Structure and gas-phase acidity of oxalic acid and its disila derivative. A theoretical study by means of the DFT quantum theoretical method

Milan Remko,[*,a] **Klaus R. Liedl**[b] **and Bernd M. Rode**[b]

[a] *Department of Pharmaceutical Chemistry, Comenius University, Odbojarov 10, 832 32 Bratislava, Slovakia*

[b] *Theoretical Chemistry Division, Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a, 6020 Innsbruck, Austria*

Density functional theory at the B3LYP/6-311 + G* level has been used to study the rotational conformers, gas-phase acidities and vibrational spectra of oxalic and disilaoxalic acid. For oxalic acid the geometry with two five-membered intramolecular hydrogen bonds is calculated to have the lowest energy. In the absence of the stabilizing effect of intramolecular H bonds in disilaoxalic acid (due to the elongation of the M–M distance to 2.35 Å) the most stable conformer corresponds to a rectangular structure making the angle between the two SiOOH groups equal to 90°. The energies calculated for stable conformers lie within 4 kcal mol^{-1}.† Experimental and B3LYP computed geometries of oxalic acid agree well. Disilaoxalic acid is, according to calculated ionizations of the first and second hydrogen, about 10–25 kcal mol^{-1} more acidic than its carboxylic acid analogue. Oxalic and disilaoxalic acid are about 15 and 25 kcal mol^{-1} stronger acids than formic and silanoic acid, respectively. Computed vibrational frequencies for oxalic, formic and silanoic acids were on average 1–3% higher than the observed values.

Introduction

The structure of oxalic acid and its protonated and deprotonated species has not been the subject of many theoretical investigations yet. Recent papers focus attention on the rotamerization and photochemical decomposition[1–4] of the oxalic acid monomer, interpretation of hydrogen bonding in the oxalic acid dihydrate[5,6] and structural investigations of oxalic acid, itself.[3–7] The protonated species has been dealt with only once[3] and the structure of oxalic acid anions has not been reported. The existence of the silicon analogue of oxalic acid, disilaoxalic acid, has not been proved experimentally and therefore no structural details are available. However, the geometry, deprotonation and decomposition energies of the amino-substituted derivative of silanoic acid, silacarbamic acid, have been investigated recently.[8,9]

The present paper reports the results of a systematic theoretical examination of oxalic acid and its anions. Of particular interest are the molecular geometries, ionization energies, dipole moments, IR frequencies and how these properties change upon the isosteric substitution of both carbon atoms in oxalic acid by silicon. The structures investigated are shown in Fig. 1 together with the notation of their conformations and the atom numbering scheme. The symbols *C* and *T* are used for the M–M conformation (the dihedral angle O=M–M=O; C, *cis*; T, *trans*). The conformations involving the M–OH bond (*i.e.* the OH rotation angles) are denoted by *c*, *t* (*cis*, *trans*) and given first and last (the dihedral angle H–O–M–M, where M=C, Si).

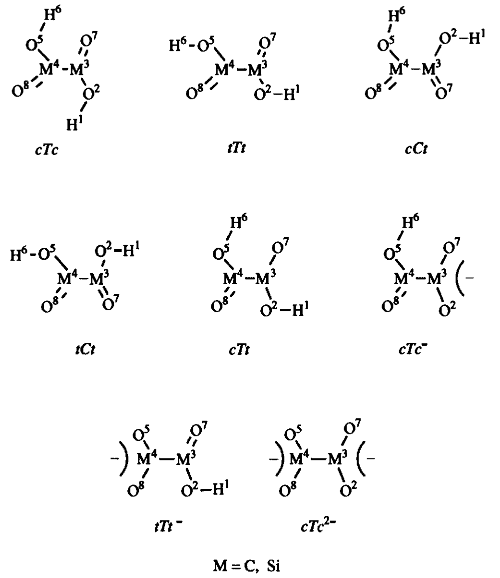

Fig. 1 Structures and atom labelling in the oxalic and disiloxalic acid species studied

Computational details

The geometries of oxalic acid, its disila-derivative and their anions (Fig. 1) were fully optimized with the GAUSSIAN-92/DFT[10] program. We used the density functional theory (DFT)[11–13] at the Becke3LYP DFT level[11,14] with the polarized spin-valence 6-311 + G* basis set.[15–17] Recent results have shown[18] that the Becke3LYP DFT performance compares well with the correlated Hartree–Fock calculations of equilibrium geometries and ionization energies and, therefore, considering its accuracy and speed, is highly attractive. Vibrational frequencies at the Becke3LYP/6-311 + G* level for the acids and their anions characterized the stationary points and gave zero-point energies (ZPE). The gas-phase acidity was defined as the enthalpy of deprotonation (ΔH^{298}) for reaction (1).

$$\mathrm{AH} \longrightarrow \mathrm{A}^- + \mathrm{H}^+ \qquad (1)$$

The enthalpy of deprotonation, ΔH^{298}, was computed using

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† 1 cal = 4.184 J.

Table 1 Total energies (in au), zero-point energies and dipole moments of oxalic acid, its disila-derivatives, isomers and anions

		B3LYP/6-311+G*‖B3LYP/6-311 + G*			
Species	Form	E^{298}[B3LYP (NIMAG)][a]	E^{298}[B3LYP + TE][b]	E_{zp}[c]/kcal mol^{-1}	μ[d]/D
$(COOH)_2$	*cTc*	−378.440 253(0)	−378.385 583	31.0	0
	tTt	−378.436 215(0)	−378.381 782	30.65	0.01
	cCt	−378.433 372(0)	−378.379 408	30.35	5.07
	tCt	−378.435 793(0)	−378.381 465	30.57	2.91
	cTt	−378.437 253(0)	−378.382 759	30.81	3.43
	cTc$^-$	−377.925 977(0)	−377.884 911	22.60	
	tTt$^-$	−377.912 548(0)	−377.871 742	22.14	
	cTc^{2-}	−377.214 947(0)	−377.186 789	14.46	
HCOOH	*syn*	−189.819 887(0)	−189.782 957	21.19	1.48
$HCOO^-$		−189.271 540(0)	−189.248 598	12.53	
$(SiOOH)_2$	*cTc*	−881.330 560(0)	−881.285 687	23.10	0.02
	tTt	−881.335 505(0)	−881.290 408	23.28	3.97
	cCt	−881.330 284(0)	−881.285 210	23.31	6.78
	tCt	−881.335 506(0)	−881.290 408	23.28	4.01
	cTt	−881.332 025(0)	−881.287 045	23.19	3.52
	cTc$^-$	−880.833 843(0)	−880.800 231	16.61	
	tTt$^-$	−880.828 530(0)	−880.795 417	16.01	
	cTc^{2-}	−880.163 739(0)	−880.142 404	9.00	
HSiOOH	*syn*	−441.260 352(0)	−441.230 681	16.21	3.08
$HSiOO^-$		−440.724 958(0)	−440.707 622	8.72	

[a] Number of imaginary frequencies: 0 = minimum. [b] Total energy plus thermal energy correction in au (1 au = 627.5095 kcal mol^{-1}). [c] Unscaled zero-point energies. [d] 1 D = 3.33564×10^{-30} C m.

eqns. (2) and (3), where E^{298} stands for the total energies of

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

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

acids and their anions (including the thermal energy correction at $T = 298.15$ K). For the work term in eqn. (2) we substituted $pV = RT$[one mol of gas is obtained in the reaction (1)]. Basis set superposition error (BSSE) corrections were not applied as they are expected to be small. The calculations were performed on an IBM-RS 6000/375 workstation.

Table 2 Relative energies (in kcal mol^{-1}) of various conformers of oxalic acid and its disila-derivative

	Compound	
	$(COOH)_2$	$(SiOOH)_2$
cTc	0	3.10
cTt	1.88	2.18
tTt	2.53	0
tCt	2.80	0
cCt	4.32	3.27

Results and discussion

General energetic considerations

The total energies and dipole moments of all calculated species are listed in Table 1 and the relative energies of various rotamers with respect to the most stable structures of acids in Table 2. Since an electron diffraction investigation[19] indicated that oxalic acid might be planar, our preliminary calculations began with the planar structures shown in Fig. 1. An analysis of the harmonic vibrational frequencies of the optimized planar species revealed that some planar structures have a rather large imaginary frequency and therefore do not correspond to the stationary points on the potential-energy surface. Finally, the non-planar conformers (in which the carboxy groups are oriented perpendicular to each other) were found to be the most stable structures for the *tTt* and *tCt* conformers of disilaoxalic acid, *tTt* for the monoanion of oxalic and disilaoxalic acids and dianions of both acids. These non-planar structures deviate from planarity in two ways. The more important is the non-planar conformation around the central C–C and Si–Si bonds displacing the oxygen atoms of one MO_2 group (M=C, Si) out of the plane of the second MO_2 moiety. Less important is the slightly non-planar configuration of the hydroxy groups. Both features can be rationalized by considering the relative importance of intramolecular hydrogen bonds and the unfavourable repulsion when negative charges of the carboxylate anions are close to each other. The intramolecular hydrogen bonds (H bonds) may form five-membered rings in the *cTc*, *cCt* and *cTt* conformers of the neutral acids as well as the *cTc* monoanions (Fig. 1) and hence stabilize planar structures. The net repulsion among oxygens in the *tTt* and *tCt* conformers of disilaoxalic acid and the *tTt*$^-$ and *cTc*$^{2-}$ anions of both acids seems responsible that the more stable non-planar structures were found for these species.

The relative stabilities of conformers of oxalic and disilaoxalic acids (Table 2) are the result of the balance between H-bond stabilization and the oxygen's electrostatic repulsion as discussed above. Two H bonds in the *cTc* conformer of oxalic acid causes this form to be the most highly populated species (94% at 298.15 K). The second conformer (stabilized by one intramolecular H bond) is 1.9 kcal mol^{-1} less stable and occurs with 4% probability. The substantial elongation of the M–M distance to about 2.35 Å in disilaoxalic acid causes a considerable weakening of the stabilizing effect of intramolecular H bonding in these compounds. In the absence of any conjugation between both silacarbonyl groups the most stable conformers are the non-planar and energetically equivalent *tTt* and *tCt* forms. The relative ordering of stable conformers of oxalic acid calculated using the DFT theory is the same as that obtained by the MP2/6-31G** HF method.[3] Among two possible monoanions (*cTc*$^-$ and *tTt*$^-$, Fig. 1) the *cTc*$^-$ species of oxalic and disilaoxalic acid are, due to the intramolecular H bond, 8.4 and 3.3 kcal mol^{-1} more stable. Table 1 also contains, for reasons of comparison, the total energies of fully optimized parent monobasic acids (formic and silanoic acids, respectively) and their anions.

The dipole moments of the different conformers of oxalic acid were of particular interest to us because their experimental values were used[20,21] in determining the conformations of various dibasic acids in solution. Our computed value for the

Table 3 Optimized geometries of various rotamers of acids studied and their ionized species (Fig. 1)

	Exp[b]	*cTc*		*tTt*		*cCt*		*tCt*	*cTt*		*cTc*$^-$		*tTt*$^-$		*cTc*$^{2-}$	
Parameter[a]	$(COOH)_2$	$(COOH)_2$	$(SiOOH)_2$	$(COOH)_2$	$(SiOOH)_2$	$(COOH)_2$	$(SiOOH)_2$	$(COOH)_2$	$(COOH)_2$	$(SiOOH)_2$	$(COOH)_2$	$(SiOOH)_2$	$(COOH)_2$	$(SiOOH)_2$	$(COOH)_2$	$(SiOOH)_2$
O2–H	1.056	0.975	0.964	0.971	0.964	0.970	0.965	0.971	0.971	0.964			0.972	0.965		
O2–M3	1.339	1.325	1.625	1.339	1.632	1.360	1.648	1.360	1.325	1.624	1.231	1.544	1.372	1.675	1.266	1.573
M3–M4	1.548	1.549	2.348	1.544	2.338	1.553	2.359	1.544	1.549	2.346	1.595	2.388	1.554	2.373	1.574	2.401
M4–O5	1.339	1.325	1.625	1.338	1.633	1.343	1.629	1.341	1.338	1.628	1.352	1.658	1.245	1.549	1.266	1.573
O5–H	1.056	0.975	0.964	0.970	0.965	0.970	0.966	0.971	0.973	0.965	0.994	0.979				
M3–O7	1.208	1.203	1.526	1.199	1.526	1.191	1.524	1.197	1.209	1.531	1.268	1.563	1.214	1.546	1.266	1.573
M4–O8	1.208	1.203	1.526	1.199	1.526	1.191	1.522	1.197	1.193	1.523	1.205	1.540	1.245	1.550	1.266	1.573
H–O2–M3	104.4	108.7	123.8	107.8	123.8	109.5	123.4	108.1	108.8	125.0			105.7	115.7		
O2–M3–M4	111.9	113.6	111.9	110.2	104.9	110.6	98.7	112.7	113.0	111.8	118.0	122.5	112.9	109.3	116.8	114.8
M3–M4–O5	111.9	113.6	111.8	110.1	105.3	115.3	106.6	112.7	111.3	104.9	110.0	99.6	113.9	109.0	116.8	114.8
M4–O5–H	104.4	108.7	123.5	108.0	123.3	111.0	120.8	108.0	109.4	122.2	101.1	108.4				
M4–M3–O7	123.1	121.3	119.7	124.5	125.0	124.7	132.5	122.0	121.4	116.8	110.9	96.7	127.5	132.7	116.8	114.8
M3–M4–O8	123.1	121.3	119.8	124.5	124.7	121.2	125.4	122.0	124.2	127.2	127.7	138.3	113.9	109.6	116.8	114.8
H–O2–M3–M4		0.0	0.0	180.0	184.6	180.0	180.0	180.0	180.0	180.0			179.9	179.5		
O2–M3–M4–O5		180.0	180.0	180.0	261.8	0.0	0.0	0.0	180.0	180.0	180.0	180.0	268.5	269.3	−90.0	−90.0
M3–M4–O5–H		0.0	0.0	180.0	182.8	0.0	0.0	180.0	0.0	0.0	0.0	0.0				
O5–M4–M3–O7		0.0	0.0	0.0	83.6	180.0	180.0	180.0	0.0	0.0	0.0	0.0	88.5	88.9	−90.0	−90.0
O2–M3–M4–O8		0.0	0.0	0.0	83.3	180.0	180.0	180.0	0.0	0.0	0.0	0.0	89.2	89.7	90.0	90.0

[a] Bond lengths in Å and bond angles in degrees. [b] Electron diffraction results, see ref. 19.

tCt conformer (Table 1) can be compared with the experimental dipole moment (in dioxane) of the oxalic acid (2.63–3.03 D, refs. 20–22) which probably possesses this conformation in solution. The known strong effect of the intramolecular H bonds on the dipole moments[23] is also supported by our investigations. In the isolated molecule of oxalic acid the most stable structure, *cTc*, is characterized by two intramolecular H bonds and zero dipole moment (Table 1). For formic acid our computed value of the dipole moment (1.51 D) fits well the experimental gas-phase dipole moment of the formic acid monomer (1.415 D, ref. 24).

Molecular structures

The fully optimized geometries of the compounds under study are given in Table 3 along with the available experimental values.[19] The *tTt* and *tCt* conformers of disilaoxalic acid are enantiomers and therefore we do not show geometric data for both species. The most important differences in geometries among various rotamers of neutral acids are connected with the stabilizing effect of the five-membered rings of intramolecular H bonds. The inspection of the distances between non-bonding H • • • O atoms in the *cTc*, *cCt* and *cTt* conformers of oxalic acid shows that these lengths are within the range of 2.0–2.1 Å, which is substantially less than the sum of the van der Waal's radii (2.6 Å) for the oxygen and hydrogen atoms. In the rotamers of disilaoxalic acid the H • • • O distances are substantially higher than the sum of the van der Waal's radii [one exception is the *cCt* conformer with $R(\mathrm{O}\cdots\mathrm{H}) = 2.5$ Å, the distance of an intramolecular H bond] and intramolecular polarization by means of the H bond does not play any part. The stabilization of the *cTc* conformer of oxalic acid by means of two intramolecular O–H • • • O=C H bonds compensates the increase in energy associated with the creation of two *anti* HO/C=O carbonyl configurations. For the case of formic and silanoic acids the potential energy minimum of the *anti* conformers was computed by us to occur 4.9 and 3.9 kcal mol^{-1} above the minimum for the *cis* configuration. The computed M–M distances (M=C, Si) (about 1.55 Å for oxalic acid and 2.35 Å in the disilaoxalic acid) correspond to the normal C–C (1.54 Å) and Si–Si (2.34 Å) bonds. This indicates that there is no conjugation between the two carboxy groups in these acids. The barrier to internal rotation for the *tTt* conformer of oxalic acid was indeed computed to be very low[1] (less than 1 kcal mol^{-1}). This barrier is apparently absent for disilanoic acid. The *tTt* and *tCt* rectangular structures of this acid are computed to be more stable by 1.3 and 1.8 kcal mol^{-1} than their planar forms.

The electron diffraction data reported by Nahlovska *et al.*[19] for oxalic acid are also shown in Table 3. On the basis of IR and electron diffraction measurements they decided for the *cTc* conformer. Comparison of the observed and calculated geometries listed in Table 3 shows the largest discrepancies in the lengths of the O–H and C–O bonds and corresponding C–O–H angles. This suggests that the strength of the H bonding is rather underestimated at the B3LYP DFT level of theory. The stabilizing effect of the intramolecular H bond results in the most stable planar cTc^- structures for both acids. The tTt^- monoanions and dianions $(\mathrm{MOO})_2{}^{2-}$ (M=C, Si) are the most stable non-planar species in which the planes of both MOO groups form an angle of about 90° (Table 3).

Gas-phase acidities

The ionization of carboxylic acids has been well studied experimentally,[25,26] and recently even in the gas phase.[27,28] The isosteric simple silacarboxylic acids are unstable compounds and no ionization and/or protonation of these compounds have been studied experimentally. Table 4 contains acidities of oxalic and disilaoxalic acids and, for reasons of comparison with the acidities of parent monohydric acids, also formic and silanoic acids, respectively. With respect to the possible existence of several stable rotational conformers of oxalic and disilaoxalic acids the enthalpies of deprotonation may be calculated between two arbitrary species. Table 4 contains all possible reactions for mono- and di-ionization of the acids studied. Of particular interest are, however, the reaction paths connected with the lowest (positive) enthalpy changes corresponding to the highest acidities. The deprotonation of the five rotamers of oxalic and disilaoxalic acids may proceed *via* two reactions paths and lead to the cTc^- and/or tTt^- anions. Out of seven possible reactions (Table 4) only the differences between the most stable conformers can have a physical meaning. Thus, the energetically easiest process could be the deprotonation of the *cTc* rotamer of oxalic acid and the *tTt* (*tCt*) conformer of disilaoxalic acid. However, the least endothermic reaction is, for both acids, the deprotonation of the *cCt* conformer and subsequent stabilization of the cTc^- anion *via* an intramolecular H bond.

The experimentally determined p*K* values[29] for formic acid (3.75) and oxalic acid (p*K* = 1.27; p*K* = 4.27) tell us that monoionization of oxalic acid is a much stronger acid than formic acid. On the other hand, the dissociation of the second proton is less favourable than the ionization of the formic acid. Computed reaction enthalpies (Table 4) for formic and oxalic acid show that the gas-phase acidities of these acids also follow the same order: $(\mathrm{COOH})_2(\mathrm{I}) < \mathrm{HCOOH} < (\mathrm{COOH})_2(\mathrm{II})$.

The higher acidity of oxalic acid can be explained by the electron-withdrawing influence of one carboxy group on the other. Moreover, the HOOC–COO$^-$ anion is stabilized by an intramolecular H bond (Table 3). The dissociation of the second proton in the monoanion of oxalic acid leads to a repulsion of the negative charges of two carboxylate groups (the most stable structure of this anion is non-planar, Table 3) resulting in a higher dissociation enthalpy and thus lower acidity in comparison with formic acid.

The acidity of silanoic and disilanoic acids must be quite different to those for carboxylic acids. Silicon has an electronegativity substantially lower (1.74) than that of carbon (2.5). In addition to this, one might expect silicon to be considerably more electron deficient than carbon in the carboxy compounds. The enhanced polarization of the Si–O

Table 4 B3LYP/6-311 + G*//B3LYP/6-311 + G* calculated gas-phase acidities

		$\Delta H^{298}(\mathrm{I})$/kcal mol^{-1}			$\Delta H^{298}(\mathrm{II})$/kcal mol^{-1}	
No.	Reaction	$(\mathrm{COOH})_2$	$(\mathrm{SiOOH})_2$	Reaction	$(\mathrm{COOH})_2$	$(\mathrm{SiOOH})_2$
1	$cTc \rightarrow cTc^-$	315.7	306.1	$cTc^- \rightarrow cTc^{2-}$	439.6	414.3
2	$cCt \rightarrow cTc^-$	311.8	305.8	$cTc^- \rightarrow cTc^{2-}$	439.6	414.3
3	$cCt \rightarrow tTt^-$	320.0	308.8	$tTt^- \rightarrow cTc^{2-}$	431.3	411.3
4	$cTt \rightarrow cTc^-$	313.9	307.0	$cTc^- \rightarrow cTc^{2-}$	439.6	414.3
5	$cTt \rightarrow tTt^-$	322.1	310.0	$tTt^- \rightarrow cTc^{2-}$	431.3	411.3
6	$tTt \rightarrow tTt^-$	321.5	312.1	$tTt^- \rightarrow cTc^{2-}$	431.3	411.3
7	$tCt \rightarrow tTt^-$	321.3	312.1	$tTt^- \rightarrow cTc^{2-}$	431.3	411.3
8	HCOOH—HCOO$^-$	336.8				
9	HSiOOH—HSiOO$^-$	329.7				

Table 5 Calculated harmonic B3LYP/6-311 + G* vibrational frequencies for acids studied

	$(COOH)_2$							HCOOH			$(SiOOH)_2$					HSiOOH		
		Calc./obs.																
No.	Obs.[a]	*cTc*	*cTc*	*cTt*	*tTt*	*tCt*	*cCt*	Obs.[b]	Calc./obs.	Calc.	*cTc*	*cTt*	*tTt*	*tCt*	*cCt*	Obs.[c]	Calc./obs.	Calc.
1			3632	3710	3723	3709	3721	3570	1.04	3699	3822	3831	3821	3821	3809			3837
2	3472	1.04	3631	3657	3721	3707	3718	2944	1.04	3076	3820	3804	3819	3819	3803			2287
3	1817	1.02	1850	1872	1838	1846	1877	1776	1.02	1819	1256	1264	1248	1248	1269	1249	1.0	1247
4	1800	1.02	1831	1792	1826	1830	1863	1387	1.02	1412	1253	1234	1241	1241	1244	891	1.03	923
5	1423	1.01	1437	1425	1403	1411	1348	1221	1.06	1300	914	933	934	934	916			868
6	1329	1.01	1337	1338	1331	1308	1321	1105	1.02	1133	887	887	892	892	867			785
7	1195	1.02	1218	1210	1216	1182	1154	1033	1.01	1047	785	798	787	787	831			592
8	1138	1.05	1197	1163	1145	1166	1121	641	1.1	708	749	744	780	780	798			487
9	815	1.01	824	832	846	846	822	625	1.01	630	452	498	487	487	481			321
10	810	1.01	822	803	787	785	781				432	448	475	477	459			
11	664	1.07	708	671	679	695	655				429	439	457	456	442			
12	651	1.07	697	661	642	645	633				328	315	299	299	314			
13	609	1.11	677	658	622	609	527				269	282	291	290	283			
14	538	1.04	561	544	527	512	504				229	221	284	284	228			
15	461	1.01	466	437	426	431	429				212	211	213	213	224			
16	405	1.01	408	424	422	418	423				196	198	114	113	193			
17	264	1.01	268	269	265	269	282				74	78	109	109	109			
18	89	1.34	120	86	22	11	53				54	40	31	30	39			

[a] Ref. 31. [b] Refs. 32 and 33. [c] Ref. 34.

bonds in comparison with the C–O bonds is also manifested in the larger dipole moments of the sila derivatives (Table 1). The computed acidities of silanoic and disilaoxalic acids are about 6–20 kcal mol^{-1} lower than the analogous values of the parent carboxylic acids (Table 4). Thus, both silanoic and disilaoxalic acids are stronger than their carbon analogues. The calculated acidities decrease in the order: $(SiOOH)_2 > (COOH)_2 > HSiOOH > HCOOH > HOOSiSiOO^- > HOOCCOO^-$. The higher acidity of sila-derivatives than their carbon isosteres could be explained by the concept of polarizability (softness) and electronegativity, which show opposite trends in a given column of the periodic table. These two effects are shown[30] to be competing. Although silicon is less electronegative than carbon, it is softer[30a] and therefore exhibits a larger charge capacity. The increased softness could lead in the gas phase to an increased stabilization of negative charge close to it which results in higher acidity of silicon acids. The same squences in acidity were recently obtained with alcohols and silanols.[30b] The silanols were found to be about 10–20 kcal mol^{-1} more acidic.

The computed acidity of formic acid is about 2.4% lower than the experimentally determined value (345.2 kcal mol^{-1}) of Cumming and Kebarle.[27]

Infrared spectra

Table 5 gives the harmonic vibrational frequencies of oxalic, disilaoxalic, formic and silanoic acid, respectively. The matrix isolation data of oxalic[31] and silanoic[34] acids and vapour phase spectra of formic acid[32,33] are also listed in this Table. The relatively large frequency shifts among various rotamers of oxalic and disilaoxalic acids are evidently associated with an opening of the intramolecular H bonds of the *cTc* conformer. The experimental spectrum of oxalic acid is well interpreted by the theoretically computed one for the *cTc* conformer (Table 5). The calculated frequencies are generally higher, however, the data of Table 1 shows that the bond lengths of oxalic acid were computed to be too short, especially the O–H and C–O bonds. These shortened bonds mean that vibrational frequencies computed with the Becke3LYP method are somewhat higher. The average increase for the set of three acids studied is not high (about 1–3%). The larger differences between the observed and computed IR spectra of oxalic acid (bands at about 600–650 cm^{-1}, and a low frequency 89 cm^{-1} band) could be partly ascribed to the uncertainties by the determination of these frequencies from IR combination mode (609 cm^{-1}) and/or to the induced matrix shift.

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