

# Silanones and metasilicates<sup>☆</sup> from negatively charged $\equiv\text{SiO}^{(-)}$ and $=\text{SiO}_2^{(2-)}$ precursors. Theoretical study

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## Abstract

Ab initio calculations were performed to compare the electronic effects in unionized, partly and fully ionized silanols,  $\text{XH}_2\text{SiOH}$ , and silanediols,  $\text{XHSi(OH)}_2$ ,  $\text{X} = \text{H, OH, OSiH}_3, \text{Cl}$ . The delocalization energy strongly increases on ionization. The silicon bond to negatively charged oxygen is significantly shortened gaining a partial double bond character, while the adjacent bonds to geminal oxygen, chlorine and hydrogen are elongated and effectively weakened. The weakening of the Si–X bond is particularly large in the dianionic structures,  $\text{XHSiO}_2^{(2-)}$ . The delocalization energy in neutral silanols is mainly due to the negative hyperconjugation ( $p_{\text{O}} \rightarrow \sigma_{\text{Si-X}}^*$ ). In silanolate anions, the ( $p_{\text{O}} \rightarrow d_{\text{Si}}$ ) $_{\pi}$  delocalization becomes more important. Thermodynamic parameters were calculated for the transformation of some ionized silanols,  $\text{X(HO)}_n\text{H}_{2-n}\text{SiO}^{(-)}$ , and silanediols,  $\text{XHSiO}_2^{(2-)}$  into silanones and metasilicates, respectively, by elimination of  $\text{X}^{(-)}$ . In the gas phase, the formation of silanones by this route is energetically very costly. However, thermodynamical calculations suggest that the process may occur in a polar solvent. In contrast, the formation of metasilicates is thermodynamically favoured even in the gas phase. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Silanols; Silanolates; Silanones; Metasilicates; Electronic effects; Ab initio

## 1. Introduction

Silanones are very important intermediates in high temperature organosilicon chemistry in the gas phase [1–4]. They are also transient species in reactions of organosilicon compounds in electronically excited states or in a high-energy radiation induced processes [1–6]. Some of these reactions are used in the industrial techniques, such as chemical vapour deposition (CVD), etching in lithography and generation of ceramic materials by pyrolysis of organosilicon precursors, see for example Refs. [7–9].

On the other hand, many attempts have been made to rationalize various transformations of organosilicon reactants in solution on the ground of mechanisms involving silanone intermediates, for review see Refs. [2–4,10]. However, although the intermediacy of

silanone is well established in the gas phase processes [11,12], silanone in solution is the elusive species. Evidence for transient formation of these species comes mostly from the isolation of products of their expected reactions with trapping agents [13–16]. Usually, alternative pathways leading to these products are possible which do not invoke silanone as intermediate [17,18].

More extensive knowledge on the generation, structure, physical properties and chemical behaviour of silanones is necessary for better understanding their role as intermediates in organosilicon chemistry. Although experimental approaches to these problems are of primary importance, theoretical calculations may also provide meaningful information. In this study, ab initio calculations were exploited to examine if a negative charge on silanolate anion and on silanediolate dianion facilitates the formation of the respective silanone species by elimination of a leaving group from silicon. The negative hyperconjugation  $p_{\text{O}} \rightarrow \sigma_{\text{Si-X}}^*$  conducive to this elimination is expected to be particularly strong in the silanolate anions [19]. Silanolates are common intermediates in the polysiloxane chemistry.

<sup>☆</sup> Species derived from the ionization of metasilicic,  $(\text{HO})_2\text{Si=O}$ , and silanoic,  $(\text{HO})\text{RSi=O}$ , acids.

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They are active propagation centres in anionic polymerization of cyclosiloxanes and appear as the transient species in silanol condensation catalysed by strong bases. Silanones were postulated to be formed from silanolate as short living species [13], although further kinetic studies did not confirm this hypothesis [17].

Silanone species formed from silanediolate dianions  $\text{XRSiO}_2^{2-}$  are of special interest as they have formal structures of monomeric metasilicates  $\text{RSiO}_2^-$ . For example, the elimination of  $\text{X}^{(-)}$  from the dianion derived from silanetriol  $\text{XSi(OH)O}_2^{2-}$  leads to the monomeric metasilicic acid anion,  $\text{HOSiO}_2^-$ . These silicon species are isoelectronic with their neutral metaphosphate analogues, which, since a long time, have been recognized as common intermediates in substitution at tetracoordinate phosphorus centre [20]. Silicon analogues of these unstable phosphorus intermediates are rarely taken into consideration as transient species in silicon chemistry [5,21], although a strong kinetic evidence of the intermediacy of metasilicates in substitution at silicon in highly basic media has been provided [22,23]. Very characteristic rate-basicity profile for the hydrolytic cleavage of a substituted benzyl group from silicate dianions derived from silanediols performed in  $\text{NaOH-DMSO-H}_2\text{O}$  system fitted well to the elimination-addition mechanism involving metasilicate intermediate. Moreover, the entropy of activation for this reaction is close to zero, which also supports the metasilicate mechanism [23].

Quantum mechanical calculations for the simple models can provide information on the negative charge assistance to elimination leading to the tricoordinate silicon compounds having silanone or metasilicate structures. Thus, the results of this study could throw more light on the possibility of the generation of metasilicates and silanones as transient species in strongly basic media.

## 2. Theoretical methods

Ab initio calculations were performed using the GAUSSIAN 98 series of programs [24]. Geometry optimizations were performed at the restricted Hartree-Fock (RHF) level of theory, using the 6-31G\* basis set and were further refined using the density functional theory (DFT) at the B3LYP/6-31 + G\* level [25]. Minima on the potential energy surface were located according to the vibrational analysis. Final energetics were obtained at the B3LYP/6-311 + G(2d,p) level [26]. Enthalpy and free energy values were calculated at 298 K using the ideal gas approximation, as implemented in GAUSSIAN 98. Scale factor of 0.98 was used for thermochemical calculations [26].

The Wiberg bond orders as well as the orbital interaction energies were obtained with the Natural Bond

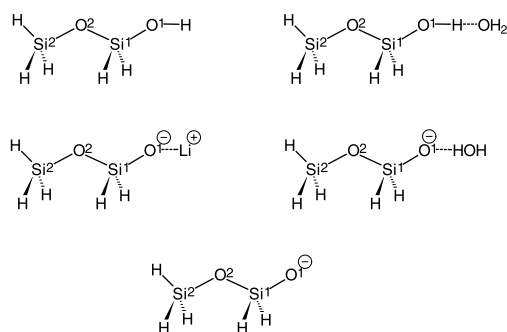
Orbital theory [27]. Orbital analyses were performed at HF/6-31 + G\*//B3LYP/6-31 + G\* level, since DFT calculations in some cases gave unreliable results. The energy associated with particular orbital interaction was calculated with the NBO deletion procedure as the difference between the total SCF energy and the energy obtained by deleting the off-diagonal Fock matrix elements corresponding to the interacting bond-antibond pair [27]. The  $p_{\text{O}}-d_{\text{Si}}$  interactions were approximated by deleting the delocalizations from the oxygen lone pairs to the respective Rydberg orbitals at Si. Only those Rydberg orbitals having the occupancy greater than 0.003e were considered for deletion. These orbitals are hybrids of 3d, 4s and 4p localized atomic orbitals with the dominating contribution from 3d orbitals.

Solvent effects were calculated using the self-consistent reaction field (SCRF) method. Gas phase geometries of the model species were re-optimized at the B3LYP/6-31 + G\* level with the Onsager method (SCRF = Dipole), assuming DMSO as a solvent. Final energies were obtained by single point calculations at B3LYP/6-311 + G(2d,p) for the SCRF geometries using the PCM model [28]. It should be stressed, that the SCRF calculations are only a crude approximate of the solvent effects, because in the dielectric continuum model the specific solvent-solute interactions are neglected.

## 3. Results and discussions

### 3.1. Electronic effects of silanol and silanolate at the polysiloxane chain terminus

Two electronic effects of oxygen lone electron pairs are regarded to have a strong impact on the structure and properties of the polysiloxane chain. One of them is the interaction with the antibonding  $\sigma^*$  orbital of the neighbouring Si-O bond, which is classified as the negative hyperconjugation. The other is the interaction with the empty 3d orbitals on silicon. Both effects can be responsible for a partial dative bonding from oxygen to silicon. The changes in electron density resulting from these effects, if unperturbed by substituents and chain ends, are symmetrical, i.e. each silicon atom in the chain receives equal charge from both neighbouring oxygens and each oxygen atom donates equal charge to both its neighbouring silicons. Thus, all the Si-O bonds in a polysiloxane chain are equivalent. They have the same length, the same bond order and the same binding energy. However, the symmetry of orbital interactions is significantly perturbed at the chain ends. A silicon atom in the terminal silanol group, although bridging two oxygen atoms, should experience some asymmetry of these electronic effects. Strong enhancement of this asymmetry is expected, if a negative charge is placed on oxygen as a result of ionization of the silanol group.



Scheme 1.

Series of derivatives of disiloxanol,  $\text{H}_3\text{SiOH}_2\text{SiOH}$ , with increasing negative charge on oxygen of the SiOH group by its partial and eventually full ionization, were used as models for ab initio calculations of the negative hyperconjugation and p–d delocalization (Scheme 1). The results are presented in Table 1. The increase of asymmetry of the two adjacent SiO bonds is strongly manifested in the equilibrium geometries of the model compounds as well as in the calculated delocalization energies related to the electronic effects.

### 3.2. Geometries

All model compounds were optimized (with the DFT method) at the B3LYP/6-31 + G\* level. Some interesting features related to the changes in the electron density in the silane molecule should be pointed out. Comparison of the disiloxanol derivatives,  $\text{H}_3\text{SiO}^2\text{H}_2\text{Si}^1\text{O}^1\text{X}$ , where X = H,  $\text{H}\cdots\text{OH}_2$ , Li,  $:(^-)\cdots\text{HOH}$ ,  $:(^-)$ , shows continuous decrease of the  $\text{Si}^1\text{—O}^1$  bond length and the increase of  $\text{O}^2\text{—Si}^1$  bond length together with the increase of the formal negative charge at  $\text{O}^1$  (Scheme 1, Table 1). In the naked siloxanolate anion,  $\text{H}_3\text{SiO}^2\text{H}_2\text{Si}^1\text{O}^{1(-)}$ , the  $\text{Si}^1\text{—O}^1$  bond distance is 1.575 Å, by 0.089 Å shorter than that in neutral disiloxanol and only by 0.039 Å longer than the  $\text{Si}=\text{O}$  double

bond in silanone (1.536 Å). The  $\text{Si}^1\text{—O}^2$  bond lengthens correspondingly, from 1.640 Å in neutral disiloxanol to 1.738 Å in the anion. These changes indicate significant strengthening of the former bond and weakening of the latter. This effect is also reflected in the Wiberg bond order of the  $\text{Si}^1\text{—O}^1$  bond, which changes from 0.58 in neutral disiloxanol to 0.93 in siloxanolate anion (Table 1). For comparison, the  $\text{Si}=\text{O}$  bond order in silanone is 1.25. Low numbers, below 2, are due to the strongly polar character of the silicon–oxygen bond [29].

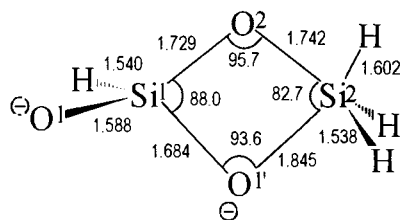
### 3.3. Comparison of the $p_{\text{O}} \rightarrow \sigma_{\text{SiO}}^*$ and $p_{\text{O}} \rightarrow d_{\text{Si}}$ electronic effects

The discussed changes in geometry of the disiloxanolate with increasing negative charge on  $\text{O}^1$  oxygen are accompanied by considerable variations in delocalization energies. The increasing asymmetry of the two SiO bonds shows up in the hyperconjugation energy. The  $p_{\text{O}1} \rightarrow \sigma_{\text{SiO}2}^*$  energy determined by the deletion procedure increases from 11.5 kcal mol<sup>-1</sup> in neutral disiloxanol to 21.5 kcal mol<sup>-1</sup> in the naked anion, while the  $p_{\text{O}2} \rightarrow \sigma_{\text{SiO}1}^*$  energy decreases in the same direction from 9.5 to 5.0 kcal mol<sup>-1</sup>. Very similar, even more pronounced variations are observed for the calculated  $p_{\text{O}1} \rightarrow d_{\text{Si}1}$  and  $p_{\text{O}2} \rightarrow d_{\text{Si}1}$  delocalization energies.

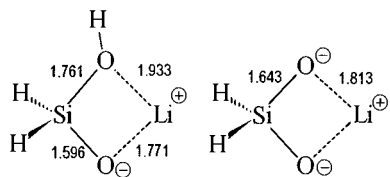
Very interesting is the comparison of the corresponding delocalization energies related to the negative hyperconjugation and the  $p_{\text{O}}\text{—}d_{\text{Si}}$  donation. According to a commonly accepted view, the hyperconjugation dominates the (p–d)<sub>π</sub> interaction in silicon compounds [30]. Recent calculations estimated the energy of the p–d interaction in silylamines to ca. 1/3 of the energy of hyperconjugation [31]. Data in Table 1 confirm smaller contribution of the (p–d)<sub>π</sub> donation for the non-ionized disiloxanol. However, they show increasing importance of this interaction for the bonding energies in the ionized species. For the naked  $\text{H}_3\text{SiOH}_2\text{SiO}^{(-)}$  ion, the energy of the  $p_{\text{O}}\text{—}d_{\text{Si}}$  orbital interaction is greater than the energy of the negative hyperconjugation (Table 1).

Table 1  
Bonding parameters and delocalization energies for disiloxane and its derivatives optimized at B3LYP/6-31 + G\* (in parentheses parameters in DMSO)

	$r(\text{Si}^1\text{—O}^1)$ (Å)	$r(\text{Si}^1\text{—O}^2)$ (Å)	$E_{\text{deloc}}$ (kcal mol <sup>-1</sup> )				Wiberg bond order	
			$p_{\text{O}1} \rightarrow \sigma_{\text{SiO}2}^*$	$p_{\text{O}2} \rightarrow \sigma_{\text{SiO}1}^*$	$p_{\text{O}1} \rightarrow d_{\text{Si}1}$	$p_{\text{O}2} \rightarrow d_{\text{Si}1}$	$\text{Si}^1\text{—O}^1$	$\text{Si}^1\text{—O}^2$
$\text{H}_3\text{SiO}^2\text{Si}^1\text{H}_2\text{O}^1\text{H}$	1.664 (1.666)	1.640 (1.638)	11.0	9.5	6.5	6.3	0.58	0.51
$\text{H}_3\text{SiO}^2\text{Si}^1\text{H}_2\text{O}^1\text{H}\cdots\text{OH}_2$	1.651	1.657	12.5	9.2	7.3	5.5	0.61	0.51
$\text{H}_3\text{SiO}^2\text{Si}^1\text{H}_2\text{O}^1\text{Li}$	1.606 (1.599)	1.713 (1.700)	15.6	5.5	16.8	2.9	0.74	0.44
$\text{H}_3\text{SiO}^2\text{Si}^1\text{H}_2\text{O}^1\cdots\text{HOH}^{(-)}$	1.579	1.726	21.5	5.4	20.1	2.6	0.85	0.43
$\text{H}_3\text{SiO}^2\text{Si}^1\text{H}_2\text{O}^{1(-)}$	1.575 (1.583)	1.738 (1.710)	21.5	5.0	25.4	2.4	0.93	0.42
$\text{H}_2\text{Si}=\text{O}$	1.536 (1.541)				16.5		1.25	



Scheme 2.



Scheme 3.

### 3.4. Anions derived from silanediols

In order to get deeper insight into the dependence of the electronic effects on the structure and charge of the siloxane species, the silanediolate,  $\text{H}_2\text{SiO}_2^{2-}$ , and disiloxanediolate,  $\text{H}_3\text{SiOHSiO}_2^{2-}$ , dianion structures were calculated. The selected bonding parameters and delocalization energies are presented in Table 2.

Dianion structures are quite unstable in the gas phase and they readily decompose, if a good leaving group is attached to silicon. For example, chlorine-substituted dianions,  $\text{ClHSiO}_2^{2-}$  and  $\text{Cl}(\text{HO})\text{SiO}_2^{2-}$ , are not defined intermediates, i.e. they are not the energy minima on the potential energy surface at the B3LYP/6-31 + G\* level of theory, and their optimization leads to dissociation of the Cl-Si bond, giving separate  $\text{Cl}^{(-)}$  and  $\text{XSiO}_2^{(-)}$  (metasilicate) anions. SCRF calculations show that chlorine-containing dianions are not stable in DMSO solution, either. Free dianions were found to be the real energy minima (intermediates) only when silicon is substituted with poor leaving group, such as H, OH,  $\text{OSiH}_3$  (Table 4). Since the negative charge in isolated species is poorly stabilized, their generation in the gas phase is associated with a high-energy input. In solution, they are stabilized by intermolecular interactions, so the amount of energy required for their formation is expected to be significantly smaller.

The optimized gas phase geometry of  $\text{H}_3\text{SiOSiHO}_2^{2-}$  dianion, is a peculiar cyclic structure, with one of the oxygens bearing negative charge forming an extra bond to the terminal ( $\text{Si}^2$ ) atom. The  $\text{Si}^2$  atom adopts distorted pyramidal configuration and the  $\text{Si}^2\text{-H}$  bonds lengthen considerably, from 1.485 Å to ca. 1.538 Å (equatorial) and 1.602 Å (apical). All Si-O bonds and SiOSi angles in the cyclodisiloxane ring are non-equivalent (Scheme 2). The SCRF calculations showed that the cyclic structure of disiloxanediolate anion is pre-

served in DMSO and the bonding parameters are very similar to those found for the gas phase.

Because of its unusual cyclic structure, the dianion  $\text{H}_3\text{SiOSiHO}_2^{2-}$  is not a good model to compare changes in geometry and delocalization energy induced by a double negative charge at oxygen atoms with those observed in the monoanion. Thus, the comparison was made for the silanolate anion,  $\text{H}_2\text{Si}(\text{OH})\text{O}^{(-)}$ , and silanediolate dianion,  $\text{H}_2\text{SiO}_2^{2-}$ .

Strong asymmetry of the discussed electronic effects is observed, as expected, for the monoanions,  $\text{XH-Si}(\text{OH})\text{O}^{(-)}$ . This implies the corresponding changes in the bond lengths. The  $p_{\text{O}} \rightarrow d_{\text{Si}}$  delocalization involving oxygens bearing a negative charge is the strongest effect, stronger than the  $p_{\text{O}} \rightarrow \sigma_{\text{SiO}}^*$  and  $p_{\text{O}} \rightarrow \sigma_{\text{SiH}}^*$  interactions. The structure of the silanediolate dianion is highly symmetrical ( $C_{2v}$  symmetry). Due to counterbalancing of the  $p_{\text{O}} \rightarrow \sigma_{\text{SiO}}^*$  interactions, the Si-O bond length has an intermediate value, between this in the non-ionized Si-OH group and that involving negatively charged oxygen in the monoanion. The Si-H bond length in  $\text{H}_2\text{SiO}_2^{2-}$  is exceptionally long, 1.597 Å, which results from the strong hyperconjugation  $p_{\text{O}} \rightarrow \sigma_{\text{SiH}}^*$ . Bond distances and hyperconjugation energies show that the Si-H bond is significantly more affected in the dianion than in the monoanion (Table 2).

Stabilization of the negative charge by formation of a cyclic structure is also observed in the case of lithium silanediolate,  $\text{H}_2\text{Si}(\text{OH})\text{O}^{(-)}\text{Li}^{(+)}$  and  $\text{H}_2\text{SiO}_2^{2-}\text{Li}^{(+)}$  (Scheme 3). The calculated stabilization energy for  $\text{H}_2\text{Si}(\text{OH})\text{OLi}$  in the gas phase, due to the formation of an extra intramolecular bond between silanol oxygen and lithium, is 4.4 kcal mol<sup>-1</sup>.

### 3.5. Thermodynamics of reactions leading to silanones

It may be concluded from data in Tables 1 and 2, that the negative charge on oxygen bonded to silicon makes the adjacent Si-O bond much weaker. The asymmetry of electronic effects is nicely illustrated in the silanolate ion,  $\text{H}_2\text{Si}(\text{OH})\text{O}^{(-)}$ , where the Si-O<sup>(-)</sup> and Si-OH bond lengths are 1.580 and 1.729 Å, respectively. In general, all Si-X bonds, where X is more electronegative than silicon, geminal to ionized hydroxyl, are expected to show similar behaviour. If the weakened bond links a good leaving group, such as  $\text{Cl}^{(-)}$ , the elimination of this group would lead to the transient formation of silanone, or, in the case of dianion, to the formation of metasilicate anion. Calculated thermodynamic parameters for some model reactions leading to silanone and metasilicate formation from negatively charged  $\equiv\text{SiO}^{(-)}$  and  $\equiv\text{SiO}_2^{2-}$  precursors are shown in Tables 3 and 4. The presented thermodynamic data refer mostly to the reactions in the gas phase. For some cases, preliminary calculations of thermodynamics in solution were performed using sim-

Table 2

Bond lengths (B3LYP/6-31+G\*) in gas phase and in DMSO (in parentheses) and delocalization energies (HF/6-31+G\*//B3LYP/6-31+G\*) for mono- and dianions derived from silanediol and disiloxanediol

	$r$ (Si <sup>1</sup> –O <sup>1</sup> ) (Å)	$r$ (Si <sup>1</sup> –O <sup>2</sup> ) (Å)	$r$ (Si <sup>1</sup> –H) (Å)	$E_{\text{deloc}}$ (kcal mol <sup>-1</sup> )						Wiberg bond order	
				PO <sub>1</sub> → σ <sub>SiO<sub>2</sub></sub> *	PO <sub>2</sub> → σ <sub>SiO<sub>1</sub></sub> *	PO <sub>1</sub> → d <sub>Si1</sub>	PO <sub>2</sub> → d <sub>Si1</sub>	PO <sub>1</sub> → σ <sub>Si1H</sub> *	PO <sub>2</sub> → σ <sub>Si1H</sub> *	Si <sup>1</sup> –O <sup>1</sup>	Si <sup>1</sup> –O <sup>2</sup>
H <sub>2</sub> Si(OH) <sub>2</sub>	1.668 (1.666)		1.479 (1.480)	10.5	10.5	4.2	4.2	4.6	4.6	0.58	
H <sub>2</sub> Si(O <sup>2</sup> H)O <sup>1(-)</sup>	1.580 (1.583)	1.734 (1.727)	1.523 (1.523)	21.2	4.1	27.2	4.5	7.8	5.0	0.92	0.48
H <sub>2</sub> SiO <sub>2</sub> <sup>(2-)</sup>	1.620 (1.621)		1.597 (1.594)	15.3	15.3	23.9	23.9	13.8	13.8	0.8	
H <sub>3</sub> SiO <sup>2</sup> Si <sup>1</sup> H(O <sup>1</sup> H) <sub>2</sub>	1.657		1.472	8.7	8.1	2.5				0.57	0.52
H <sub>3</sub> SiO <sup>2</sup> Si <sup>1</sup> H(O <sup>1</sup> H)O <sup>1(-)</sup>	1.572	1.713	1.499							0.92 (O <sup>1</sup> )	0.43
										0.50 (O <sup>1</sup> )	
H <sub>3</sub> SiO <sup>2</sup> Si <sup>1</sup> HO <sub>2</sub> <sup>1,1(2-)</sup> <sup>a</sup>	1.588 (O <sup>1</sup> )	1.729	1.540	18.6 (O <sup>1</sup> )	5.8	23.8 (O <sup>1</sup> )	5.2	13.2 (O <sup>1</sup> )	5.1 (O <sup>2</sup> )	0.88 (O <sup>1</sup> )	0.47
	1.684 (O <sup>1</sup> )			1.8 (O <sup>1</sup> )		7.1 (O <sup>1</sup> )		7.2 (O <sup>1</sup> )		0.55 (O <sup>1</sup> )	

<sup>a</sup> Cyclic structure, bond order (Si<sup>2</sup>–O<sup>1</sup>) = 0.39; see Scheme 2.

Table 3  
Electronic energies, enthalpies and free enthalpies (298 K) of elimination reactions proceeding with generation of silanones

Reaction	X	Gas			DMSO		
		$\Delta E$	$\Delta H$	$\Delta G$	$\Delta E$	$\Delta H$	$\Delta G$
$\text{XH}_2\text{SiO}^{(-)} \rightarrow \text{H}_2\text{Si=O} + \text{X}^{(-)}$	H	103.4	100.3	92.6	80.7	77.6	69.9
	HO	101.9	99.6	90.4	24.3	22.0	12.8
	$\text{H}_3\text{SiO}$	76.3	73.7	64.4	9.3	6.8	-1.7
	Cl	50.1	49.5	42.0	12.0	12.5	5.1
$\text{XH}(\text{HO})\text{SiO}^{(-)} \rightarrow \text{H}(\text{HO})\text{Si=O} + \text{X}^{(-)}$	H	100.6	96.9	90.6	58.0	54.1	46.5
	HO	100.5	98.4	88.9	42.3	40.1	30.9
	$\text{H}_3\text{SiO}$	74.6	72.3	62.4			
	Cl	46.7	46.4	33.5	8.0	7.7	0
$\text{X}(\text{HO})_2\text{SiO}^{(-)} \rightarrow (\text{HO})_2\text{Si=O} + \text{X}^{(-)}$	H	105.7	102.6	95.9	61.8	57.6	51.1
	OH	101.4	99.3	89.9	61.8	59.7	50.1
	Cl	46.7	46.8	39.7	24.3	24.2	16.7

ple reaction field method. For SCRF calculations DMSO was arbitrary chosen as a solvent, because DMSO has a high dielectric constant ( $\epsilon = 46.70$ ) and, in principle, cannot serve as a proton donor in hydrogen bonding. This solvent was also used in kinetic studies of reactions, where silanone and metasilicate intermediates were postulated [22,23,32,33].

SCRF geometries optimized at the B3LYP/6-31 + G\* level in DMSO differ only slightly from the gas phase structures (Table 1). However, the SCRF energies of reactions considered here are significantly different from those calculated for the gas phase, particularly, when ionic species are involved. This could be expected, as the polar solvent strongly interacts with the charged species. The SCRF results should be treated as a very rough approximation, because the dielectric continuum model does not reproduce the specific interactions between solvent and a solute. Moreover, calculations of isolated molecules neglect interactions between the counter-ions or ion-pairs. It is well known, for example, that lithium compounds form strong aggregates in solution. These interactions play a primary role in stabilization of the ionic species. However, calculations involving such aggregates, or their complexes with solvent are much more computationally demanding. Further studies are in progress. Thus, the SCRF calculations of isolated molecules give only a qualitative idea about the changes in reaction energetics, when going from gas phase to solution.

The data in Table 3 reveal a high thermodynamic instability of silanone. A considerable energy input is needed to transform the model reactants into silanones in the gas phase. Even elimination of as good leaving group as  $\text{Cl}^{(-)}$  requires about 50 kcal mol<sup>-1</sup>. Thus, the  $\equiv\text{SiO}^{(-)}$  anions are not good precursors of silanones in the gas phase. The solution system is more favourable for the silanone formation. Data presented in Table 3

indicate that the interaction of a polar solvent such as DMSO is able to increase dramatically the thermodynamic stability of silanone. Thus, the enthalpy of the elimination of  $\text{Cl}^{(-)}$  in DMSO becomes lower by about 40 kcal mol<sup>-1</sup>. For some reactions of silanone formation in Table 3, free enthalpy ( $\Delta G$ ) achieves low values indicating that thermodynamics is not an obstacle for the formation of silanone from silanolate anion in these systems. This inference could be strengthened, if specific interactions were taken into account as they are likely to increase the thermodynamic stability of the products of elimination reaction.

On the other hand, it should be remembered that silanones show very high kinetic reactivity connected with a great polarization of the Si=O group, which is extremely strong electrophile and a highly reactive nucleophile. Thus, the oligomerization of silanones and their addition to polar compounds, such as water, proceed virtually without energy barrier [34]. From this point of view, silanones may appear in solution only as diffusional non-equilibrated intermediates, difficult to

Table 4  
Electronic energies, enthalpies and free enthalpies (298 K) of elimination reactions of silanediolates proceeding with generation of metasilicates (Eq. (2))

Reaction	X	Gas		
		$\Delta E$	$\Delta H$	$\Delta G$
$\text{XHSiO}_2^{(2-)} \rightarrow \text{HSiO}_2^{(-)} + \text{X}^{(-)}$	H	-40.6	-42.8	-50.2
	HO	-36.9	-38.7	-48.7
	$\text{H}_3\text{SiO}$	-38.1	-39.2	-51.5
	Cl	dissociation		
$\text{X}(\text{HO})\text{SiO}_2^{(2-)} \rightarrow \text{HOSiO}_2^{(-)} + \text{X}^{(-)}$	H	-32.0	-34.5	-41.8
	HO	-33.0	-34.8	-44.8
	Cl	dissociation		

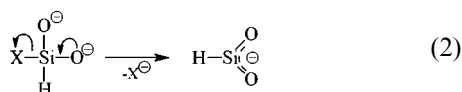
Table 5  
Electronic energies, enthalpies and free enthalpies (298 K) of elimination reactions of silanulates proceeding with generation of metasilicates (Eqs. (2) and (3))

Reaction	X	Gas			DMSO		
		$\Delta E$	$\Delta H$	$\Delta G$	$\Delta E$	$\Delta H$	$\Delta G$
$\text{XHSi}(\text{OH})\text{O}^{(-)} \rightarrow \text{HSiO}_2^{(-)} + \text{HX}$	H	20.3	16.5	8.6	22.2	18.5	10.6
	HO	43.9	42.4	32.2	37.1	35.2	25.1
	$\text{H}_3\text{SiO}$	51.6	49.8	39.0			
	Cl	52.9	49.6	40.1	45.4	42.4	32.6
$\text{X}(\text{HO})_2\text{SiO}^{(-)} \rightarrow \text{HOSiO}_2^{(-)} + \text{HX}$	H	25.0	21.4	13.7	16.3	12.7	5.3
	HO	44.5	43.3	33.3	42.7	41.0	30.9
	Cl	52.5	49.9	40.6	47.8	45.2	35.9

detect by kinetic methods. The boundary mechanisms, in which they are the incipient species are also feasible. In such mechanisms, the formation and conversion of the incipient silanone would occur in one step but the structure of the transition state of this step would be very close to the structure of silanone.

### 3.6. Thermodynamics of reactions leading to metasilicates

Thermodynamic parameters of some decomposition reactions of negatively charged precursors leading to metasilicates according to Eq. (2) are presented in Table 4. Inspection of data leads to the conclusion that the decomposition of dianions derived from silanediols and silanetriols to metasilicates is thermodynamically more favourable than the formation of silanones from the corresponding monoanions. Attempts of optimization of the chlorosilanediolate dianion structure showed that it is not a minimum on the potential energy surface, neither in the gas phase nor in DMSO solution. Thus, the decomposition of the chlorosilanediolate dianion to metasilicic acid anion occurs spontaneously without energy barrier. The transformation of other dianion precursors into metasilicates presented in Table 4 proceed with an exothermic effect. Negative free enthalpy values for these reactions indicate that metasilicate anions are more stable in the gas phase than their dianion precursors.

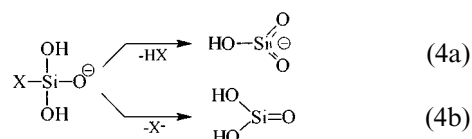
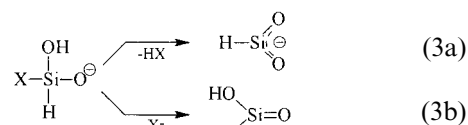


Although ionization of silanediol to silanediolate dianion in the gas phase is energetically costly, it should occur more readily in solution, where the dianion is strongly solvated.

The calculated structures of tricoordinate silicon species, i.e. the anions of silanoic acid (Eq. (3a)) and metasilicic acid (Eq. (4a)) are symmetrical with the

charge equally distributed over both oxygen atoms. High facility of formation of metasilicates from negatively charged precursors is reflected in data presented in Table 5.

The elimination reactions of monoanions derived from silanediol and silanetriol leading to metasilicates, according to Eqs. (3a) and (4a), proceeds easier than the elimination leading to silanone, according to Eqs. (3b) and (4b) (compare the corresponding data in Tables 3 and 5).



## 4. Conclusions

According to ab initio calculations, negative charge localized on oxygen bonded to silicon strongly decreases the energy of the adjacent bond of silicon to an atom X, more electronegative than silicon, by the  $\text{p}_\text{O} \rightarrow \sigma_{\text{Si-X}}^*$  negative hyperconjugation. Energies of negative hyperconjugation and  $\text{p}_\text{O} \rightarrow \text{d}_{\text{Si}}$  back donation effects strongly increase when a negative charge is developed on oxygen. Although the p-d effect is significantly lower in energy compared to hyperconjugation in the neutral moieties,  $\text{X}-\text{SiR}_2-\text{O}(\text{R}')$ , it becomes dominating in the anionic species,  $\text{X}-\text{SiR}_2-\text{O}^{(-)}$ .

The formation of silanone by elimination of an  $\text{X}^{(-)}$  anion from negatively charged  $\text{XR}_2\text{SiO}^{(-)}$  species requires a considerable amount of energy, when carried out in the gas phase. However, thermodynamics may be

not an obstacle for this type of reaction in a polar solvent.

On the other hand, the elimination of  $X^{(-)}$  from  $XHSiO_2^{2(-)}$  dianion proceeds much easier and is thermodynamically favoured ( $\Delta G < 0$ ) even in the gas phase. Metasilicates are likely to appear as intermediates in some processes carried out in strongly basic media.

## 5. Supplementary material

Supplementary material contains the Cartesian coordinates of the model species, optimized at B3LYP/6-31 + G\* and are available from author on request.

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