INVESTIGATION OF THE ELECTRONIC STRUCTURES OF SILANONES AND HYDRATION MECHANISM

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Abstract: Conformational analysis and semiempirical calculation were carried out for some derivatives of silanones with the common skeleton I by means of the **PM3** method. The analysis of the electron density distribution as a function of the nature of substituents was performed on the basis of the data obtained. The reactions of H_2O with silanone have been studied by **PM3** semiempirical calculations in gas phase. Attack by H_2O through four membered cyclic transition states is found. It was determined that the addition of H_2O to Si=O bond of silanone gave silandiol.

Keywords: Silanones, Semiempirical calculations, Electronic structure, Transition state

SİLANONLARIN ELEKTRONİK YAPILARININ VE HİDRASYON MEKANİZMALARININ TEORİK İNCELENMESİ

Özet: Bazı Silanon türevlerinin konformasyon analizleri ve semiempirik hesaplamaları **PM3** metodu ile yapıldı. Ayrıca model olarak alınan silanon ile suyun reaksiyonu gaz fazunda **PM3** semiempirik metodu hesaplamaları ile incelendi. Bu reaksiyonda suyun silanona atağı ile ara kademede dört üyeli halkalı yapıda geçiş hali bulundu. Silanon' un Si=O bağı ile H_2O arasındaki katılma reaksiyonu sonucunda bir silandiol bileşiğinin oluştuğu saptandı.

Anahtar Kelimeler: Silanonlar, yarı deneysel hesaplamalar, elektronik yapı, geçiş durumu

1. Introduction

The elucidation of structure-reactivity relationships of chemical compounds (in terms of their electronic features) seems to be the most important problem from both theoretical and experimental point of view. Over the last three decates years, there has been considerable interest on reactive π-multi-bonded indicates π-character, in every case silicon intermediates [1], such as silanones; which contain a silicon- oxygen double bond [2]. These compounds are particularly reactive and can not be normally isolated under normal reaction conditions.

They are generated by methods which involve conversion of an initial reactive silicon containing intermediate, having a Si-O bond, into a silanone, a very labile compound of silicon [3].

The intermediacy of free silanones has been proposed for many reactions [4]. Much of the evidence for silanone formation is inferred from the presence of small silicone cyclics in the reaction mixtures [4]. Although a few simple silanones ($R_2Si=O$, R: H, Me, X) have been characterized by a variety of spectroscopic techniques, including IR at low T, the bulk of present knowledge of silanone properties originates from studies on transients, the radical anion of $(tBu)_2Si=O$ [4]. Transient organic silanones $(CH_3O)_2SiO$ and $(C_6H_5)_2SiO$ were generated by vacuum pyrolysis from 3,3-dimethyl-6-oxo-3-silabicyclohexane and its 3,3-diphenyl derivative, respectively and after being trapped in

Argon cryogenic matrices at 12 K directly studied by IR spectroscopy [5].

During recent years, Voronkov developed a concept stating that the silanones are generally produced as a result of a geminal cleavage (the α -elimination) of organic compounds containing a Si(OR)X group as depicted by the following scheme;
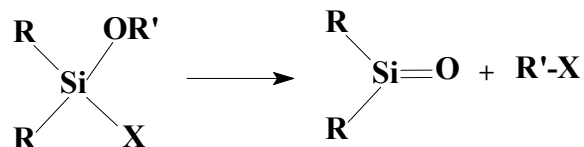
Many low-energetic silanone intermediate involving processes, occur according to this scheme at reasonably low temperatures [3]. The trapping of the generated silanones and their incorporation into other molecules may be a synthetically very useful approach in organosilicon chemistry [2]. Unlike the other silicon-based reactive intermediates, silanones constitiute one of the few classes of compounds, for which synthetic routes to create stable species have yet to be developed.

Silanones are reactive towards nucleophilic addition across Si=O bonds. They undergo rapid addition by nucleophilic attack at Si. The general reactivity of silanones have recently been investigated by means of *ab initio* methods [6]. The bimolecular reaction of silanone with water was examined and found to proceed with no overall barrier, indicating very high reactivity of the silicon-oxygenn double bond toward polar reagents [7].

Especially , the reactivity of silanones in cycloaddition reactions has renewed the theoretical interest in the mechanism and kinetics of their reactions. In the absence of a reactive substrate, silanone combines with itself to form cyclic products [8].

In this work, some silanone derivatives were examined for their structural parameters and thermodynamics by semiempirical PM3 method in gas phase. In the light of increasing current interest in the possible existence of Si-O doubly bonded compounds, the lowest singlet potential energy surface of the parent unsubstituted silanone, $H_2Si=O$, was investigated by means of PM3 method. Furthermore, the reaction mechanism of the simplest silanone $H_2Si=O$ with water is investigated.

2. Methodology

To study the mechanism of the rections, all calculations were carried out by means of semiempirical **PM3** method with full geometry optimization for reactants and products. Transition structures, located with saddle calculations, were refined by minimizing the scalar gradient of energy with respect to the geometry and characterized as saddle points by diagonalising the Hessian Matrix and establishing the presence of one and only one negative force constant, whereas the ground state of the rectants and the products had no imaginary force constants. As a result, the transition states were located

in **PC SPARTAN PRO** and obtained structures were refined with option.The **PM3** calculations were carried out with the help of **PC SPARTAN PRO** for the reaction and **MOPAC 7** for the subtituted silanone derivatives. Alkyl groups are replaced by H atoms in the model compounds prior to theoretical calculations.
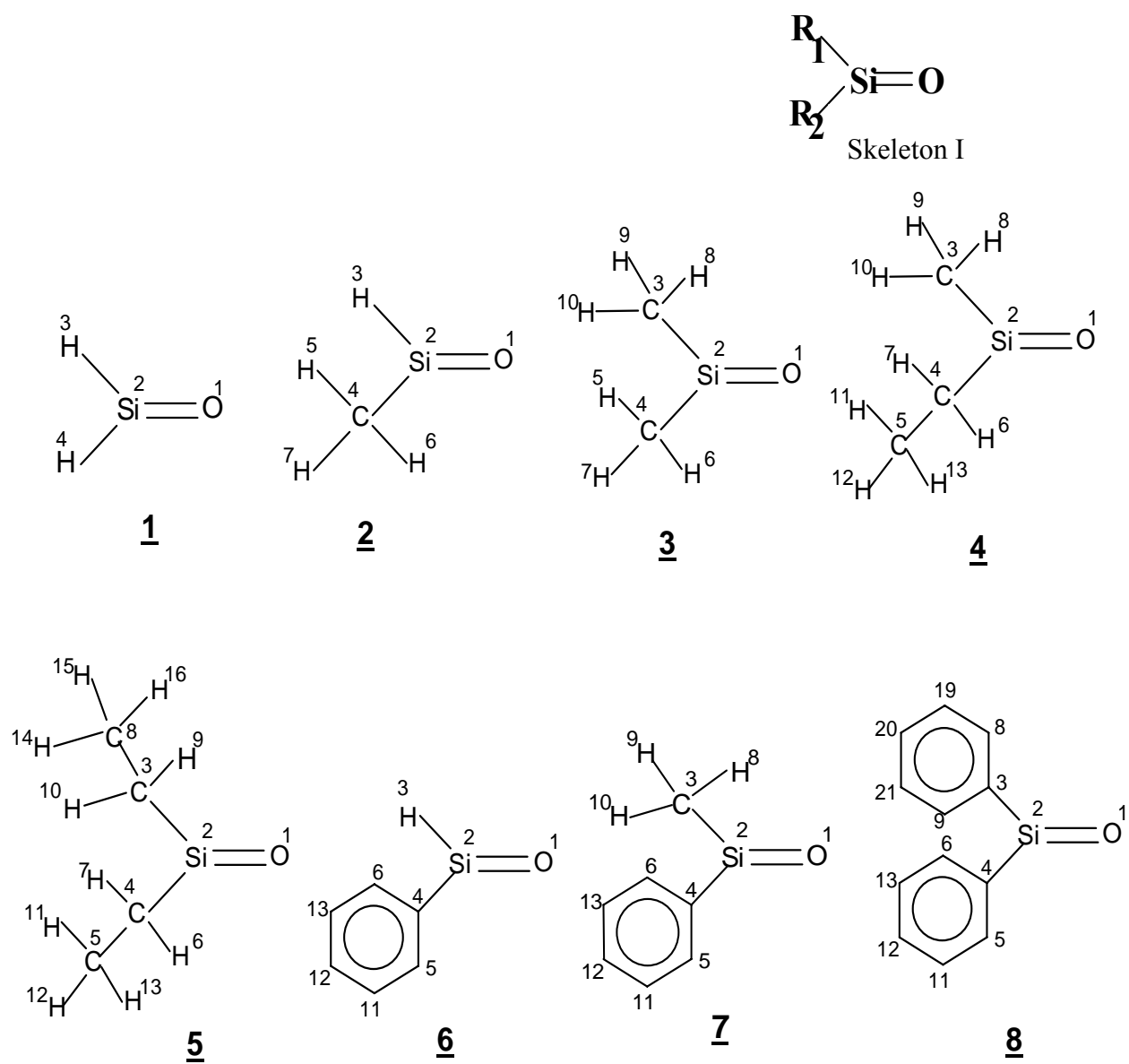
Figure 1. The structural skeletons of some silanone derivatives.

3. Result and Discussion:

The compounds of variously substituted silanones, shown in Figure 1, were studied.

1

2
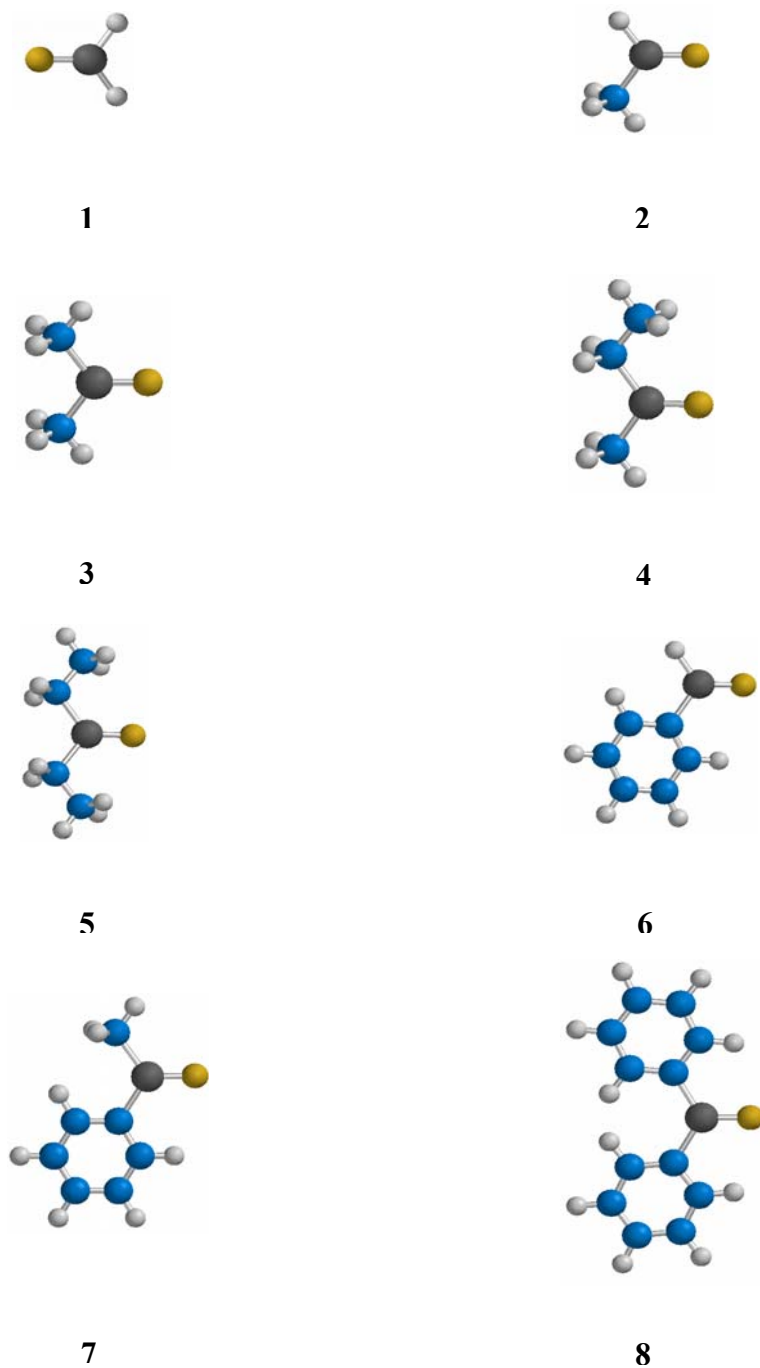
3

4

5

6

7

8

Figure 2. The spatial arrangements of compounds 1-8.

Structural parameters of the compounds 1-8 have been calculated and presented in Table 1. It can be seen in Table 1 that O-Si bond length for the compounds 1-8 is unaffected by the substituents aligned to Si. Si-O bond length is also not effected because of precise doublet bond.

Bond lengths are affected by the state of hybridization of the atom bonded. The more **s** charecter in a hybrid atomic orbital the closer it lies to nucleus. In Si-H_3 bond, the bond is formed by **sp^2** hybrid orbital of Si and **s** orbital of H. The positive lobe of **sp^2** orbital of Si overlaps with the positive **1s** orbital of H to form a bond. When C is aligned to Si (compounds 2 to 8), this time an **sp^3** and a **sp^2** orbital should combine. As **sp^3** orbital has more **p** character and are larger in shape, the increase in the bond length could be understood. The more stubby its geometry so that effective overlap will require a closer approach. Another major source of perturbation of bond length is conjugation. Substitution of a phenyl group leads to the bond length of 1,80A° (see compounds 6 to 8). This value is smaller than a -CH_3 or -C_2H_5 group because of the resonance structure and conjugation of the phenyl group which makes the delocalizon of **π** electrons over the ring possible.

The bond angle change for R_3-Si-R_4 is of our interest (Table 1). The angle increases as large substituents are aligned to Si due to the steric effects. The very small calculated distosions are in agreement with this prediction. Substitution of larger groups cause sıgnıfıcant increase in the value because of the steric effects. The bond angle for O-Si-R_3 is calculatet effected by the substituends and changes within the range of 112° to 124°.

Table 1. Geometrical parameters of compounds.

Geometrıcal Parameters	1	2	3	4	5	6	7	8
O_1-Si_2	1.5252	1.5272	1.5283	1.5281	1.5276	1.5295	1.5295	1.5334
Si_2-R_3	1.4943	1.4959	1.8549	1.8736	1.8559	1.4984	1.8598	1.8136
Si_2-R_4	1.4943	1.8514	1.8552	1.8725	1.8724	1.8026	1.8089	1.8143
C_4-R_5	------	1.0938	1.0949	1.4995	1.5014	1.3921	1.3907	1.3910
C_4-R_6	------	------	------	1.1051	1.1036	1.0948	1.0949	1.9460
C_3-R_8	------	------	------	------	------	------	1.0950	1.3916
C_3-R_9	------	------	------	------	------	------	1.0948	1.3916
O_1-Si_2-R_3	123.48	124.25	114.29	113.57	122.80	112.69	112.08	119.98
O_1-Si_2-R_4	123.48	122.08	122.80	124.05	114.48	122.14	123.42	119.98
O_1-Si_2-R_4-R_7	------	-59.19	66.52	133.75	90.38	0.3704	-179.85	-151.19

In particular, the chemistry of silicon but not of carbon is expected to have the possibility of being infulenced by the avability of empty **3d** orbitals that are not greatly higher in energy than the **3s** and **3p** orbitals of silicon [8]. The **3d** orbitals of silicon are involved in a different way in compounds of the type Si-X , where X is an atom or group having electrons in a **p** orbital so situated as to be able to overlap with an empty **3d** orbitals of silicon. The result is a Si-X bond with partial double bond character of the **d-p** type , in which the silicon has an expanded valence shell [9]. Because of this from as it can be seen from Table 1 that Si-O bond length is smaller than Si-R_3 and Si-R_4 bond lengths. That support the conclusions of , Si-O bonds are double bonds.

Table 2 shows the effective charges on the atoms of compounds1-8. The greatest positive charge is concentrated on

Si because of being bonded to a relatively electronegative element, O. Si-H bond in silanones may be attributed to charge speration $Si\delta+...H\delta$-that results from the greater electronegativitiy of H than of Si (Table 2, compounds 1,2,6). Bearing a C attached to Si displays negative charge in the position R_3 or R_4 (Table 2, compounds 3, 4, 5, 7, 8). C atoms in the positions R_3 or R_4 are bigger negative charges than H atoms . The greater polarity of the bond $Si^{\delta+}....C^{\delta-}$ allows easier nucleophilic attack on Si and electrophilic attack on C than for C-C compounds [10].

Table 2. The charges on the atoms of compounds 1-8.

Charge	1	2	3	4	5	6	7	8
O_1	-0.54	-0.54	-0.54	-0.53	-0.53	-0.53	-0.52	-0.51
Si_2	0.82	0.80	0.79	0.77	0.78	0.84	0.83	0.87
R_3	-0.14	-0.13	-0.31	-0.29	-0.31	-0.11	-0.29	-0.26
R_4	-0.14	-0.31	-0.31	-0.28	-0.28	-0.30	-0.29	-0.26

The analysis of the electron density distributions at the bonds for compounds 1-8 are listed Table 3. The higher the bond order is the stronger the bond and the shorter the bond length. The values correlate with the bond such as O-Si bond degree is around 1.85-1.89 for all compounds, and there is a double bond appearing between these two atoms. The bond order gives a strong indication of both bond length and bond strength. Upon going from a bond order of 1.85 to 1.89 the bond will both become stronger and shorter.

Table 3. The Wiberg's ındices (bond orders) of the compounds 1-8.

Bond Order	1	2	3	4	5	6	7	8
O_1-Si_2	1.89	1.87	1.86	1.87	1.86	1.87	1.85	1.85
Si_2-R_3	0.92	0.91	0.92	0.90	0.92	0.92	0.93	0.90
Si_2-R_4	0.92	0.93	0.92	0.91	0.90	0.91	0.89	0.90
C_3-R_8	----	----	0.98	0.01	0.98	----	0.98	1.40
C_4-R_5	----	0.98	0.98	0.01	1.00	1.39	1.39	1.40
C_3-H_{10}	----	----	0.98	0.97	0.98	----	----	----

Figure 3 is the graphical and extended version of listed energy levels in Table 5. From this graph we can conclude that the substitution of C groups increases **HOMO** and **LUMO** values (due to hyperconjugation).

Table 4 include entalpy of formation (ΔH), total energy of the system (Etot), ionization potential (IP) and dipol moments (μ) of the compounds. The more stable the compound in the lower the enthalpy of the molecule. In molecule **4** the ΔH value has the more negative value so it is the most stable one out of **8** compounds. $E_{electronic}$ value is maximum as well as the core core repulsion in molecule **8** because of the phenyl substituents. Values of E_{HOMO} and E_{LUMO} can be experimentally determined from measurements of ionization potentials and electron affinies.

Table 4. The structural parameters of compounds 1-8.

MOLECULES	ΔH (kcal)	E_{TOT} (eV)	E_{EL} (eV)	C-C $_{REP}$ (eV)	I_P (eV)	μ DEBYE	HOMO (eV)	LUMO (eV)
1	-21.52	-426.32	-662.46	266.44	9.61	2.684	-9.61	-0.46
2	-42.38	-546.22	-1248.41	702.18	9.59	3.029	-9.58	-0.38
3	-63.00	-696.42	-1967.63	1271.21	9.54	3.309	-9.54	-0.30
4	-74.20	-995.51	-3806.27	2810.75	9.28	3.136	-9.28	-0.36
5	-68.79	-845.97	-2841.97	1995.99	9.40	3.243	-9.40	-0.33
6	-11.88	-1168.76	-4695.88	3527.11	9.60	2.874	-9.61	-0.76
7	-32.34	-1318.95	-5792.58	4473.62	9.55	3.084	-9.55	-0.69
8	0.42	-1941.40	-10660.39	8718.99	9.52	2.872	-9.52	-0.89

E(ev)

1 2 3 4 5 6 7 8
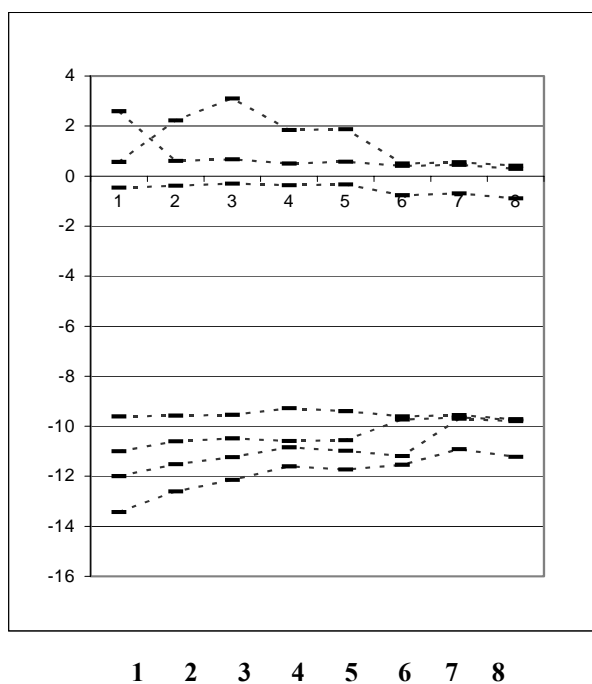
Figure 3. Energy levels of "active zero" for the compounds 1-8.

Table 5. The main orbital components and the E_{HOMO} and E_{LUMO} values of compounds 1-8.

| 1	$\psi =0.76py(O_1)-0.27py(Si_2)+0.42s(H_3)-0.42s(H_4)$	E_{HOMO}=- 9.61eV
	$\psi =-0.57pz(O_1)+0.82pz(Si_2)$	E_{LUMO}= -0.46eV
2	$\psi =0.74py(O)-0.23py(Si2)-0.41s(H_3)-0.17px(C4)+0.38py(C4)$	E_{HOMO}= -9.58eV
	$\psi =0.55pz(O_1)-0.81pz(Si_2)$	E_{LUMO}= -0.38eV
3	$\psi =-0.72py(O_1)+0.21py(Si_2)+0.21px(C_3)-0.34py(C_3)-0.20px(C_4)-0.37py(C_4)$	E_{HOMO}= -9.54eV
	$\psi =-0.54pz(O_1)+0.81pz(Si)$	E_{LUMO}= -0.30eV
4	$\psi =-0.61py(O_1)+0.26py(Si_2)-0.24px(C_3)-0.35py(C_3)+0.21px(C_5)+0.39py(C_5)+0.15s(H_{11})$	E_{HOMO}= -9.28eV
	$\psi =0.54Pz(O_1)-0.81Pz(Si_2)$	E_{LUMO}= -0.36eV
5	$\psi = -0.66py(O_1)+0.24py(Si_2)-0.18px(C_4)-0.34py(C_4)+0.23px(C_5)-0.4py(C_5)-0.15s(H_{11})$	E_{HOMO}= -9.40eV
	$\psi = 0.54pz(O_1)-0.81pz(Si_2)$	E_{LUMO}= -0.33eV
6	$\psi =0.42pz(O_1)-0.53pz(C_3)-0.3pz(C_4)+0.21pz(C_6)-0.25pz(C_{11})+0.26pz(C_{12})+0.5pz(C_{13})$	E_{HOMO}= -9.61eV
	$\psi =-0.5pz(O_1)+0.69pz(Si_2)+0.19pz(C_3)+0.23pz(C_4)-0.24pz(C_{11})+0.29pz(C_{13})$	E_{LUMO}= -0.76eV
7	$\psi =-0.43pz(O_1)+0.53pz(C_4)+0.25pz(C_6)+0.29pz(C_8)+-0.50pz(C_7)-0.26pz(C_5)$	E_{HOMO}= -9.55eV
	$\psi =-0.49pz(O_1)+0.69pz(Si_2)+0.20pz(C_4)+0.30pz(C_6)-0.24pz(C_5)-0.23pz(C_8)$	E_{LUMO}= 0.69eV
8	$\psi=0.48pz(O_1)-0.31pz(C_3)-0.15pz(C_4)-0.17pz(C_5)+0.29pz(C_7)-0.34pz(C_9)-0.18pz(C_{10})-0.17pz(C_{11})+0.15pz(C_{12})+0.31pz(C_{13})$	E_{HOMO}= -9.52eV
	$\psi=0.49pz(O_1)-0.66pz(Si_2)+0.15pz(C_4)+0.15pz(C_5)+0.17pz(C_7)+0.17pz(C_{10})+0.18pz(C_{11})-0.21pz(C_{13})$	E_{LUMO}= -0.89eV

R1 + R2   **TS**   **P**
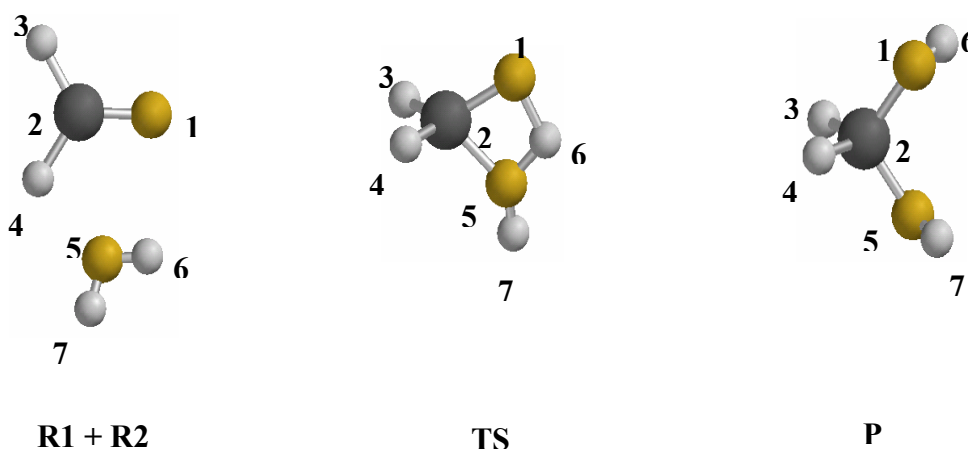
Figure 4. The spatial arrangements of the reacting species.

As mentioned before, the kinetics and mechanism of some rections of silanone have recently been investigated by a few authors [7]. In this paper, the kinetics and mechanism of H_2O addition to silanones were studied. The reactants, transition state and the product is shown in Figure 4.

Each reaction stage is characterized by electronic properties and energy states. With Si-O_5 bond length of 3.86 there is no interaction between **R1** and **R2**, in the case of formation energy for **R1+R2** (E_{R1+R2}=-74.96 kcal / mol) is equal to some of the formation energies of the reactant,**R1** (E_{R1}= -21.53 kcal / mol) and R2 (E_{R2}= -53.43 kcal / mol). The following reaction mechanism energies are calculated relative to the total energy of **R1**+ **R2** by considering the total energy of reactants as 0 kcal / mol. When Si-O_5 bond length becomes 1.74 interaction occuring between reactants, **R1**-**R2**, leads to the transition state. The transition structure, **TS**, corresponds to the nucleophılic addition of the waters O atom to the **sp²** hybridized silicon atom of the electrophilic silanone to give silandiol. The reacting atom's approach cause O_5-Si bond length to decrease and Si=O_1 double bond was weakened. As seen from Table 6 the formation of Si-O_5 and O_1-H_6 bonds leads simultaneously to weakening of O_5-H_6bond.

Table 6. The geometrical parameters of the reaction mechanism.

Parameters	1+2	TS	P
Si_1-O_2	1.53	1.64	0.92
Si_1-O_5	---	1.74	0.92
Si_1-H_3	1.49	1.5	0.94
Si_1-H_4	1.49	1.5	0.94
O_2-H_6	---	1.34	0.94
O_5-H_6	0.97	1.15	---
O_5-H_7	0.97	0.95	0.94
O_2-Si_1-H_3	123.48	120.22	71.53
H_3-Si_1-H_4	113.06	111.11	109.73
O_2-Si_1-O_5	---	72.83	107.21
$E_{(kcal / mol)}$	0	-18.1	-70.34

Vibration which is impossiple, ie, would cause molecule to spontaneously break down finding exactly one indicates that molecule is a transition structure [11]. The transition state **TS** is characterized by the presence of a four membered cycle for **TS**, the bond distances Si-O_1, O_1-H_6, H_6-O_5, Si-O_5 were found to be 1.64 ; 1.34 ; 1.15 ; 1.74 A° respectively. The transition state is characterized by the relative energy of –18.10 kcal\mol and the only imaginary frequency of 2002.71 cm⁻¹. Further approach of the atoms O_5 and Si finally leads to the formation of Si-O_5 and O_1-H_6 bonds and breaking of O_5-H_6 bond in the form of silandiol in which the bond distances Si-O_1,O_1-H_6, Si-O_5 are 1.70; 0.94; 1.70 for which the relative energy was found to be –70.34 kcal /mol .

Table 7. The bond order values for the reaction mechanism.

Bond Order	R1+R2	TS	P
Si_1-$O2$	1.9	1.22	0.92
Si_1-O_5	0	0.67	0.92
Si_1-H_3	0.93	0.93	0.94
Si_1-H_4	0.93	0.93	0.94
O_2-H_6	0	0.44	0.44
O_5-H_6	0.97	0.45	0.45
O_5-H_7	0.97	0.9	0.9

Table 8. The charges on atoms.

Atoms	Charges		
	R1+R2	TS	P
Si_1	0.82	0.81	0.87
O_2	-0.54	-0.62	-0.5
H_3	-0.14	-0.13	-0.13
H_4	-0.14	-0.13	-0.13
O_5	-0.36	-0.42	-0.5
H_6	0.18	0.31	0.2
H_7	0.18	0.18	0.2

For the reaction of silanones with H_2O, we observed that the **HOMO** of the water molecule and the **LUMO** of the silanone will react. The main property of the silanones for this reaction is their low **LUMO** energies. The **LUMO** energy values of each silanones studied in this work, the smallest energy value was found for compound 8 (E_{LUMO}=-0.89eV). The energy difference between **HOMO** of the water molecules (E_{HOMO}= -12.32eV for H_2O) and **LUMO** of the silanones is the least for this molecule, thus compound 8 will react more rapidly with water, compared to the others.

The $n_{o5} \rightarrow \pi$ interaction takes place when the lone pair electrons of O atom delocalize into the antibonding orbital π^* of Si atoms. During this interactions change in the charge of the atoms is presented in Table 8.

Acknowledgement

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