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Stereoelectronic Effects and Gas-phase Affinities of Dicoordinated Borinium Cations

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The relative affinities of the borinium cations $(CH_3O)_2B^+$ and CH_3OB^+H towards pyridines were determined by the kinetic method using a pentaquadrupole mass spectrometer and the absolute affinities of these ions towards pyridine itself were estimated with the aid of *ab initio* calculations at the MP2/6–31G(d,p)//6–31G(d,p) level to be 75.7 and 82.2 kcal mol^{-1}, respectively (1 kcal = 4.184 kJ). The affinities were found to correlate linearly with the proton affinities of the *meta*- and *para*-substituted pyridines, but steric effects decrease the affinities for *ortho*-substituted pyridines. A set of gas-phase stereoelectronic parameters (S^k) for these isomers was measured from the deviation of the value of the logarithm of the experimentally measured ion abundance ratio from the regression line established for *meta*- and *para*-substituted pyridines. The S^k value of 2,6-dimethylpyridine with $(CH_3O)_2B^+$ is smaller than that for other dimethylpyridines, owing to the stabilizing effects of auxiliary hydrogen bonding interactions between one hydrogen of each of the *ortho*-methyl substituents and the two oxygens of the $(CH_3O)_2B^+$ ion. The dimethoxy boron cation $(CH_3O)_2B^+$ is shown to have smaller steric effects than CH_3OB^+H, even though the former ion has two bulky methoxy groups. This is ascribed to the relatively longer B—N bond in $(CH_3O)_2B^+$—Py as a result of reduced charge density on the boron atom due to resonance stabilization within the dimethoxy boron cation. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Dicoordinated borinium cations are proposed to exist as intermediates in solution[1,2] where these electron-deficient species bearing two empty p-orbitals on the boron appear to act as strong electrophiles.[3,4] Their extreme reactivity towards solvent molecules and counterions, however, limits study to ions such as $B(NR_2)_2{}^+$ and $B(NR_2)R'^+$ (R = alkyl or aryl) with bulky ligands which are capable of π-back-bonding to offset the large positive charge at the boron center and to inhibit nucleophilic attack sterically.[5]

The gas phase allows the study of the chemical and physical properties of ions and molecules without such perturbing influences as solvation and ion pairing. Accordingly, the stabilities of borinium ions and their structures have long been of interest in mass spectrometry. Early results[6] showed that cyclic structures are thermodynamically unstable relative to their non-cyclic analogues which can adopt the favored linear O—B—O (or N—B—N) configuration. More recent gas phase studies of dicoordinated borinium cations include the determination of halide affinities of $(CH_3)_2B^+$ by halide transfer[7] and studies of the reactivities of $(CH_3O)_2B^+$ and $(CH_3)_2B^+$ ions towards organic ethers.[8] These ions were found to be exceedingly reactive towards oxygen lone pair electrons in organic substrates in reactions proposed to take place via consecutive 1,2-eliminations of two neutral alkene molecules from the ethers to yield $(CH_3O)_2BOH_2{}^+$ and $(CH_3)_2BOH_2{}^+$ product ions. Similar results were obtained for reactions with alcohols.[9] Further, it was demonstrated by Kenttämaa and co-workers[10] that the dimethoxy boron cation $(CH_3O)_2B^+$ can be used to differentiate stereoisomeric diols by investigation of their ion–molecule reactions. These results showed that only the adduct formed from the *cis*-diols could react further by abstraction of a methanol. More recently, the special reactivity of the borinium ion $(CH_3O)_2B^+$ to form adducts with barbiturate derivatives, which then dissociate by elimination of methanol followed by attachment of a trimethylborate molecule in a secondary ion–molecule reaction, has been reported by Colorado and Brodbelt.[11]

Even though the gas-phase ion chemistry of dicoordinated borinium cations has received some attention, thermochemical data are very limited and have large uncertainties.[12,13] For example, the values reported for the heat of formation of $(CH_3O)_2B^+$ differ by more than 43 kcal mol^{-1} (1 kcal = 4.184 kJ).[13,14] Thermochemical information has played a particularly important role in the development of ion–molecule chemistry in the elucidation of product ion structures and the prediction of mechanisms. Therefore, it is highly desirable that further information on the thermochemical properties of dicoordinated borinium cations be available. Recently, Isbell and Brodbelt[15] reported the relative free energies of bonding of dimethoxyborinium ion to several substituted pyridines using an equilibrium

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method in an ion trap instrument and steric effects of *ortho*-substituted pyridine were illustrated by a comparison of the relative borinium ion affinities and gas-phase basicities. Here, we report a study of the gas phase $(CH_3O)_2B^+$ and CH_3OB^+H affinities of a large set of pyridines using the kinetic method. The kinetic method is an alternative to equilibrium methods for determining thermochemical properties.[16,17] It is based on the rates of competitive dissociation of mass-selected cluster ions (A—M$^+$—B) under collision-induced dissociation (CID) or metastable ion conditions to form the individual cationized monomers (AM^+ and BM^+). The ratio of the rates of the competitive dissociations of the cation-bound dimer, expressed as the ratio of the abundances of the individual monomers, can be used to estimate the cation affinity difference between A and B:

$$\ln\left(\frac{[AM^+]}{[BM^+]}\right) = \frac{\Delta(M^+ \text{ affinity})}{RT_{\text{eff}}} \quad (1)$$

where $[AM^+]$ and $[BM^+]$ are the abundances of the two monomers, $\Delta(M^+$ affinity) is the cation affinity difference between the two compounds A and B and T_{eff} is the effective temperature of the activated cation-bound dimer and represents the excess energy per degree of freedom normalized to the critical energy for cluster ion fragmentation.[18,19] The derivation of Eqn (1) is presented elsewhere.[17,20] The kinetic method is sensitive to small thermochemical differences (<1 kcal mol^{-1}), and is applicable to polar and non-volatile samples even when they are not pure.[17c] On the other hand, special attention must be paid to the possibility that entropic factors adversely affect the enthalpic measurements,[21,22] and this is usually done by limiting comparisons to closely related compounds. The kinetic method has been widely used to measure the proton affinities of various compounds.[23–27] More significantly, the method has been extended to estimate the proton affinities of free radicals,[28] the electron affinities of polycyclic aromatic hydrocarbons (PAHs) and nitrobenzenes,[29] NH_4^+ affinities of crown ethers,[30] NO_2^+ affinities of various organic ligands[31] and the affinities of substituted pyridines towards Cl^+,[32] $OCNCO^+$,[33] $SiCl^+$, $SiCl_3^+$ [34] and SF_3^+.[35] In the last series of studies, various cations are being studied in order to develop an understanding of the relationship between the affinities for different cations using a common set of Lewis bases. A series of pyridines was chosen because they are strong bases in which ring substituents can be introduced to modify systematically their electronic and steric effects.

The objectives of this study were (i) to order the relative $(CH_3O)_2B^+$ and CH_3OB^+H affinities with respect to a group of alkyl-substituted pyridines, (ii) to seek stereoelectronic effects which might arise for *ortho*-substituted alkyl pyridines and (iii) to compare the stereoelectronic effects of the *ortho*- substituent(s) in $(CH_3O)_2B^+$- and CH_3OB^+H-bound dimers.

EXPERIMENTAL

All multiple mass spectrometric experiments (MS^2 and MS^3) were performed using a custom-built pentaquadrupole mass spectrometer[36] with three mass-analyzing quadrupoles (Q1, Q3 and Q5) and two collision quadrupoles (Q2 and Q4). Samples were introduced into the ion source via a leak valve (Granville Phillips, Boulder, CO, USA) and the ions $(CH_3O)_2B^+$ and CH_3OB^+H were generated by 70 eV electron impact (EI) ionization of trimethyl borate (Aldrich Chemicals, Milwaukee, WI, USA) in the mass spectrum of which they have relative abundances of ~100% and ~25%, respectively.

Ion–molecule reactions of mass analyzed reagent ions (MS^2 experiment) were performed in Q2 between the ion of interest generated in the ion source and mass selected in Q1 and a mixture of neutral pyridines. The spectrum of ion–molecule reaction products was recorded by scanning Q5 while setting both Q3 and Q4 in the r.f.-only mode. To characterize the individual ion–molecule reaction products a sequential product scan[37] (MS^3 experiment) was performed, product ions formed in Q2 being mass selected in Q3 and allowed to undergo CID with argon in Q4, while Q5 was scanned to record the sequential product spectrum.

The nominal sample pressure was typically 5×10^{-6} Torr (1 Torr = 133.3 Pa) as monitored by a single ionization gauge located in the vacuum chamber near Q5. The pressure rose to 4×10^{-5} Torr on addition of the pyridine mixture to Q2, and further to 6×10^{-5} Torr on addition of argon collision gas to Q4. The collision energy, given as the potential difference between the ion source and the offset voltage of the collision quadrupole, was typically near 0 eV for ion–molecule reactions and 10 eV for CID. The attenuation of the ion beam upon introducing the argon collision gas was about 80%. The pyridines and trimethyl borate are commercially available and were used as received. Mass-to-charge ratios are reported using the Thomson unit (Th) (1 Th = 1 atomic mass per unit positive charge).[38]

RESULTS AND DISCUSSION

Dicoordinated borinium cations can be generated readily upon EI ionization of boron-containing compounds.[39] The EI mass spectrum of trimethyl borate has been reported previously.[39,40] The fragment at 43 Th is assigned as CH_3OB^+H by high-resolution MS, while the fragment at 73 Th is $(CH_3O)_2B^+$. Both ions contain a —B$^+$—O—moiety and are highly susceptible to nucleophilic attack. Here, we use substituted pyridines as nucleophiles.

Ion–molecule reactions of $(CH_3O)_2B^+$ (73 Th) with a mixture of pyridines, in this case pyridine (Py) and 3-methylpyridine (3-MePy), were investigated and gave the set of products shown in Fig. 1. These ion–molecule reaction products include (i) the protonated molecules PyH$^+$ (80 Th) and 3-MePyH$^+$ (94 Th), (ii) the $(CH_3O)_2B^+$ addition products $(CH_3O)_2B^+$—Py (152 Th) and $(CH_3O)_2B^+$—3-MePy (166 Th), (iii) proton-bound dimers PyH$^+$Py (159 Th), 3-MePyH$^+$Py (173 Th) and 3-MePyH$^+$3-MePy (187 Th) and (iv) $(CH_3O)_2B^+$-bound dimers Py—$(CH_3O)_2B^+$—Py (231 Th), 3-MePy—$(CH_3O)_2B^+$—Py (245 Th) and 3-MePy—$(CH_3O)_2B^+$—3-MePy (259 Th). Note that $(CH_3O)_2B^+$ fragments readily to form CH_3OB^+H (43

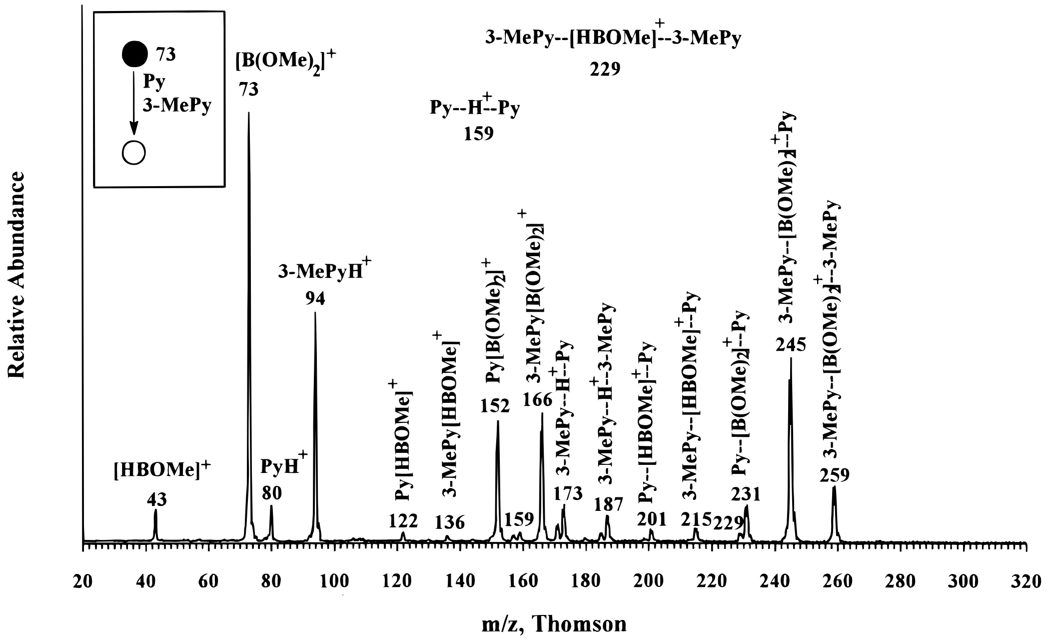


Figure 1. Reaction product spectrum displaying products of ion–molecule reactions of $(CH_3O)_2B^+$ (73 Th) with a mixture of pyridine (Py) and 3-methylpyridine (3-MePy).

Th) by loss of neutral CH_2O and consequently CH_3OB^+H-bound monomers and dimers of pyridines are also observed among the ion–molecule reaction products. The protonated pyridines and the proton-bound dimers probably arise via charge exchange between the pyridines and the mass-selected reagent ion due to proton transfer and subsequent association reactions.

The ion at 245 Th, assigned as the $(CH_3O)_2B^+$-bound dimer of pyridine and 3-methylpyridine, was generated as just described then mass selected in Q3 and fragmented by CID with argon in Q4 while scanning Q5 to record the sequential product mass spectrum (MS^3). The spectrum (Fig. 2) shows only two fragments, $(CH_3O)_2B^+$—Py (152 Th) and $(CH_3O)_2B^+$—3-MePy (166 Th). This simple behavior, which is characteristic of loosely bound dimers, was not observed by Isbell and Brodbelt,[15] who observed methanol elimination from the $(CH_3O)_2B^+$-bound pyridine dimers and therefore could not apply the kinetic method. The reasons for this difference were not studied.

Ion–molecule reactions between the ion CH_3OB^+H and the pyridines were also investigated and the analogous product, 3-MePy—CH_3OB^+H—Py (215 Th), was also characterized by MS^3 experiments. The only fragments observed are the corresponding CH_3OB^+H-

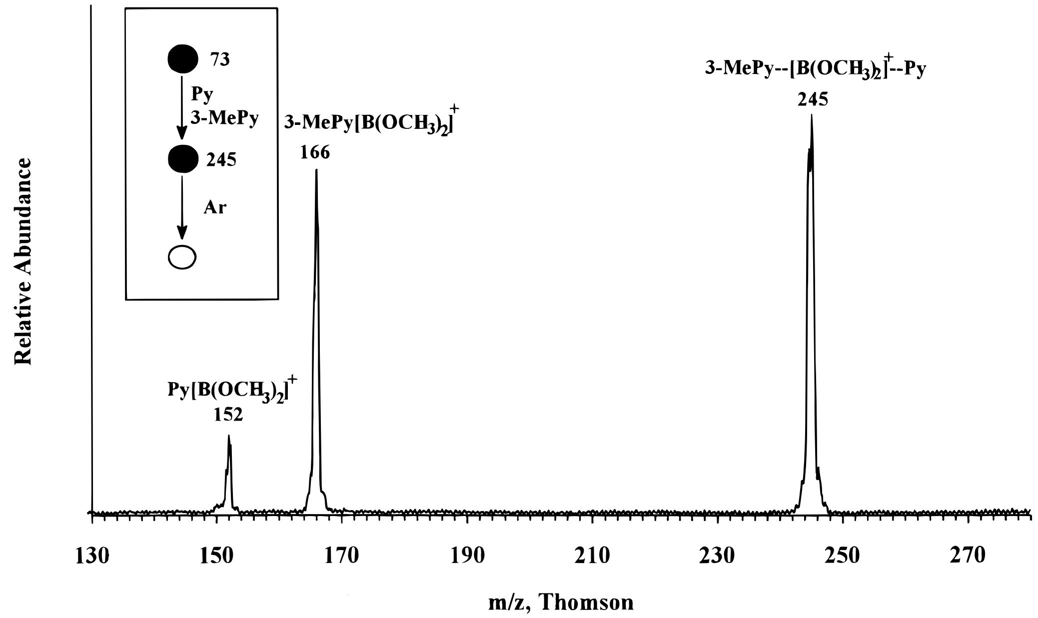


Figure 2. Sequential product spectrum (MS^3) showing fragmentation of the mixed dimeric adduct (245 Th) generated upon reaction of $(CH_3O)_2B^+$ (73 Th) with a mixture of pyridine (Py) and 3-methylpyridine (3-MePy).

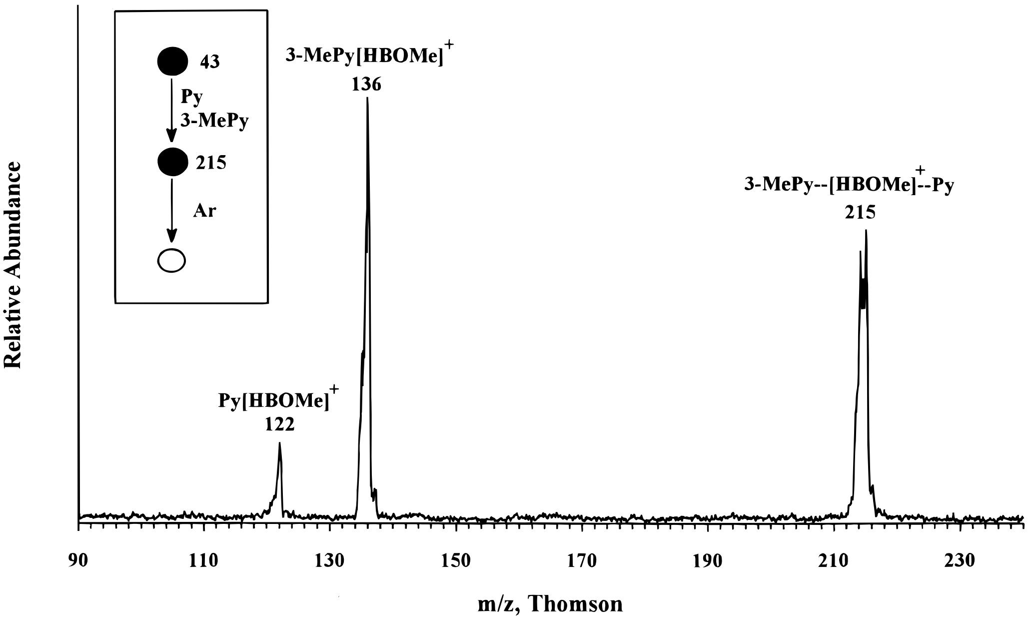


Figure 3. Sequential product spectrum (MS^3) showing fragmentation of the mixed dimeric adduct (215 Th) generated upon reaction of CH_3OB^+H (43 Th) with a mixture of pyridine (Py) and 3-methylpyridine (3-MePy).

bound monomers, Py—CH_3OB^+H (122 Th) and 3-MePy—CH_3OB^+H (136 Th), as shown in Fig. 3. The fact that the cluster ions fragment readily under mild collision energy (10 eV) and pressure (6×10^{-5} Torr) conditions suggests that they are loosely bound.[17,32] The relative abundances of the two fragments indicate that 3-MePy has a higher affinity towards $(CH_3O)_2B^+$ and CH_3OB^+H than does pyridine itself.

According to the kinetic method, loosely bound dimers should fragment competitively to give the two monomeric product ions in relative abundances which are logarithmically related to the difference in the borinium cation affinities:

$$\ln\left(\frac{[\mathrm{Py}_1(\mathrm{R}_1\mathrm{B}^+\mathrm{R}_2)]}{[\mathrm{Py}_2(\mathrm{R}_1\mathrm{B}^+\mathrm{R}_2)]}\right) = \frac{\Delta[(\mathrm{R}_1\mathrm{B}^+\mathrm{R}_2)\ \text{affinity}]}{RT_{\mathrm{eff}}} \qquad (2)$$

where Py_1 and Py_2 represent two pyridines, $R_1 = R_2 = CH_3O$ in the $(CH_3O)_2B^+$ system and $R_1 = CH_3O$ and $R_2 = H$ in the CH_3OB^+H case. Therefore, it is possible to compare the relative magnitudes of the borinium cation affinities using the quantity $\ln\{[\mathrm{Py}_1(\mathrm{R}_1\mathrm{B}^+\mathrm{R}_2)]/[\mathrm{Py}_2(\mathrm{R}_1\mathrm{B}^+\mathrm{R}_2)]\}RT_{\mathrm{eff}}$ if one knows the effective temperature for the activated dimers. Effective temperatures in the range 555–782 K have been reported in previous studies of other pyridine clusters.[32–35] Given that all these experiments were performed under the similar conditions, an average temperature of 650 K was used here to estimate the relative borinium ion affinities. The relative affinities so determined are listed in Table 1. Note that the value of the effective temperature does not significantly affect the affinities.[34] For example, errors in the temperature by even 100 K correspond to changes in affinities of less than ± 1.0 kcal mol^{-1}. The absolute $(CH_3O)_2B^+$ and CH_3OB^+H affinities of pyridine itself were estimated by *ab initio* calculations (Spartan version 4.0 at the level of MP2/6–31G(d,p)//6–31G(d,p)) to be 75.7 and 82.2 kcal mol^{-1}, respectively. These calculated affinity values can be used in combination with the relative borinium ion affinities to calculate the absolute $(CH_3O)_2B^+$ and CH_3OB^+H affinities of other pyridines, and the results are also listed in Table 1.

If the same electronic effects known to influence proton affinities (*PA*) also affect $(CH_3O)_2B^+$ and CH_3OB^+H affinities, and if these effects parallel each other, then the same order for both borinium ion ($R_1B^+R_2$) affinities and proton affinities is expected. Excellent linear correlations are observed between the relative $(CH_3O)_2B^+$ and CH_3OB^+H affinities of *meta*- and *para*-substituted pyridines and their proton affinities as shown in Figs 4 and 5. The linear correlations observed in these cases suggest that the pyridines are oriented symmetrically with respect to binding at the central boron atom. This has been proved in studies of Cl^+,[32] CN^+ [41] and $OCNCO^+$ cations,[33] where the symmetrical binding to the central atom has been confirmed to be the most stable structure by *ab initio* calcu-

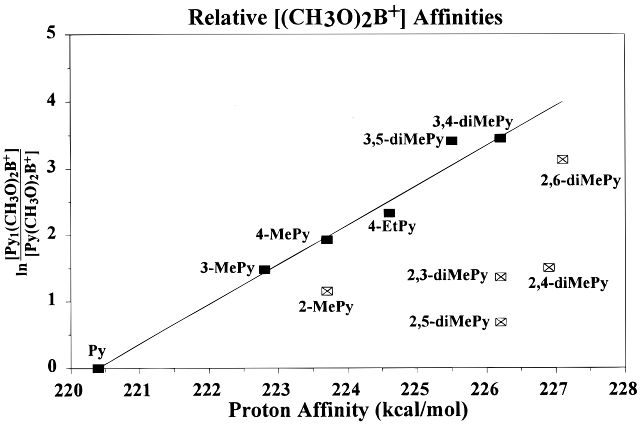


Figure 4. Linear correlation between $\ln\{[\mathrm{Py}_1(\mathrm{CH_3O})_2\mathrm{B}^+]$ $[\mathrm{Py}(\mathrm{CH_3O})_2\mathrm{B}^+]\}$ and the corresponding proton affinities (correlation coefficient (r^2) = 0.98). Open symbols represent ortho substituted pyridines which do not correlate due to steric effects.

Table 1. $(CH_3O)_2B^+$ and CH_3OB^+H affinities and proton affinities of pyridines

Entry	Pyridine	$Py_1:Py_2$[a]	$\ln\left(\frac{[Py_1(CH_3O)_2B^+]}{[Py(CH_3O)_2B^+]}\right)$	$\ln\left(\frac{[Py_1(CH_3OB^+H]}{[Py(CH_3OB^+H]}\right)$	Proton affinity[d] (kcal mol^{-1})	Relative $(CH_3O)_2B^+$ affinity[e]	Relative CH_3OB^+H affinity[e]	Absolute $(CH_3O)_2B^+$ affinity[f]	Absolute CH_3OB^+H affinity[f]
1	Py		0	0	220.4	0	0	75.7	82.2
2	3-MePy	2:1	1.48	1.73	222.8	1.9	2.2	77.6	84.4
3	4-MePy	3:1	1.93	2.06	223.7	2.5	2.7	78.2	84.9
4	4-EtPy	4:3	2.33	2.59	224.6	3.0	3.3	78.7	85.5
5	3,5-DiMePy	5:3	3.41	3.17	225.5	4.4	4.1	80.1	86.3
6	3,4-DiMePy	6:3	3.45	3.6	226.2	4.5	4.6	80.2	86.8
7	2MePy	7:1	1.15	−0.14	223.7	1.5	−0.2	77.2	82.0
8	2,5-DiMePy	8:3	0.68	0.25	226.2	0.9	0.3	76.6	82.5
9	2,3-DiMePy	9:3	1.36	0.58	226.2	1.8	0.7	77.5	82.9
10	2,4-DiMePy	10:3	1.5	1.51	226.9	1.9	1.9	77.6	84.1
11	2,6-DiMePy	11:3	3.13	0.75	227.1	4.0	1.0	79.7	83.2

[a] The entry number of the pyridine forming the borinium cation-bound dimer used to estimate the borinium cation affinity.
[b] Experimental results from the dissociation of $(CH_3O)_2B^+$-bound dimers.
[c] Experimental results from the dissociation of CH_3OB^+H-bound dimers.
[d] Proton affinities are taken from Ref. 45. This older set of values is used in preference to others because it is more internally consistent and it facilitates comparison of the present data with those for pyridine binding to other cations. See Ref. 41 for a discussion of this point.
[e] The relative borinium cation affinities (kcal mol^{-1}) are obtained by using Eqn (2) and an assumed effective temperature of 650 K.
[f] The absolute borinium cation affinities (kcal mol^{-1}) of pyridine are obtained by *ab initio* calculations while those of substituted pyridines are calculated by adding the relative affinities to this value. The estimated error is ±2 kcal/mol.

lations. The present results indicate that the two pyridines in the $(CH_3O)_2B^+$- and CH_3OB^+H-bound dimers are symmetrically bound to the central boron atom.

From the linear plots in Figs 4 and 5 and the results in Table 1, the relative gas-phase $(CH_3O)_2B^+$ and CH_3OB^+H affinities of a series of pyridines can be ordered as Py < 3-MePy < 4-MePy < 4-EtPy < 3,5-diMePy < 3,4-diMePy. The linear correlations can be expressed (kcal mol^{-1}) as

$$\ln(k_1/k_2) = 0.60PA - 131.5 \qquad (3)$$

for $(CH_3O)_2B^+$-bound dimers and

$$\ln(k_1/k_2) = 0.61PA - 134.1 \qquad (4)$$

for CH_3OB^+H-bound dimers, where k_1 and k_2 are the two rate constants for the competitive dissociations of the borinium cation-bound dimers.

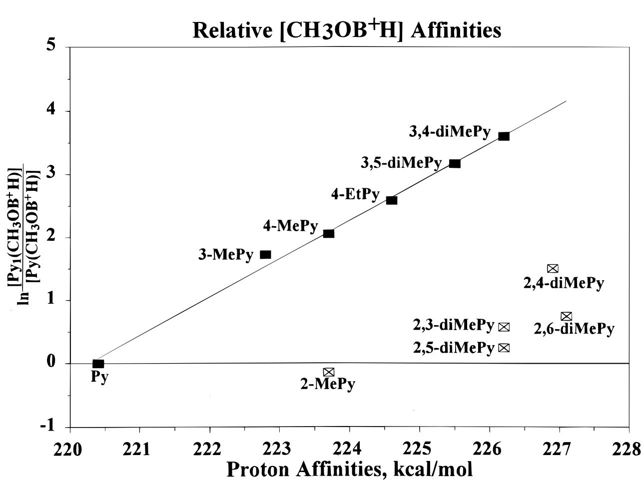
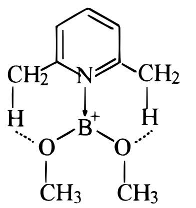


Figure 5. Linear correlation between ln{$[Py_1(CH_3OB^+H)]$/$[Py(CH_3OB^+H)]$} and the corresponding proton affinities ($r^2 = 0.99$). Open symbols represent *ortho*-substituted pyridines which do not correlate due to stereoelectronic effects.

As shown in Figs 4 and 5, the correlations between the logarithm of the ion abundance ratio and the proton affinity are excellent for *meta*- and *para*-substituted pyridines but poor for *ortho*-substituted pyridines, which show lower affinities. Such behavior can best be understood as a result of steric interactions between the *ortho*-alkyl substituent and the central cation in the dimers, as shown in previous studies of several cations.[32–35] The steric repulsion causes a lengthening of the B—N bond and consequently decreases the bond strength and hence the apparent cation affinity of the pyridine.

When a cluster ion comprising a sterically hindered pyridine (Py^h) and an unhindered pyridine (Py^u) is studied, the decrease in the logarithm of the ratio of the ion abundances $[Py^h(CH_3O)_2B^+]/[Py^u(CH_3O)_2B^+]$ or $[Py^h(CH_3OB^+H)]/[Py^u(CH_3OB^+H)]$ is assumed to be due to the stereoelectronic effects of the *ortho* group. The offset from the regression line established using *meta*- and *para*-substituted pyridines is defined as the gas-phase stereoelectronic parameters (S^k).[32] Steric effects depend on the size of the central cation, the geometry of the dimer and the bond length, which in turn affects the distance between the *ortho*-alkyl group and the central cation. Owing to the very small size of the proton, steric effects are expected to be negligible in proton-bound dimers. For example, 2-MePy and 4-MePy have similar proton affinities, both of which are higher than that of 3-MePy (Table 1), which can be understood by the fact that *o*- and *p*-methyl groups have very similar electronic effects on the pyridine molecules and these effects are larger than those of the *m*-methyl group. No steric effects are expected or observed for the proton affinity of 2-MePy. However, in the cases of $(CH_3O)_2B^+$- and CH_3OB^+H-bound dimers, the relative borinium cation affinities lie in a different order, 2-MePy < 3-MePy < 4-MePy. The decreased affinity of 2-MePy is clearly due to the steric hindrance arising from the *ortho* substituent. The same trend is observed for the dimethylpyridines. The gas phase stereoelectronic parameters (S^k) are ordered as 2-MePy (-0.82) < 2,6-diMePy (-0.87) < 2,3-diMepy (-2.10) < 2,4-diMePy (-2.38) < 2,5-diMePy (-2.78) in the $(CH_3O)_2B^+$-bound dimers and 2-MePy (-2.23) < 2,4-diMePy (-2.53) < 2,3-diMePy (-3.03) < 2,5-diMePy (-3.36) < 2,6-diMePy (-3.41) in the CH_3OB^+H-bound dimers, as listed in Table 2, which also includes S^k values obtained for other cations from previous studies. It is interesting that the stereoelectronic parameter for 2-MePy is smaller than that of the dimethyl mono-*ortho*-substituted pyridines. This is due to the buttressing effect of the greater binding strength of the dialkylpyridines to the borinium cation, which reduces the N—B bond length and thus increases the steric effects. For pyridines having two *ortho*-methyl substituents, the steric effect is expected to increase as it does in the cases of Cl^+, $SiCl_3{}^+$ and $OCNCO^+$ (Table 2). However, the dimethylborate cation $(CH_3O)_2B^+$ shows a smaller steric effect with 2,6-dimethylpyridine than with any other dimethylpyridine. This indicates the operation of an opposing electronic effect which increases the cation affinities. In this case, it is probably due to C—H···O hydrogen bonding interactions between hydrogens in the two *ortho*-methyl substituents and the oxygens in the central $(CH_3O)_2B^+$ ion, as shown in Scheme 1. The importance of C—H···O hydrogen bonds is well known[42] and has been verified both by experimental data[43] and theoretical calculations.[44] The energies of such C—H···O bonds are reported to be in the range 1–7 kcal mol^{-1}. In the case of CH_3OB^+H, this effect is expected to be smaller since there is only one possible interaction of this type and this only slightly offsets the relatively large steric effect as a result of the short B—N bond. Note that a similar situation in which agostic effects compete with steric effects was previously encountered in the cases of $SiCl^+$ and $SF_3{}^+$.[34,35]



Scheme 1. Proposed hydrogen bonds in the case of the adduct of 2,6-dimethylpyridine with the $(CH_3O)_2B^+$ ion.

The steric effects in the case of CH_3OB^+H are larger than those in Cl^+, $SiCl_3{}^+$ and $SF_3{}^+$, but similar to those in the bulky $OCNCO^+$. It is interesting that CH_3OB^+H has a larger steric effect than $(CH_3O)_2B^+$, although $(CH_3O)_2B^+$ has two bulky methoxy groups. This is probably due to resonance stabilization of the borinium ion by the two methoxy groups:

$$CH_3O^+{=}B{-}OCH_3 \leftrightarrow CH_3O{-}B^+ - OCH_3$$
$$\leftrightarrow CH_3O{-}B{=}O^+CH_3$$

The charge delocalization reduces the charge density on the boron atom, increases the B—N bond length in the $(CH_3O)_2B^+$—Py complex and thus reduces its bond strength. This is consistent with the results from *ab initio* calculations which yield $(CH_3O)_2B^+$ and CH_3OB^+H affinities of pyridine of 75.7 and 82.2 kcal mol^{-1}, respectively. The lengthening of the B—N bond reduces the steric repulsion between the *ortho*-methyl group of the pyridine and the central borinium ion $(CH_3O)_2B^+$.

CONCLUSIONS

The kinetic method provides insights into the binding of dicoordinated borinium cations to pyridine and allows borinium ion affinities to be estimated. Together with previous studies,[32–35] a variety of cations having central bonding atoms belonging to different groups and of different size have now been studied. Similar trends in bond strength with the nature of the substituent on pyridine have been observed in each case and the cation affinities are always found to correlate linearly with the proton affinities for the *meta*- and *para*-substituted pyridines. The slopes of these correlations fall in the order $OCNCO^+ \approx SiCl_3{}^+ > Cl^+ > SF_3{}^+ \approx CH_3OB^+H \approx (CH_3O)_2B^+ > SiCl^+$, the smaller slopes indicating weaker bonding but also depending on the number of degrees of freedom of the ion–pyridine complex.[18] Although the $(CH_3O)_2B^+$ affinity of pyridine is lower than that of CH_3OB^+H, the $(CH_3O)_2B^+$–pyridine system has more degrees of freedom and these effects offset each other and result in similar slopes in the

Table 2. Stereoelectronic parameters (S^k) for *ortho*-substituted pyridines

Pyridine	$(CH_3O)_2B^+$ [a]	CH_3OB^+H [b]	$SF_3{}^+$ [c]	$OCNCO^+$ [d]	Cl^+ [e]	$SiCl_3{}^+$ [f]	$SiCl^+$ [g]
2-MePy	−0.82	−2.23	−1.09	−1.39	−0.43	−0.47	0.15
2,4-diMePy	−2.38	−2.53	−2.4	−3.15	—	−0.71	−0.17
2,3-diMePy	−2.1	−3.03	−2.15	−3.29	−0.64	−0.22	0.55
2,5-diMePy	−2.78	−3.36	−2.25	−3.02	—	−0.32	0.78
2,6-diMePy	−0.87	−3.41	−1.11	−5.09	−1.6	−0.94	1.62

[a] S^k value obtained from the deviation of experimental data from the regression line in Fig. 4.
[b] S^k value obtained from the deviation of experimental data from the regression line in Fig. 5.
[c] S^k value obtained from Ref. 35.
[d] S^k value obtained from Ref. 33.
[e] S^k value obtained from Ref. 32.
[f] S^k value obtained from Ref. 34.
[g] S^k value obtained from Ref. 34. The positive value indicates agostic binding which increases the affinity of the *ortho*-substituted pyridine towards $SiCl^+$.

correlations against *PA* for $(CH_3O)_2B^+$ and CH_3OB^+H ions. The weak bonding found in this study is probably due to the electron-donating character of the methoxyl group, which decreases the positive charge at the boron center and, therefore, decreases the bond strength between the central cation and pyridine. The remarkably similar trends in binding energy for such a wide variety of cations are the most important finding of the series of studies. This regularity in behavior points to systematic trends in the underlying electronic effects.

The decreased cation affinities observed for *ortho*-substituted pyridine are explained, as was the case for the other cations studied earlier, by steric effects. Similar results were obtained by Isbell and Brodbelt.[15] They used dimethoxyborinium ions as probes to investigate steric effects and found that 2,3-dimethylpyridine binds to borinium ion less effectively than does 3-methylpyridine, while 3,5-dimethylpyridine and 3,4-dimethylpyridine bind more strongly to borinium ion than 3-methylpyridine. The decreased bonding strength of 2,3-dimethylpyridine to borinium ion is clearly due to the steric effects arising from the *ortho* substituent.

In addition to steric effects, in special cases auxiliary interactions are evident, as in the case of the complex of 2,6-dimethylpyridine with the $(CH_3O)_2B^+$ cation, where two weak hydrogen bonding interactions slightly increase the cation affinity. In the case of CH_3OB^+H, the large steric effects which result from the short B—N bond and the possibility of forming only a single auxiliary hydrogen bond make the stereoelectronic parameter slightly greater for the 2,6-dimethylpyridine than for the 2,3- and 2,5-isomers.

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