

## Acid–Base Equilibria in Nonpolar Media. 4. Extension of the Self-Consistent Basicity Scale in THF Medium. Gas-Phase Basicities of Phosphazenes

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Eleven new phenyl-substituted phosphazenes (P<sub>1</sub>-, P<sub>3</sub>-, and P<sub>4</sub>-bases) have been synthesized by the Staudinger or the Kirsanov reactions. The UV–vis spectrophotometric titration method was used to establish the relative basicity of them, and to extend the ion-pair basicity scale for THF medium. These measurements together with our previous work give a continuous basicity scale in THF ranging from 2.6 (2-MeO-pyridine) to 26.6 (2-Cl-C<sub>6</sub>H<sub>4</sub>P<sub>4</sub>(pyrr) phosphazene) in pK<sub>a</sub> units: that is for 24 orders of magnitude and containing 58 compounds (pyridines, anilines, amines, guanidines, amidines, phosphazenes). Ion-pair formation was taken into account by using the Fuoss equation. ΔpK<sub>ip</sub> values of some phosphazene indicators estimated earlier by the <sup>13</sup>C NMR method were revised. For some of the phosphazenes gas-phase basicities were measured.

### Introduction

In an earlier publication of this series we have presented a self-consistent basicity scale in THF spanning over 17 pK units on the basis of various N-bases.<sup>1</sup> In particular, the scale includes more than 20 phosphazene bases of P<sub>1</sub> and P<sub>2</sub> type (Scheme 1). The UV–vis spectrophotometric and <sup>13</sup>C NMR methods have been used for basicity measurements. The ion-pairing was taken into account by using the Fuoss equation.<sup>2</sup> The scale was anchored to the corrected for ion-pairing value of pK<sub>a</sub> 12.5 for triethylamine<sup>3</sup> as proposed by Morris et al.<sup>4</sup>

The first goal of this work was to extend the basicity scale into the region of stronger bases. Eleven new P<sub>3</sub>- and P<sub>4</sub>-phosphazene superbases (see Scheme 1, here and henceforth “dma” denotes dimethylamino (–N(CH<sub>3</sub>)<sub>2</sub>) and “pyrr” denotes 1-pyrrolidinyl (–N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>) group) were synthesized for this purpose. Together with some other phosphazene and amidine bases these were used to extend the self-consistent basicity scale in THF toward the more basic region for 5 pK units by use of the UV–vis spectrophotometric method.

In the previous work<sup>1</sup> a number of pK<sub>a</sub> values were estimated by using the <sup>13</sup>C NMR method. Due to higher

concentrations used with this method it is possible that the results are not as reliable as those with the UV–vis spectrophotometric method. Thus the second goal of this work was to recheck the earlier <sup>13</sup>C NMR data by using the UV–vis spectrophotometric method.

There has been a long quest for the gas-phase basicity data for phosphazene bases, which started almost as soon as these bases were first introduced to the chemical community in the beginning of nineties. The very serious practical problem with gas-phase basicity measurements of phosphazenes has been their very low volatility and extremely “sticky” nature. These properties have made it very difficult to introduce them into the mass spectrometers that are used for gas-phase basicity measurements. The first attempts of our group to tackle this problem date back to 1993 when one of us made several attempts to measure the gas-phase basicities of MeP<sub>1</sub>(dma) and *t*-BuP<sub>1</sub>(dma). No definitive quantitative results were obtained except the recognition of the much stronger basicity of those compounds as compared with DBU.

To the best of our knowledge, the only available gas-phase basicity values of phosphazenes have been published in a review paper by Raczynska et al.<sup>5</sup> The values are given for HP<sub>1</sub>(dma) (GB = 249.6 kcal/mol), MeP<sub>1</sub>(dma) (GB = 253.6 kcal/mol), and HP<sub>1</sub>(pyrr) (GB = 255.1 kcal/mol). However, the experimental details of the measurements made to obtain these values are not readily accessible to the chemical community because they have been published only in a conference presentation (see ref 5).

(5) Raczynska, E. D.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Woźniak, K.; Kurg, R.; Carins, S. N. *Trends Org. Chem.* **1998**, 7, 95–103.

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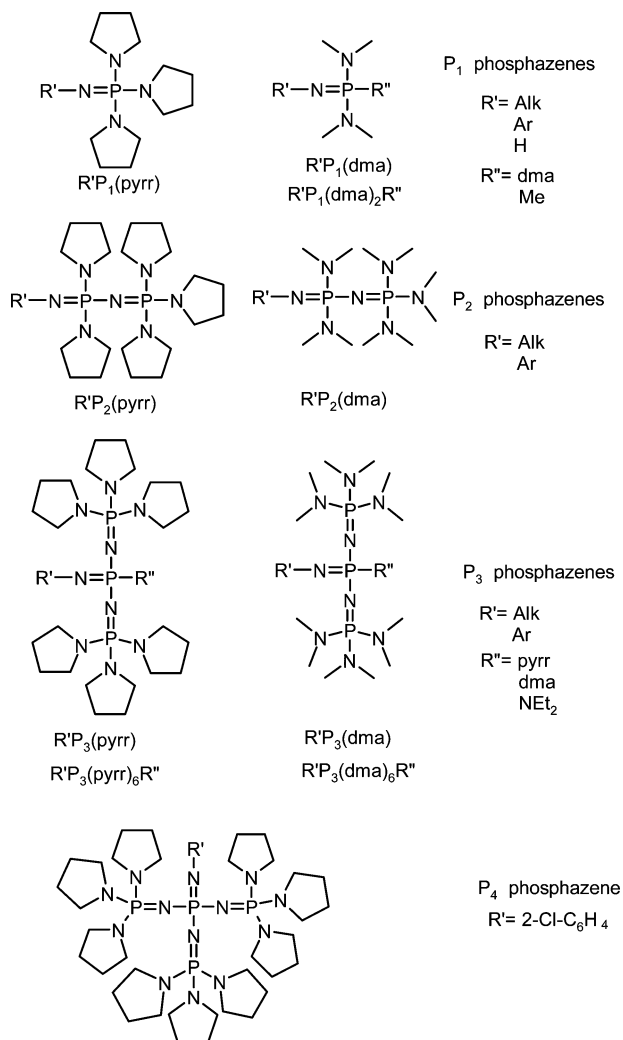
(1) Part 2 of this series: Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. *J. Org. Chem.* **2002**, 67, 1873–1881.

(2) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, 80, 5059–5061.

(3) Throughout this paper we have adopted the common usage of organic chemists where “pK<sub>a</sub> of a base” means in fact the pK<sub>a</sub> value of the conjugate acid of the base.

(4) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, 122, 9155–9171.

## SCHEME 1



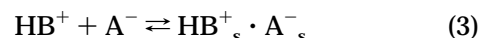
Thus, the third goal of this work was to develop the methodology for gas-phase basicity measurements of phosphazenes and to measure the gas-phase basicities of several of these.

The simple acid dissociation equilibrium (eq 1) used to describe the strength of an acid in polar solvents (water, acetonitrile, etc.) does not describe fully the actual

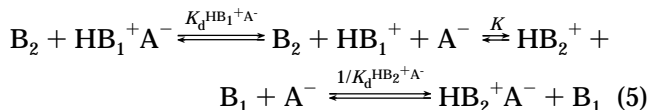


$$K_a = \frac{a(\text{B}) \cdot a(\text{HS}^+)}{a(\text{HB}^+)} \quad (2)$$

situation in media of relatively low polarity ( $D \leq 15$  to 20).<sup>6</sup> Here the solvent molecules are not capable of shielding the attraction forces of oppositely charged free ions and an extensive ion-pairing takes place. The extent of ion-pairing depends on the solvent, the size of the ions, and the charge distribution in ions. The general trend is that small ions tend to form solvent-separated ion-pairs (SSIP) (eq 3) while large ions with delocalized charge tend to form contact ion-pairs (CIP) (eq 4).



To exclude the necessity for measuring the hydrogen ion activity (see eq 2) the equilibrium between two bases B<sub>1</sub> and B<sub>2</sub> was studied:



The  $K_d$  values are the dissociation constants of the respective ion-pairs. The directly measured quantity is the relative ion-pair basicity,  $\Delta pK_{\text{ip}}$ , of bases B<sub>1</sub> and B<sub>2</sub>. It is expressed as follows:

$$\Delta pK_{\text{ip}} = pK_{\text{ip}}(\text{HB}_2^+ \text{A}^-) - pK_{\text{ip}}(\text{HB}_1^+ \text{A}^-) = \log \frac{K \cdot K_d^{\text{HB}_1^+ \text{A}^-}}{K_d^{\text{HB}_2^+ \text{A}^-}} = \log \frac{a(\text{HB}_2^+ \text{A}^-) \cdot a(\text{B}_1)}{a(\text{HB}_1^+ \text{A}^-) \cdot a(\text{B}_2)} \quad (6)$$

If the  $K_d$  values can be measured or estimated then  $pK_{\alpha}$  (an estimate of the  $pK_a$ ) can be found as follows:

$$\Delta pK_{\alpha} = pK_{\alpha}(\text{HB}_2^+) - pK_{\alpha}(\text{HB}_1^+) = \Delta pK_{\text{ip}} - \log \frac{K_d^{\text{HB}_1^+ \text{A}^-}}{K_d^{\text{HB}_2^+ \text{A}^-}} \quad (7)$$

The term gas-phase basicity (GB) refers to the following equilibrium:



GB is defined as negative Gibbs' free energy of reaction 8:

$$\text{GB} = -\Delta G_b \quad (9)$$

The directly measured quantity, as in the case of THF, is the relative basicity of two bases  $\Delta \Delta G_b$ :



where:

$$\Delta \Delta G_b = \Delta G_b(\text{B}_2) - \Delta G_b(\text{B}_1) = -RT \ln K \quad (11)$$

$$K = \frac{p(\text{B}_1) \cdot p(\text{B}_2 \text{H}^+)}{p(\text{B}_2) \cdot p(\text{B}_1 \text{H}^+)} \quad (12)$$

The  $p$  values are the partial pressures of the respective species.

## Experimental Section

**Chemicals, Synthesis, Purification, and Characterization of Compounds.** Descriptions of chemicals, synthesis, and purification procedures and characterization data of compounds can be found in the Supporting Information.

**Methods of  $pK_a$  Determination.** The spectrophotometric titration method and  $\Delta pK_{\text{ip}}$  calculation method used in this

(6) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; VCH: Weinheim, Germany, 2002.

**TABLE 1. Ionic Radii of the Protonated Forms of the New Phosphazene Bases and Methanesulfonate Anion**

ion	ion-pair radius, Å <sup>a</sup>	ion	ion-pair radius, Å <sup>a</sup>
R'P <sub>4</sub> (pyrr)H <sup>+</sup>	6.6	R'P <sub>1</sub> (pyrr)H <sup>+</sup>	4
R'P <sub>3</sub> (pyrr)H <sup>+</sup> ; R'P <sub>3</sub> (pyrr) <sub>6</sub> R''H <sup>+</sup>	6	R'P <sub>1</sub> (dma)H <sup>+</sup> ; R'P <sub>1</sub> (dma) <sub>2</sub> MeH <sup>+</sup>	4
R'P <sub>3</sub> (dma)H <sup>+</sup> ; R'P <sub>3</sub> (dma) <sub>6</sub> R''H <sup>+</sup>	5	DBUH <sup>+</sup> ; CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	2.5
R'P <sub>2</sub> (pyrr)H <sup>+</sup>	5.4	TBDH <sup>+</sup> ; MTBDH <sup>+</sup>	3
R'P <sub>2</sub> (dma)H <sup>+</sup>	4.8		

<sup>a</sup> Ionic radii from previous work (ref 1). In cases when no data were available, the radii were estimated by PM3 calculations; R' = alkyl, aryl, or H; R'' = dma, pyrr, or NEt<sub>2</sub>. TBD denotes 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine and MTBD denotes 1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidine, respectively.

work are the same as described earlier,<sup>1,7,8</sup> i.e., the simultaneous titration of two free bases of comparable basicity was carried out and the data for  $\Delta pK_{ip}$  were obtained from mathematical treatment of the spectra. A professional glovebox was used to ensure that the environment was free from humidity and oxygen. The measurements were carried out in an external cell compartment, situated in the glovebox. The cell compartment was connected to the UV-vis spectrophotometer by means of two quartz fiber optic cables. The correction for ion-pairing was calculated by using the Fuoss equation as described in refs 1 and 4. The ionic radii are those from ref 1. Ionic radii for compounds not encountered in ref 1 are given in Table 1. Additional information on the experiments is given in the Supporting Information.

**Measurements of Gas-Phase Basicity (GB).** The FT-ICR spectrometric GB measurements were carried out at Kyushu University. Each equilibrium measurement is a measurement of relative basicity of bases B<sub>1</sub> and B<sub>2</sub> (that is "each arrow" in Table 3) according to the eqs 10–12. The partial pressures of the neutrals were measured by using the Bayard-Alpert gauge and were corrected for the differences in ionization cross-sections (see ref 9 for details). The ratio of the intensities of the ions in the mass spectrum was used as the estimate of the ratio of partial pressures of the ions. The substituted phenylphosphazenes were introduced by means of a direct inlet.<sup>9</sup> Constant partial pressures of the compounds were obtained by cooling the probe tip. The rest of the bases were introduced from the conventional sample introduction system, the so-called "oven" that was maintained at 150 °C. See ref 9 for further details on the introduction of low-volatility samples into the Kyushu University FT-ICR spectrometer.

The equilibrium measurements were carried out at different partial pressures of the neutrals. Good agreement was obtained between the  $\Delta\Delta G_b$  values (difference mostly not more than 0.3 kcal/mol, in one case 0.6 kcal/mol). At given partial pressures of the neutrals the equilibrium measurements were carried out as a series of pulse sequences with different reaction times. Each sequence consisted of generating ions (by an electron impact pulse from a few to 10 ms), giving them time to react (reaction time), and detecting the ions (see ref 10 for more details). From the ion intensity ratios at different reaction times (and at constant partial pressures of the neutrals) time plots were constructed. From the time plots it was found that between 1 and 20 s of reaction time was necessary to reach the equilibrium (depending on the reacting bases and their partial pressures). To ensure that the equilibrium has been reached reaction times significantly longer than what was required to reach the plateau on the time plot were used in all cases. All experiments were carried out at a cell temperature of 373 K.

(7) Kaljurand, I.; Rodima, T.; Leito, I.; Koppel, I.; Schwesinger, R. *J. Org. Chem.* **2000**, *65*, 6202–6208.

(8) Leito, I.; Rodima, T.; Koppel, I. A.; Schwesinger, R.; Vlasov, V. M. *J. Org. Chem.* **1997**, *62*, 8479–8483.

(9) Koppel, I. A.; Koppel, J.; Leito, I.; Koppel, I.; Mishima, M.; Yagupolskii, L. M. *J. Chem. Soc., Perkin Trans. 2* **2001**, 229–232 and references therein.

## Results

**Basicity Measurements in THF.** The results are presented in Table 2. Altogether 47 new basicity measurements were carried out involving 16 new bases. These measurements together with our previous work<sup>1</sup> give a continuous basicity scale in THF ranging from 2.6 to 26.6 in the p*K*<sub>α</sub> units, that is for 24 orders of magnitude. The absolute p*K*<sub>ip</sub> and p*K*<sub>α</sub> values were assigned to the bases as described in ref 1. The whole spectrophotometric basicity scale in THF (this work and ref 1) has in total: number of measurements *n*<sub>m</sub> = 115, number of p*K*<sub>α</sub> values determined *n*<sub>c</sub> = 58, and the consistency of measurements *s* = 0.08 (for  $\Delta pK_{ip}$  *s* = 0.08) (see refs 1 and 11 for further details).

Multiple overlapping measurements were made to make the results more reliable and help to estimate their self-consistency. The entire basicity range covered involves at least two independent pathways of measurements and the relative basicity of any two bases can be obtained by combining at least two independent sets of measurements. Reversibility of protonation/deprotonation process of all bases was checked. All equilibria presented in Table 2 were reached in minutes and were stable. The absolute basicities were obtained as described previously.<sup>1</sup> Both ion-pair (p*K*<sub>ip</sub>) values and values corrected for ion pairing (p*K*<sub>α</sub>) are given in Table 2. Although somewhat arbitrary, the correction for ion-pairing is useful because it makes our data comparable to the data of the Morris' group.<sup>4</sup> The same practice was followed in the previous work.<sup>1</sup> The scale anchored to the p*K*<sub>α</sub> value of triethylamine as described in ref 1.

**Rechecking the Previous <sup>13</sup>C NMR Results with the UV-Vis Spectrophotometric Method.** The <sup>13</sup>C NMR measurements performed in the previous work<sup>1</sup> were rechecked in this work by using the UV-vis spectrophotometric method and discrepancies were found. In most cases these amounted to 0.1 to 0.5 p*K*<sub>α</sub> units. In one case the discrepancy is significantly larger: the p*K*<sub>α</sub> value of TBD found in this work (21.0) differs from the previous one (19.4) by 1.6 p*K*<sub>α</sub> units.

TBD was taken under deeper study as we suspected that its p*K*<sub>ip</sub> is dependent on the base concentration. Its concentration was varied over 4 orders of magnitude (10<sup>-5</sup> to 10<sup>-2</sup> M) while keeping the concentration of the reference indicator base 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>P<sub>3</sub>(pyrr) around 3 × 10<sup>-5</sup> M. We did not observe significant change in relative ion-pair basicities ( $\Delta pK_{ip}$ ) of these bases; for details see Table S1 in the Supporting Information. However, the methanesulfonyl salt of TBD started to precipitate at around 15% neutralization of TBD at its analytical concentration of 2.09 × 10<sup>-2</sup> M.

TABLE 2. Continuous Self-Consistent UV–Vis Spectrophotometric Basicity Scale of Neutral Bases in THF Solution<sup>a</sup>

No	Compound	$\Delta pK_{ip}(\text{THF})^c$	$pK_{ip}(\text{THF})^c$	$pK_{\alpha}(\text{THF})^c$
1	2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>4</sub> (pyrr)		25.6	26.6
2	EtP <sub>2</sub> (dma)		24.9	25.3
3	4-MeO-C <sub>6</sub> H <sub>4</sub> P <sub>3</sub> (pyrr)		24.8	25.7
4	PhP <sub>3</sub> (pyrr)		24.1	25.0
5	4-MeO-C <sub>6</sub> H <sub>4</sub> P <sub>3</sub> (dma)		23.5	24.0
6	PhP <sub>3</sub> (dma)		23.0	23.5
7	4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> P <sub>3</sub> (pyrr)		22.3	23.1
8	EtP <sub>1</sub> (pyrr)		21.7	21.7
9	TBD		21.7	21.0
10	4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> P <sub>3</sub> (dma)		21.2	21.7
11	2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>3</sub> (pyrr) <sub>6</sub> NEt <sub>2</sub>		21.1	22.0
12	4-MeOC <sub>6</sub> H <sub>4</sub> P <sub>2</sub> (pyrr)		20.8	21.5
13	HP <sub>1</sub> (pyrr)		20.8	20.8
14	MeP <sub>1</sub> (dma)		20.7	20.7
15	2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>3</sub> (dma) <sub>6</sub> NEt <sub>2</sub>		20.3	20.8
16	PhP <sub>2</sub> (pyrr)		20.2	20.9
17	t-ButP <sub>1</sub> (pyrr)		20.2	20.2
18	HP <sub>1</sub> (dma)		19.7	19.7
19	PhP <sub>2</sub> (dma)		19.4	19.8
20	2,5-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>3</sub> (pyrr) <sub>6</sub> NEt <sub>2</sub>		19.3	20.2
21	t-ButP <sub>1</sub> (dma)		18.9	18.9
22	MTBD		18.6	17.9
23	DBU		18.0	16.8
24	4-Me <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)		17.3	17.3
25	TMG		17.0	15.5
26	2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>2</sub> (pyrr)		16.8	17.5
27	4-MeO-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)		16.8	16.8
28	PhP <sub>1</sub> (pyrr)		16.0	16.0
29	PhP <sub>1</sub> (dma) <sub>2</sub> Me		15.4	15.5
30	PhTMG		15.0 <sup>b</sup>	14.0 <sup>b</sup>
31	4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)		14.6 <sup>b</sup>	14.6 <sup>b</sup>

<sup>a</sup> The numbers on the arrows are the direct experimental  $\Delta pK_{ip}$  values (uncorrected for ion pairing) obtained from UV–vis spectrophotometric titration of neutral bases with methanesulfonic acid. <sup>b</sup> Value from ref 1. <sup>c</sup> Absolute  $pK_{ip}(\text{THF})$  and  $pK_{\alpha}(\text{THF})$  estimated values for conjugate acids of the respective bases. TMG denotes *N,N,N,N*-tetramethylguanidine.

Because NMR spectrometry has the intrinsic disadvantage that higher concentrations are used, we decided to drop all NMR data from this scale<sup>1</sup> and the scale presented in Table 2 is fully spectrophotometric.

**Basicity Measurements in the Gas Phase.** For eight of the phosphazenes measured in THF also the gas-phase basicities were obtained. The results of the gas-phase measurements are presented in Table 3. MTBD (GB = 246.2 kcal/mol<sup>12</sup>) and ITBD (1,3,4,6,7,8-hexahydro-1-isopropyl-2*H*-pyrimido[1,2-*a*]pyrimidine) (GB = 248.2

kcal/mol<sup>12</sup>) served as reference bases. The absolute GB values were found the same way as with THF measurements. The consistency of the measurements was as follows:  $s = 0.35$  kcal/mol,  $n_m = 14$ ,  $n_c = 8$  (see ref 11 for details).

## Discussion

**Comparison of the Solution Basicities (THF) with the Gas-Phase Basicities.** The comparison of the  $pK_{\alpha}$  values in THF and the GB values is presented in Figure 1. Several compounds have been added to Figure 1 for

(10) Mishima, M.; Mustanir; Fujio, M.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2009–2018.

(11) Leito, I.; Kaljurand, I.; Koppel, I. A.; Yagupolskii, L. M.; Vlasov, V. M. *J. Org. Chem.* **1998**, *63*, 7868–7874.

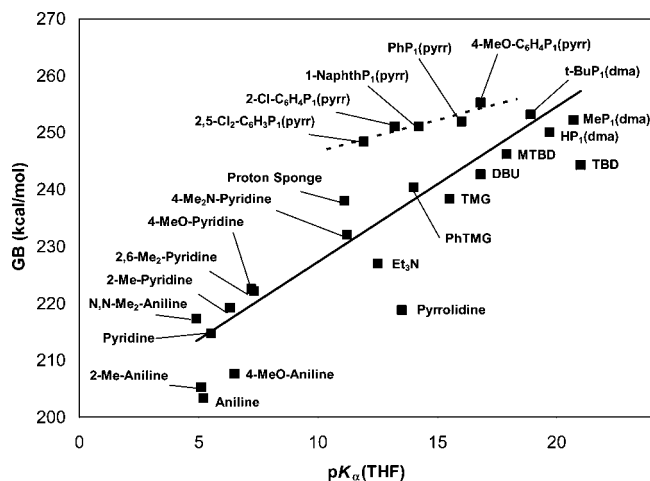
(12) Hunter, P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413–656.



**TABLE 3. Results of the Gas-Phase Basicity Measurements<sup>a</sup>**

No	Base	GB <sup>c</sup>
27	4-MeO-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)	255.2
21	<i>t</i> -BuP <sub>1</sub> (dma)	253.2
14	MeP <sub>1</sub> (dma)	252.2
28	PhP <sub>1</sub> (pyrr)	252.0
32	1-NaphtP <sub>1</sub> (pyrr)	251.1
33	2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)	251.1
18	HP <sub>1</sub> (dma)	250.0
34	2,5-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	248.4
35	ITBD	248.2 <sup>b</sup>
22	MTBD	246.2 <sup>b</sup>

<sup>a</sup> The numbers on the arrows are the direct experimental  $\Delta\Delta G_b$  (kcal/mol) values obtained from FT-ICR measurements. <sup>b</sup> Values from ref 12. <sup>c</sup> Estimated absolute GB (kcal/mol) values for bases.

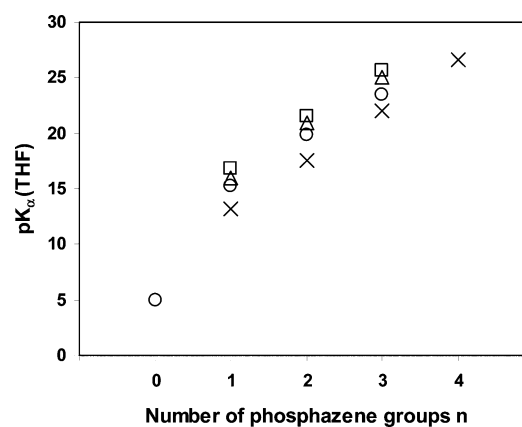


**FIGURE 1.** Comparison of the basicity data in THF ( $pK_a$  values) and in the gas phase (GB). The solid line corresponds to overall correlation (all available data included) and the dotted line corresponds to the series of aryl-P<sub>1</sub>(pyrr) phosphazenes.

which the  $pK_a$  values in THF are available from this or previous work but the GB values come from the literature.<sup>12</sup>

The overall correlation is as follows:  $GB \text{ (kcal}\cdot\text{mol}^{-1}) = 200.0 + 2.73 \cdot pK_a$ , the standard deviations of the intercept and slope are 4.6 and 0.34, respectively,  $R^2 = 0.74$ ;  $n = 25$  and  $s = 8.84 \text{ kcal}\cdot\text{mol}^{-1}$ . The graph is rather diffuse and it is difficult to find well-defined family relationships: neither pyridines nor anilines form any well-defined line. The attenuation factor calculated from the slope is  $2.73/2.30RT = 2.00$  for the overall correlation.

A clearly visible general trend is that small bases with unhindered basicity centers (pyrrolidine, anilines) tend to be below the line, while bulky and crowded ones (pyrrolidinyl phosphazenes, proton sponge) tend to be above the line. This means that the small bases are



**FIGURE 2.** Dependence of the  $pK_a$  values of substituted phenylphosphazenes on the number of phosphazene groups  $n$ .  $\square$ , 4-MeO-C<sub>6</sub>H<sub>4</sub>P<sub>n</sub>(pyrr);  $\Delta$ , C<sub>6</sub>H<sub>5</sub>P<sub>n</sub>(pyrr);  $\circ$ , C<sub>6</sub>H<sub>5</sub>P<sub>n</sub>(dma), where the compound with zero number of phosphorus atoms is the *N,N*-dimethylaniline; X, 2-Cl-C<sub>6</sub>H<sub>4</sub>P<sub>n</sub>(pyrr).

relatively more basic in the THF medium than in the gas phase. The ability of THF to solvate smaller ions better is clearly in action here.

Only the pyrrolidinyl phosphazenes forms a more or less straight line. The line has noticeably smaller slope than the general correlation. These phosphazenes are the bulkiest phosphazenes included in our gas-phase study. The correlation, however, is only fair:  $GB \text{ (kcal}\cdot\text{mol}^{-1}) = 235.3 + 1.13 \cdot pK_a$ , the standard deviations of the intercept and the slope are 4.1 and 0.28, respectively,  $R^2 = 0.84$ ;  $n = 5$  and  $s = 1.13 \text{ kcal}\cdot\text{mol}^{-1}$ . The attenuation factor for the pyrrolidinyl phosphazene family is  $1.13/2.30RT = 0.83$ . This cannot be interpreted as the THF medium having better differentiating ability than the gas phase, because the standard deviation of the attenuation factor is 0.21 and the attenuation factor can be well over 1. So, the current results are inconclusive and clearly additional data are needed.

The GB values of the phosphazenes HP<sub>1</sub>(dma) and MeP<sub>1</sub>(dma) have been measured by Raczyńska et al.<sup>5</sup> the GB values are 249.6 and 253.6 kcal/mol, respectively. The GB value of HP<sub>1</sub>(dma) agrees well with our result, the GB value of MeP<sub>1</sub>(dma), however, differs from ours by 1.4 kcal/mol. The GB values of HP<sub>1</sub>(dma) and MeP<sub>1</sub>(dma) have also been calculated at the DFT B3LYP 6-311+G\*\* level by some of us:<sup>13</sup>  $GB(\text{HP}_1(\text{dma})) = 249.2 \text{ kcal/mol}$ ,  $GB(\text{MeP}_1(\text{dma})) = 252.3 \text{ kcal/mol}$ . The agreement is good for HP<sub>1</sub>(dma) and very good for MeP<sub>1</sub>(dma).

**Dependence of the Basicity on the Number of Phosphorus Atoms in the Phosphazenes.** It has been found previously that the basicity of small phosphazene bases increases with increasing number of phosphorus atoms  $n$ . The increase is, however, not monotonic and at higher  $n$  a plateau is reached where the basicity is essentially independent of  $n$ .<sup>14,13</sup> Figure 2 shows the dependence of the  $pK_a$  values of substituted phenylphosphazenes in THF on the number of phosphorus atoms  $n$ . No plateau is reached at  $n = 3$  or 4 and the figure suggests that the plateau will be reached not before  $n = 5$ . In DMSO solution with *t*-BuP<sub>n</sub>(pyrr) phosphazenes the

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plateau is reached at  $n = 5$ .<sup>14</sup> In the gas phase there is currently no clear answer because no measurements have been made with higher phosphazenes. Some of us have carried out a computational study on phosphazene bases,<sup>13</sup> but alkyl-substituted phosphazenes that contain several phosphorus atoms are large molecules and could not be studied at high computational levels. Therefore model compounds had to be used and the beginning of the plateau was found to range from  $n = 4$  to 9 depending on the type of model compound and on the computational method used.<sup>13</sup>

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**Supporting Information Available:** Table (Table S1) of detailed experimental data (includes data for all the UV–vis equilibrium measurements: concentrations, acid used, calculation method, comments), <sup>13</sup>C NMR spectra of selected compounds (Figures S2), and the UV–vis titration spectra for all these bases, where the UV–vis spectra were used for  $\Delta pK_{ip}$  calculations as well as descriptions of chemicals, synthesis, and purification procedures, and characterization data of compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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