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Thermodynamic and kinetic investigations of silathioformohydroxamic acid conformers

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ABSTRACT

The Silathioformohydroxamic acid conformers were studied in the gas phase by a high level density functional theory. The global isomeric structure was S2 at the CBS-Q levels of theory. The stability order for the conformers were 1E>1Z>4Z>2Z>2E>3Z>S1. Thirteen anions and seven cations of various conformers have been studied. The protonation and deprotonation reactions in the gas phase are investigated at the CBS-Q level. The 2EOA showed the highest relative enthalpy and Gibbs free energy (ΔH= 249.57 kJ/mol, ΔG=240.62 kJ/mol) in the anions section and the 4ZOC showed the highest relative enthalpy and Gibbs free energy (ΔH= 285.12 kJ/mol, ΔG=234.13 kJ/mol) in the cations section. Energetically easiest process is the deprotonation of 2ZNA with the computed enthalpy and Gibbs free energy of 1274.52 kJ/mol and 1282.49 kJ/mol. The equilibrium constants at 298.15 K of the deprotonation reactions are very small which means the reaction at this temperature favor the reactants.

Keywords: CBS-Q, Gibbs free energy, equilibrium constant and stability.
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INTRODUCTION

The structure and the ionization of hydroxamic acid derivatives has been the subject of several theoretical investigations [1-4]. Because of the ease of formation of metal complexes these compounds are important in analytical chemistry [5]. The existence of the silicon analogue of thioformohydroxamic acid, silathioformohydroxamic acid has not been proved experimentally and therefore, no structural details are available. The substitution of the central carbon atom with the silicon in thioformohydroxamic acid can significantly influence the structure and acidity by comparison with the parent compounds. Silathioformohydroxamic acid has thus far not been characterized by theoretical or experimental method. The present study reports the results of a systematic theoretical investigation of silathioformohydroxamic acid and its anions. additional interest are the molecular geometries, enthalpies, Gibbs free energies and infrared frequencies, and how these properties change upon isosteric substitution of carbon atom in thioformohydroxamic acid molecule by silicon.

2. Computational Details
The calculations were investigated the relative stabilities of the various isomeric forms of silathioformohydroxamic acid. The study included the analysis of the reaction enthalpies and Gibbs free energies. The geometries of silathioformohydroxamic acid and its derivatives (Fig. 1.) were completely optimized at MP2(FC)/6-31G(d) level within the CBS-Q theory [6-9]. The gas-phase basicity was defined as the enthalpy of protonation (ΔH^{298}) for reaction (1).
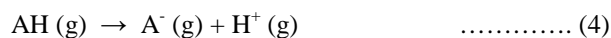
$$X(g) + H^+(g) \rightarrow XH^+(g) \qquad \ldots\ldots.. \quad (1)$$

The enthalpy of protonation, ΔH^{298}, was computed using Eqs. (2) and (3).

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$$\Delta H^{298} = \Delta E^{298} + \Delta(pV) \qquad\qquad \text{.................(2)}$$

$$\Delta E^{298} = E^{298}(XH^{+}) - [E^{298}(X) + 3/2RT] \qquad \text{...........(3)}$$

The gas-phase acidity was defined as the enthalpy of deprotonation (ΔH^{298}) for reaction (1)

$$AH\ (g)\ \rightarrow\ A^{-}\ (g) + H^{+}\ (g) \qquad\qquad \text{............. (4)}$$

The enthalpy of deprotonation, ΔH^{298} was computed using the following two equations 5,6:

$$\Delta H^{298} = \Delta E^{298} + \Delta(pV) \qquad\qquad \text{................(5)}$$

$$\Delta E^{298} = [E^{298}(A^{-}) + 3/2RT] - E^{298}(AH) \qquad \text{..............(6)}$$

Notice that there is an inverse relationship between the magnitude of the ΔH^{298} and the strength of the acid. E^{298} stands for the total energies of the most stable conformations of acids and their anions (including the thermal energy correction at 298.15 K). In equation 2, the substitution of $(\Delta pV)=-RT$ is carried out since, one mole of gas is lost in reaction 1). Again In equation 5, the substitution of $(\Delta pV)=RT$ is carried out since, one mole of gas is obtained in reaction 4).

The equilibrium constants (K_{eq}) of the reactions were calculated from Gibbs free energies using $\Delta G = -RTlnK_{eq}$.

The optimized structures were confirmed to be real minima by frequency calculation. The vibrational frequencies were scaled by a factor of 0.9614 [10]. The calculations were performed using Gaussian03 version 6.0 package [11].

RESULTS AND DISCUSSION

The calculations at this level predict eight local minima structures for silathioformohydroxamic acid. Four thione forms (1Z, 2Z, S2, 1E), Three thiol forms (2E, 3Z, 4Z) and one iminol form with separating charge S1.The Selected structures are presented in Fig. 1. The description of the anions (A) and the cations (C) for the structures are as follows, deprotonation of N-H in 1Z is labelled 1ZNA and the protonation of N atom in 3Z molecule is labelled 3ZNC (i.e. 1ZNA is an anion form of 1Z molecule in which the proton is dissociated from nitrogen atom and 3ZNC is a cation form of 3Z molecule in which the proton is added to nitrogen atom). The structural parameters from the full optimized geometry of the structures are given in Table 1.

Table 1: The selected bond lengths of the molecules at CBS-Q level of theory.

	Si-S	Si-N	N-O	Si-H	S-H	O-H	N-H
1Z	1.935	1.688	1.374	1.466	-	0.945	0.997
S1	2.172	2.012	1.163	1.499	1.327	-	1.024
2Z	1.959	2.136	1.155	1.477	-	-	1.025
S2	1.943	1.925	1.422	1.461	-	-	1.001
1E	1.938	1.692	1.379	1.461	-	0.944	0.997
2E	2.106	1.590	1.380	1.465	1.328	0.941	-
3Z	2.127	1.558	1.346	1.454	1.328	0.994	-
4Z	2.129	1.846	1.178	1.466	1.328	-	-

The energies of the molecules are often calculated for geometries optimized at a lower level due to the large computational time required for geometry optimization; however in this paper the optimized structures at CBS-Q level of theory gave a good value for the bond distances in comparison with the available experimental related data [12]. Even though, there are four structures in which the S-Si-N-O is planar, only the 2E molecule has a planar configuration. There are two interesting pentacoordinate silicon structures 2Z and S2, both structures have the Si→N coordinate bond. These two have been verified since the structures have the longest Si→N bond length in the series. Similar structures to 2Z and S2 have been reported previously [13-14]. The relative energy profile is schematically plotted in Figure 2.
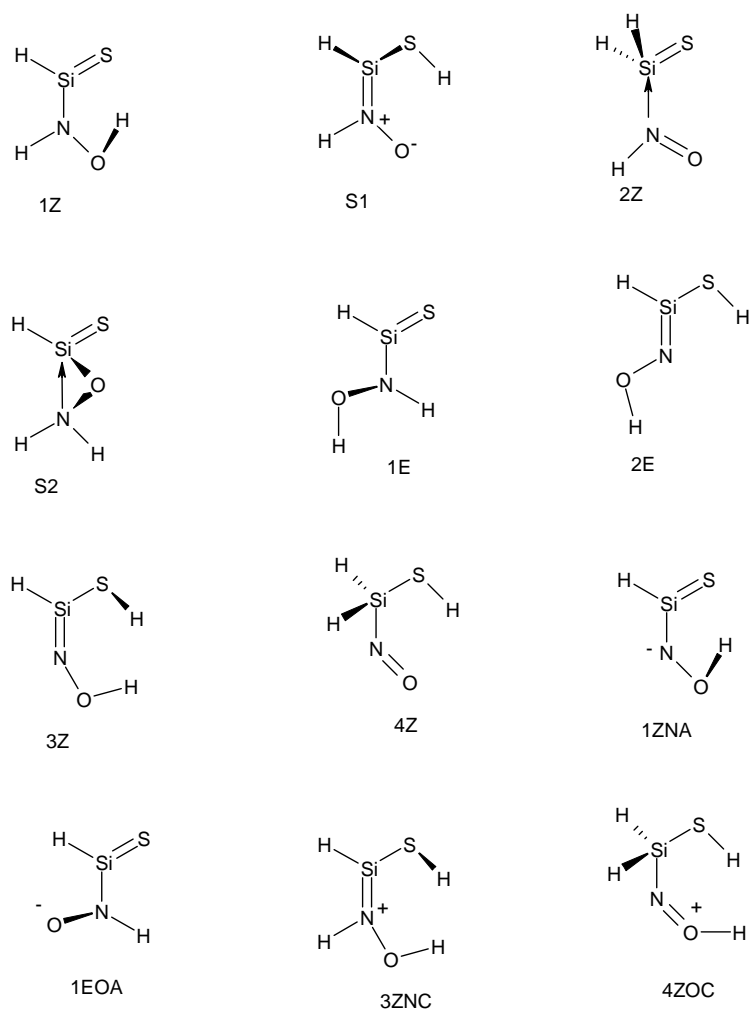
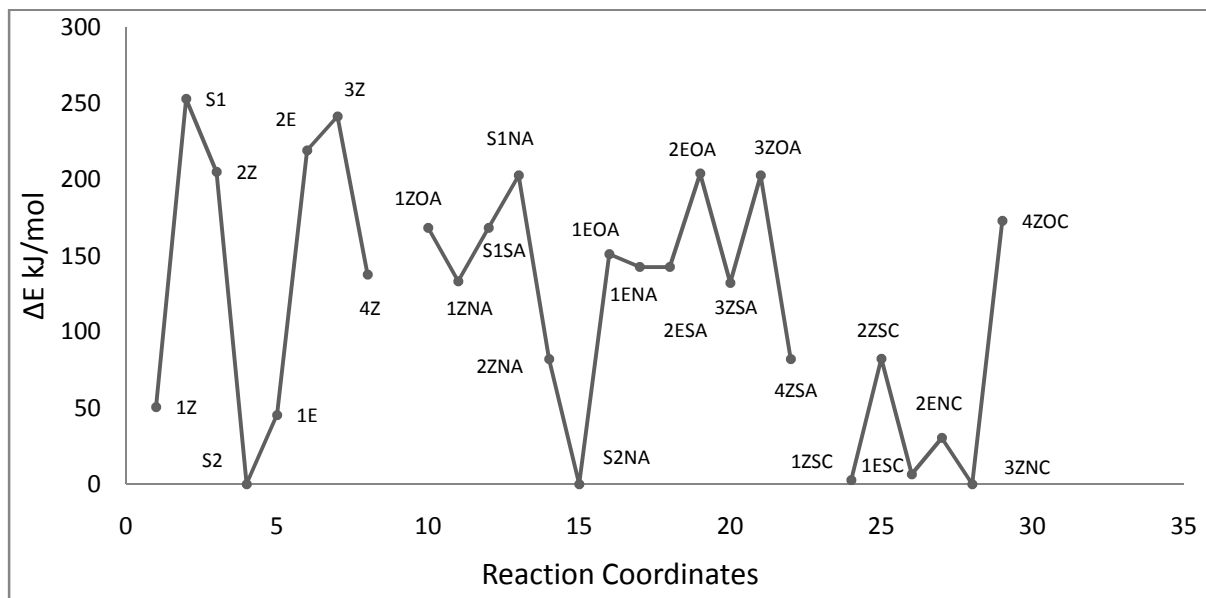**Fig. 1: The selected structures of the silathioformohydroxamic acid with anions and cations derivatives**

Figure 2: The relative energy (ΔE) profile of the tautomers, anions and cations derivatives of silathioformohydroxamic acid.
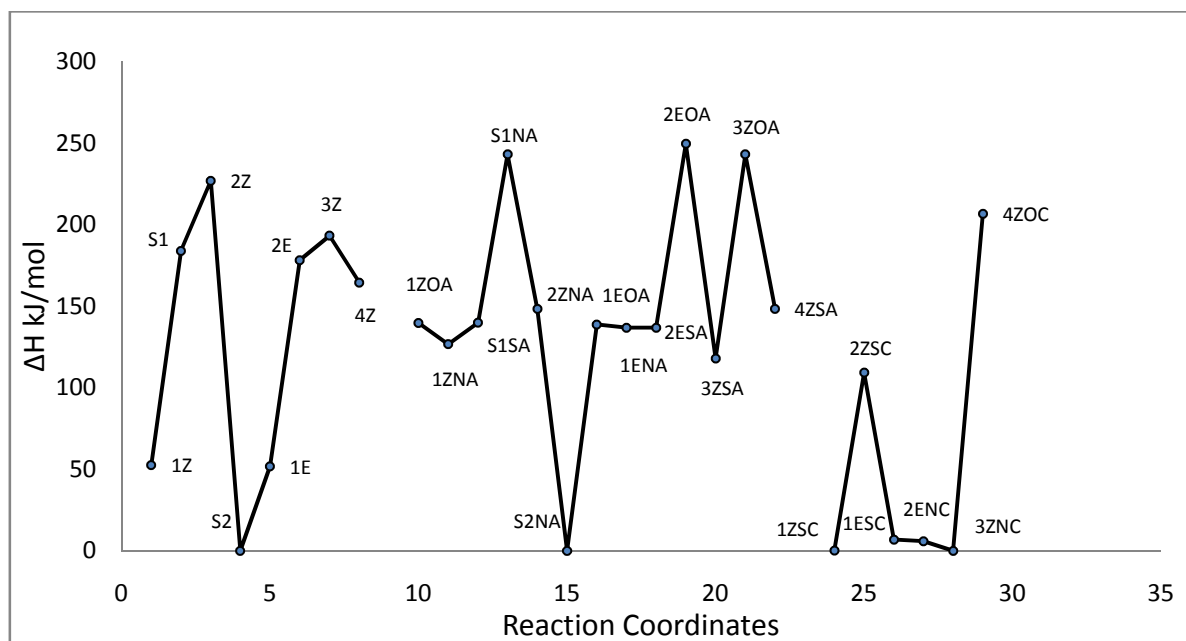
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Figure 3: The relative enthalpy (ΔH) profile of the tautomers, anions and cations derivatives of silathioformohydroxamic acid.

Table 2: The relative energies, enthalpies and free energies (KJ/mol) for the molecules at CBS-Q level of theory

Molecules	ΔE	ΔH	ΔG
1Z	50.74	52.67	49.17
S1	252.99	183.90	176.33
2Z	204.99	226.82	217.79
S2	0.00	0.00	0.00
1E	45.37	51.82	48.49
2E	219.26	178.21	171.67
3Z	241.53	193.26	184.95
4Z	137.59	164.49	156.46
Anions			
1ZOA	168.37	139.79	136.88
1ZNA	133.28	126.74	121.44
S1SA	168.37	139.81	136.91
S1NA	202.81	243.08	235.28
2ZNA	82.08	148.24	142.42
S2NA	0.00	0.00	0.00
1EOA	151.09	138.78	135.65
1ENA	142.68	136.84	130.07
2ESA	142.68	136.84	130.07
2EOA	204.09	249.57	240.62
3ZSA	132.19	117.93	113.80
3ZOA	202.81	243.08	235.29
4ZSA	82.08	148.24	142.42
Cations			
1ZSC	85.10	82.06	74.16
S2SC	0.00	0.00	0.00
2ZSC	194.02	186.25	144.45
1ESC	91.72	87.77	77.68
2ENC	90.71	87.77	97.66
3ZNC	84.81	82.12	71.43
4ZOC	291.41	285.12	234.13

The S2 tautomer is located as a global minimum on the reaction coordinates at the CBS-Q level of calculation and the energy values are reported related to S2 in the silathioformohydroxamic acid tautomers. The 1E and 1Z conformers have the lowest energies (45.37 and 50.74 kJ/mol) above the S2 energy. The 2Z and 3Z have the highest energies (204.99 and 241.53 kJ/mol) above the global minimum S2. The stability order of the tautomers are 1E>1Z>4Z>2Z>2E>3Z>S1. The anions study revealed that the 4ZSA has the lowest energy (82.08 kJ/mol) above the S2NA and the 2EOA possessed the highest energy (204.09 kJ/mol) related to global minimum in anions section S2NA. The cations energies exhibited the 3ZNC as a global minimum in the cation section. The 1ZSC tautomer had

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the lowest energy (2.73 kJ/mol) above the 3ZNC whereas the 4ZOC tautomer was the highest energy form above the cations global minimum 3ZNC tautomer. The relative enthalpies and Gibbs free energies are listed in Table 2.

Again, the values of ΔH and ΔG are reported related to S2 in the silathioformohydroxamic acid because S2 possessed the lowest ΔH and ΔG values. The 2EOA showed the highest relative enthalpy and Gibbs free energy (ΔH= 249.57 kJ/mol, ΔG=240.62 kJ/mol) in the anions section and the 4ZOC showed the highest relative enthalpy and Gibbs free energy (ΔH= 285.12 kJ/mol, ΔG=234.13 kJ/mol) in the cations section. The ionization of substituted hydroxamic acids have been investigated experimentally and in the gas phase [15]. Nevertheless, no ionization or protonation of silathioformohydroxamic acid has been studied. The acidities and basicities of silathioformohydroxamic acid are presented in Table 3.

Table 3: The gas-phase acidity, basicities (enthalpies ΔH , Gibbs free energies ΔG in kJ/mol) and the equilibrium constants of the reactions at CBS-Q level of theory at 298.15 K.

Reaction	ΔH^{298}	ΔG^{298}	K_{eq}
1Z + H+ → 1ZSC	-820.75	-819.85	1.12E+107
2Z + H+ → 2ZSC	-893.21	-884.29	2.89E+115
S2 + H+ → S2SC	-846.70	-852.75	2.21E+111
1E + H+ → 1ESC	-812.11	-813.47	1.64E+106
2E + H+ → 2ENC	-953.64	-936.65	1.98E+122
3Z + H+ → 3ZNC	-1002.81	-955.57	5.87E+124
4Z + H+ → 4ZOC	-726.68	-724.09	3.51E+94
1Z - H+ → 1ZOA	1511.27	1445.57	1.78E-189
2Z - H+ → 2ZNA	1274.52	1282.49	3.51E-168
S2 - H+ → S2NA	1392.88	1357.86	5.05E-178
1E - H+ → 1ENA	1491.10	1439.44	1.12E-188
2E - H+ → 2EOA	1380.60	1426.80	5.02E-187
3Z - H+ → 3ZOA	1356.69	1408.20	1.34E-184
4Z - H+ → 4ZSA	1351.38	1343.81	3.44E-176

The enthalpy of deprotonation may be computed between two arbitrary species. Those between two species with most similar structures (1E and 1EOA), for example, the reaction (1E → 1EOA + H⁺) might be of theoretical interest, but only the differences between the most stable species can have physical meaning and can be compared with experiments. Of the six anions of silathioformohydroxamic acid (1ZOA, 2ZNA, 1ENA, 2EOA, 3ZOA and 4ZSA) two anions with equal energies are located in deprotonation processes; S-anion for 4ZSA and the N-anions are the most stable. Previously reported results of formohydroxamic acid are predicated to behave as an N-acid in the gas-phase [16]. Energetically easiest process is the deprotonation of 2ZNA with the computed enthalpy and Gibbs free energy of 1274.52 kJ/mol and 1282.49 kJ/mol. The equilibrium constants of the processes are given in Table 4. The equilibrium constants at 298.15 K of the deprotonation reactions are very small which means the reaction at this temperature favor the reactants and the protonation reactions at the same temperature showed a reverse trend.

The computed vibrational frequencies are calculated at MP2(Full)/6-31(d) level, the infrared frequencies are listed in Table 4.

Table 4: Calculated MP2(Full)/6-31G(d) vibrational frequencies (cm⁻¹) of some selected tautomers of silathioformohydroxamic acid

1Z		1E		2E		4Z	
130		111		129		70	
204		169		139		93	
244		296		200		183	
398		363		276		363	
481		466		279		487	
527		589		452		503	
633		675		518		585	
753		827		676		642	
918		848		749		775	
1068	υ(N-O)	1038	υ(N-O)	839		859	
1332		1339		1018	υ(N-O)	918	
1364		1342	υ(N….HO)	1357	υ(N….HO)	1358	υ((N=O)
2196	υ(Si-H)	2224	υ(Si-H)	2197	υ(Si-H)	2193	υ_s(Si-H)
3393	υ(N-H)	3397	υ(N-H)	2609	υ(S-H)	2232	υ_{as} (Si-H)
3502	υ(O-H)	3505	υ(O-H)	3537	υ(O-H)	2613	υ(S-H)

The 2E isomer showed a υ(SH) at 2609 cm^{-1} which is excellent agreement with previously reported experimental results [16,17]. The vibration stretching frequencies for υ(SiH), υ(Si-N) and υ(NO) are observed at 2197 and 1018 cm^{-1} respectively. The experimental value for υ(Si-H) stretching is 2167 cm^{-1} [18], which is in conformity with the current value of 2197 cm^{-1}. The intramolecular hydrogen bonding stretching frequencies are noted for 2E and 1E isomers. The computed stretching frequencies for 1Z and 4Z structures are in accord with the expected values for υ(OH) and υ(NH), the υ(N=O) in 4Z is observed at 1358 cm^{-1} and the υ(SH) is noted at 2613 cm^{-1}. The expected shift towards the lower frequency of υ(NH) in 1E and 2E, which has been attributed previously to intramolecular hydrogen bonding, is not noted, this is clearly due to the basis set influence.

REFERENCES

[1] Deng HW, Jia JH, *J. Phys. Chem. A*, **1988**, 102, 3582.

[2] El yazal J, Ping PY, *J. Phys. Chem*. A **1999,** 103, 8324.

[3] Remko M, Lyne PD, Richards, WG, *Phys. Chem. & Chem. Phys*. **1999**, 1, 5353.

[4] Stinchomb M D, Pranata J*, J. Mol. Struct*. (Theochem) **1996**, 370, 25.

[5] Bagno A, Comuzzi C, Scorrano G, *J. Amer. Chem. Soc*. **1994**, 116, 916.

[6] Petersson GA, Al-Laham MA, *J. Phys. Chem*. **1991,** 94, 6081.

[7] Montgomery JA, Ochterski JW, Peterson GA*, J. Phys. Chem*. **1994,** 101, 5900.

[8] Peterson GA, Tensfeldt T, Montgomery JA, *J. Phys. Chem*. **1991,** 94, 6091.

[9] Ochterski JW, Peterson GA, Montgomery JA, *J. Phys. Chem*. **1996,** 104, 2598.

[10] Scott AP, Radom L, *J. Phys. Chem.;* **1996** 100, 16502.

[11] Gaussian 03, Revision C.02. Gaussian, Inc., Wallingford CT, **2004**.

[12] Sohn WY, Lee JS, *J. Phys. Chem. A*, **2010**, 114, 7537.

[13] Csonka G, Elias K, Csizmadia G, *Chem. Physi. Lett*. **1996**, 257, 49.

[14] Allen FA, Kennard O, Watson DG, Brammer L, Orpen GA, Taylar R, *J. Chem. Soc. Perkin Trans* 2. **1987** S1.

[15] Dissanayake D. P, Senthilnithy R, *J. Mol. Struct*. (Theochem), **2009**, 910, 93.

[16] Kakkar R, Dua A, Zaidi S, *J. Org. Biomol. Chem*. **2007**, 5, 247.

[17] Yuen CW, Ku SK. A, Choi PS, Kan CW, Tsang YS, *Res. J. Texti. & App*. (RJTA). **2005**, 9, 25.

[18] Mitzel NW, Christoph C, Rankin DW, *Organometal*. **1999**, 18, 3437.