Experimental and Theoretical Studies of the Gas-Phase Protonation of Aliphatic Phosphine Oxides and Phosphoramides

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Abstract: Gas-phase basicities were determined in an ion cyclotron resonance spectrometer for 13 aliphatic organophosphorus compounds: OPX_3 (X = Me, Et, n-Pr, i-Pr, OEt, NEt_2, CH_2NMe_2); $OPMe_{3-x}(NMe_2)_x$, x = 1–3; $OPNH_2(NMe_2)_2$; OPX-$(NMeCH_2)_2$, X = Me or NMe_2. The results are discussed by comparison with the corresponding P^{III} derivatives and also in terms of the effects of substituents on basicity. A good correlation is observed between gas-phase basicities and the σ^{ϕ} Kabachnik's constants. Ab initio SCF calculations using four different basis sets were performed on the representative compounds OPX_3 (X = H, Me, NH_2) and $OPMe_2NMe_2$, and on their protonated analogues, so as to allow for a better interpretation of the experimental results. They lead to a reasonable description of the protonation process in these bases, indicating, for example, that O-protonation is favored over N-protonation by ca. 100 kcal/mol, an important result which is more clearly visualized in a molecular electrostatic potential map representation.

The structure of the products formed upon protonation of phosphoramides remains a controversial issue despite extensive investigations reported in the recent literature.[2] The interest in these compounds arises because of their use as chemosterilant pesticides[3a] or as drugs in anticancer chemiotherapy;[3b] they have also been suspected of having potentially carcinogenic properties,[3c] although a recent study indicates that some of these compounds are not mutagenic.[3d]

In solution,[4] a clear-cut interpretation of protonation site (O vs. N) is masked by complexities arising from solvent, composition, and other factors. In an attempt to circumvent some of these difficulties, we began a series of gas-phase basicity (GB) studies of several phosphoramides and phosphine oxide derivatives which led us to conclude[5] that oxygen protonation seems to be favored in these systems. In order to understand more clearly the role of substituents on GB, and thus the relative stability and structure of the protonated products, we report here the determination of GB values for a larger number of related derivatives.

However, such a study would not be comprehensive without performing quantum chemical calculations on some of these compounds in order to substantiate the experimental conclusions. Indeed, in the absence of complicating solvation phenomena, the GB values can be compared directly with the calculated proton affinities (PA), which will provide a reliable confirmation of the interpretation of O vs. N protonation in phosphoramides. In addition, the calculations are expected to lead to a vast amount of unique information concerning the structural features and

Table I. Physical Constants for the Phosphorus Compounds and Reference Bases Studied in the Present Work[a]

compound	M	d^{25}_4	n^{25}_D	α_{calcd} (Å^3)	ref
2	134.16			15.2	b
4	176.24	0.9404	1.4695	20.7	c
9	151.15			15.4	b
10	263.35	0.9655	1.4615	29.7	d
11	221.28			24.3	b
12	148.15	1.0847	1.4682	15.1	c
13	177.18	1.0815	1.4720	18.2	c
14	163.20	0.900	1.4686	20.0	e

base	M	d^{20}_4	n^{20}_D	α_{calcd} (Å^3)	ref
MeNHEt	59.11	0.688	1.376	7.8	f
3-methyl-pyridine	93.13	0.9566	1.5040	11.4	g,h
$MeNEt_2$	87.17	0.7034	1.3879	11.6	g
Et_3N	101.19	0.7275	1.4010	13.4	g
n-Pr_3N	143.28	0.7558	1.4181	18.9	g
Me_2NEt	73.14	0.677	1.374	9.8	f
Me_2NH	45.09	0.6804 (0 °C)	1.350 (17 °C)	5.6	g
indoline	119.17	1.069	1.5923	15.0	g

[a] For other compounds, see ref 5. [b] Physical properties not available; α estimated from the other values and from group polarizabilities given in ref 25. [c] This work. [d] Yvernault, T.; Yvernault, G.; Bollinger, J. C. (*R. Acad. Sci., Ser. C.*) **1978**, *287*, 519. [e] Besserre, D.; Troquet, M. *Bull. Soc. Chim. Fr.* **1974**, 845. [f] Fluka catalog, 1984/85 edition. [g] "CRC Handbook of Chemistry and Physics", 52nd ed; CRC Press: Boca Raton, FL, 1971/72. [h] Same values of α used for 2- and 4-methylpyridine.

chemical bonding characteristics of the species studied and their protonated analogues. To this end, we have chosen the Hartree–Fock ab initio model using various basis sets, ranging from minimal to double zeta (ζ) augmented by a 3d polarization function on phosphorus. Correlation and zero-point vibrational energy corrections have been evaluated in the case of OPH_3, in order to see whether these contributions could possibly modify the O vs. N protonation conclusions. Finally, molecular electrostatic potential (MEP) maps also have been obtained (at the ΔSCF level) to facilitate the theoretical interpretation. The utility of this technique as an aid to visualize protonation sites is illustrated for phosphoric triamide.

Experimental Section

Gas-phase basicities were determined in an ion cyclotron resonance (ICR) spectrometer under conditions previously described,[6] from the

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(2) (a) Modro, T. A.; Liauw, W. G.; Peterson, M. R.; Csizmadia, I. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1432. (b) Modro, T. A. *J. Chem. Soc., Chem. Commun.* **1980**, 201. (c) Davidowitz, B.; Modro, T. A. *S. Afr. J. Chem.* **1980**, *33*, 74. (d) Rahil, J.; Haake, P. *J. Am. Chem. Soc.* **1981**, *103*, 1723. (e) Modro, T. A.; Graham, D. H. *J. Org. Chem.* **1981**, *46*, 1923. (f) Matrosov, E. I.; Kryuchkov, A. A.; Nifantyev, E. E.; Kozachenko, A. G.; Kabachnik, M. I. *Phosphorus Sulfur* **1982**, *13*, 69. (g) Modro, T. A.; Rijkmans, B. P. *J. Org. Chem.* **1982**, *47*, 3208. (h) Bonicamp, J. M.; Haake, P. *Tetrahedron Lett.* **1982**, *23*, 3127. (i) Moerat, A.; Modro, T. A. *Phosphorus Sulfur* **1983**, *14*, 179. (j) Mizrahi, V.; Modro, T. A. *J. Org. Chem.* **1983**, *48*, 3030.

(3) (a) Labrecque, G. C.; Fye, R. L. *Mutat. Res.* **1978**, *47*, 99. (b) Lalka, D.; Bardos, T. J. *Biochem. Pharmacol.* **1975**, *24*, 455. (c) Ashby, J.; Styles, J. A.; Paton, D. *Br. J. Cancer* **1978**, *38*, 418. (d) Labadie, M.; Devaud, D.; Debord, J.; Bollinger, J. C.; Yvernault, T.; Nicolas, A. *Mutat. Res.*, submitted for publication.

(4) (a) Bollinger, J. C.; Yvernault, G.; Yvernault, T. *Thermochim. Acta* **1983**, *60*, 137. (b) Bollinger, J. C.; Faure, R.; Yvernault, T. *Can. J. Chem.* **1983**, *61*, 328.

(5) Bollinger, J. C.; Houriet, R.; Yvernault, T. *Phosphorus Sulfur* **1984**, *19*, 379.

(6) Houriet, R.; Rüfenacht, H.; Carrupt, P. A.; Vogel, P.; Tichy, M. *J. Am. Chem. Soc.* **1983**, *105*, 3417.

Table II. GB Values for B_1 = OPXYZ and Related Compounds (All Values in kcal/mol)

B_1	X	Y	Z	B_2	$GB(B_2)^a$	ΔG_r^b	$GB(B_1)^c$
1	Me	Me	Me				209.4^d
2	Et	Et	Et	MeNHEt	214.8	−0.3	214.1 ± 0.4
				3-methylpyridine	215.0	−1.3	
3	n-Pr	n-Pr	n-Pr				216.7^d
4	i-Pr	i-Pr	i-Pr	n-Pr$_2$NH	219.2	−1.2	217.8
				indoline	218.0	−0.3	
5	OEt	OEt	OEt				209.2^d
6	Me	Me	NMe$_2$				213.6^d
7	Me	NMe$_2$	NMe$_2$				216.7^d
8	NMe$_2$	NMe$_2$	NMe$_2$				219.3^d
9	NH$_2$	NMe$_2$	NMe$_2$	Et$_2$NH	216.9	−1.2	215.6
				2-methylpyridine	215.9	−0.4	
10	NEt$_2$	NEt$_2$	NEt$_2$	MeNEt$_2$	221.1	0.1	221.7 ± 0.5
				Et$_3$N	223.4	−0.9	
				n-Pr$_2$NH	219.2	2.3	
11	CH$_2$NMe$_2$	CH$_2$NMe$_2$	CH$_2$NMe$_2$	n-Pr$_3$N	225.6	1.0	226.6
				n-Bu$_3$N	227.0	−0.4	
12	[structure: OP with two N–Me groups, Me, Me]			2-methylpyridine	215.9	−0.2	215.6
				4-methylpyridine	215.9	−0.4	
13	[structure: OP with NMe$_2$, N–Me groups, Me]			Me$_2$NEt	218.8	−0.6	218.1
				indoline	218.0	0.1	
14	P(NMe$_2$)$_3$			Me$_2$NH	212.3	0.3	212.6 ± 0.5

^{a} From ref 18. $^b \Delta G_r$ is the free energy change for reaction 1 carried out at 323 K. $^c \pm 0.2$ kcal/mol unless otherwise indicated (deviation on the experimental determination of ΔG_r). ^{d} From ref 5.

equilibrium constant for the proton-transfer reaction between bases B_1 (phosphorus compound) and B_2 (reference base).

$$B_1H^+ + B_2 \rightleftharpoons B_1 + B_2H^+ \qquad (1)$$
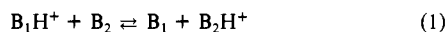
Reaction times up to 1 s were used; an example of the time-dependent concentrations is given in Figure 1. At least three independent measurements were carried out for each couple with pressure ratio of the bases varying in about a fivefold range. The concentration of the neutrals was determined from the pressure measurements of an ionization gauge. In order to convert the gauge readings into concentrations, we estimated the relative ionization cross section σ from the polarizability α of the neutrals. The α values were obtained from the molar refraction (R) according to the relationship

$$R = (n^2 - 1)M/((n^2 + 2)d) = \tfrac{4}{3}\pi\alpha N_A$$

where n = refractive index, M = molar mass, and d = density (see Table I). Values for σ were obtained from the correlation of σ with ($\alpha + 1$) as explained in ref 5.

The organophosphorus compounds **1**, **2**, **3**, **5**, and **14** were obtained from commercial suppliers (Ventron, Strem) and used without further purification. The synthesis and purification procedures of aliphatic phosphoramides have been described previously (see ref 5 and references therein). The other compounds were obtained as follows. OP(NH$_2$)-(NMe$_2$)$_2$, **9**, was synthesized according to Baldwin et al.:[7a] mp 115–116 °C; lit. mp 112.5 °C,[7a] 109–114 °C (deliq).[7b] OP(CH$_2$NMe$_2$)$_3$, **11**, was prepared according to Maier:[8] mp = 163 °C (subl); lit. mp 154–157 °C (subl). To synthesize OP(i-Pr)$_3$, **4**, OPCl$_3$ (30 g) in THF (200 mL) was added slowly while stirring to the Grignard reagent obtained from i-PrBr (100 g) in ether. Ether was distilled off (with vigorous stirring in order to avoid solidification); then the mixture was hydrolyzed in dilute aqueous HCl and the remaining ether and THF were evaporated. After extraction with CHCl and concentration, 5 g (14%) of a liquid was distilled: bp 81 °C; d^{25}_4 = 0.9404; n^{25}_D = 1.4695.

(7) (a) Baldwin, M. A.; Loudon, A. G.; Webb, K. S.; Cardnell, P. C. *Org. Mass. Spectrom.* **1977**, *12*, 279. (b) Constant, L. A.; Pepperman, A. B.; Vail, S. L. *Text. Res. J.* **1978**, *48*, 557.

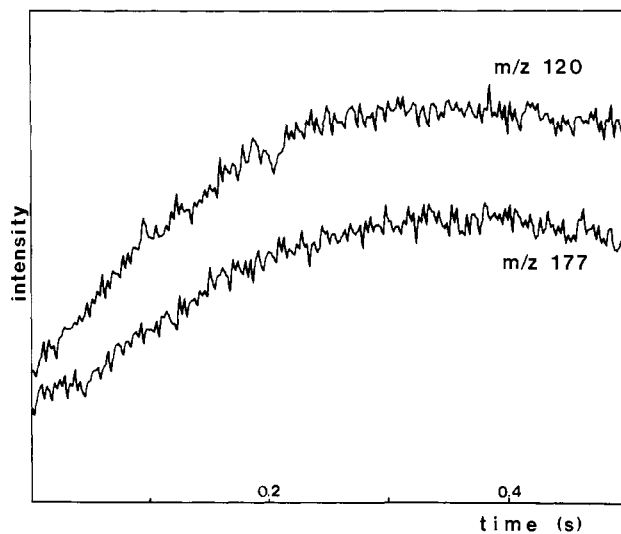(8) Maier, L. *Helv. Chim. Acta* **1967**, *50*, 1723; procedure no. 7, p 1739.

Figure 1. Time plot for the determination of the equilibrium constant for reaction 1 where B_1 = OP-i-Pr$_3$ (1.2×10^{-6} torr) and B_2 = indoline (0.7×10^{-6} torr).

Results

A. Gas-Phase Basicity. The GB values for compounds **1–14** determined in the equilibrium proton transfer (eq 1) are reported in Table II. It was difficult to stabilize the pressure of compounds **2, 10**, and **14** which seemed to have unusual adsorption properties; these cases are indicated by somewhat larger error limits on the GB values (Table II). In order to check the basicity of OP(NEt$_2$)$_3$, **10**, additional determinations of GB were performed using the method of dissociation of proton-bound dimers initially described by Cooks et al.[9] A value of GB(**10**) = 222.3 ± 0.8 kcal/mol was

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Table III. Ab Initio and Experimental Structures of Phosphine Oxides and Phosphoramides[a]

molecule	parameter[b]	I	II	III	IV	exptl[c]
OPH$_3$	r(PO)	1.656	1.587	1.605	1.475	
	r(PH)	1.383	1.406	1.405	1.387	
	$\angle$(OPH)	118.7	117.1	116.0	116.6	
1[d]	r(PO)	1.619	1.575	1.592	1.480	1.476
	r(PC)	1.840	1.853	1.828	1.800	1.809
	r(CH)	1.083	1.083	1.087	1.089	1.107
	$\angle$(OPC)	116.2	114.9	113.9	114.4	114.4
	$\angle$(PCH)	110.5	110.1	110.3	110.5	110.3
6[e]	r(PO)	1.604	1.566	1.583	1.485	
	r(PC)	1.842	1.850	1.831	1.808	
	r(PN)	1.718	1.711	1.700	1.654	
	r(NC)	1.468	1.469	1.470	1.476	
	r(CH$_p$)	1.082	1.082	1.087	1.089	
	r(CH$_n$)	1.091	1.083	1.088	1.087	
	$\angle$(OPC)	116.3	114.6	114.0	114.4	
	$\angle$(OPN)	112.2	111.6	110.6	110.5	
	$\angle$(PNC)	121.6	121.5	121.5	121.9	
	$\angle$(NCH$_n$)	112.2	110.7	111.4	111.3	
	$\angle$(PCH$_p$)	110.4	110.2	110.2	110.4	
15[f]	r(PO)	1.582	1.550	1.570	1.471	
	r(PN)	1.738	1.697	1.693	1.650	
	r(NH)	1.027	0.999	0.995	0.996	
	$\angle$(OPN)	116.6	115.2	114.2	114.1	
	$\angle$(PNH)	110.3	119.7	120.5	121.4	

[a] Distances in ångströms, angles in degrees; I, STO-3G; II, 6-21G; III, double-ζ basis set of Dunning (ref 13, 14); IV, basis set III plus d AO on phosphorus. [b] Subscripts used on hydrogen atoms: H$_p$, hydrogen of a methyl group bonded to phosphorus; H$_n$, hydrogen of a methyl group bonded to nitrogen. [c] Reference 31. [d] The OPCH dihedral angles were optimized to be ±60 and 180°. [e] For the two methyl groups bonded to phosphorus, the OPCH dihedral angles were fixed at ±60 and 180°; for the methyl groups bonded to nitrogen, the PNCH dihedral angles were fixed at ±60 and 180° for the first one, and 0 and ±120° for the second one, the OPNC dihedral angles being 0 and 180°, respectively. [f] The OPNH$_1$ and OPNH$_2$ dihedral angles have been assumed to be the same in all the NH$_2$ groups, respectively, and both have been optimized in each case.

found, thus confirming the results of Table II.

B. Theory. Ab initio calculations at the SCF level were performed for compounds **1**, **6**, and phosphoric triamide, OP(N-H$_2$)$_3$, **15**, which is the simplest triamidophosphine oxide and also a prototype of **8** and **10**. All computations were performed on a VAX-11/780 computer using versions of both GAUSSIAN 80 and 82 programs.[10] Gradient optimization techniques[11,12] have been employed to optimize fully the geometries of these bases and their corresponding protonated species. Four different sets of calculations were made to examine the dependence of the results upon the basis set: the minimal STO-3G set (hereafter referred to as basis set I), the split-valence 6-21G set (II), the (11s7p/9s5p)-(4s)/[6s4p/3s2p][2s] contracted set proposed by Dunning[13,14] (III), and set III augmented by a single 3d polarization function on phosphorus, with an exponent optimized separately for each neutral compound (IV). Test calculations showed that the optimum value of this exponent is not changed significantly when the species is protonated. The SCF optimized geometries of the neutral and protonated species are presented in Tables III and IV for the basis sets I–IV. In order to estimate correlation effects and zero-point vibrational energy corrections on the proton af-

finities of phosphine oxide derivatives, Hartree–Fock and fourth-order Møller–Plesset[15] calculations with the same basis sets and also the 6-31G* and 6-31G** basis sets were carried out for OPH$_3$ (Table V).

Discussion

I. Experimental Basicities. (A) Protonation of Phosphines and Phosphine Oxides. Recent experimental and theoretical studies[16] have shown that the protonation of phosphines occurs on the phosphorus atom to form phosphonium ions. In addition to the expected effects of alkyl substituents on the basicity of phosphines, it was observed that phenyl groups were more efficient than methyl groups at stabilizing phosphonium ions. This was interpreted as a resonance effect made possible by π-donation from phenyl groups to empty orbitals of the phosphorus.[16,17] It was also deduced that significant stabilization of phosphonium ions could occur by rehybridization and mixing of occupied orbitals of alkyl groups with unoccupied orbitals of the phosphorus atom.[16] This possibility seems to be confirmed by the results reported in the first column of Table VI for PMe$_3$ and PEt$_3$. The effects of substituents on the basicity of phosphines are seen to be more pronounced than on the basicity of aliphatic amines, in agreement with previous observations.[16] The other PX$_3$ compounds of Table VI show that quite spectacular effects on basicity are brought about by the introduction of OMe, NMe$_2$, and particularly F substituents directly attached to the phosphorus. The inductive effects of these substituents obviously play an important role, but it is not possible at the present stage to separate the respective contributions of resonance, inductive, and polarization effects on the basicity of these PX$_3$ derivatives, even in a semiquantitative manner (see ref 18 and references therein; see also ref 19).

The protonation of phosphoryl compounds OPX$_3$ has been examined previously by both experiment and theory.[2,5,20] Most studies indicate that protonation of these systems occurs at the oxygen site. The series of compounds **1–4** exemplifies the effects of alkyl substituents on the basicity of phosphine oxides; effects comparable to those in aliphatic ketones and amines are observed. The GB values of some of the latter compounds are listed for comparison: Me$_3$PO, 209.4; Me$_2$CO, 189.9; Me$_3$N, 216.5; Et$_3$PO, 214.1; Et$_2$CO, 194.8; Et$_3$N, 223.4; n-Pr$_3$PO, 216.7; n-Pr$_2$CO, 196.5; n-Pr$_3$N, 225.6 (all GB values in kcal/mol, taken from ref 18, except for Et$_2$CO and n-Pr$_2$CO which are from ref 21). It is also of interest to compare the basicity data for the PX$_3$ and OPX$_3$ compounds (Table VI). For the first three pairs of compounds, it is seen that the change in protonation site (P to O) is accompanied by a *decrease* in basicity by about 9 kcal/mol. This decrease can be attributed to the fact that the d orbitals of the phosphorus atom in P^V compounds participate in the bonding; therefore, the possibility for resonance stabilization is reduced in the O-protonated form of these phosphoryl compounds. The case provided by the trifluoro-substituted compounds shows an inverse trend; i.e., OPF$_3$ is slightly *more* basic than PF$_3$, thus indicating that the basicity of the latter is lowered substantially by the destabilizing inductive effects of the fluorine atoms located next to the charged center.

By contrast, in the tris(dimethylamino) compounds, the basicity of the phosphine oxide *increases* by 6.7 kcal/mol with respect to

(9) McLuckey, S. A.; Cameron, D.; Cooks, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1313. We thank Dr. D. Stahl (EPF-Lausanne) for performing these checking experiments on a ZAB-2F (VG-Analytical) instrument.

(10) (a) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406. (b) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, 1983.

(11) Binkley, J. S. *J. Chem. Phys.* **1976**, *64*, 5142.

(12) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1973**, *6*, 163.

(13) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(14) Dunning, T. H.; Hay, J. P. In "Modern Theoretical Chemistry. Vol. III. Methods of Electronic Structure Theory"; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; p 1.

(15) (a) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1. (b) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1976**, *14*, 91.

(16) (a) Ikuta, S.; Kebarle, P.; Bancroft, G. M.; Chan, T.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 5899. (b) Ikuta, S.; Kebarle, P. *Can. J. Chem.* **1983**, *61*, 97.

(17) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 6252.

(18) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Chapter 9.

(19) Taft, R. W.; Taagepera, M.; Abboud, J. L. M.; Wolf, J. F.; DeFrees, D. J.; Hehre, W. J.; Bartmess, J. E.; Scott, J. A.; McIver, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 7765.

(20) Hodges, R. V.; McDonnell, T. J.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1327.

(21) Bouchoux, G.; Houriet, R. *Tetrahedron Lett.*, in press.

(22) Collyer, S. M.; McMahon, T. B. *J. Phys. Chem.* **1983**, *87*, 909.

Table IV. Proton Affinities and Protonation Sites of Phosphine Oxides and Phosphoramides[a]

molecule	parameter	I	II	III	IV	exptl[b]
OPH_3	$E_{tot}(M)$	−412.356 74	−417.068 27	−417.183 07	−417.306 37	
	$E_{tot}(MH^+)$	−412.854 68	−417.434 02	−417.542 92	−417.644 22	
	PA[c]	312.5	229.5	225.8	212.0	d
	$r(OH^+)$	0.995	0.974	0.958	0.954	
	$\angle(POH^+)$	106.1	121.9	128.4	142.3	
	$\angle(HPOH^+)$	60.0	56.3	56.1	56.1	
	$r(PO)$	1.680	1.642	1.636	1.530	
	$r(PH)$	1.386	1.389	1.391	1.372	
	$\angle(OPH)$	110.5	110.1	109.1	110.4	
1	$E_{tot}(M)$	−528.141 29	−534.119 16	−534.049 00	−534.167 90	
	$E_{tot}(MH^+)$	−528.674 83	−534.512 54	−534.439 93	−534.538 03	
	PA[c]	334.8	246.8	245.3	232.3	217.2
	$r(OH^+)$	0.991	0.971	0.954	0.952	
	$\angle(POH^+)$	106.9	122.5	128.2	135.5	
	$\angle(CPOH^+)$	60.0	59.9	55.2	55.6	
	$r(PO)$	1.674	1.649	1.647	1.556	
	$r(PC)$	1.828	1.839	1.806	1.771	
	$\angle(OPC)$	108.3	108.3	107.4	108.5	
6	$E_{tot}(M)$	−621.025 50	−628.055 21	−627.960 71	−628.094 33	
	$E_{tot}(MH^+)$	−621.555 15	−628.449 26	−628.349 45	−628.468 61	
	PA[c]	332.4	249.2	243.9	234.9	221.4
	$r(OH^+)$	0.990	0.970	0.954	0.952	
	$\angle(POH^+)$	107.3	122.7	128.3	133.1	
	$\angle(CPOH^+)$	47.8	45.2	43.2	29.1	
	$r(PO)$	1.666	1.640	1.638	1.562	
	$r(PC)$	1.830	1.834	1.808	1.779	
	$r(PN)$	1.693	1.684	1.673	1.618	
	$\angle(OPC)$	107.8	106.9	107.2	108.2	
	$\angle(OPN)$	107.8	107.6	106.4	106.5	
15	$E_{tot}(M)$	−575.367 79	−582.052 45	−582.337 84	−582.508 55	
	$E_{tot}(MH^+)$	−575.867 00	−582.441 84	−582.714 25	−582.878 97	
	PA[c]	313.3	244.5	236.2	232.4	e
	$r(OH)^+$	0.990	0.970	0.954	0.952	
	$\angle(POH^+)$	108.2	125.0	129.9	136.3	
	$\angle(NPOH^+)$	60.3	73.6	76.5	69.9	
	$r(PO)$	1.659	1.624	1.631	1.548	
	$r(PN)$	1.683	1.660	1.657	1.611	
	$\angle(OPN)$	110.2	108.9	108.4	108.7	

[a] Total energies in hartrees, distances in ångströms, angles in degrees: I, STO-3G; II, 6-21G; III, double-ζ basis set of Dunning (ref 13, 14); IV, basis set III plus d AO on phosphorus. [b] The experimental PAs have been calculated from the GB values of Table II by taking into account only the translational effect of the proton on the entropy, 7.8 kcal/mol; see also ref 18. [c] PA = $E_{tot}(M) - E_{tot}(MH^+)$ in kcal/mol. [d] Hypothetical compound; no experimental GB. [e] This compound polymerizes in the inlet of the ICR instrument; no experimental GB.

Table V. Electron Correlation (ΔE_c) and Zero-Point Vibrational (ΔE_{zp}) Energy Corrections to Proton Affinities Calculated for OPH_3[a]

	I	II	III	IV	V	VI
ΔE_c	+4.9	−10.7	−10.1	−10.3	−6.6	−5.6
ΔE_{zp}	−8.8	−7.5	−7.7	−6.9	−7.3	−7.4

[a] Correlation corrections calculated at corresponding SCF geometries by Møller–Plesset perturbation theory at fourth order, including all single, double, triple, and quadruple substitutions (MP4SDTQ); energies in kcal/mol: I, STO-3G; II, 6-21G; III, double-ζ basis set of Dunning (ref 13, 14); IV, basis set III plus d AO on phosphorus; V, 6-31G*; VI, 6-31G**.

Table VI. GB Values for P^{III} and P^V Compounds[a]

X	GB(PX₃)	GB(OPX₃)
Me	217.9[b]	209.4
Et	223.9[c]	214.1
OMe	213.1[b]	204.4[b]
F	160.1[d]	161.2[d]
NMe₂	212.6	219.3

[a] All values in kcal/mol, adjusted to the reference value GB(NH₃) = 196.4 kcal/mol. [b] From ref 17. [c] From ref 18. [d] From ref 22.

the phosphine. The properties of these triamide compounds have been rationalized by Labarre et al.[23] in terms of p_π–d_π back-donation between the N and P atoms, which gives the P–N bond some multiple-bond character. Moreover, the phosphoryl bond has also been considered as a σ bond reinforced by some π

back-bonding.[24] Consequently, the highly delocalized electronic cloud in $OP(NMe_2)_3$, **8**, allows for additional stabilization in the protonated forms of the system. We have arrived at similar conclusions from the computational results (vide infra).
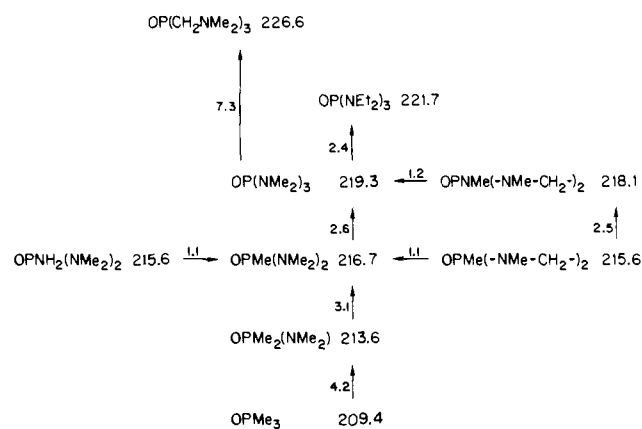
(B) Protonation of Phosphoramides. It has been concluded previously that the thermodynamically favored protonation of phosphoramides occurs at the oxygen site.[5] The present results on a significantly enlarged set of compounds confirm these earlier conclusions and permit more specific comparisons. For example, the GB of **4** (OP-i-Pr₃) differs only slightly from the GB of **8** (HMPT). Considering that the substituents have comparable polarizabilities,[25] this result suggests that the structures are similar for both protonated forms, thus confirming the formation of *oxygen protonated structures* for both phosphine oxides and phosphoramides. It is interesting to notice that when replacing a methyl group in **7** by an amino group, as realized in **9**, a slight destabilization of the protonated form occurs, thus evidencing the influence of the more electronegative nitrogen atom. Still, this effect remains much less pronounced than when it operates on P^{III} compounds (Table V), and it is no more apparent in the case of more polarizable substituents such as N-alkylated groups. Such examples are provided by compounds **10** and **11** which show a continuous increase in basicity. Scheme I summarizes the effects of substituents on GB in this series of compounds.

The results obtained for the two cyclic compounds **12** and **13** agree with the conclusion about oxygen being the preferred site

(23) (a) Labarre, M. C.; Labarre, J. F. *J. Chim. Phys.* **1971**, *68*, 539. (b) Labarre, M. C.; Coustures, Y. *Ibid.* **1973**, *70*, 534.

(24) (a) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. (b) Schmidt, M. W.; Yabushita, S.; Gordon, M. S. *J. Phys. Chem.* **1984**, *88*, 382.
(25) Ketelaar, J. A. A. "Chemical Constitution"; Elsevier: Amsterdam, 1958.

Scheme I[a]

OP(CH₂NMe₂)₃ 226.6

7.3

OP(NEt₂)₃ 221.7

2.4

OP(NMe₂)₃ 219.3 ←1.2— OPNMe(-NMe-CH₂-)₂ 218.1

2.6   2.5

OPNH₂(NMe₂)₂ 215.6 —1.1→ OPMe(NMe₂)₂ 216.7 ←1.1— OPMe(-NMe-CH₂-)₂ 215.6

3.1

OPMe₂(NMe₂) 213.6

4.2

OPMe₃   209.4

[a] All GB values in kcal/mol. Arrows point in the direction of increased stability.

of protonation; the difference in their GB (2.5 kcal/mol) corresponds to replacing a methyl substituent by a demethylamino group as in compounds **7** and **8** (ΔGB = 2.6 kcal/mol). It is also interesting to note that the GB values for **12** and **13** are lower by about 1 kcal/mol than the GB values for their corresponding open-chain compounds **7** and **8**. These differences might be related to the possibility of a favored resonance structure of the protonated phosphoramides:

$$>P^+—O^- \longleftrightarrow >P=O \xrightarrow{H^+} >P^+—OH \longleftrightarrow$$

I

$$>P=O^+H$$

II
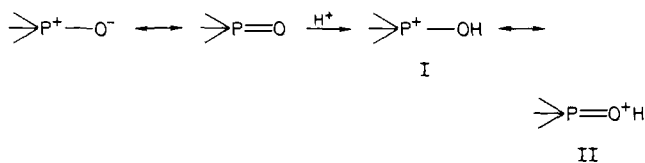
In a recent study on the protonation of the carbonyl group,[21] it was concluded that the carbocation structure (analogous to I) plays an important role in determining the basicity properties of aliphatic ketones. The cyclic substituents associated with **12H⁺** and **13H⁺** could alter the mixing coefficients of the wave functions associated with resonance forms I and II in such a manner as to favor structure II, thereby destabilizing those forms relative to their unhindered counterparts (e.g., GB(**12**) < GB(**7**)). Further studies are planned to elaborate this important point.

(C) Comparison of Gas-Phase and Solution Reactivities. It has been shown that gas-phase basicity can correlate well with the properties used to describe electrophilic reactivity in solution, such as Hammett-type constants.[26] For the presently studied phosphoryl derivatives OPXYZ, their characteristic properties can be described by the σ^φ constants according to Kabachnik[27] which are Hammett-like constants specific for substituents linked to a phosphoryl group. Excellent correlations have been obtained for ionization constants of phosphorus acids and bases in aqueous and organic media and also for the rate constants of various reactions.[27] Figure 2 represents the correlation between GB and the σ^φ parameter: GB = (174 ± 6) − (12.3 ± 0.9)Σσ^φ (correlation coefficient = 0.986, GB in kcal/mol). From the excellent correlation observed, it can be concluded that the electrophilic reactions on phosphoramides (and more specifically their protonation) involve the oxygen atom in both the gas and condensed phases. The following substituent constants σ^φ can also be deduced from Figure 2: −CH₂NMe₂, -1.43; NH₂, −0.94; (NMeCH₂)₂, −2.39.

II. Ab Initio Basicities. The nature of the PO bond has been the subject of numerous theoretical investigations. As discussed above, these studies generally lead to a consensus that bonding
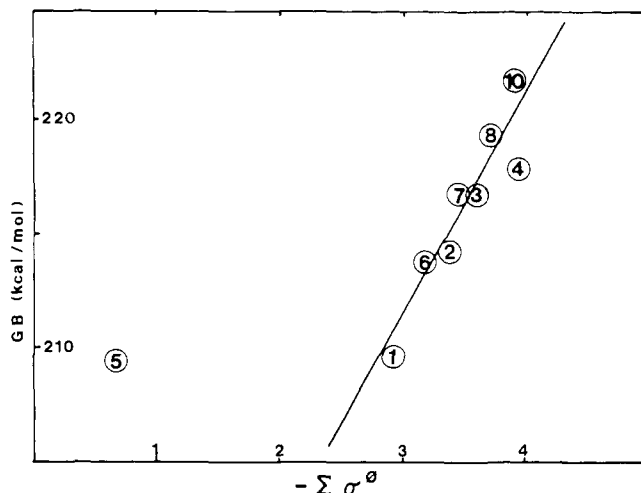

Figure 2. Plot of GB vs. Kabachnik's substituent constant σ^φ. Later values taken from ref 27: Me, −0.96; Et, −1.10; n-Pr, −1.18; i-Pr, −1.30; NMe₂, −1.22; OEt, −0.21; NEt₂, −1.28 (this value from ref 35). Note that **5** and **4** were not considered in establishing the correlation.

between P and O may be described as a single σ bond, arising from the σ donation of the phosphorus lone pair to a vacant p orbital on the oxygen, enhanced by some degree of π back-bonding from the oxygen lone pairs to the low-lying vacant d orbitals of phosphorus.[24] For a realistic description of the nature of the PO bond, it is therefore essential to use a comprehensive one-electron basis set including d atomic orbitals (AOs) on phosphorus.[24,28-30] Kutzelnigg has indeed shown[24a] in the case of OPH₃ that, despite their relatively small population (0.30 e), the d AOs on phosphorus are indispensable for a proper prediction of both PO bond distance (1.47 vs. 1.60 Å without d AOs) and characteristics (partial triple bond). However, the role of d AOs on oxygen is much less important since they accomodate only 0.05 e according to the same calculation.[24a] We presume, therefore, that a basis set of double ζ quality plus d polarization on phosphorus only (i.e., basis set IV) should be adequate for describing the protonation of the present compounds, which has been confirmed by test calculations performed for OPH₃ using the 6-31G* (d AOs on P and O) and 6-31G** (idem plus p AOs on H) basis sets (vide infra).

It is seen in Table III, which compares the SCF optimized geometries for basis sets I–IV, that adding a d function (i.e., changing the basis set from III to IV) shortens the PO bond by 0.11 Å on average for the molecules OPX₃ (X = H, Me, . . .), in agreement with the conclusions of Kutzelnigg.[24a] One finds also significant shortening of the PN (∼0.045 Å) and PC (∼0.025 Å) bond lengths, which again has its origin to some degree in π back-bonding toward the d orbitals of phosphorus, though to a lesser extent than in the PO case. The most complete calculation (basis set IV) at the ab initio SCF level leads, for the optimized equilibrium geometry of compound **1**, to very good agreement with the electron diffraction data reported by Wilkins et al.[31] The importance of adding d orbitals on phosphorus can also be seen from the gross atomic population of this AO which amounts to 0.5–0.6 e for all four compounds. Returning to Table III, we note another feature: that extension of the basis set leads generally to smaller equilibrium distances, in agreement with the well-known trend observed in ab initio calculations.[32] It is interesting to compare the results in Table III with those obtained for OPH₃ at the SCF level using the 6-31G* and 6-31G** basis sets. These two calculations lead to PO bond distances of 1.465 and 1.466

(26) (a) Lau, Y. K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452. (b) Harrison, A. G.; Houriet, R.; Tidwell, T. T. *J. Org. Chem.* **1984**, *49*, 1302. (c) For a recent review, see: Taft, R. W. *Prog. Phys. Org. Chem.* **1982**, *14* 248.
(27) Mastryukova, T. A.; Kabachnik, M. I. *Russ. Chem. Rev.* **1963**, *38*, 795; *J. Org. Chem.* **1971**, *36*, 1201.
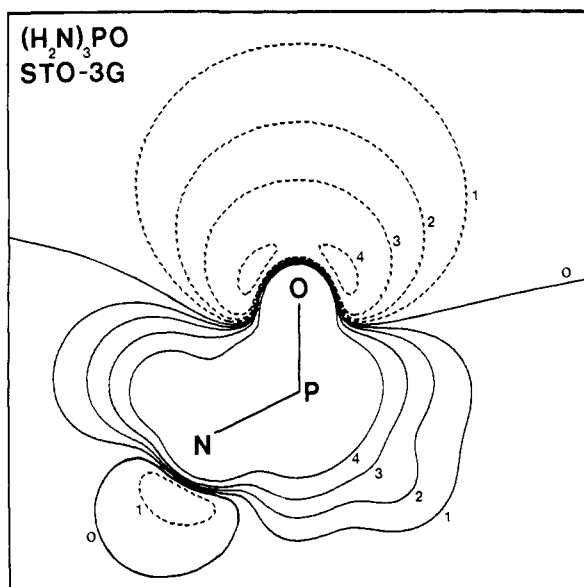
(28) Guest, M. F.; Hillier, I. H.; Saunders, V. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 867.
(29) Wallmeier, H.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1979**, *101*, 2804.
(30) Mardsen, C. J. *Inorg. Chem.* **1984**, *23*, 1703.
(31) Wilkins, C. J.; Hagen, K.; Hedberg, L.; Shen, Q.; Hedberg, K. *J. Am. Chem. Soc.* **1975**, *97*, 6352.
(32) Carsky, P.; Urban, M. "Lecture Notes in Chemistry. Vol. 16. Ab Initio Calculations: Methods and Applications in Chemistry"; Springer: Berlin, 1980; p 136.

Figure 3. STO-3G MEP map calculated for $OP(NH_2)_3$ in the OPN plane. Contour values of 0, 1, 2, 3, and 4 correspond to energies of 0, 6, 13, 25, and 63 kcal/mol, respectively. Positive (negative) contours are indicated by a solid (dashed) line.

Å, PH bond distances of 1.393 and 1.396 Å, and OPH bond angles of 117.0 and 116.9°, respectively, these results being very similar to those obtained with basis set IV.

Table IV presents the proton affinities and the structural parameters of protonated species obtained at the ab initio SCF level. All the geometrical parameters of the protonated structures have been optimized so as to provide a consistent comparison of the PA values. We have reported in Table IV the results for the O-protonated structures only, since *additional calculations performed for the N-protonated species* **6H⁺** *have shown that its thermodynamic stability is lower by as much as 100 kcal/mol* (basis set I). The same qualitative conclusion would undoubtedly also apply to **15**, as the ab initio results of Modro et al.[2a] obtained for $H_2P(O)NH_2$ indicate that oxygen protonation is favored by 50 kcal/mol, though these calculations might be questionable because of the minimum basis set used (without d AOs on P). In the case of **15H⁺**, a further confirmation of the larger stability of the oxygen-protonated form is provided by a STO-3G MEP map (Figure 3) which shows clearly the much smaller depth of the minimum at the nitrogen site. *It is therefore clear that protonation of the phosphoramides occurs at the oxygen site, at least for the molecules examined here.*

As a result of the O-protonation, Table IV shows that the PO bond length increases significantly for the four compounds, its value being much closer to that of a single PO bond (1.60 Å). This effect is undoubtedly due to a smaller π back-bonding donation because one lone pair of oxygen is involved in OH bonding, as exemplified by the reduced 3d populations on phosphorus (by roughly 0.1 e) in the protonated bases, which indicates that O-protonation reinforces the single σ-bond character of the PO bond. Decreases in PC and PN bond distances are also found upon protonation: $r(PC)$ decreases by 0.029 Å in **1** and **6**, whereas $r(PN)$ decreases by 0.036 Å in **6** and 0.039 Å in **15** (basis set IV). The origin of this shortening lies probably in the larger polarity of the PO unit in the protonated form, which in turn leads to a somewhat larger σ and π back-donation from the substituents of phosphorus. We also report in Table IV the optimized equilibrium geometry of the proton in each of the O-protonated forms. Basis set effects on the POH⁺ bond angles and XPOH⁺ dihedral angles are rather spectacular. Finally, as the energies of the structures are reported in Table IV, it is possible to compare them with the corresponding values obtained for OPH_3 (unprotonated) using the 6-31G* and 6-31G** basis sets, i.e., −417.306 81 and −417.313 20 hartrees, respectively, which leads to the following PA values: 209.7 kcal/mol (6-31G*) and 214.8 kcal/mol (6-

31G**). This demonstrates that the quality of basis set IV is practically equivalent to that of the fairly large 6-31G* basis, suggesting that our SCF results obtained using basis set IV are reliable.

It is known that the absolute values of proton affinities are overestimated by the STO-3G basis set.[33] This feature is again observed in the present results which exhibit a monotonous decrease of the calculated PAs along the basis sets I–IV. The results obtained with basis set IV are in satisfactory agreement with experiment. The ordering PA(1) < PA(6) is the same as that obtained for experimental GB values, and the predicted PA values are about 10% larger than the experimental ones, which is not surprising. Indeed, two corrections to the PA values calculated at the ∆SCF level should be taken into account, namely, electron correlation and zero-point vibrational energies. It has been shown by Pople et al. that, whereas the small correlation corrections to PA values should be determined by using large basis sets and may be of both signs,[34a] the zero-point correction leads always to a decrease in PA values (on the order of 5 to 10 kcal/mol for a series of bases of AH_n and H_mABH_n type).[34b] In order to evaluate the importance of these corrections, we have performed two series of additional calculations: (i) with correlation included using Møller–Plesset perturbation theory up to fourth order;[15] (ii) with harmonic vibrational analysis included, which leads to an estimation of zero-point vibrational corrections.[10b] The results are presented in Table V. It is seen that whereas both correlation (ΔE_c) and zero-point vibrational (ΔE_{zp}) effects decrease the computed PA values by 5–10 kcal/mol, basis set dependence is very different in both cases. Indeed, convergence of ΔE_{zp} as a function of basis set size is very rapid and the results tend smoothly to a ΔE_{zp} of $\sim$−7 kcal/mol. Correlation corrections, however, are much more unpredictable and, in agreement with Pople et al.,[34a] we conclude that "unless very extensive basis are used, the inclusion of correlation corrections to computed protonation energies cannot necessarily be expected to improve accuracy". All one can say is that, at the 6-31G** level, both ΔE_c and ΔE_{zp} are of the same sign and order of magnitude, the former being smaller by roughly 2 kcal/mol. We can therefore reasonably expect that by taking these two corrections into account, the best SCF values for PA in Table IV will decrease by 15 to 20 kcal/mol, thereby yielding very good agreement with the measurements. In other words, the SCF ab initio models in Table IV contain two well-studied quantitatively recoverable errors which should not invalidate the main conclusions and trends drawn from the present calculations.

Another interesting feature that emerges from Table IV lies in the variations in predicted basicities. Not unexpectedly, replacing hydrogen by methyl groups in OPH_3 produces an increase in basicity (20.3 kcal/mol, basis set IV) because of the polarizability enhancement due to the methyl group.[5,18] Then, replacing one methyl by a dimethylamino group leads again to an increase in PA of 2.6 kcal/mol, in qualitative agreement with experiment (4.2 kcal/mol). For compound **15**, one would expect qualitatively a smaller basicity than for **1**, in accordance with the ordering in basicity GB(7) − GB(9) = 1.1 kcal/mol (vide supra). The calculated proton affinities show indeed the trend PA(1) > PA(15) for basis sets I, II, and III, but Pa(1) $\simeq$ PA(15) for set IV. We have seen above that the neglect of correlation corrections is sufficiently basis-set dependent to produce such a result. Finally, the SCF models predict consistently PA(6) > PA(15), which would be in contradiction with the experimental values if **15** were interpreted as a perfect prototype of **8**. However, the destabilizing substituent effects caused by replacing all methyl groups in **8** by hydrogen atoms in **15** may be easily important enough to account for the relative proton affinities of compounds **6** and **15**. Thus, taken as a whole, the present calculations appear to establish a

(33) Newton, M. D.; Ehrenson, S. *J. Am. Chem. Soc.* **1971**, *93*, 4971.
(34) (a) Frisch, M. J.; Del Bene, J.; Raghavachari, K.; Pople, J. A. *Chem. Phys. Lett.* **1981**, *83*, 240. (b) Del Bene, J.; Frisch, M. J.; Raghavachari, K.; Pople, J. A. *J. Phys. Chem.* **1982**, *86*, 1529.
(35) Yakshin, V. V.; Tymonyuk, M. I.; Sokal'skaya, L. I.; Laskorin, B. N. *Dokl. Akad. Nauk. SSSR* **1979**, *247*, 128.

rather satisfactory framework for the interpretation of the gas-phase protonation of phosphoramides and phosphine oxide derivatives.

Conclusion

The determination of experimental gas-phase basicities indicates that the protonation of phosphines, phosphine oxides, and phosphoramides all lead to formation of phosphonium ions. Stabilization of the latter via π back-donation to the d orbitals of the phosphorus is evidenced by the spectacular effects of substituents in P^{III} and P^V compounds. In the case of phosphoramides, these effects permit us to conclude that O-protonation is the thermodynamically favored process.

These conclusions are substantiated by ab initio calculations on the protonation of model compounds. They point out the importance of including the d orbitals on phosphorus in order to describe the properties (geometry, energy) of these compounds. They also show that O-protonation of phosphoramides is the lowest energy process of protonation. These conclusions are in accordance with general concepts used to describe chemical reactivity. On the one hand, the principle of "hard and soft acids and bases" developed by Pearson can be applied.[36] Gas-phase protonation

is concerned with bare reactants and thus deals with hard acid reagents. The oxygen atom is known to be a harder base than a nitrogen center, in agreement with our experimental and calculational conclusions. On the other hand, the versatile behavior of phosphoramides in solution (change in site of protonation) can be understood on the basis of the experimentally determined solvation energies for onium ions.[37] The larger solvation energies have been determined for the stronger Brønsted acids BH^+; thus this effect tends to weaken the difference in basicity between O and N as solvation increases.

(36) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643. (c) Ho, T. L. "Hard and Soft Acids and Bases Principle in Organic Chemistry"; Academic Press: New York, 1977.

(37) (a) Davidson, W. R.; Sunner, J.; Kebarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1675. (b) Meot-Ner (Mautner), M. *Ibid.* **1984**, *106*, 1265.

Gas-Phase Reactions of Free Vinyl Cation with Benzene and Free Phenylium Ion with Ethylene. A Comparative FT–ICR and Nuclear Decay Study

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Abstract: The results of a comparative FT–ICR (ca. 10^{-6} torr) and nuclear-decay study (6–65 torr) of the gas-phase reaction of vinyl cation with benzene and of phenylium ion with ethylene are reported. The isomeric population of the $C_8H_9^+$ intermediates obtained from both reactions and their interconversion pattern have been sampled by direct analysis of the reaction products. Stable (lifetime $>10^{-7}$ s) ring-protonated styrenes are primarily formed by vinyl cation attack on benzene, while ethylenebenzenium ion arises from phenylium ion addition to ethylene. At low pressures (ca. 10^{-6} torr), both species undergo appreciable hydrogen scrambling prior to fragmentation. At higher pressures (6–65 torr), fragmentation of $C_8H_9^+$ is efficiently prevented in favor of rapid isomerization to the thermodynamically more stable α-methylbenzyl cation. The present investigation provides no evidence for further isomerization to other conceivable structures. The benzene vinylation and the ethylene phenylation reaction mechanisms, as well as the isomerization pathways of the ensuing primary adducts, are discussed and compared to relevant mass spectrometric and kinetic data.

Spontaneous β decay of a tritium atom in multitritiated compounds affords a convenient means to generate free carbocations of defined structure into any system of interest and to study their reactions by tracer techniques.[1] The method was recently applied to gather otherwise inaccessible information on the reactivity of a free vinyl cation toward liquid benzene and methanol.[2] The results point to the high reactivity of the vinyl cation which efficiently adds to the nucleophilic site of the substrate to give as the major products, respectively, styrene and methyl vinyl ether. In the liquid phase, no evidence of further isomerization of the vinylated adducts was observed.

In the gas phase, the $C_2H_3^+$ ions can easily be produced by mass spectrometric methods and their heat of formation evaluated.[3]

However, very little is known about the reactivity of vinyl cation toward organic substrates and the nature of the ionic intermediates involved. In fact, the gas-phase reaction of a $C_2H_3^+$ cation with benzene has been examined thus far only in a triple quadrupole mass spectrometer.[4] The unexpected hydrogen abstraction 1 was

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(1) (a) Cacace, F. *Adv. Phys. Org. Chem.* **1970**, *8*, 79. (b) Cacace, F. In "Interaction between Ions and Molecules"; Ausloos, P., Ed.; Plenum Press: New York, 1975. (c) Cacace, F. In "Kinetics of Ion-Molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, 1979. (d) Speranza, M. *Gazz. Chim. Ital.* **1983**, *113*, 37.

(2) Fornarini, S.; Speranza, M. *Tetrahedron Lett.* **1984**, *25*, 869.

(3) (a) Lossing, F. P. *Can. J. Chem.* **1971**, *49*, 357. (b) Lossing, F. P. *Ibid.* **1972**, *50*, 3973. (c) Field, F. H.; Lampe, F. W. *J. Am. Chem. Soc.* **1958**, *80*, 5587. (d) Smith, R. D.; Futrell, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *20*, 71.

(4) Morrison, J. D.; Stanney, K.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 838.