2-methyl-1-nitro-1-(4-nitrophenyl) propane (MNPNP)) and phosphazenes (BEMP, BTPP, P_1-t-Oct) in tetrahydrofuran have been measured, and the activation parameters were determined. The results are compared with those previously obtained for P_1-t-Bu phosphazene, guanidines and amidines.

Keywords: *Proton/deuteron transfer • Carbon acids • Phosphazene bases*

1. Introduction

Phosphazenes developed by R. Schwesinger are non-ionic, strong organic bases with low nucleophilicity and pK_a ranging from 26 to 42 (Table 1) [1-10]. Our previous study reported the results obtained for the proton transfer reaction between P_1-t-Bu phosphazene base and a series of nitroalkanes with increasing substituent masses at the reaction center [11]. The rate constant for the reaction of 1-nitro-1-(4-nitrophenyl)alkane with P_1-t-Bu phosphazene base is 9357 dm^3 mol^{-1} s^{-1}. The exchange of the hydrogen atom attached to the α-carbon atom for the methyl group decreases the rate constant by three orders of magnitude [11]. The increase of the alkyl substituent mass by replacement of the methyl with an ethyl or iso-propyl group causes a further decrease of the rate constant a few times over. The second order rate constants obtained for P_1-t-Bu and nitroalkanes were: 9357, 2.31, 0.66, 0.09 dm^3 mol^{-1} s^{-1} for H, Me, Et, and i-Pr substituents, respectively [11]. These results show that the steric factor and ordering effects in forming the transition state play an important role, confirmed by negative and relatively large entropies of activation: $\Delta S^{\ddagger}$ = – 149.7, –176.5, –178.7, –227.8 J mol^{-1} K^{-1}. The reactions between nitroalkanes with different steric hindrance and classic nitrogenous bases such as amidines or guanidines in acetonitrile and tetrahydrofuran have been disscussed previously [12-15].

In this work the equilibrium and kinetic study of the proton transfer reaction between phosphazenes and nitroalkanes has been studied (Fig. 1). The scope of phosphazene bases has been broadened. Three P_1-phosphazene bases: P_1-t-Oct, BTPP and BEMP with different steric hindrances and pKa values were used in the experiments. Reproducibility problems with more basic phosphazenes prevented us from detailed study of deprotonation of carbon acids promoted by P_2 or P_4-phosphazenes [1,4,16].

P_1-Oct has very similar basicity to that of P_1-t-Bu, used previously, but has a bulkier substituent at the imine nitrogen. BTTP has the same substituent at the imine nitrogen as P1-t-Bu but the dimethylamino groups are replaced by pyrrolidine rings. This is the strongest base used in this study. BEMP, which has t-Bu group at the imine nitrogen, and a phosphorine ring displays an intermediate basicity.

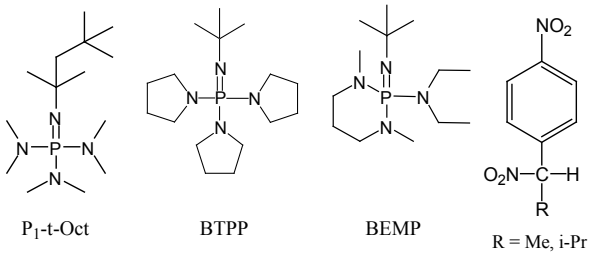

Figure 1. Phosphazenes and carbon acids.

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2. Experimental Procedure

Tetrahydrofuran, anhydrous 99.9%, inhibitor-free from Aldrich was stored over sodium and then distilled over Na/benzoquinone ketyl in the apparatus under argon. Careful purification of THF is critical for reproducibility of the equilibrium and kinetic results because peroxides react readily with phosphazenes. We found that untreated commercial "high quality" solvent should not be used even for preliminary rinsing of the stopped flow instrument since the peroxides apparently penetrate the tubing and are not easily removed. In our experience the solvent must be freshly distilled, and transferred in an inert atmosphere.

Phosphazenes: BEMP, BTPP, P_1-t-Oct from Aldrich were used without any purification.

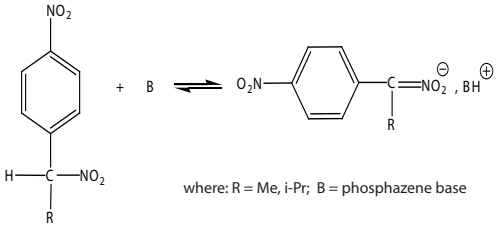
Previously prepared samples of carbon acids: 1-nitro-1-(4-nitrophenyl)ethane (NPNE), 2-methyl-1-nitro-1-(4-nitrophenyl)propane (MNPNP) and deuterated analogues have been used experimentally [13].

The solutions of phosphazene and carbon acid were freshly prepared before each experiment using freshly distilled tetrahydrofuran and flasks with septa.

Equilibrium measurements were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer fitted with a thermostatted cell holder. The kinetic experiments were performed on an Applied Photophysics spectrophotometer stopped-flow apparatus or on a Hewlett-Packard 8452A diode-array spectrophotometer, at λ_{max} of the reaction products (Table 2). The observed rate constants were measured for five different base concentrations, always in large excess over carbon acid to ensure pseudo-first-order kinetic conditions. The second order rate constants were found from the plots of k_{obs} versus base concentration. For the deuterated analogues the initial part of the kinetic curves was ignored to minimize the possible error caused by D/H exchange [17,18]. The activation parameters were calculated from the temperature dependence of the second order rate constants, k_f.

Table 1. pK_a val ues of strong organic bases in acetonitrile [2,4].

Base	pK_a
BEMP	27.58
BTPP	28.4
P_1-t-Bu	26.88
P_1-t-Oct	26.49
P_2-t-Bu	33.49
P_2-t-Oct	33.27
P_4-t-Bu	42.7
TBD	25.96
DBU	23.90
MTBD	25.43



where: R = Me, i-Pr; B = phosphazene base

Figure 2. Scheme of the reaction between nitroalkanes and phosphazene bases in tetrahydrofuran.

Table 2. λ_{max} values for the proton transfer reaction products in tetrahydrofuran.

C-acid	λ_{max}, nm		
	BEMP	BTPP	P1-t-Oct
MNPNP	500	502	496
NPNE	500	500	500

Table 3. Equilibrium constants for proton transfer reaction between MNPNP (5×10^{-5} M) and BEMP in tetrahydrofuran.

Temp., °C	K, dm^3 mol^{-1}	ε, dm^3 mol^{-1} cm^{-1}	reaction parameters
15	24 ± 1	16000 ± 500	
25	12,8 ± 0,5	15300 ± 500	ΔH = – 52 ± 3 kJ mol^{-1}
35	6,6 ± 0,3	15000 ± 800	ΔS = – 155 ± 10 J mol^{-1} K^{-1}
45	2,7 ± 0,7	19000 ± 5100	

3. Results and discussion

The carbon acids studied, NPNE and MNPNP, in the reaction with phosphazenes in THF (Fig. 2) give coloured ion pair products with a corresponding λ_{max} shown in Table 2.

The values of equilibrium constants shown in Tables 3, 4 and 5 were calculated from the Benesi-Hildebrand equation. The equilibrium constant, K, for the proton transfer reaction between NPNE and DBU was found to be 2060 M^{-1} (Table 8), while for the phosphazenes studied the equilibrium constants were too large to be measured. In the reaction between the more hindered MNPNP carbon acid, equilibrium constants are lower and are very similar to 5 M^{-1} for MNPNP-DBU or 3.7 M^{-1} for the MNPNP-P_1-t-Oct system. The previous results obtained by Wisłocka *at al.* [11] for the reaction between P_1-t-Bu and MNPNP or NPNE are very comparable with the equilibrium constant and rate constants presented for BEMP presented in Table 8. However, the equilibrium constant for the reaction of MNPNP with BTPP is ten times larger. This increase of equilibrium constant corresponds with the difference of pK_a of these bases (Table 1).

As can be seen, equilibrium constants for the reaction of carbon acids with phosphazenes were unexpectedly comparable to the results obtained for the weaker DBU base (Table 8). This effect could be caused by weaker interaction between ions in ion-pairs formed by phosphazene cation in comparison with ion-pairs formed by $DBUH^+$ in THF. This weaker hydrogen bonding between ion-pairs involving phosphazenium cations is supported by the fact that absorption bands for the phosphazene reaction products (see λ_{max} values collected in Table 2) are shifted by ~25 nm to the red compared to the bands of the $DBUH^+$ salts in the same THF solvent [13].

The results previously obtained for DBU, TBD and MTBD bases showed that these reactions are faster than with phosphazenes (Table 8), despite the Schwesinger bases are stronger than classic bases. The reason for this effect may be the steric factor in the vicinity of reaction center brought by the phosphazenes.

The activation parameters of the reaction systems studied are characterized by large negative entropy of activation values. For the reaction of MNPNP, $\Delta S^{\ddagger}$ = – 211 J mol^{-1} K^{-1} and –22 J mol^{-1} K^{-1} with BTPP and with P_1-t-Oct, respectively. The entropies of activation for MNPNP are smaller: $\Delta S^{\ddagger}$ = –146 and –123 J mol^{-1} K^{-1}, for the reactions with DBU and TBD respectively [13,14]. Moreover, the large difference in entropy of activation can be seen between values obtained for the reaction of phosphazene with NPNE and MNPNE. This was not observed for amidines and guanidine bases. These results might suggest a specific conformation of the substrates for the reaction

Table 4. Equilibrium constants for proton transfer reaction between MNPNP (5×10^{-5} M) and BTPP in tetrahydrofuran.

Temp., °C	K, dm^3 mol^{-1}	ε, dm^3 mol^{-1} cm^{-1}	reaction parameters
15	357 ± 6	19000 ± 200	
25	187 ± 4	18300 ± 300	ΔH = – 46 ± 2 kJ mol^{-1}
35	110 ± 7	17000 ± 1000	ΔS = – 111 ± 6 J mol^{-1} K^{-1}
45	57 ± 2	17000 ± 400	

Table 5. Equilibrium constants for proton transfer reaction between MNPNP (5×10^{-5} M) and P_1-t-Oct in tetrahydrofuran.

Temp., °C	K, dm^3 mol^{-1}	reaction parameters
15	7,6 ± 1,7	
25	5 ± 1	ΔH = – 36 ± 1 kJ mol^{-1}
35	3,2 ± 0,6	ΔS = – 106 ± 3 J mol^{-1} K^{-1}
45	2,4 ± 0,6	

Table 6. Observed and second order rate constants for proton transfer reaction between MNPNP and phosphazenes in tetrahydrofuran.

Temp., °C	[base], M	$k_{obs} \times 10^2$, s^{-1}	k_f, $dm^3mol^{-1}s^{-1}$	activation parameters
		BTPP		
15	0,03 - 0,15	0,99 – 9,5	0,71 ± 0,03	
25	0,03 - 0,15	1,8 – 11,7	0,84 ± 0,02	
35	0,03 - 0,15	2,68 – 14.8	0,98 ± 0,03	ΔH‡ = 10,5 ± 0,2 kJ mol^{-1}
45	0,03 - 0,15	4,37 – 18,21	1,18 ± 0,02	ΔS‡ = –211 ± 1 J mol^{-1} K^{-1}
		P_1-t-Oct		
15	0,03 – 0,3	0,46 – 1,16	0,026 ± 0,002	
25	0,03 – 0,3	0,97 – 2,05	0,039 ± 0,005	ΔH‡ = 22 ± 3 kJ mol^{-1}
35	0,03 – 0,3	2,15 – 3,67	0,05 ± 0,01	ΔS‡ = –198 ± 10 J mol^{-1} K^{-1}
45	0,03 – 0,3	5,46 – 10,86	0,19 ± 0,01	

Table 7. Observed and second order rate constants for proton transfer reaction between NPNE and phosphazenes in tetrahydrofuran.

Temp., °C	[base], M	$k_{obs} \times 10^2$, s^{-1}	k_f, $dm^3mol^{-1}s^{-1}$	activation parameters
		BEMP		
15	0,006 - 0,03	1,47 – 4,88	1,2 ± 0,1	
25	0,006 - 0,03	2,29 – 6,90	2,13 ± 0,22	
35	0,006 - 0,03	3,98 – 10,24	2,3 ± 0,1	ΔH‡ = 34 ± 9 kJ mol^{-1}
45	0,006 - 0,03	7,02 – 21,71	5,9 ± 0,3	ΔS‡ = –126 ± 30 J mol^{-1} K^{-1}
		P_1-t-Oct		
15	0,002 – 0,016	0,46 – 1,45	0,68 ± 0,03	
25	0,002 – 0,016	0,57 – 1,97	0,99 ± 0,03	
35	0,002 – 0,016	0,83 – 2,84	1,44 ± 0,07	ΔH‡ = 27,3 ± 1,2 kJ mol^{-1}
45	0,002 – 0,016	1,50 – 4,60	2,20 ± 0,05	ΔS‡ = –153 ± 4 J mol^{-1} K^{-1}

Table 8. Comparison of equilibrium constants and second-order rate constants for the reactions of carbon acids (MNPNP, NPNE) with strong organic bases in tetrahydrofuran at 25 °C.

Base (pKa)[a]	K (dm^3 mol^{-1})	k_f (M^{-1} s^{-1}), 25 °C
	NPNE	
BEMP	-	2,13 ± 0,004[b]
P_1-t-Oct	-	0,99 ± 0,03
P_1-t-Bu	2200 ± 80 [c]	2,31 ± 0,05 [c]
MTBD	-	161 ± 1 [d]
TBD	-	19000 ± 200 [d]
DBU	2060 ± 30 [e]	800 ± 20 [e]
	MNPNP	
BEMP (27,6)	12,8 ± 0,5	0,038 ± 0,004
BTPP (28,4)	187 ± 4	0,84 ± 0,02
P_1-t-Oct (26,5)	5 ± 1	0,04 ± 0,005
P_1-t-Bu (26,9)	11,8 ± 0,1 [c]	0,09 ± 0,001 [c]
MTBD (25,43)	44 [d]	3,05 ± 0,09 [d]
DBU (23,90)	3,7 ± 0,2 [e]	7,75 ± 0,26 [e]
TBD (25,96)	11000 [d]	880 ± 20 [d]

[a] pK_a in acetonitrile (from Table 1), [b] 15°C, [c] [11], [d] [13], [e] [14]

of phosphazene with nitroalkanes. It has been noted that the energy barriers for the reaction of nitroalkanes with tetramethylguanidine or DBU are very low. Lower barriers could be expected for deprotonations of nitroalkanes promoted by phosphazenes which exhibit larger basicity than amidines or guanidines. However, other factors such as steric hindrance or differences in the strength of electronic interactions between the base and carbon acid within the reaction complex may also play a role. The enthalpies of activation for the reaction of NPNE with phosphazenes are larger than those obtained for the reactions of weaker nitrogen bases. Our results imply a large energy demand caused by steric hindrance. However, low energetic barriers obtained for phosphazene reactions with MNPNP, similar to those of the DBU reaction, do not confirm this hypothesis.

The 22 kJ mol^{-1} energy barrier for the reaction

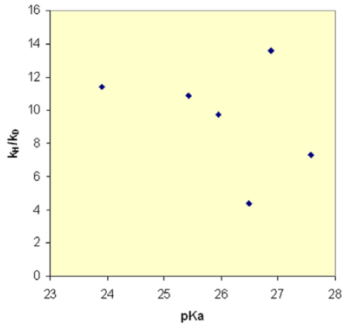


Figure 3. The dependence of kinetic isotope effects for the deprotonations of NPNE on pK_a of protonated base (data of Tables 1 and 9).

Table 9. Comparison of primary deuterium kinetic isotope effects for the reaction of C-acids (NPNE, MNPNP) and strong organic bases in tetrahydrofuran at 25 °C.

Base	k_H/k_D
	NPNE
P1-t-Oct	4,4
BEMP	7,3
P1-t-Bu	13,6 [a]
MTBD	10,9 [b]
TBD	9,7 [b]
DBU	11,4 [c]
	MNPNP
P1-t-Oct	6,8
MTBD	8,5 [b]
TBD	14,8 [b]
DBU	9,7 [c]

[a] [11], [b] [14], [c] [13]

ofMNPNP with P_1-t-Oct is unexpectedly lower than the 27.2 kJ mol^{-1} barrier for the NPNE reaction. It is interesting that a similar anomaly has been observed by Wisłocka *et al.* [11] for the reaction of these carbon acids with P_1-t-Bu, having energetic barriers of 18 and 11 kJ mol^{-1} for the NPNE and MNPNP reaction, respectively. These variations in energetic barriers, which are sometimes not much larger from the value for viscous flow, are difficult to explain.

The primary deuterium kinetic isotope effects for the reaction of the phosphazenes studied shown in Table 9 are relatively small. Initially, it was believed that steric hindrance leads to increased primary deuterium kinetic isotope effects by making the energetic barrier steeper [19,20] or by desolvation of the transition state [15]. However, there are examples of kinetic isotope effects insensitive to the bulk of substituent or even decreasing with steric hindrance either on C-acid or on the base [15]. Phosphazenes are more sterically hindered than DBU, TBD or MTBD. The energetic barriers for the reactions promoted by phosphazenes are very low, so the desolvation of the transition state rather than steep energy barriers could be considered a factor. The low kinetic isotope effect values obtained in this work clearly do not support the original concept of kinetic isotope effect increasing with steric hindrance. There are other factors influencing the magnitude of kinetic isotope effects, such as symmetry of the transition state which may change substantially on going from guanidines or amidines to phosphazenes. The symmetry of the transition state have been believed to depend on ΔpK_a between C-acid and protonated base [21]. The relatively large variance of the kinetic isotope effect values depicted in Fig. 3 eludes a clear cut explanation of the problem.

4. Conclusions

In conclusion, the systems of reactions between nitroalkanes and strongly basic phosphazenes characterize lower values of rate constants and primary deuterium kinetic isotope effects when compared to weaker guanidine and amidine bases.

Abbreviation:

NPNE 1-nitro-1-(4-nitrophenyl)ethane
MNPNP 2-methyl-1-nitro-1-(4-nitrophenyl)propane
BEMP 2-*tert*-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3-diaza-2-phosphorine
BTPP *tert*-butylimino-tris(pirolidyno)phosphorane
P_1-t-Oct *tert*-octylimino-tris(dimethylamino) phosphorane
P_1-t-Bu *tert*-butylimino-tris(dimethylamino) phosphorane
P_2-t-Bu 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2Λ^5,4Λ^5-catenadi(phosphazene)
P_2-t-Oct *tert*-octylimino-tris(dimethyloamino) phosphorane
P_4-t-Bu 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene)
TBD 1,5,7-triazabicyclo[4,4,0]dec-5-ene
DBU 1,8-diazabicyclo[5,4,0]un-dec-7ene
MTBD 7-methyl-1,5,7-triazabicyclo[4,4,0]dec-5-ene

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