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Gas phase basicity of silanaldehydes and silanones

H.E. Audier*, J. Fossey, J.P. Denhez, J.P. Jacquet, P. Mourgues

Laboratoire des Mécanismes Réactionnels, UMR CNRS 7651, Ecole Polytechnique, F-91128 Palaiseau, France

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Abstract

Gas basicities (GBs) and proton affinities (PAs) of $CH_3SiH{=}O$, $CH_3CH_2SiH{=}O$, $(CH_3)_2Si{=}O$ $(CH_3CH_2)_2Si{=}O$, were determined by using the kinetic method as well as calculations. From experiment, GB of these molecules were respectively measured to be 203.3, 206.3, 213.4 and 218.0 kcal mol^{-1}. The precision is estimated to be 0.5 kcal mol^{-1}. Calculations are in excellent agreement with experiment.

GB and PA of the $R_1R_2Si{=}O$ compounds are far above those of their counterparts $R_1R_2C{=}O$, containing exclusively carbon. The difference lies between 25 and 30 kcal mol^{-1} and slightly decreases as the substitution degree of silicon increases. This behavior strongly contrasts with that of silanols or silanamines whose GB and PA are close to those of the corresponding alcohols or amines. This can be explained by the high ΔH_f of neutral low coordinate molecules containing silicon.

Keywords: Gas basicity; Proton affinity; Silanones; Silanaldehydes; Kinetic method; Proton-bound dimer; Calculation

1. Introduction

Gas basicity (GB) and proton affinities (PAs) of a great number of small and medium sized molecules (M) are now well known [1]. Determination of GB(M) and PA(M), respectively defined as $-\Delta G^\circ$ and $-\Delta H^\circ$ of the reaction $[M + H^+ \Rightarrow MH^+]$, are obtained by experiment and, more and more often, by calculation. In contrast, with high level ab initio calculations leading to absolute values of PA [2], experiments only allow relative GB and PA measurements.

When the molecule is stable and available in the gas phase, the "equilibrium method" is the most accurate. In the equilibrium reaction (1) between MH^+ and a base, the equilibrium constant K, estimated from the partial pressures and from the $[MH^+]/[BH^+]$ ratio, leads to the PA(M) by the equation $-RT \ln K = PA(M) - PA(B)$. FT-ICR [3], high pressure mass spectrometry [4] and flowing afterglow [5] can be used to perform these experiments.

$$MH^+ + B \Leftrightarrow BH^+ + M \qquad (1)$$

The equilibrium method cannot be used when the molecule is either unstable or not available in the gas phase. It cannot be used also for the determination of PA of radicals. However, when the cation corresponding to the protonated molecule can be generated, other methods can be used. In the "bracketing method" [6], the reactions in the cell of a FT-ICR spectrometer of MH^+ with a series of bases are performed in order to observe whether the base is protonated or not. With the same data, the "thermokinetic method" [7]

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* Corresponding author. Tel.: +33-169-33-4878; fax: +33-169-33-3041.

E-mail address: hea@dcmr.polytechnique.fr (H.E. Audier).

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Table 1
Proton affinities (in kcal mol^{-1}) of some silanols, silyl-ethers and silylamines from reference [1]

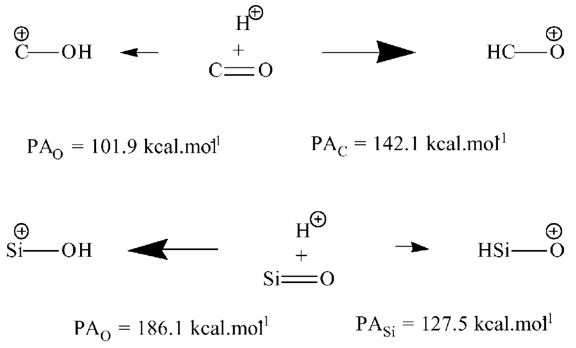
	PA		PA	ΔPA
SiH_3OH	178.4	CH_3OH	180.5	−2.1
$(CH_3)_3Si–OH$	192.0	$(CH_3)_3C–OH$	192.0	0
$(CH_3)_3Si–OCH_3$	202.4	$(CH_3)_3C–OCH_3$	204.4	−2.4
$[(CH_3)_2SiH]_2O$	202	$[(CH_3)_2CH]_2O$	197.2	−2.5
$(CH_3)_3SiNH_2$	216	$(CH_3)_3CNH_2$	221.2	−5.2

leads to more accurate determination. In the “kinetic method” [8], the decomposition of the proton-bound dimer (PBD) MBH^+, spontaneously or upon collision, leads to a $\ln([BH^+]/[MH^+])$ value which allows PA(M) determination.

It is rare that small molecules containing a silicon atom are commercially available. Furthermore, even when stable, their synthesis is difficult. For instance, the $(CH_3)_2Si{=}O$ silanone has been synthetized only ten years ago. For this reason, the thermochemical data are rather rare.

However, from calculations [9] and from the measurements performed by Stone and co-workers, it has been shown that PA of silanols [10] lies only some kcal mol^{-1} under those of the corresponding alcohols. The same observation can be done for the PA of alkoxysilanes [1] or silylamines [11] compared to those of the corresponding alkylethers or alkylamines (Table 1).

Behavior of low coordinated compounds is completely different. For instance, whereas CO is preferentially protonated at carbon, SiO is protonated at oxygen [1] (Scheme 1). Furthermore, from ICR measurements, it has been shown that GB of silenes lie far above those of alkenes [12].



Scheme 1.

In this work, GB of $CH_3SiH{=}O$, $CH_3CH_2SiH{=}O$, $(CH_3)_2Si{=}O$, $(CH_3CH_2)_2Si{=}O$, were determined by using the kinetic method as well as calculations.

2. Experimental

2.1. Measurements

Measurements were mainly performed with a VG-ZAB-2F double focusing mass spectrometer. Ions were produced in a high pressure ion source as described further below. Their unimolecular dissociations were studied in the second field free region (MIKE technique). The pressure in the ion source was about 5×10^{-5} mbar.

In some cases, in order to perform high resolution measurements or collision-induced dissociations (CID), the reactions were studied with a Bruker CMS-47X FT-ICR mass spectrometer equipped with an external ion source and an infinity cell [13,14]. The neutral reactants were introduced into the cell through a leak valve at a pressure of 1×10^{-8} to 4×10^{-8} mbar depending on the experiment, and then diluted with argon, to give a total pressure of 2×10^{-7} mbar.

The ion–molecule reactions were examined after isolation and thermalization of the reactant ions. After transfer into the cell, the ion of interest was first isolated by radio frequency (rf) ejection of all unwanted ions. After a 1 s delay, usually sufficient to thermalize the ions by successive collisions with argon, the isolation procedure was repeated by the use of low voltage single rf pulses (soft shots) at the resonance frequencies of the product ions formed during the relaxation time.

Argon was also used to perform CID spectra. The target gas pressure was 10^{-7} mbar. A rf pulse at the cyclotron frequency of the ions was used (0.1–0.4 ms duration) to excite the ions translationally. Collision time was chosen so as to ensure few-collisions conditions.

$$(CH_3)_2Si(OC_2H_5)_2{}^{\bullet+} \rightarrow CH_3{}^{+}Si(OC_2H_5)_2 \rightarrow CH_3{}^{+}SiH(OC_2H_5) \rightarrow CH_3{}^{+}SiH{=}OH^{+}$$

Scheme 2.

The exact elemental composition of ions was checked by systematic high resolution mass measurements, during which the argon pressure was reduced to 8×10^{-8} mbar.

2.2. Generation of the studied cations

Protonated $R_1R_2Si{=}OH^+$ ions (MH^+) were produced in the CI ion-source of a mass spectrometer by fragmentation of appropriate compounds commercially available. Structures of the so formed ions were ascertained by labeling, by their MIKE and CID spectra and by their reactivity. $(CH_3)_2Si{=}OH^+$ was formed by simple cleavage of ionized *tert*-butyldimethylsilanol. $(CH_3CH_2)_2Si{=}OH^+$ was produced by simple cleavage of ionized triethylsilanol, which, in turn, yields $CH_3CH_2SiH{=}OH^+$ by loss of ethylene. Finally, as shown by Tobita et al. [15], successive fragmentations of ionized diethoxydimethylsilan yields $CH_3SiH{=}OH^+$ (Scheme 2).

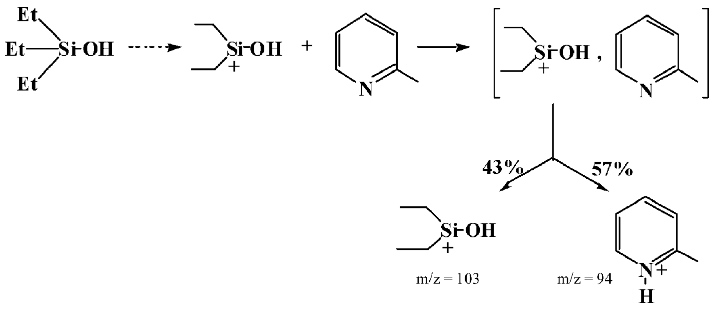
2.3. GB determination

GB were determined by the "kinetic method" [8]. Proton-bound dimers $M\cdots H^+\cdots B$ were generated in the ion source by reaction of the protonated ions with bases of known proton affinities. Their dissociation, in the second field free region, leads to the MH^+ and BH^+ products, whose abundances are related to the difference in the PA of the studied molecule M and the reference base B. The natural logarithms of the $[MH^+]/[BH^+]$ branching ratio may correlate linearly with PA[M]–PA[B] as well as with GB[M]–GB[B], if the entropy changes in the following reactions can be considered as comparable (Eq. (2), Scheme 3).

$$\begin{aligned} MH^+ + B \Rightarrow MBH^+ &\Rightarrow MH^+ + B \\ &\Rightarrow BH^+ + M \end{aligned} \tag{2}$$

A difficulty encountered in studying gas phase reactions of silyl cations, is that a large majority of compounds (alcohols, ethers, ketones, amines, amides and even furans) react with the $R_1(R_2)^+Si$–OH cations by a nucleophilic attack and do not lead to the formation of proton-bound dimers [16]. Only some aromatic compounds yield the latter reaction. Therefore, pyrazine, pyridazine, pyrimidine, quinoleine, isoquinoleine and R-substituted pyridines (R = H, CH_3, CH_2CH_3, OCH_3, F, Cl, Br, etc.) were the reference bases mostly used. The use of such an homogeneous series of substituted heterocyclic compounds as reference bases justifies the above assumption that entropy changes are comparable for the reported experiments.

For each GB determination, at least 12 proton transfer reactions were performed, with two or three measurements for each of them. By using $R_1(R_2)^+Si$–OD cations, it has been verified that the proton borne by oxygen is the one transferred to the base.



Scheme 3.

2.4. Calculations

Calculations were performed as described in previous works [2,17].

Standard ab initio molecular orbital calculations were carried out using the GAUSSIAN 98 [18] program package. Equilibrium geometries of $R_1(R_2)Si{=}O$ and $R_1(R_2)^+Si{-}OH$ were calculated at the MP2(FU) [19] level of theory (second-order Møller–Plesset perturbation including all electrons) using the split-valence shell 6-31G(d,p) basis set [20].

Diagonalization of the analytically calculated Hessian matrix at the MP2(FU)/6-31G(d,p) level using the MP2(FU)/6-31G(d,p) optimized geometries was performed to calculate harmonic vibrational frequencies, from which equilibrium geometries were characterized as minima. Thermal energies ($E_{298}[R_1(R_2)Si{=}O]$ and $E_{298}[R_1(R_2)^+Si{-}OH]$) were determined at 298 K (1 atm) using MP2(FU)/6-31G(d,p) vibrational frequencies scaled by 0.95.

Finally, PA and GB were calculated according to the G2′MP2 method [17] which is a slightly modified G2-MP2 method [21] by using, the MP2(FU)/6-31G(d,p) optimized geometries instead of the MP2(FU)/6-31G(d) ones for the single point calculations, and the thermal energy correction, at the MP2/6-31G(d,p) level, in place of the zero-point correction E_{ZPE}.

3. Results and discussion

3.1. Shape of the curves

Correlation between the logarithms of $[MH^+]/[BH^+]$ branching ratio and the GB of the reference bases are reported in Figs. 1–4, respectively for the reactions of the $CH_3SiH{=}OH^+$, $CH_3CH_2SiH{=}OH^+$, $(CH_3)_2Si{=}OH^+$ and $(CH_3CH_2)_2Si{=}OH^+$ ions. As expected, a linear correlation is observed for the two latter ions. In the case of the two first ions, the logarithm

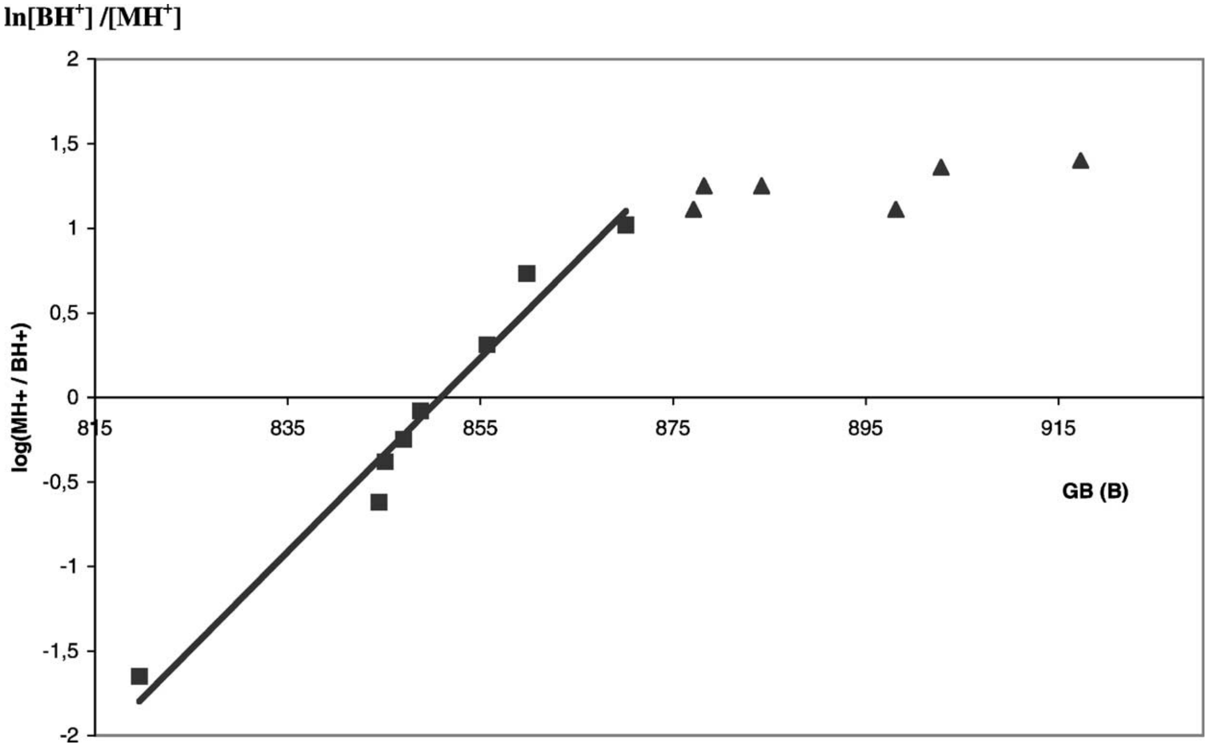


Fig. 1. Correlation between the logarithms of $[BH^+]/[MH^+]$ and GB(B) for the reactions of $CH_3SiH{=}OH^+$.

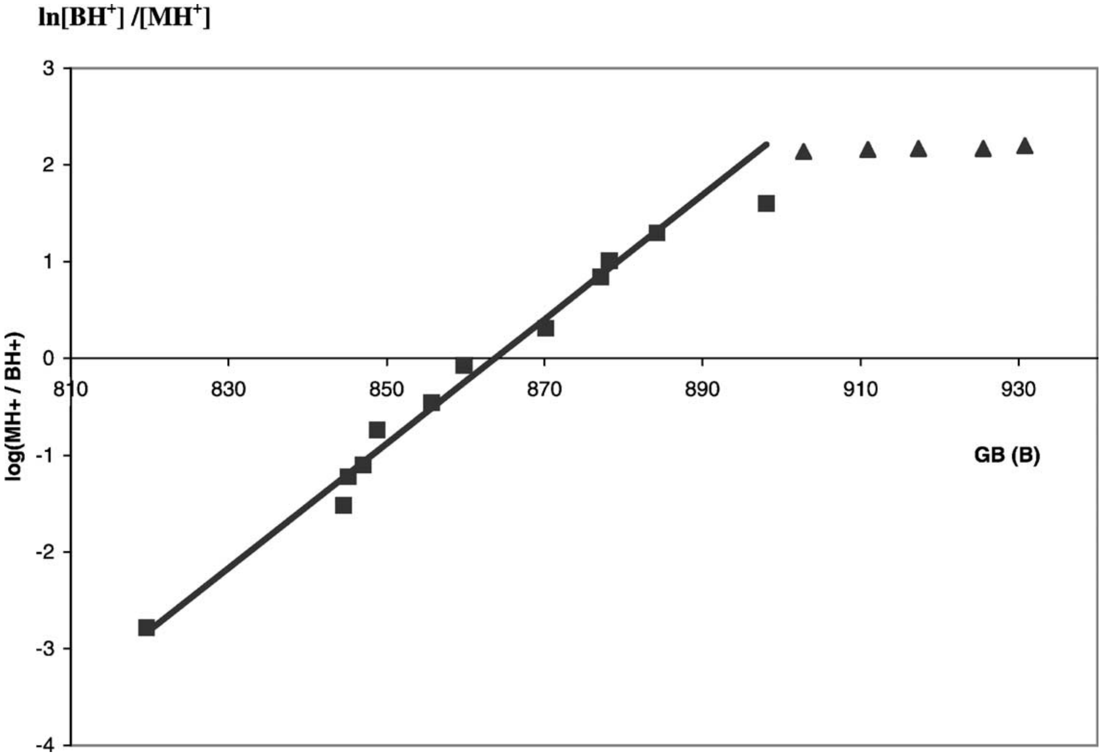


Fig. 2. Correlation between the logarithms of [BH$^+$]/[MH$^+$] and GB(B) for the reactions of $CH_3CH_2SiH{=}OH^+$.

of the branching ratio increases linearly with the PA of the base, but this linear correlation is no longer observed for very strong bases. This behavior indicates that, somewhere in the pathway, there are two isomer structures. A first hypothesis is that the cation formed in the ion source possesses mainly the $R_1(R_2)^+Si$–OH expected structure but that a very minor fraction corresponds to another isobaric cation. A second hypothesis is that, for the adduct, besides the dominant PBD structure, exists a minor proportion of a covalent structure. This structure could be formed by the nucleophilic attack of the neutral molecule at the positively charged silicon atom of the ion as observed for the reactions of aliphatic compounds.

In order to answer this question, $CH_3CH_2SiH{=}OH^+$ (*m*/*z* 75) formed in the external ion-source of a FT-ICR spectrometer, was allowed to react in the cell with pyridine, which is one of the strong bases corresponding to the plateau of the curve shown in Fig. 2. Pyridine is rapidly protonated and for long reaction times, the *m*/*z* 75 cation is no longer observed. The logarithmic plot of the *m*/*z* 75 ion vs. time is linear (correlation coefficient: 0.998). This shows that the ion does not possess two structures.

In the course of this reaction, the abundance of the *m*/*z* 154 product, corresponding to the adduct between the *m*/*z* 75 ion and pyridine, increases. This fact, rather exceptional, suggests the formation of a covalent structure since it has been shown [22,23] that the covalent adducts, formed by reaction of silicon containing cation with molecules, are long-lived enough to be observed upon FT-ICR conditions.

Furthermore, the high energy required to dissociate this adduct, more than 2 eV, is in agreement with a covalent structure [12] and discards a PBD structure since their dissociation energies lie below 35 kcal mol^{-1} [8].

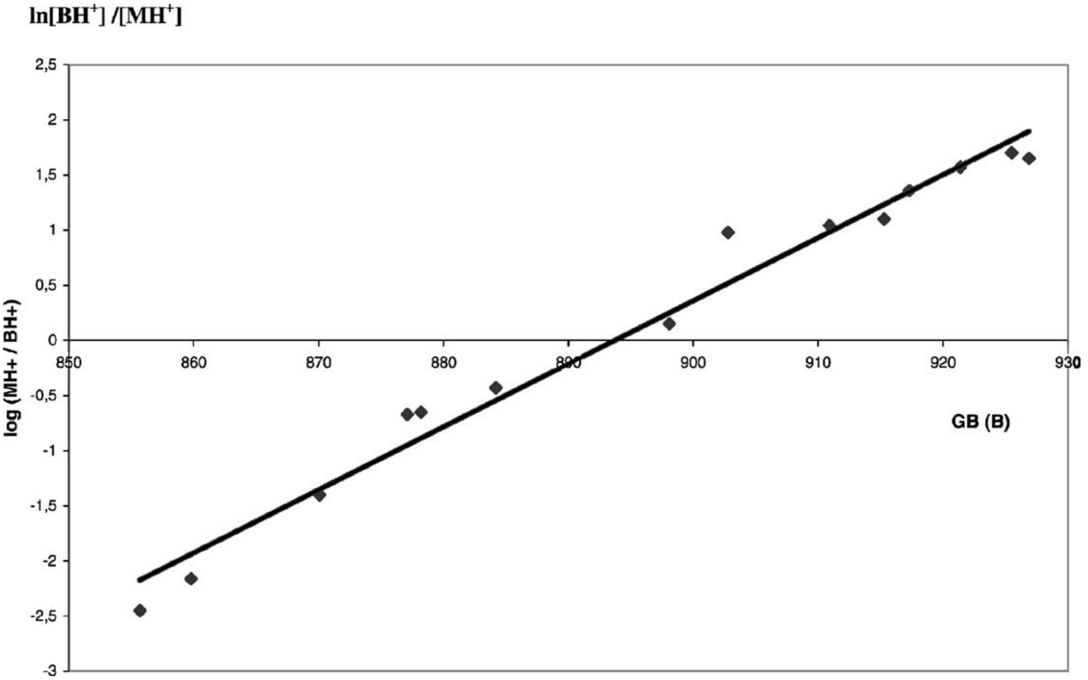


Fig. 3. Correlation between the logarithms of $[BH^+]/[MH^+]$ and GB(B) for the reactions of $(CH_3)_2Si{=}OH^+$.

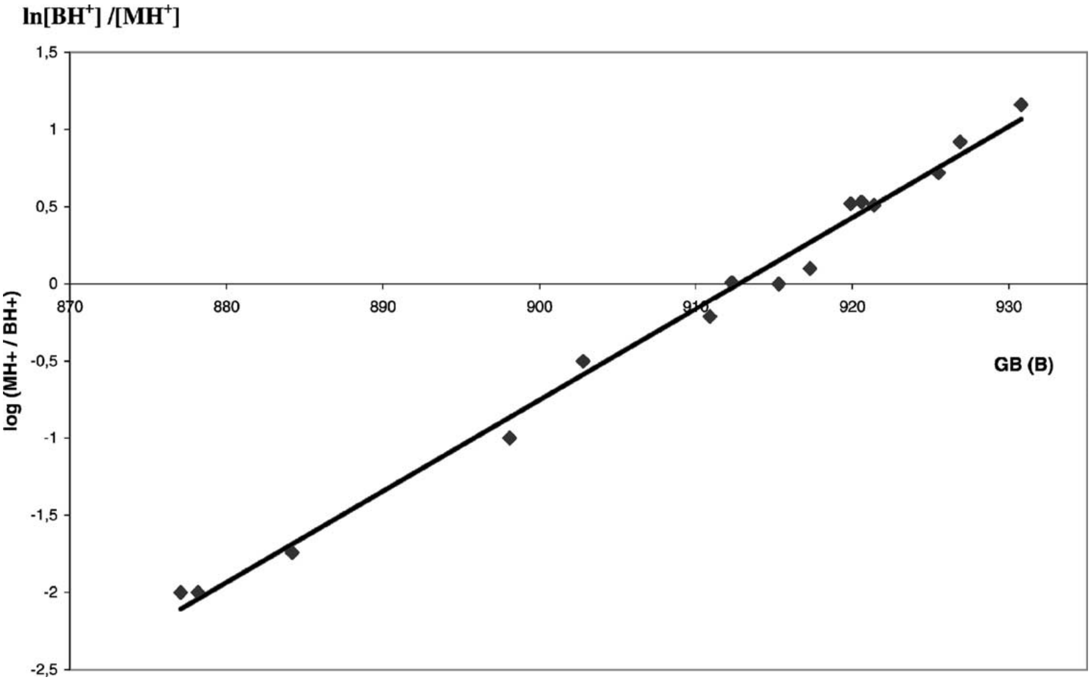


Fig. 4. Correlation between the logarithms of $[BH^+]/[MH^+]$ and GB(B) for the reactions of $(CH_3CH_2)_2Si{=}OH^+$.

Finally, in the FT-ICR experiment, the adduct dissociates at the threshold to yield protonated pyridine which is the most stable final state. However, when the energy increases, the simple cleavage giving *m/z* 75 increases.

In conclusion, the studied ion possesses only one structure but, besides a dominant PBD structure, a minor part of the adduct has a covalent structure and, therefore, the kinetic method must be used carefully.

3.2. Experimental and calculation results

For the reasons explained just above, only the beginning of the curves, shown in Figs. 1–4, were taken in account for GB[M] determination. These curves show a good linear correlation between the logarithm of $[MH^+]/[BH^+]$ and GB[B]. The correlation coefficient of the least square fit is 0.95 for $CH_3SiH{=}OH^+$ and 0.98–0.99 for the three other ions.

A good correlation is also found between $\ln[BH^+]/[MH^+]$ and PA[B] which shows that the approximation considering that entropy changes are similar in the formation of HM^+ and of BH^+ is a valuable approximation for those reactions.

From experiment, GB of the $CH_3SiH{=}O$, $CH_3CH_2SiH{=}O$, $(CH_3)_2Si{=}O$ and $(CH_3CH_2)_2Si{=}O$ molecules are respectively measured to be 203.3, 206.3, 213.4 and 218.0 kcal mol^{-1} (Table 2). The kinetic method is likely to detect differences as small as 0.1 kcal mol^{-1} in the relative PA when the PA of the bases are well known. However, in the present case, it is not sure that PA of substituted pyridines are known with a good precision. Therefore, the precision of our measurements can be considered to be about 0.5 kcal mol^{-1} [7].

For PA, 210.6, 213.8, 220.9 and 225.5 kcal mol^{-1} are respectively found (Table 3).

Calculations, performed at the G′2MP2 level (Tables 2 and 3), are in excellent agreement with the GB and PA measured in this work and those of aldehydes and ketones listed in the NIST table [1]. They agree also with the PA value for $SiH_2{=}O$ previously calculated [1].

3.3. Silicon vs. carbon containing ions

Tables 2 and 3 indicate that GB and PA of the $R_1R_2Si{=}O$ compounds are far above those of their counterparts $R_1R_2C{=}O$, containing only carbon. The

Table 2
Measured and calculated GB (in kcal mol^{-1})

	GB			GB		ΔGB	
	Experimental	Calculated		Experimental	Calculated	Experimental	Calculated
H_2SiO		192.8 (193.1)*	H_2CO	163.2*	162.1		30.7
CH_3SiHO	203.3	203.8	CH_3CHO	176*	176	27.3	27.8
CH_3CH_2SiHO	206.3		CH_3CH_2CHO	180.2*		25.9	
CH_3SiOCH_3	213.4	213.5	CH_3COCH_3	186.9*	186.3	26.1	27.2
$C_2H_5SiOC_2H_5$	218		$C_2H_5COC_2H_5$	192.9*		25.2	

Values with an asterisk are taken from reference [1].

Table 3
Measured and calculated PA (in kcal mol^{-1})

	PA			PA		ΔPA	
	Experimental	Calculated		Experimental	Calculated	Experimental	Calculated
H_2SiO	–	200.2 (200.9)*	H_2CO	170.3*	169.6		30.6
CH_3SiHO	210.6	210.9	CH_3CHO	183.5*	183.6	27.1	27.3
CH_3CH_2SiHO	213.8		CH_3CH_2CHO	187.8*		26	
CH_3SiOCH_3	220.9	219.3	CH_3COCH_3	194.0*	193.8	27	25.5
$C_2H_5SiOC_2H_5$	225.5		$C_2H_5COC_2H_5$	200.0*		25.5	

Values with an asterisk are taken from reference [1].

differences lie between 25 and 30 kcal mol^{-1} and slightly decreases as the substitution degree of silicon increases. This strongly contrasts with GB and PA of silanols or silanamines that are almost similar to those of the corresponding alcohols or amines (Table 1).

This behavior of low coordinate silicon compounds seems to be widespread. It has been recently shown that a similar difference is observed between acids or esters and RSi(O)OR′ compounds [16]. Early works have shown that PA of silenes are 35–40 kcal mol^{-1} greater than those of their corresponding alkenes [11]. Important differences are also observed between PA of enols or vinylethers and those of $R_1O(R_2O)Si{=}CH_2$ compounds [23].

3.4. Thermochemistry

Therefore, a question arises: whereas PA of silanols and PA of alcohols are very close, why PA of silanones lie far above those of ketones? From the definition of PA (Eq. (3)), the difference can either come from a particularly unfavorable ΔH_f of neutral silanone compared with that of acetone or from a relatively favorable ΔH_f of protonated silanone compared to that of protonated acetone.

$$\mathrm{PA}\,[\mathrm{A}] = \Delta H_f[\mathrm{H}^+] + \Delta H_f[\mathrm{A}] - \Delta H_f[\mathrm{AH}^+] \qquad (3)$$

In order to answer this question, the thermochemistry of the reaction shown in Eq. (4) was calculated, at the G2′MP2 level, to be 20 kcal mol^{-1} endothermic. Starting from $\Delta H_f[SiH_3OH] = -65$ kcal mol^{-1} [24] and from the values of the NIST table [25] for carbon containing ions, $\Delta H_f[H_2Si{=}O] = -22.8$ kcal mol^{-1} is obtained, in excellent agreement with previous work [24]. From our calculated value $\mathrm{PA}[H_2Si{=}O] = 200.2$ kcal mol^{-1}, $\Delta H_f[H_2SiOH^+] = 142.7$ kcal mol^{-1} is obtained (Table 4).

Table 4 suggests that the high value of $\mathrm{PA}[H_2Si{=}O]$ comes dominantly from the high value of $\Delta H_f[H_2SiO]$ and for a minor part from the better stabilization of the charge in the H_2SiOH^+ ion. As already observed for the Si=C double bonds [11], the formation of the Si=O double bond is strongly unfavorable.

Table 4
Enthalpies of formation (in kcal mol^{-1})

	ΔH_f		ΔH_f	$\delta\Delta H_f$
H_3SiOH	−65.0[a]	H_3COH	−48.2[b]	−16.8
$H_3SiOH_2{}^+$	122.3[a]	$H_3COH_2{}^+$	136.0[b]	−13.7
$H_2Si{=}O$	−22.6[a]	$H_2C{=}O$	−26.0[b]	+3.4
	−22.8[c]			+3.2
$H_2{}^+Si–OH$	143.1[a]	$H_2{}^+C–OH$	168.0[b]	−24.9
	142.7[c]			−25.3

[a] Reference [24].
[b] Reference [25].
[c] This work.

This is in agreement with the strong endothermicity of the reaction (4) (20 kcal mol^{-1}) involving only neutral molecules, as well as that of the reaction (5) (17 kcal mol^{-1}) involving molecules and ions, leading both to $H_2Si{=}O$ formation. In contrast, reaction (6), which does not lead to the formation of a Si=O bond, is about 10 kcal mol^{-1} exothermic.

$$H_2C{=}O + SiH_3OH \rightarrow H_2Si{=}O + CH_3OH \qquad (4)$$

$$H_2C{=}O + SiH_3OH_2{}^+ \rightarrow H_2Si{=}O + CH_3OH_2{}^+ \qquad (5)$$

$$H_2C–OH^+ + SiH_3OH \rightarrow H_2Si–OH^+ + CH_3OH \qquad (6)$$

$$(CH_3)_2C{=}O + SiH_3OH \rightarrow (CH_3)_2Si{=}O + CH_3OH \qquad (7)$$

The same approach applied to silanone leads to a similar conclusion (Eq. (7)), but the direct measurement of $\Delta H_f[(CH_3)_2{}^+Si–OH]$, which will be performed in a near future, will allow to definitively answer the question.

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