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# Structure, reactivity and vibrational spectra of formohydroxamic and silaformohydroxamic acids: a comparative ab initio study

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## Abstract

Ab initio molecular orbital methods at the CBS-Q level of theory have been used to study the structure, gas-phase acidities and vibrational spectra of formohydroxamic acid  $\text{HC(=O)NHOH}$ , and its sila derivative  $\text{HSi(=O)NHOH}$ . The geometries of various tautomers and rotamers of formohydroxamic and silaformohydroxamic acids, their anions and protonated forms were optimized at the MP2(FC)/6-31G(+) level of theory. The calculations showed that the molecules of neutral acids should exist in several forms very close in energy. The molecules of neutral formohydroxamic and silaformohydroxamic acids exist in more stable keto form. The formohydroxamic tautomer is by about  $20 \text{ kJ mol}^{-1}$  more stable than the hydroximic structure. The result of the effect of the carbon-by-silicon substitution is considerable destabilization of the hydroximic tautomer. In the structure of the neutral form and anion of the parent hydroxamic acid the intramolecular hydrogen bond stabilizes the structure and makes the most stable conformations more planar. In both acids the  $\text{HON}^-$  anion is more stable than the O-anion, hence formohydroxamic and silaformohydroxamic acids in the gas phase are N-acids. Formohydroxamic acid is a weak acid with calculated acidity of about  $1427 \text{ kJ mol}^{-1}$ . The acidity increases in the order:  $\text{HSiONHOH} < \text{HCONHOH}$ . The proton affinity of formohydroxamic acid was computed to be  $-821.0 \text{ kJ mol}^{-1}$ . Silaformohydroxamic acid is a stronger base with computed proton affinity  $\Delta H^{298} = -883.0 \text{ kJ mol}^{-1}$ . The fundamental vibrational frequencies have been computed using the MP2(Full)/6-31G(d) method. Sila substitution produces an appreciable shift of the corresponding harmonic vibrational frequencies of formohydroxamic acid. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Acidity; Basicity; Formohydroxamic and Silaformohydroxamic acids; CBS-Q; Infrared spectra

## 1. Introduction

The structure and ionization of hydroxamic acid derivatives has been the subject of several theoretical investigations [1–14]. Because of the ease of formation of metal complexes these compounds are important in analytical chemistry [6] and  $-\text{CONHO}-$  grouping occurs in numerous biologically active

compounds [15–20], e.g. fungicides, bactericides, and lipogenase inhibitors. The existence of the silicon analogue of formohydroxamic acid, silaformohydroxamic acid, has not been proved experimentally and, therefore, no structural details are available. The substitution of the central carbon atom with the silicon in the formohydroxamic acid can significantly influence the structure and acidity by comparison with the parent compounds. Although many theoretical studies on derivatives containing  $> \text{Si=O}$  groups have been reported [21–31], silaformohydroxamic

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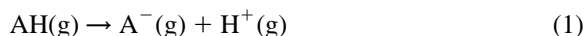
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acid has, thus far, not been characterized by any theoretical or experimental method.

The present paper reports the results of a systematic theoretical examination of formohydroxamic acid, its cations and anions. Of particular interest are the molecular geometries, acidities, basicities, IR frequencies and how these properties change upon isosteric substitution of carbon atom in formohydroxamic acid by silicon. The structures studied are shown in Fig. 1 together with the notation of their conformations and the atom numbering scheme.

## 2. Computational details

The geometries of formohydroxamic acid and its derivatives (Fig. 1) were completely optimized at MP2(FC)/6-31G(†) level within the CBS-Q theory [32–35]. The gas-phase acidity was defined as the enthalpy of deprotonation ( $\Delta H^{298}$ ) for reaction (1)



The enthalpy of deprotonation,  $\Delta H^{298}$ , was computed

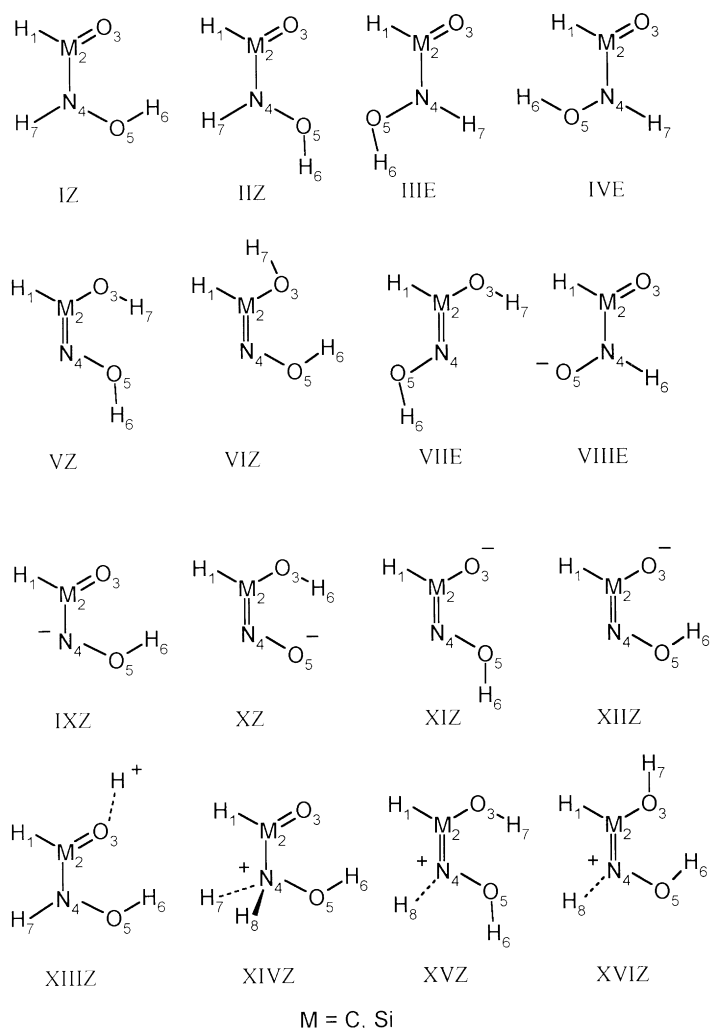


Fig. 1. Structure and atom numbering of the species studied.

Table 1

CBS-Q enthalpies and free energies (in hartree) of formohydroxamic acid species and their silicon derivatives (at 298.15 K)

Rotamer	Enthalpy	Free energy
<i>Formohydroxamic acid</i>		
<b>I</b> Z	–244.727930	–244.760507
<b>II</b> Z	–244.724199	–244.755993
<b>III</b> E	–244.725149	–244.756714
<b>IV</b> E	–244.725149	–244.756714
<b>V</b> Z	–244.725944	–244.757407
<b>VI</b> Z	–244.713926	–244.745854
<b>VII</b> E	–244.719849	–244.751571
<b>VIII</b> E	–244.166889	–244.197774
<b>IX</b> Z	–244.185462	–244.216084
<b>X</b> Z	–244.185460	–244.216079
<b>XI</b> Z	–244.171170	–244.203115
<b>XII</b> Z	–244.185466	–244.216096
<b>XIII</b> Z	–245.035769	–245.067534
<b>XIV</b> Z	–245.011251	–245.044383
<b>XV</b> Z	–245.038283	–245.069761
<b>XVI</b> Z	–245.035766	–245.067539
<i>Silaformohydroxamic acid</i>		
<b>I</b> Z	–495.783303	–495.817401
<b>II</b> Z	–495.783299	–495.817396
<b>III</b> E	–495.784238	–495.818260
<b>IV</b> E	–495.784241	–495.818262
<b>V</b> Z	–495.766050	–495.800872
<b>VI</b> Z	–495.755329	–495.790559
<b>VII</b> E	–495.761767	–495.796548
<b>VIII</b> E	–495.228743	–495.262001
<b>IX</b> Z	–495.234347	–495.268242
<b>X</b> Z	–495.202516	–495.237009
<b>XI</b> Z	–495.233338	–495.267613
<b>XII</b> Z	–495.237347	–495.268248
<b>XIII</b> Z	–496.115817	–496.150721
<b>XIV</b> Z	–496.069438	–496.105083
<b>XV</b> Z	–496.118212	–496.152838
<b>XVI</b> Z	–496.115819	–496.150729

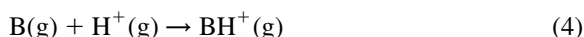
using Eqs. (2) and (3),

$$\Delta H^{298} = \Delta E^{298} + \Delta(pV) \quad (2)$$

$$\Delta E^{298} = [E^{298}(A^-) + 3/2RT] - E^{298}(AH) \quad (3)$$

where  $E^{298}$  stands for the total energies of the most stable conformations of acids and their anions (including the thermal energy correction at  $T = 298.15$  K). In Eq. (2) we substituted  $\Delta(pV) = RT$  (one mole of gas is obtained in reaction (1)). Notice that there is an inverse relationship between the magnitude of the  $\Delta H^{298}$  and the strength of the acid.

The larger the value of  $\Delta H^{298}$ , the weaker is the acid. The gas-phase basicity was defined as the enthalpy of protonation ( $\Delta H^{298}$ ) for reaction (4).



The enthalpy of protonation,  $\Delta H^{298}$ , was computed using Eqs. (5) and (6),

$$\Delta H^{298} = \Delta E^{298} + \Delta(pV) \quad (5)$$

$$\Delta E^{298} = E^{298}(BH^+) - [E^{298}(B) + 3/2RT] \quad (6)$$

where  $E^{298}$  stands for the total energies of bases and their cations (including thermal energy correction at  $T = 298.15$  K). In Eq. (5) we substituted  $\Delta(pV) = -RT$  (one mole of gas is lost in reaction (4)). Ab initio calculations were carried out with the aid of the GAUSSIAN98 package of computer codes [36].

### 3. Results and discussion

#### 3.1. Molecular structures

The enthalpies and free energies of all calculated species are listed in Table 1 and the relative enthalpies and free energies of various conformers with respect to the most stable structures of acids in Table 2. An analysis of the harmonic vibrational frequencies at the HF/6-31G(d) level of theory of the optimized species revealed that all structures are minima (no imaginary frequencies). The neutral molecules ( $MH_3O_2N$ ,  $M = C, Si$ ) were considered in two sets of tautomeric hydroxamic (**I**Z–**IV**E) and hydroximic (**V**Z–**VII**E) structures, the anion ( $MH_2O_2N^-$ ,  $M = C, Si$ ) in five sets (**VIII**E–**XII**Z), and the protonated forms ( $MH_2O_2N^+$ ,  $M = C, Si$ ) in four sets (**XIII**Z–**XVI**Z), Fig. 1.

Four planar conformations (**I**Z–**IV**E) of the keto tautomer of formohydroxamic acid were used as initial structures for geometry optimization. Three distinct final non-planar structures were obtained (Table 2). **IV**E optimized to the **III**E conformation. These non-planar structures deviate from planarity in two ways. The more important is the non-planar conformation around the N–O bond displacing the OH hydrogen atom out of the plane of N–C=O heavy atoms. In conformer **I**Z this displacement is very small ( $-9.1^\circ$ , Table 3), which is due to the

Table 2

Relative enthalpies and free energies (kJ mol<sup>-1</sup>) of studied rotamers and tautomers of formohydroxamic acid and their silicon derivatives

No.	Formohydroxamic acid		No.	Silaformohydroxamic acid	
	$\Delta H$ (298)	$\Delta G$ (298)		$\Delta H$ (298)	$\Delta G$ (298)
Neutral molecules					
<b>IZ</b>	0 (0) <sup>a</sup>	0	<b>III E (IV E)</b>	0	0
<b>VZ</b>	5.2 (7.5) <sup>a</sup>	8.1	<b>IZ (II Z)</b>	2.5	2.3
<b>III E (IV E)</b>	7.3 (7.9) <sup>a</sup>	10.0	<b>VZ</b>	47.8	45.7
<b>II Z</b>	9.8	11.9	<b>VII E</b>	59.0	57.0
<b>VII E</b>	21.2 (21.3) <sup>a</sup>	23.5	<b>VIZ</b>	75.9	72.7
<b>VIZ</b>	36.8	38.5			
Anions					
<b>IXZ</b>	0	0	<b>IXZ</b>	0	0
<b>XIZ</b>	39.2	35.3	<b>XIZ</b>	2.6	1.7
<b>VIII E</b>	50.5	49.3	<b>VIII E</b>	14.7	16.4
			<b>XZ</b>	83.6	82.0
Cations					
<b>XVZ</b>	0	0	<b>XVZ</b>	0	0
<b>XIII Z</b>	6.6	5.8	<b>XIII Z</b>	6.3	5.5
<b>XIVZ</b>	71.0	66.6	<b>XIVZ</b>	128.1	125.4

<sup>a</sup> Values computed by using the G2 theory [12].

mutual electrostatic attraction of hydrogen and oxygen atoms via hydrogen bond (a value of 2.063 Å was computed for  $d(\text{O}_3 \cdots \text{H}_6)$  in **IZ**. Less important is a non-planar configuration on the nitrogen atom. For all three (**IZ**, **II Z**, **III E**) conformers of formohydroxamic acid the structures with pyramidal nitrogen conformation were found. As regards of hydroxamic acids all three structures are planar (Table 3). The intramolecular electrostatic stabilization is important in **VZ** and **VIZ**. The  $\text{O} \cdots \text{H}$  bond length in these conformers varies within a narrow interval of around 2 Å, which is much less than the sum of the van der Waals radii of oxygen and hydrogen (2.6 Å).

In the case of silicon species the intramolecular electrostatic stabilization is in comparison with the parent formohydroxamic acid less important. The  $\text{Si}=\text{O} \cdots \text{H}$  bond length in all sila derivatives investigated varies within a wide interval of 3.4–4.6 Å, Table 3 which is much higher than the sum of the van der Waals radii of oxygen and hydrogen. In the absence of intramolecular electrostatic stabilization the full optimization of four rotamers (**IZ**–**IV E**) of silaacid leads to two geometrically different structures (**IZ** and **III E**). Both are planar. Upon optimization **II Z** became **IZ**, and **IV E** became **III E**.

Geometry optimizations were performed starting from each of the five anions (**VIII E**–**XII Z**) of formohydroxamic acid. Rotamers **XZ** and **XII Z** spontaneously underwent internal rotation to form a **IXZ** conformer. In all, three structures (**IXZ**, **XIZ** and **VIII E**) were successfully optimized at the MP2(FC)/6-31G(†) level. Among the five anions of silaformohydroxamic acid four anions “survived” optimization procedure. **XII Z** optimized to the **IXZ**. The optimization of the protonized structures **XIII Z** and **XVIZ** of both carbon and silicon acids converged to one stable form.

The CBS-Q calculations of the relative stability of tautomers of formohydroxamic acid in agreement with experiments show hydroxamic form to be more stable than hydroxamic tautomer. Some experimental studies on the structure of hydroxamic acid derivatives using X-ray [37] and <sup>17</sup>O NMR [1] concluded that the most stable structure was **IZ**. In the crystalline phase, conformations **II Z** and **III E** are usually found [38], but this is due to the additional stabilization derived from networks of intermolecular hydrogen bonds. The **IZ** conformer of formohydroxamic acid has been computed previously [13] (at a G2 level of theory) to be the most stable structure. The hydroxamic form was computed by about 5.2 (CBS-Q) and

Table 3

MP2(FC)/6-31G(†) optimized geometries of: (a) formohydroxamic acid species; and (b) silicon derivatives of formohydroxamic acid species

Parameter	I <sub>Z</sub>	II <sub>Z</sub>	III <sub>E</sub>	V <sub>Z</sub>	VII <sub>Z</sub>	VIII <sub>E</sub>	Exp. <sup>a</sup>
(a)							
<i>d</i> (C2H1)	1.105	1.111	1.107	1.086	1.088	1.090	
<i>d</i> (C2O3)	1.224	1.211	1.213	1.341	1.367	1.347	1.217
<i>d</i> (C2N4)	1.367	1.386	1.391	1.288	1.283	1.281	1.312
<i>d</i> (N4O5)	1.401	1.400	1.407	1.423	1.386	1.411	1.388
<i>d</i> (O5H6)	0.978	0.967	0.967	0.964	0.975	0.965	
<i>d</i> (N4H7)	1.013	1.014	1.017				
<i>d</i> (O3H7)				0.974	0.964	0.972	
<i>d</i> (H6...O3)	2.063	2.951	4.046		2.042		
<i>d</i> (H7...O5)				2.004			
∠(H1C2O3)	124.6	124.2	125.1	114.6	119.3	113.9	121.0
∠(H1C2N4)	112.6	110.0	111.4	118.5	118.4	125.2	113.0
∠(O3C2N4)	122.6	125.5	123.4	126.9	122.4	121.0	125.3
∠(C2N4O5)	115.8	116.1	113.7	107.7	114.9	109.7	118.3
∠(N4O5H6)	102.1	104.2	104.0	102.7	108.4	102.2	111.0
∠(C2N4H7)	119.6	116.8	114.2				123.0
∠(C2O3H7)				106.3	110.2	107.0	
∠(O5N4C2H1)	−170.2	−163.6	26.4	180.0	−180.0	0.0	
∠(O5N4C2O3)	14.0	21.8	−157.2	−0.0	0.0	180.0	
∠(H7N4C2O3)	149.9	153.3	−28.7				
∠(H7N4C2H1)	−35.1	−32.1	154.8				
∠(H6O5N4C2)	−9.1	−92.3	−118.7	180.0	0.0	180.0	
∠(H7O3C2N4)				−0.0	−180.0	−0.0	
(b)							
<i>d</i> (Si2H1)	1.480		1.475	1.462	1.467	1.474	
<i>d</i> (Si2O3)	1.534		1.535	1.649	1.653	1.644	
<i>d</i> (Si2N4)	1.703		1.710	1.623	1.608	1.628	
<i>d</i> (N4O5)	1.408		1.415	1.411	1.382	1.417	
<i>d</i> (O5H6)	0.969		0.968	0.966	0.970	0.965	
<i>d</i> (N4H7)	1.015		1.014			2.914	
<i>d</i> (O3H7)				0.965	0.963	0.965	
<i>d</i> (H6...O3)	3.676		4.602		3.375		
<i>d</i> (H7...O5)				3.423			
<i>d</i> (N4...H7)						2.914	
∠(H1Si2O3)	127.3		127.7	109.2	114.5	107.6	
∠(H1Si2N4)	103.6		106.6	115.8	114.3	134.5	
∠(O3Si2N4)	129.0		125.6	135.1	131.2	117.9	
∠(C2N4O5)	122.0		118.1	123.0	137.6	120.1	
∠(N4O5H6)	104.8		104.5	102.3	108.6	102.0	
∠(Si2N4H7)	123.8		124.5				
∠(Si2O3H7)				119.3	121.3	117.8	
∠(O5N4Si2H1)	168.6		18.4	−180.0	180.0	−0.0	
∠(O5N4Si2O3)	−15.6		−165.0	−0.0	0.0	180.0	
∠(H7N4Si2O3)	−172.4		−16.3				
∠(H7N4Si2H1)	11.8		167.1				
∠(H6O5N4Si2)	95.2		−109.0	−180.0	−0.0	180.0	
∠(H7O3Si2N4)				0.0	−180.0	−0.0	

<sup>a</sup> Experimental values, Ref. [37].

Table 4

CBS-Q gas-phase acidities and basicities (enthalpies  $\Delta H$ , and Gibbs free energies  $\Delta G$ ) of the formohydroxamic and silaformohydroxamic acids (at 298.15 K)

Reaction	Formohydroxamic acid		Reaction	Silaformohydroxamic acid	
	$\Delta H^{298}$	$\Delta G^{298}$		$\Delta H^{298}$	$\Delta G^{298}$
<b>IZ</b> – $H^+ \rightarrow$ <b>IXZ</b>	1430.4	1435.6	<b>IIIE</b> – $H^+ \rightarrow$ <b>IXZ</b>	1449.9	1450.3
<b>VZ</b> – $H^+ \rightarrow$ <b>IXZ</b>	1425.2	1427.4	<b>IIIE</b> – $H^+ \rightarrow$ <b>XIZ</b>	1452.6	1451.9
<b>IZ</b> + $H^+ \rightarrow$ <b>XVZ</b>	–821.0	–818.1	<b>IZ</b> – $H^+ \rightarrow$ <b>XZ</b>	1447.5	1448.0
<b>IZ</b> + $H^+ \rightarrow$ <b>XIIIIZ</b>	–814.4	–812.3	<b>IZ</b> – $H^+ \rightarrow$ <b>XIZ</b>	1450.1	1449.7
<b>VZ</b> + $H^+ \rightarrow$ <b>XVZ</b>	–826.2	–826.3	<b>IIIE</b> + $H^+ \rightarrow$ <b>XVZ</b>	–883.0	–884.6
<b>VZ</b> + $H^+ \rightarrow$ <b>XIIIIZ</b>	–819.6	–820.4	<b>IIIE</b> + $H^+ \rightarrow$ <b>XIIIIZ</b>	–876.8	–879.1
			<b>IZ</b> + $H^+ \rightarrow$ <b>XVZ</b>	–885.5	–886.9
			<b>IZ</b> + $H^+ \rightarrow$ <b>XIIIIZ</b>	–879.2	–881.3

7.4 kJ mol<sup>–1</sup> (G2) less stable (Table 2). Upon the carbon-by-silicon substitution the stability of hydroxamic tautomers considerably increase. However, there is no unambiguous enthalpy preference for two geometrically different silaformohydroxamic acid rotamers (Table 2). The relative free energies of formohydroxamic acid species and its sila derivatives follow the enthalpy changes and conformational entropy contribution for isomerization and tautomerization reactions is small.

The calculated geometries of formohydroxamic and silaformohydroxamic acids are summarized in Table 3. There are significant structural differences between conformers of formohydroxamic acid. Thus the C=O bond is longer in **IZ** than in **IIIZ** and **IIIE** but the C–N bond is shorter. These differences and those in the angles are due at least in part to the intramolecular hydrogen bond which is present in **IZ**. The dihedral angle C–N–O–H in **IIIZ** and **IIIE** is from the interval of 92–118° and orients OH group perpendicularly to the plane of N–C=O heavy atoms. These values correspond well to the experimentally determined intervals of the C–N–O–H angle for the 15 syn-periplanar (*Z*) hydroxamic acids [38] (50–140°). This orientation of the OH group is more appropriate for intermolecular hydrogen bonding. The presence of C=N double bonds in **VZ**, **VIZ** and **VIIIE** results in considerable changes of all bond lengths and angles compared with **IZ**–**IVE** (Table 3). For formohydroxamic acid the planar conformers are characteristic. In the absence of gas phase structural data (microwave spectroscopy of formohydroxamic acid in the gas phase has been prevented by low volatility and easy

decomposition of the compound [5]) the computed geometry of studied conformers can be compared with the X-ray data on formohydroxamic acid [38] (Table 3). The carboxyl group is found to be longer in the crystal than in the isolated molecule. However, the C=O bond lengthening in the crystal is probably due to intermolecular hydrogen bonding [39]. The bond angles, which are generally more reliable in crystal structures, correspond better to the conformer **IZ**; the actual form of the molecule in the crystal is nearer to **IIIZ** than to **IZ**. The substantial elongation of the M–N distance to about 1.7 Å in silaacid causes a considerable weakening of the stabilizing effect of intramolecular hydrogen bond in these species. In the absence of any conjugation between Si=O and NOH groups the most stable conformer is the non-planar **IIIE** form (Table 3).

### 3.2. Gas phase acidities

The ionization of substituted hydroxamic acids has been investigated experimentally [1,15,40], more recently even in the gas phase [41,42]. However, no ionization and/or protonation of silahydroxamic acids has been studied. Table 4 contains acidities and basicities of formohydroxamic and silaformohydroxamic acids. With respect to the possible existence of several stable rotational conformers and tautomers (Table 2) the enthalpy of deprotonation and/or protonation may be computed between two arbitrary species. Those between two species with most similar structures (e.g. **IVE**  $\rightarrow$  **VIIIE** +  $H^+$ ) might be of theoretical interest, but only the differences between

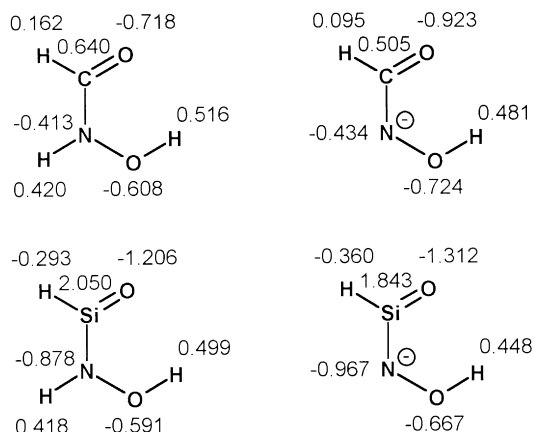


Fig. 2. MP2(FC)/6-31G(d) natural atomic charges calculated for formohydroxamic, silaformohydroxamic acids and their anions.

the most stable species can have physical meaning and can be compared with experiments.

Of the three anions of formohydroxamic acid (**IXZ**, **XIZ** and **VIII<sub>E</sub>**) the N-anion **IXZ** is most stable. This structure is stabilized by the five-membered intramolecular hydrogen bond O–H...<sup>−</sup>O (a value of 1.896 Å was calculated for  $d(\text{H}\cdots\text{O}^-)$ ). Hence formohydroxamic acid is predicted to behave as an N-acid in the gas phase, which agrees with the results of theoretical calculations for this acid carried out at various levels of theory [6,11,13]. The energetically easiest process is deprotonation of **VZ** with the computed enthalpy and Gibbs free energy of 1425.2 and 1427.4 kJ mol<sup>−1</sup>. This value corresponds well to the empirically estimated  $\Delta H^{298} = 1435$  kJ mol<sup>−1</sup> value [5] obtained from experimental thermodynamic data of acetohydroxamic acid [41] by an empirical correction based on the difference between formic and acetic acid [43]. The estimated value [5] of  $\Delta G^{298} = 1405$  kJ mol<sup>−1</sup> is substantially lower (Table 4). This large discrepancy between experimental and computed  $\Delta G^{298}$  values may be, to some extent, due to the different method for evaluation of experimental and theoretical Gibbs free energies of ionization. Theoretically we computed intrinsic gas-phase acidities referring to the thermodynamic equilibrium described by Eq. (1). Experimental acidities were evaluated from proton transfer equilibria [44]  $\text{A}_1\text{H} + \text{A}^- \rightleftharpoons \text{A}_0\text{H} + \text{A}_1^-$ , describing the transfer of proton between a given ( $\text{A}_1\text{H}$ ) and reference base ( $\text{A}^-$ ). The experimental  $\Delta G^0$  acidities have been tied

to the “marker” thermodynamic value for HBr [43,45] which means a lowering of  $\Delta G^0$  value of acid by some 30 kJ mol<sup>−1</sup> in comparison with the corresponding enthalpy change. Ventura’s [8] enthalpy and Gibbs free energy for formohydroxamic acid (1302.9 and 1311.3 kJ mol<sup>−1</sup>, MP2/6-311++G(2d,2p)/MP2/6-311++G(2d,2p) calculation) are much lower than our CBS-Q values (Table 4).

Of the four stable anions of silaformohydroxamic acid investigated the HO–N<sup>−</sup> anion **IXZ** is most stable (Table 2), hence silaformohydroxamic acid is predicted to behave as an N-acid in the gas phase. The second most stable anion (by 1.7 kJ mol<sup>−1</sup> less stable) is O-anion **XIZ** of hydroximic tautomer. Thus, in the absence of intramolecular hydrogen bond in silaacid species the net preference for one stable form is substantially reduced. The calculated population ratios for these two most stable anions (at 298.15 K) are 67:33. The energetically easiest process could be the deprotonation of **IZ** with the computed  $\Delta G^0 = 1448.0$  kJ mol<sup>−1</sup>. The computed enthalpies and Gibbs free energies for possible deprotonation mechanisms of the most stable rotamers (**III<sub>E</sub>** and **IZ**) are close to each other and there is no clear preference for one reaction (Table 4).

The acidity of the silaformohydroxamic acids must be quite different from the parent formohydroxamic acids. The electronegativity difference between silicon, oxygen and nitrogen (Si;  $\chi = 1.74$ ; O,  $\chi = 3.50$ ; N,  $\chi = 3.07$ ) suggests that considerable charge may be on oxygen and nitrogen atoms. In addition, one might expect that the silicon would be considerably more electron deficient than the carbon atom in the carboxyl compounds. The natural atomic charges [46–49] computed for the formohydroxamic acid, silaformohydroxamic acid and their anions are shown in Fig. 2. More electropositive silicon in the silaacids induces much higher polarization in the –Si(=O)NH moiety in comparison with the –C(=O)NH group and hence a wider electron delocalization (Fig. 2). Ionization results in a substantial increase of polarization of the Si–N bond in comparison with the C–N one. The negative charge is located on the most electronegative element of the hydroxamate ion, oxygen. However, the nitrogen atom carries substantially higher negative charge in comparison with the same nitrogen atom in hydroxamic acid anion (Fig. 2). The higher acidity of



silaacids in comparison with the parent carboxylic acid has been explained [31] on the basis of electronegativity and the concept of charge capacity introduced by Politzer et al. [50]. The less electronegative silicon has a higher charge capacity than carbon which results in a larger stabilization of silicon containing anions in comparison with formate. The dispersion of charge is largest in the acids containing the Si=O double bond. For formohydroxamic acid and its sila-derivative the reverse order of acidity was found. The acidity increases in the order:  $\text{HSiONHOH} < \text{HCONHOH}$  (Table 4). The reverse acidity order of formohydroxamic and silaformohydroxamic acids by comparison with carboxylic acids could be explained by the extraordinary stabilization of formohydroxamic acid anion by strong intramolecular hydrogen bond. This intramolecular hydrogen bond is even more important than in rotamers and tautomers of neutral formohydroxamic acid. Higher charge capacity of the less electronegative silicon which results in a larger stabilization of silicon containing anions in comparison with parent carbon acids is not sufficient to overcome the hydrogen bond stabilization in the formohydroxamate.

### 3.3. Gas phase basicities

The nitrogen and carbonyl oxygen protonation of

hydroxamic and hydroxamic tautomers considerably changed the stability of keto and imine species (Table 2). The most stable structure of both silaacid and formohydroxamic acid is protonized imine structure **XVZ**. Slightly less stable is the delocalized form resulted from the optimization of **XIII**Z. The conformers (**XIV**Z) protonated at the nitrogen of both acids lie much higher in enthalpy (71.0 and 128.1 kJ mol<sup>-1</sup>) and need not be further considered (Table 2). Lower level ab initio calculations [5,6] of formohydroxamic acid and the experimental NMR data for aceto-hydroxamic acid [6] have been shown that these compounds are protonated at the carbonyl oxygen. The highest proton affinity ( $\Delta H^{298} = -826.2$  kJ mol<sup>-1</sup>) was found for the reaction **VZ** +  $\text{H}^+ \rightarrow \text{XVZ}$ , but only the equilibrium between the most stable species **IZ** +  $\text{H}^+ \rightarrow \text{XVZ}$  is physically meaningful ( $\Delta H^{298} = -821.0$  kJ mol<sup>-1</sup>). From the thermodynamic data about the protonation of aceto-hydroxamic acid, formamide and acetamide [41,43] an estimated value of approximately  $\Delta H^{298} = -826$  kJ mol<sup>-1</sup> [5] was determined for protonation of formohydroxamic acid. Silaformohydroxamic acid is a stronger base (Table 4). The energetically easiest protonation **IZ** +  $\text{H}^+ \rightarrow \text{XVZ}$  gives proton affinity  $\Delta H^{298} = -885.5$  kJ mol<sup>-1</sup>. However, physically meaningful is the process **III**E +  $\text{H}^+ \rightarrow \text{XVZ}$  with proton affinity  $\Delta H^{298} = -883.0$  kJ mol<sup>-1</sup>.

Table 5

Calculated MP2(Full)/6-31G(\*) vibrational frequencies (cm<sup>-1</sup>) and IR intensities (km mol<sup>-1</sup>) of most stable rotamers of formohydroxamic acid (FA) and silaformohydroxamic acid (SFA)

FA ( <b>IZ</b> )				SFA ( <b>III</b> E)		
	Vibrational frequency	IR intensity	Assignment	Vibrational frequency	IR intensity	Assignment
$\omega_1$	3631	69	NH	3724	48	OH
$\omega_2$	3563	42	OH	3614	46	NH
$\omega_3$	3112	47	CH	2375	85	SiH
$\omega_4$	1784	202	C=O	1425	113	N(H)OH
$\omega_5$	1583	37	N(H)OH	1424	8	N(H)OH
$\omega_6$	1423	103	N(H)OH	1234	59	Si=O
$\omega_7$	1412	52	C(=O)H	1083	15	HSi(=O)NHOH
$\omega_8$	1235	9	HC(=O)NHOH	904	34	HSi(=O)NHOH
$\omega_9$	1016	18	HC(=O)NHOH	838	59	HSi(=O)NHOH
$\omega_{10}$	981	31	HC(=O)NHOH	635	68	HSi(=O)NHOH
$\omega_{11}$	864	51	HC(=O)NHOH	528	178	HSi(=O)NHOH
$\omega_{12}$	520	135	HC(=O)NHOH	411	79	HSi(=O)NHOH
$\omega_{13}$	455	180	HC(=O)NHOH	336	51	HSi(=O)NHOH
$\omega_{14}$	334	65	HC(=O)NHOH	219	21	HSi(=O)NHOH
$\omega_{15}$	307	52	HC(=O)NHOH	130	2	HSi(=O)NHOH

### 3.4. Infrared spectra

Matrix isolated infrared spectroscopy is one of the most powerful techniques for the experimental characterization of many unstable species. Because experimental IR spectra of the investigated derivatives of formohydroxamic and silaformohydroxamic acids are not known until now, we also computed theoretical spectra using the MP2(Full)/6-31G(d) method. The theoretical prediction of the vibrational frequencies could, therefore, be an important step towards the identification of these compounds. The MP2 calculated harmonic vibrational frequencies of most stable conformers of these acids are summarized in Table 5. The details of the vibrational calculations have shown that sila substitution produces an appreciable shift of the corresponding harmonic vibrational frequencies of formohydroxamic acid. Most intense band of formohydroxamic acid corresponds to the C=O stretching vibration ( $1784\text{ cm}^{-1}$ ) and should be used for eventual experimental identification of this compound. This band is close to the typical ketonic  $\nu(\text{C=O})$  of  $1731\text{ cm}^{-1}$  in acetone [51]. The analogous Si=O band in silaformohydroxamic acid is found at substantially lower frequencies ( $1234\text{ cm}^{-1}$ ). Our computed frequency for the Si=O mode in  $\text{HSi(=O)NHOH}$  agrees well with the experimentally found Si=O fundamentals ( $1249\text{ cm}^{-1}$ ) in structurally related silanoic acid [52]. The N–H stretching vibrations for both compounds are close to one another (Table 5). The larger differences in the frequencies of the O–H stretches for formohydroxamic acid and its silicon derivative may be attributed (besides the effect of the carbon-by-silicon substitution) to intramolecular hydrogen bonding in the case of most stable conformer of formohydroxamic acid.

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