SiCl_3^+ and SiCl^+ Affinities for Pyridines Determined By Using the Kinetic Method with Multiple Stage Mass Spectrometry: Agostic Effects in the Gas Phase

Sheng Sheng Yang, Philip Wong, Shuguang Ma, and R. Graham Cooks

Department of Chemistry, Purdue University, West Lafayette, Indiana, USA

Cluster ions, $\text{Py}_1\text{SiCl}_3^+\text{Py}_2$ and $\text{Py}_1\text{SiCl}^+\text{Py}_2$, where Py_1 and Py_2 represent substituted pyridines, formed upon reactive collisions of mass-selected SiCl_3^+ or SiCl^+ cations with a mixture of pyridines, are shown to have loosely bound structures by multiple stage mass spectrometry experiments in a pentaquadrupole mass spectrometer. The fragment ion abundance ratio, $\ln([\text{Py}_1\text{SiCl}_n^+]/[\text{Py}_2\text{SiCl}_n^+])$ ($n = 1$ or 3) is used to estimate the relative SiCl_3^+ or SiCl^+ affinities of the constituent pyridines by the kinetic method. In the case of clusters comprised of meta- and/or para-substituted pyridines (unhindered pyridines), the SiCl_3^+ and SiCl^+ affinities are shown to display excellent linear correlations with the proton affinities (PAs). On the assumption that the effective temperatures of the SiCl_3^+ - and SiCl^+ -bound dimers are 555 K (i.e., the same as those of the corresponding Cl^+ -bound dimers), SiCl_3^+ and SiCl^+ affinities of the substituted pyridines, relative to pyridine, are estimated to be 3-MePy (2.1 kcal/mol), 4-MePy (3.2 kcal/mol), 3-EtPy (3.7 kcal/mol), 4-EtPy (4.2 kcal/mol), 3,5-diMePy (4.8 kcal/mol), and 3,4-diMePy (5.4 kcal/mol). The SiCl_3^+ and SiCl^+ cation affinities are related to the proton affinities by the expressions: relative (SiCl_3^+) affinity = $0.95 \Delta\text{PA}$ and relative (SiCl^+) affinity = $0.60 \Delta\text{PA}$. The smaller constant in the relationship between the relative SiCl^+ affinity and the relative proton affinity is the result of weaker bonding.

Steric effects between the ortho-substituted alkyl group and the central SiCl_3^+ cation reduce the SiCl_3^+ affinities of dimers that contain ortho-substituted pyridines. The magnitude of the steric acceleration of fragmentation is used to measure a set of gas-phase steric parameters (S^A). The steric effects in the SiCl_3^+ dimers are similar in magnitude to those in the corresponding Cl^+ -bound dimers but weaker than those produced by the bulky $[\text{OCNCO}]^+$ group. An inverted steric effect is observed in those SiCl^+ -bound dimers that incorporate ortho-substituted pyridines and is ascribed to auxiliary $\text{Si}-\text{H}-\text{C}$ bonding, which stabilizes the ortho-substituted pyridine- SiCl^+ bond. This auxiliary bonding appears to correspond to agostic bonding, which is well characterized in solution and occurs in competition with steric effects that weaken the pyridine- SiCl^+ interaction.

Ion-molecule reactions of pyridines with halosilicon radical cations $\text{SiCl}_2^{\cdot+}$ and $\text{SiCl}_4^{\cdot+}$ as well as alkylated halosilicon cations $\text{Si}(\text{CH}_3)_2\text{Cl}^+$ and $\text{Si}(\text{CH}_3)\text{Cl}_2^+$ also are investigated. In these cases, charge exchange and associated reactions are the main reaction channels, and clustering is not observed. (*J Am Soc Mass Spectrom* 1996, 7, 198–204)

Recently, there has been considerable interest in gas-phase silicon chemistry [1]. This interest is typified by a recent ion cyclotron resonance study on the relative affinities of SiCl_3^+ toward H^- and Cl^- [2] and a high pressure mass spectrometric study on the gas-phase $(\text{CH}_3)_3\text{Si}^+$ affinities of alkylamines [3]. Similarly, the reactivity and heats of formation of SiCl , SiCl^+ , and SiCl_2^+ have been studied by using a guided beam instrument [4]. The reasons to study ion-molecule reactions in the gas phase under solvent- and counterion-free conditions are well known [5]. In

this way, the intrinsic physical properties of ionic species can be investigated readily and their reactivity can be characterized. By contrast, electron-deficient species are both highly reactive and difficult to characterize in solution [6].

The thermochemistry of electron-deficient cations and their ion-molecule reactions are of interest in our laboratory. A prototypical case is that of the ion Cl^+ , which has been investigated in electrophilic aromatic halogenation [7] by using multiple stage mass spectrometry (MS^3). In these experiments, mass-selected ClCO^+ was allowed to react with aromatic substrates, and the Cl^+ -addition products were selected and characterized by using a pentaquadrupole mass spectrometry.

Address reprint requests to R. G. Cooks, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

ter. The same instrumentation has been used to determine thermochemical properties of electron-deficient ions by the kinetic method [8]. These measurements utilize a cluster ion (a cation-bound dimer) comprised of a compound with an unknown proton affinity (PA) bound by a cation to a reference compound. This cluster ion is generated and allowed to dissociate to form the individual cationized monomers. The relative rates of competitive dissociations of the cation-bound dimer to give the individual cationized monomers can be used to calculate the cation affinity difference between the two compounds that constitute the dimer. Details on the kinetic method [8] are given elsewhere, but it is significant to note that it has been used to estimate proton affinities as well as other thermochemical properties for numerous classes of organic compounds, which include amino acids and peptides [9], and even free radicals [10]. Most significantly for this study, the kinetic method has been extended to measure pyridines affinities toward Cl⁺ [11], CN⁺ [12], and OCNCO⁺ [13]. In the studies of Cl⁺ and OCNCO⁺, excellent linear correlations were observed between the cation affinities and the proton affinities of meta- and para-substituted alkylpyridines. Lower than expected affinity values were obtained for ortho-alkylpyridines, and this was assigned to gas-phase steric effects, the magnitudes of which are quantified by the extent to which the experimental results depart from linearity.

We report here a study of SiCl₃⁺ and SiCl⁺ affinities toward pyridines—again by using the kinetic method. As such, this study continues the investigation of the thermochemistry and stereoelectronic effects of polyatomic cations. The specific goals are (1) to measure relative affinities toward SiCl₃⁺ and SiCl⁺ of a group of alkyl-substituted pyridines; (2) to investigate stereochemical and electronic effects in the SiCl₃⁺ and SiCl⁺ systems; (3) to evaluate dimer formation in such related ions as SiCl₄⁺, SiCl₂⁺, Si(CH₃)Cl₂⁺, and Si(CH₃)₂Cl⁺.

Experimental

The tandem (MS²) and multiple stage (MS³) mass spectrometry experiments were performed by using a custom-built pentaquadrupole mass spectrometer described elsewhere [14]. This instrument consists of three mass analyzing quadrupoles (Q1, Q3, and Q5) and two collision quadrupoles (Q2, Q4). For MS² experiments, the SiCl₃⁺ or SiCl⁺ ion generated in the ion source was mass-selected by using Q1. Mass-selected SiCl₃⁺ or SiCl⁺ ions were then allowed to undergo ion-molecule reactions with a vaporized pyridine mixture in Q2 at nominally zero collision energy, as established by the potential difference between the ion source and Q2. The reaction products were then analyzed by scans of Q5 with both Q3 and Q4 set in the broad-band transmission rf-only mode. To perform MS³ experiments [15] ion-molecule reaction products formed in Q2 were

mass-selected by using Q3 and allowed to undergo energetic collisions with argon in Q4, while Q5 was scanned to record the sequential product ion spectrum.

The ions SiCl₃⁺ and SiCl⁺ were generated by 70-eV electron ionization of silicon tetrachloride (Aldrich Chemical Co., Milwaukee, WI), which was introduced into the ion source via a Granville Phillips leak valve (Granville Phillips Co., Boulder, CO). Pressure was read on a single ionization gauge located in the main vacuum housing. Silicon tetrachloride was added until a nominal pressure of 4×10^{-6} torr was achieved. The indicated pressure rose to 4×10^{-5} torr upon addition of the pyridine mixture to Q2, and further increased to 7×10^{-5} torr upon addition of argon gas to Q4. The collision energy—the nominal voltage difference between the ion source and the collision quadrupole—was set near 0 eV in Q2 for ion-molecule reactions and 10 eV in Q4 for MS³ experiments, respectively. The pyridines (Aldrich Chemical Co.) are commercially available samples and were used as received. In the mass spectra presented in this study, the Thomson (Th) unit [16] has been used.

Results and Discussion

Thermochemical and Structural Studies

Ion-molecule reactions of SiCl₃⁺ and SiCl⁺ with pyridines were investigated by using a custom-built pentaquadrupole mass spectrometer. Figure 1a shows a typical ion-molecule reaction product spectrum (an MS² spectrum) for reaction of mass-selected SiCl₃⁺ (133 Th) with a mixture of two pyridines: 3-methylpyridine (3-MePy) and pyridine (Py). The ion-molecule reaction products include (1) the protonated monomers PyH⁺ (80 Th) and 3-MePyH⁺ (94 Th), (2) the mono-SiCl₃⁺ addition products PySiCl₃⁺ (212 Th) and 3-MePySiCl₃⁺ (226 Th), (3) the two symmetrical proton-bound dimers Py—H⁺—Py (159 Th) and 3-MePy—H⁺—3-MePy (187 Th), (4) the mixed proton-bound dimer Py—H⁺—3-MePy (173 Th), and, finally, (5) the SiCl₃⁺-bound dimers Py—SiCl₃⁺—Py (291 Th) and 3-MePy—SiCl₃⁺—3-MePy (319 Th), and the ion of most interest, the mixed dimer Py—SiCl₃⁺—3-MePy (305 Th). Analogous results were obtained for the ion-molecule reactions of SiCl⁺ (63 Th) with the 3-methylpyridine and pyridine mixture. The excellent yield of the monomeric and dimeric adducts in both cases is noteworthy. Note also the presence of the protonated pyridines and the proton-bound dimers. These products probably occur via charge exchange of the pyridines with the SiCl₃⁺ and SiCl⁺ cations, and subsequent proton transfer and association reactions. In both cases the relative abundances of the protonated pyridines and the dimers are much lower than those of corresponding SiCl₃⁺ and SiCl⁺ monomers and dimers and they do not interfere in the study.

Structural assignments of the dimeric ions 3-MePy—SiCl₃⁺—Py (305 Th) and 3-MePy—SiCl⁺—Py (235

Figure 1. (a) Reaction product spectrum that displays ion-molecule reactions of SiCl_3^+ (m/z 133) with a mixture of pyridine and 3-methylpyridine. (b) Sequential product spectrum that shows fragmentation of the mixed dimeric adduct (m/z 305) generated upon reaction of SiCl_3^+ with a mixture of pyridine and 3-methylpyridine.

Th) were pursued by using MS^3 experiments. The mixed SiCl_3^+ - or SiCl^+ -bound dimer was mass-selected in Q3 and fragmented by collision-induced dissociation with argon in Q4 while scanning Q5 to record the sequential product mass spectrum (Figure 1b). The only fragments observed in this spectrum are the two mono-adducts PySiCl_3^+ (212 Th) and 3-MePySiCl_3^+ (226 Th). Another feature of the MS^3 spectra is the readiness with which fragmentation occurs under mild activation conditions. This indicates that the dimers are bound loosely. With this evidence from MS^3 studies and analogies from earlier studies on Cl^+ , CN^+ , and OCNCO^+ -bound systems, the two possible dimeric structures are (1) the Si^+ -bound dimer and (2) the π -bound complex (Scheme I). However, *ab initio* calculations on the chlorine cation [11] and $[\text{OCNCO}]^+$ cation [13] clusters have shown that the π -complexes are not stable and the Si^+ -bound structure (1), therefore, is the probable structure for this dimer also.

According to the kinetic method [8], loosely bound dimers should fragment to give the two monomers in relative abundances that should be linearly related to the difference in the SiCl_3^+ and SiCl^+ affinities of the

Scheme I. Possible structures for pyridine SiCl_3^+ dimers.

two pyridines provided that entropic effects on the competitive reactions cancel. Under these circumstances,

$$\ln \frac{[\text{Py}_1\text{SiCl}_3]^+}{[\text{Py}_2\text{SiCl}_3]^+} = \frac{\Delta(\text{SiCl}_3^+ \text{ affinity})}{RT_{\text{eff}}} \quad (1)$$

where T_{eff} is the effective temperature of the dissociating cluster ion and the terms in brackets are the product ion abundances. Application of this relationship is limited by the lack of independently known SiCl_3^+ and SiCl^+ affinity values and the difficulty of independently measuring the effective temperature of the dimer. However, relative SiCl_3^+ and SiCl^+ affinities can be ordered and if the same electronic effects that influence proton affinities also affect SiCl_3^+ and SiCl^+ affinities, a linear relationship between the relative proton affinities and the experimentally measured ΔSiCl_3^+ and ΔSiCl^+ affinities is expected. The relative SiCl_3^+ and SiCl^+ affinities, expressed as $RT_{\text{eff}} \ln\{[\text{Py}_1\text{SiCl}_3]^+ / [\text{Py}_2\text{SiCl}_3]^+\}$, were therefore calculated with the assumption that the effective temperature is 555 K. This temperature is obtained from the slope of the linear correlation of the logarithm ratio of individual chlorine cation monomer abundance versus the chlorine cation affinities; the latter was referenced to the value for pyridine itself, which was calculated by using the semiempirical AM1 method [11]. Note that similar effective temperatures have been reported for other clusters [17] and that the value of 555 K is in the range often observed for proton-bound dimers. Table 1 summarizes the relative SiCl_3^+ and SiCl^+ affinities derived from eq 1 by using the experimentally measured ratios and the effective temperature 555 K. Linear correlations indeed are observed between the relative SiCl_3^+ and SiCl^+ affinities of a series of meta- and para-alkylpyridines and their proton affinities (Figures 2 and 3). Note that the choice of effective temperature does not affect the quality of the correlation: errors in this temperature by even 50 K correspond to changes in affinities of only ± 0.3 kcal/mol. The linear correlations observed in the SiCl_3^+ and SiCl^+ cases suggest that the pyridines are oriented symmetrically with respect to binding at the central silicon atom. This in fact has been proven in the cases of Cl^+ , CN^+ , and OCNCO^+ cations, where the symmetrical binding to the central atom has been confirmed by *ab initio* calculations. It is proposed that the two pyridines in the SiCl_3^+ -bound dimer (Scheme I) are bound to silicon

Table 1. Relative (SiCl₃⁺) affinity, SiCl⁺ affinity, and proton affinity

Entry	Pyridines	Py ₁ :Py ₂ ^a	$\ln \left\{ \frac{[\text{Py}_1(\text{SiCl}_3^+)]}{[\text{Py}_2(\text{SiCl}_3^+)]} \right\}^b$	Rel. (SiCl ₃ ⁺) affinity ^c	$\ln \left\{ \frac{[\text{Py}_1(\text{SiCl}^+)]}{[\text{Py}_2(\text{SiCl}^+)]} \right\}^b$	Rel. (SiCl ⁺) affinity ^c	Proton affinity ^d
1	Py		0	0	0	0	220.4
2	3-Me	2:1	1.92	2.12	1.55	1.71	222.8
3	4-Me	3:1	2.93	3.23	1.61	1.77	223.7
4	3-Et	4:2	3.31	3.65	1.94	2.14	223.9
5	4-Et	5:2	3.78	4.17	2.67	2.94	224.6
6	3,5-diMe	6:3	4.39	4.84	2.78	3.07	225.5
7	3,4-diMe	7:3	4.9	5.4	3.16	3.49	225.5
8	2,6-diMe	8:3	4.88	5.38	5.34	5.89	227.1
9	2-Me	9:1	2.41	2.66	2.01	2.22	223.7
10	2,3-diMe	10:3	4.82	5.32	3.75	4.14	226.2
11	2,5-diMe	11:3	4.72	5.21	4.01	4.42	226.2
12	2,4,6-triMe	12:7	—	—	6.92	7.63	230.3 ^e
13	2,4-diMe	13:3	4.94	5.45	3.44	3.79	226.9

^a The entry number of the pyridine that forms the SiCl₃⁺- and SiCl⁺-bound dimer used to estimate the SiCl₃⁺ and SiCl⁺ affinities.^b Experimental results.^c Obtained from eq 1 (assuming $T_{\text{eff}} = 555$ K); estimated uncertainty is $\pm 15\%$.^d Proton affinities are taken from Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2. A referee has questioned the use of proton affinity data from Aue and Bowers when more recent data are available. Because this question pertains not only to this study, but also the earlier Cl⁺ (ref 11), CN⁺ (ref 12), and OCNCO⁺ studies (ref 13) we have reexamined this question. In doing so, we have plotted the experimental abundance ratios against PA from Aue and Bowers and also by using preferred values from the well-known NIST compilation (Lias, Bartmess, Liebman, Holmes, Levin, Mallard *J. Phys. Chem. Ref. Data* 1988, 17, Suppl. 1). The results for dimers bound by H⁺, CN⁺, Cl⁺, and OCNCO⁺ show that the PA values of Aue and Bowers (obtained by an equilibrium method in an ICR instrument) give virtually identical slopes to those given when one uses the preferred NIST PA values. The same applies to the gas-phase basicity plot, which is reproduced but with more scatter when the NIST rather than the Aue and Bowers data are used. We conclude that the use of Aue and Bowers values is not only satisfactory but preferable: the high correlation coefficient presumably arises because the data are from a single set of experiments.^e Estimated by using the combined inductive and resonance effect of 3.2 kcal/mol for a 4-methyl group and by adding this value to the PA of 2,6-dimethylpyridine. (see ref 11).

normal to the plane that contains the three chlorine atoms. The structure for SiCl⁺-bound dimer is similar except that the silicon bears two non-bonding electrons.

From the linear plots (Figures 2 and 3) and the data in Table 1, the relative gas-phase SiCl₃⁺ and SiCl⁺ affinities can be ordered as Py < 3-MePy < 4-MePy < 3-EtPy < 4-EtPy < 3,5-diMePy < 3,4-diMePy. Relative

SiCl₃⁺ and SiCl⁺ affinities can be summarized using eqs 2 and 3, respectively:

$$\text{Relative (SiCl}_3^+) \text{ affinities} = 0.95 \Delta \text{PA} \quad (2)$$

$$\text{Relative (SiCl}^+) \text{ affinities} = 0.60 \Delta \text{PA} \quad (3)$$

The smaller slope 0.60 in eq 3 in comparison with the slope 0.95 in eq 2 reflects weaker bonding in this case.

Figure 2. Linear correlation between $\ln[\text{Py}_1(\text{SiCl}_3^+)/\text{Py}_2(\text{SiCl}_3^+)]$, which is proportional to the relative SiCl₃⁺ affinities of substituted pyridines and their proton affinities. **Figure 3.** Linear correlation between $\ln[\text{Py}_1(\text{SiCl}^+)/\text{Py}_2(\text{SiCl}^+)]$, which is proportional to the relative SiCl⁺ affinities of substituted pyridines and their proton affinities.

Stereoelectronic Effects

There has been considerable interest in gas-phase stereoelectronic effects on ion–molecule reactions and in stereochemical effects on fragmentation [18]. The main challenge in quantification of steric effects is the separation of steric from inductive and resonance effects and one of the simplest methods of doing so is to compare results for a substituent in the ortho position with the same group located at the para position. Recently, a new scale of ortho-steric parameters S^0 was introduced by Berg and co-workers [18a] by using the N-alkylation of pyridines in solution. The measurement is based on the fact that all ortho-substituted pyridines fall below the correlation line that relates the logarithm of k/k_H and pK_a of the pyridines, where k is the quaternization rate constant of the substituted (non-ortho) pyridines. These authors measured solution phase steric parameters as $S^0 = \log(k'/k_H) - (\alpha pK_a + c)$, where k is the quaternization rate constant of the ortho-substituted pyridine and α and c are the Brønsted parameters with non-ortho-substituted pyridines. In an analogous approach, a method of quantification of steric effects in the gas phase was introduced by Eberlin et al. [11] in studies of the affinities of chlorine cation toward alkyl-substituted pyridines. Gas-phase steric parameters were determined from the deviation of the experimentally measured logarithm of relative dissociation rates from the linear correlation established by the meta- and para-substituted pyridines. It is also worthy of note that there exist no steric effects in the proton-bound pyridine system, at least for the substituents studied so far. In agreement with this, proton affinities of methyl-substituted pyridine fall in the order 3-methylpyridine < 2-methylpyridine = 4-methylpyridine (Table 1).

Via the procedures just described, steric effects were measured for SiCl_3^+ cations toward ortho-substituted pyridines. Because it is evident from the excellent correlations with PA already shown that there are no steric effects in the meta- and para-substituted pyridines, it is feasible to pair a para- or meta-substituted pyridine with an ortho-substituted pyridine in

a dimer to measure the steric effect of the ortho-substituted compound. As shown in Figure 2, the correlation ($r = 0.991$) of relative SiCl_3^+ affinities with proton affinities is generally excellent for meta- and para-substituted pyridines and poor for ortho-substituted pyridines. Lower than expected SiCl_3^+ affinities are observed for the ortho-substituted pyridines, behavior which is analogous to that reported previously for Cl^+ and OCNCO^+ cations. These lower than expected affinity values for the ortho-substituted pyridines are attributed to steric interactions of the ortho substituent(s) with the central SiCl_3^+ ion in the dimers that weaken the bond and accelerates fragmentation. The deviation from the regression line established for the meta- and para-substituted compounds then can be quantified in terms of steric parameters S^k [18g]. Values are listed in Table 2. Comparisons between the steric effect for 2-methylpyridine in the Cl^+ bound dimer ($S^k = -0.43$) [11], the $[\text{OCNCO}]^+$ bound dimer ($S^k = -1.39$) [13], and the SiCl_3^+ bound dimer ($S^k = -0.47$) clearly demonstrate the similarity of the Cl^+ and SiCl_3^+ systems in steric bulk and the much stronger steric effects in the $[\text{OCNCO}]^+$ system. Interestingly, the steric effects observed with the dimethylpyridines for the SiCl_3^+ cation are buttressed by electronic effects as described earlier for Cl^+ [11] and $[\text{OCNCO}]^+$ [13]. Di-ortho-substituted compounds display large steric parameters for 2,6-dimethylpyridine, and the S^k values for the ions SiCl_3^+ , Cl^+ , and $[\text{OCNCO}]^+$ are -0.94 , -1.6 [11], and -5.09 [13], respectively. Smaller steric effect values also are observed for other dimethylpyridines toward SiCl_3^+ (Table 2).

Although SiCl_3^+ behaves analogously to other cations studied earlier, the most interesting result of this study is the apparently inverse steric effect observed for SiCl_3^+ with ortho-substituted pyridines (Figure 3). Remarkably, all of the ortho-substituted pyridines except 2-methylpyridine and 2,4-dimethylpyridine show abundance ratios that lie significantly above the linear correlation line (Figure 3), whereas they are expected to fall below it. Such reverse effects are not observed in the SiCl_3^+ system or in previously studied cations. As previously noted, dimers that con-

Table 2. Steric parameters for ortho-substituted pyridines in SiCl_3^+ - and SiCl^+ -bound dimers

Pyridine	Expt. $\ln \left\{ \frac{[\text{Py}_1(\text{SiCl}_3^+)]}{[\text{Py}_2(\text{SiCl}_3^+)]} \right\}^a$	Calc. $\ln \left\{ \frac{[\text{Py}_1(\text{SiCl}_3^+)]}{[\text{Py}_2(\text{SiCl}_3^+)]} \right\}^b$	$S^{k,c}$ (SiCl_3^+)	Expt. $\ln \left\{ \frac{[\text{Py}_1(\text{SiCl}^+)]}{[\text{Py}_2(\text{SiCl}^+)]} \right\}^a$	Calc. $\ln \left\{ \frac{[\text{Py}_1(\text{SiCl}^+)]}{[\text{Py}_2(\text{SiCl}^+)]} \right\}^b$	$S^{k,c}$ (SiCl^+)
Py	0	0	0	0	0	0
2-Me	2.41	2.88	-0.47	2.01	1.86	0.15
2,5-diMe	4.72	5.04	-0.32	4.01	3.23	0.78
2,4-diMe	4.94	5.65	-0.71	3.44	3.61	-0.17
2,3-diMe	4.82	5.04	-0.22	3.75	3.23	0.55
2,6-diMe	4.88	5.82	-0.94	5.34	3.72	1.62
2,4,6-triMe	—	—	—	6.92	5.48	1.44

^a Experimental data.

^b Calculated data from linear regression equation.

^c S^k value is the difference between the experimental data and the calculated data.

Scheme II. Auxiliary bonding in the case of an ortho-substituted pyridine.

sist of a sterically hindered, ortho-substituted pyridine and an unhindered pyridine are used to study steric effects on relative affinities. The anomalous behavior of SiCl⁺ is believed to be due to the availability of vacant *d*-orbitals or the presence of two unpaired electrons on the silicon atom of the SiCl⁺ cation and the sterically favorable orientation of the ortho-substituted methyl group, which promotes intramolecular auxiliary bonding between the methyl group to the central silicon atom (1, Scheme II). This auxiliary bonding stabilizes the Si—N bond and increases the affinity of the ortho-substituted pyridines toward SiCl⁺. The auxiliary bonding may take the form of three-center two-electron bonding Si—H—C or full Si insertion into the C—H bond of the ortho-methyl group (2, Scheme II). The appearance of 4-MePySiCl⁺ (156 Th) and 2,6-diMePySiCl⁺ (170 Th) and the lack of 4-MePySiClH⁺ in the MS³ spectrum of 4-MePy—SiCl⁺—2,6-diMePy (Figure 4) suggest that full insertion does not occur.

Auxiliary bonding has been encountered previously in isolated cases in the study of Cl⁺-bound dimers, where smaller than expected steric effects were observed in the cases of 2-methoxypyridine and quinoline. It was proposed that the steric effects of the ortho-methoxyl group and static peri-hydrogen are compensated for by chelation of the Cl⁺, that is, bonding to oxygen and the fused benzene ring, respectively.

Figure 4. Sequential product spectrum that shows fragmentation of the mixed dimeric adduct (*m/z* 263) generated upon reaction of SiCl⁺ with a mixture of 4-methylpyridine and 2,6-dimethylpyridine.

Note that an analogous phenomenon has been suggested to explain the unexpectedly large gas-phase basicity of the formate anion. The reason behind this anomalous behavior is that the proton-bound dimers that contain formate have cyclic structures that involve the hydrogen of the formate group [19]. A similar case has been reported by Squires and co-workers [20] from measurements of gas-phase acidities of carboxylic acids and alcohols from collision-induced dissociation of dimer cluster ions via the kinetic method.

It is worthy of note that the deviation from linearity in the cases of the ortho-substituted pyridines is the combined result of the electronic and steric effects and that both effects approximately cancel in the 2-methylpyridine and 2,4-dimethylpyridine cases (Figure 3). Auxiliary bonding is much stronger than the opposing steric effect in 2,6-dimethylpyridine and 2,4,6-trimethylpyridine as shown in Figure 3.

In parallel to these gas-phase observations on auxiliary bonding, solution phase auxiliary bonding, known as agostic bonding, has been known since its description by Brookhart and Green [21]. Agostic bonding (M—H—L) has been observed in many organometallic molecular systems where the ligand L binds through carbon, boron, silicon to hydrogen and where M is a transition metal. Physical and chemical properties of species with agostic bonding have been studied by a variety of spectroscopic methods [22], and instances of equilibria [23] and stable isomers [24] that have the M—H—C unit have been reported.

Dimer Formation that Involves Other Silicon Cations

The factors that control the tendency to form cation-bound dimers of pyridine have been investigated further by examination of several substituted silicon cations such as SiCl₄⁺, SiCl₂⁺, Si(CH₃)Cl₂⁺, and Si(CH₃)₂Cl⁺. Formation of cation-bound pyridine dimers was not observed but cation-pyridine monomers, protonated monomers, and proton-bound dimers were produced in large amounts. These studies showed that odd-electron silicon cations undergo mainly charge exchange and subsequent proton transfer reactions, whereas their fragmentation yields even-electron silicon cations that react with pyridines to form silicon cation-bound monomers and dimers. Alkyl-substituted silicon cations form silicon-cation bound monomers with pyridine along with a large amount of charge exchange and proton transfer reactions. The lack of observable dimers in these cases may be due to steric weakening of the pyridine-silicon bonds.

Conclusions

It is possible to generate the SiCl₃⁺- and SiCl⁺-bound dimers of pyridines via gas-phase ion-molecule reac-

tions and characterize their fragmentation in a pentaquadrupole mass spectrometer. The MS³ studies indicate that the dimers are loosely bound and the relative abundances of the individual monomers depend upon the relative affinities of the neutral molecules toward the central ion. Linear correlations are observed between the logarithm of the product ion abundance ratio and the proton affinity difference for meta- and para-substituted pyridines for SiCl₃⁺ and SiCl⁺ cations. The linear correlations for both systems suggest that pyridine molecules are bound to the central silicon atom symmetrically. Relative SiCl₃⁺ and SiCl⁺ affinities of substituted pyridines to pyridine are ordered with the assumption of an effective temperature 555 K obtained from the previous Cl⁺-bound dimer study. In future work, the effective temperatures for those dimers will be measured and the correlations of relative cation affinities and proton affinities will be considered further.

Steric effects are observed in SiCl₃⁺-bound dimers that contain ortho-substituted pyridines. The steric effects decrease the affinities of the ortho-substituted pyridines through interactions between the SiCl₃⁺ cation and the ortho substituent(s). A set of gas-phase steric parameters is measured from the deviation of the experimentally measured ratio to the regression line, established for meta- and para-substituted compounds, and the steric parameters for SiCl₃⁺ are found to be similar to those for the corresponding Cl⁺-bound dimers. Anomalously high SiCl⁺ affinities are observed for SiCl⁺-bound dimers that consist of ortho-substituted pyridines. This is believed to be due to auxiliary bonding that involves Si—H—C. This is the first systematic demonstration of gas-phase agostic bonding, although previous scattered studies have suggested the existence of analogous electronic interactions.

Acknowledgment

This work was supported by the National Science Foundation, CHE 92-23791. We thank Detlef Schröder for valuable discussions.

References

- (a) Oppenstein, A.; Lampe, F. W. In *Review of Chemical Intermediates*; Strusz, O. P., Ed.; Elsevier: Amsterdam, 1986; Vol. 6, p 275; (b) Schwartz, H. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; p 445; (c) Depuy, C. H.; Damrauer, R.; Bowie, J. H.; Sheldon, J. C. *Acc. Chem. Res.* **1987**, *20*, 127; (d) Bowie, J. H. *Mass Spectrom. Rev.* **1984**, *3*, 1.
- Murthy, S.; Beauchamp, J. L. *J. Phys. Chem.* **1992**, *96*, 1247.
- Li, X.; Stone, J. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *101*, 149.
- Weber, M. E.; Armentrout, P. B. *J. Phys. Chem.* **1989**, *93*, 1596.
- (a) Sieck, L. W.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1976**, *5*, 1123; (b) Meot-ner (Mautner), M. In *Gas Phase Ion Chemistry*; Bower, M. T., Ed.; Academic: New York, 1979; Vol. 2; (c) Depuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146.
- (a) Foucaud, A. In *The Chemistry of Functional Groups*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1983; Suppl. D, Chap. 11, p 441; (b) Lwowski, W., Ed. *Nitrenes*; Interscience: New York, 1970; (c) Jones, M., Jr.; Moss, R. A., Eds. *Carbenes*; Wiley-Interscience: New York, 1973; Vol. 1; (d) Saunders, M.; Jimmet-Vazueez, H. A. *Chem. Rev.*, **1991**, *91*, 375; (e) Lam-mertsma, K. *Rev. Chem. Intermed.* **1988**, *9*, 141; (f) Cox, R. A. *Org. React. Mech.* **1989**, 283; (g) Creary, X., Ed. *Advances in Carbonation Chemistry*; JAI Press: Greenwich, CT, 1989.
- (a) Kotiaho, T.; Shay, B. J.; Cooks, R. G.; Eberlin, M. N. *J. Am. Chem. Soc.* **1993**, *115*, 1004; (b) Bortolini, O.; Yang, S. S.; Cooks, R. G. *Org. Mass Spectrom.* **1993**, *28*, 1313.
- (a) Patrick, J. S.; Kotiaho, T.; McLuckey, S. A.; Cooks, R. G. *Mass Spectrom. Rev.* **1994**, *13*, 287; (b) Cooks, R. G.; Kruger, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 3274; (c) Wright, L. G.; McLuckey, S. A.; Cooks, R. G.; Wood, K. V. *Int. J. Mass Spectrom. Ion Processes* **1982**, *42*, 115.
- (a) O'Hair, R. A. J.; Bowie, J. H.; Gronert, S. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 23; (b) Bojesen, G. *J. Am. Chem. Soc.* **1987**, *109*, 5557; (c) Wu, Z.; Fenselau, C. *Tetrahedron* **1993**, *49*, 9197; (d) Cheng, X. H.; Wu, Z.; Fenselau, C. *J. Am. Chem. Soc.* **1993**, *115*, 4844; (e) Zhang, K.; Zimmerman, D. M.; Chung-Phillips, A.; Cassidy, C. *J. Am. Chem. Soc.* **1993**, *115*, 10812.
- Hoke, S. H., II; Yang, S. S.; Cooks, R. G.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 4888.
- Eberlin, M. N.; Kotiaho, T.; Shay, B. J.; Yang, S. S.; Cooks, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2457.
- Yang, S. S.; Bortolini, O.; Steinmetz, A.; Cooks, R. G. *J. Mass Spectrom.* **1995**, *30*, 184.
- Yang, S. S.; Chen, G.; Ma, S.; Cooks, R. G.; Gozo, F.; Eberlin, M. N. *J. Mass Spectrom.* **1995**, *30*, 807.
- Schwartz, J. C.; Schey, K. L.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1990**, *1*, 101.
- (a) Schwartz, J. C.; Wade, A. P.; Enke, C. G.; Cooks, R. G. *Anal. Chem.* **1990**, *62*, 1809; (b) Cooks, R. G.; Amy, J.; Bier, M.; Schwartz, J. C.; Schey, K. L. *Adv. Mass Spectrom.* **1989**, *11A*, 33.
- Cooks, R. G.; Rockwood, A. L. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 93.
- Cedra, B. A.; Wesdemiotis, C. Presented at the 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, IL, June 1994.
- (a) Gallo, R.; Roussel, C. Berg, U. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1988, Vol. 43, p 173; (b) Berg, U.; Gallo, R.; Klatte, G.; Metzger, J. *J. Chem. Soc., Perkin Trans.* **1980**, *2*, 1350; (c) Meyerson, S.; Weitkamp, A. W. *Org. Mass Spectrom.* **1968**, *1*, 659; (d) Tureček, T. *Collect. Czech. Chem. Commun.* **1987**, *52*, 1928; (e) Tureček, F. *Int. J. Mass Spectrom. Ion Processes* **1991**, *108*, 137; (f) Green, M. M. *Tetrahedron* **1980**, *36*, 2687; (g) Jenkins, H. D. B.; Kelly, E. J.; Samuel, C. J. *Tetrahedron Lett.* **1994**, *35*, 6543; (h) Splitter; Tureček, F., Eds. *Application of Mass Spectrometry to Organic Stereochemistry*; VCH Publishers: New York, 1994.
- Wright, L. G.; McLuckey, S. A.; Cooks, R. G.; Wood, K. V. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 115.
- Graul, S.; Schnute, M. E.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1990**, *96*, 181.
- Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.
- (a) Green, M. L. H. *Pure Appl. Chem.* **1984**, *56*, 47; (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1988; Vol. 36, p 1.
- Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.
- Carmona, E.; Contreras, L.; Poveda, M. L.; Sánchez, J. *Am. Chem. Soc.* **1991**, *113*, 4322.