Determination of equilibrium distances of Si-F and Si-Cl, certain thermodynamic values and electron affinities of silanes and silyl radicals using the Hartree-Fock (HF) and density functional theory (DFT) *ab initio* methods

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ABSTRACT: The two quantum methods Hartree-Fock HF/6-31G* (d, p) and density functional theory DFT/3-21G* (d, p) were used to calculate the equilibrium of the Si-F and Si-Cl bonds in SiH_3X compounds where X may be F^- or Cl^-; the atomic electron affinity of chloride (Cl^-), fluoride (F^-), chlorine (Cl) and fluorine (F); entropy (S), heat capacity (C_v), total energy and reaction enthalpy of fluorosilanes, chlorosilanes and silyl radicals; and bond angles and bond lengths of SiH_3F and SiH_3Cl. Inter-atomic distances of the Si-F and Si-Cl bonds in SiH_3F and SiH_3Cl calculated using HR and DFT are in good agreement with the experimental values. The optimal distance of the Si-F bond is shorter than that of the Si-Cl bond in SiH_3X. Electron affinities calculated using HF and DFT are not in agreement with those obtained experimentally. The values of entropy (S) increase in parallel with the increase in the number of fluorine atoms in the silanes. The geometric structures of SiH_3F and SiH_3Cl both belong to the C_{3v} point group. Their bond angles are slightly different. SiH_3F has slightly higher energy than SiH_3Cl. This might be due to the value of the bond angle in SiH_3F, which is 109.18°. This is the same value obtained using the MP_2 quantum method.

KEYWORDS: Bond angle, electron affinity, enthalpy, entropy, energy of reaction, calorific capacity, state correlation diagramme, SN₂ reaction.

1 INTRODUCTION

In the field of chemical reactivity, quantum chemistry is an indispensable complement to experimentation, and has become an important tool for studying the stereoselectivity of concerted reactions. Quantum methods are used to solve problems relating to structure and chemical reactivity.

The application of quantum methods to molecular spectroscopy has become increasingly important in recent years [1], [2], [3], [4], [5], [6]. The majority of studies use *ab initio* rather than semi-empirical methods, although most molecular properties (e.g. enthalpy of formation, molecular geometry, dipole moments, ionization energy, and zero-point vibrational energy) have been obtained by semi-empirical methods [7], [8], [9], [10].

All calculations presented in this work were carried out using Hartree-Fock (HF) and density functional theory (DFT) methods in Gaussian 09 [11].

2 RESULTS AND DISCUSSION

2.1 STUDY OF REACTION BETWEEN THE NUCLEOPHILE F^- AND THE SUBSTRATE SiH_4

The attack by the nucleophile F^- on the SiH_4 substrate is represented as a nucleophilic substitution of type SN$_2$ (Figure 1).
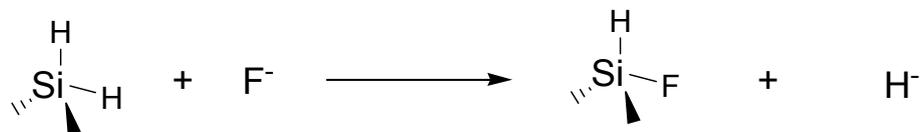

Fig. 1. Attack by the nucleophile F^- on SiH_4

The state correlation diagram (Fig. 2) shows two dips, marked B and D. The energy difference between states A and B is ΔE_1, equal to -98.75 atomic units (a.u.) The energy difference between states C and D is ΔE_2, equal to -99.352 a.u. The energy differences ΔE_1 and ΔE_2 correspond to intrinsic barriers. The final energy E is significantly lower than the initial energy A. The probability of the inverse reaction is very low and the system evolves fully to the final state E.
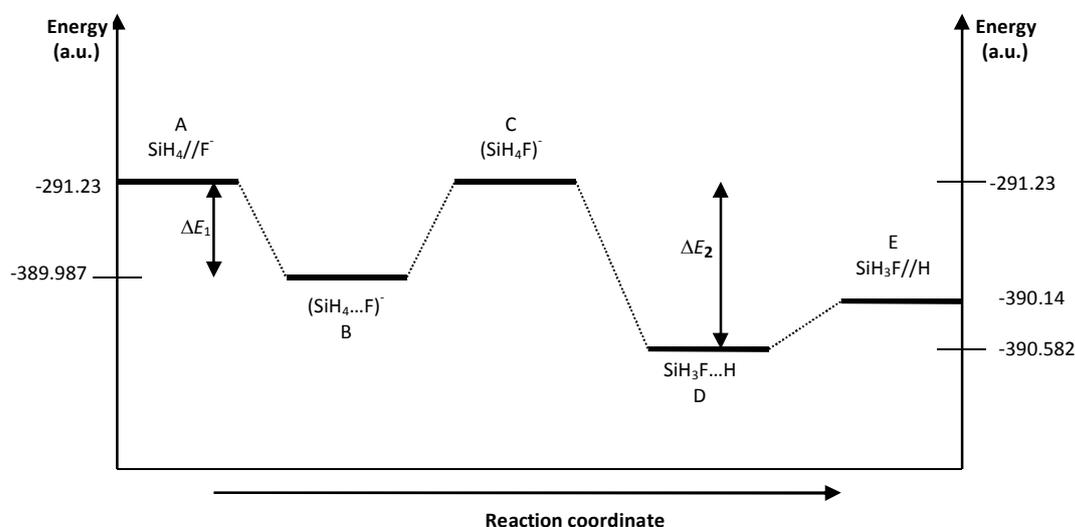

Fig. 2. State correlation diagram showing reaction between nucleophile F^- and substrate SiH_4

Energy as a function of equilibrium distance of the Si-F bond calculated using the HF and DFT methods is shown in Figure 3. Reaction energies and inter-nuclear equilibrium distances of the SiH_3X substrate with X=F^- are shown in Table 1.

Fig. 3.   Energy as a function of equilibrium distance of the Si-F bond (HF and DFT respectively)

Energy graphs of SiH_3F in Figure 3 show that the optimal distance for the silicon-fluorine bond is 1.6 Å according to HF/6-31G*, compared to 1.7Å according to DFT. The value calculated by the HF method is in good agreement with the result obtained by H.B. Schlegel, S. Wolf and F. Bernardi [12]. Total energy calculated by HF is -390.056 a.u., compared to -389.135 a.u. calculated by DFT. Energy calculated by the HF method is more stable than that calculated by DFT.

Table 1.   Energy of the reaction between nucleophile F⁻ and SiH_4 substrate

d (Å)	Energy (a.u.) HF/6-31G* (d, p)	Energy (a.u.) DFT/3-21G* (d, p)
0.9	-388.177	-383.582
1.0	-388.985	-385.835
1.1	-389.455	-387.220
1.2	-389.732	-388.032
1.3	-389.894	-388.511
1.4	-389.986	-388.976
1.5	-390.035	-388.112
1.6	-390.056	-388.135
1.7	-389.705	-389.142
1.8	-390.140	-389.138
1.9	-388.941	-389.129
2.0	-387.242	-389.116
2.1	-387.421	-389.102
2.2	-386.554	-389.083

2.2   STUDY OF REACTION BETWEEN THE NUCLEOPHILE CL⁻ AND THE SiH_4 SUBSTRATE

The attack by the nucleophile Cl⁻ on the SiH_4 substrate is represented as a nucleophilic substitution of type SN_2 (Figure 4).
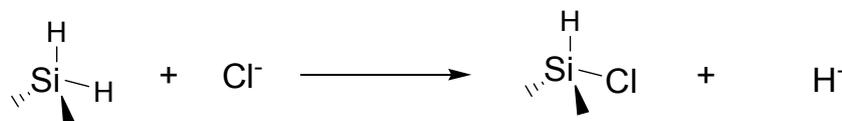

Fig. 4.   Attack by the nucleophile Cl⁻ on SiH_4

The state correlation diagram (Figure 5) shows two dips, marked B' and D'. The energy difference between states A' and B' is ΔE'1, equal to -0.11 a.u. The energy difference between states C' and D' is ΔE'2, equal to -0.1 a.u. The reaction between Cl^- and SiH_4 shows the same behaviour as that between F^- and SiH_4, which means that this too evolves to the final state E'.
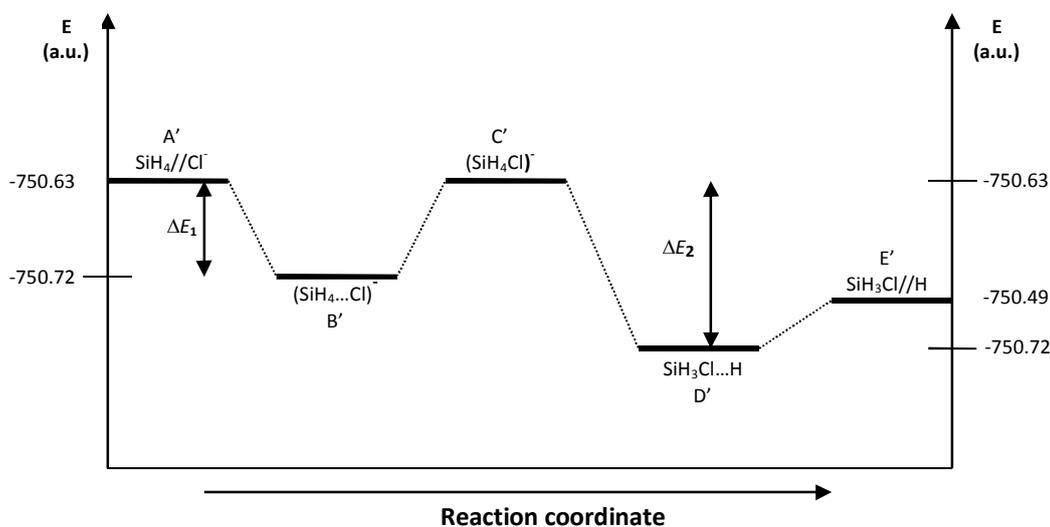

Fig. 5.   *State correlation diagram showing reaction between nucleophile Cl^- and substrate SiH_4*

Reaction energies and inter-nuclear equilibrium distances of the SiH_3X substrate with X= Cl^- are given in Table 2. Energy as a function of the equilibrium distance of the Si-F bond calculated using the HF and DFT methods are shown in Figure 6.

Table 2. Energy of the reaction between nucleophile Cl^- and substrate SiH_4

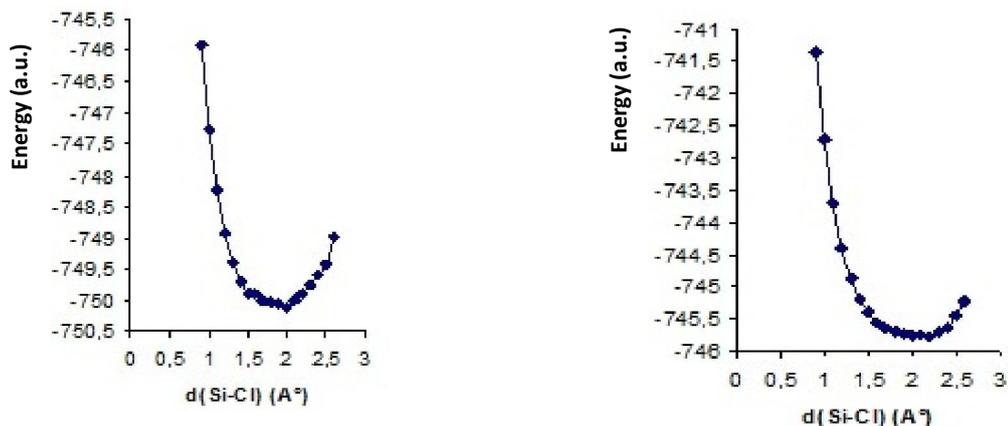| d (Å)	Energy (a.u.) HF/6-31G* (d, p)	Energy (a.u.) DFT/3-21G* (d, p)
0.9	-745.923	-741.354
1.0	-747.275	-742.722
1.1	-748.241	-743.702
1.2	-748.920	-744.391
1.3	-749.383	-744.867
1.4	-749.691	-745.190
1.5	-749.893	-745.406
1.6	-750.022	-745.549
1.7	-750.102	-745.640
1.8	-750.150	-745.698
1.9	-750.176	-745.732
2.0	-750.187	-745.750
2.1	-750.188	-745.757
2.2	-750.183	-745.758
2.3	-750.174	-745.754
2.4	-750.163	-745.747
2.5	-750.150	-745.739
2.6	-750.138	-745.729

Fig. 6.   Energy as function of equilibrium distance of the Si-Cl bond (HF and DFT respectively)

Energy graphs of SiH_3Cl in Figure 6 show that the optimal distance for the silicon-chlorine bond is 2.1 Å according to HF/6-31G*, compared to 2.2 Å according to DFT. The value calculated by the HF method is in good agreement with the theoretical result obtained using the MP_4 method [13].

SiH_3F and SiH_3Cl belong to the some point group C_{3v}, although bond angles and bond lengths of SiH_3F and SiH_3Cl are slightly different. SiH_3F has slightly greater energy than SiH_3Cl, possibly because of the bond angle in SiH_3F, which is 109.18°. This value is in good agreement with theoretical results obtained by the MP_2 method using the base 6-31++G [14].

2.3   CERTAIN THERMODYNAMIC PROPERTIES OF SILANES AND SILYL RADICALS

Table 3 shows the thermodynamic and reaction energy results and equilibrium distances for the reaction between the halogen X (F^-, Cl^-) and the substrate SiH_4, calculated by the more reliable method, namely low HF 6-31G*:

Table 3. Thermodynamic properties of silanes and silyl radicals

Species	Distance Si-X (Å)	Entropy (S) (Cal/mol.K)	Heat capacity (C_v) (Cal/mol.K)	Theoretical energy (Kcal/mol)	Enthalpy ΔH_r (H)
H^-	------	26.014	2.981	889	-0.420
SiH_4	1.47	48.658	7.685	22.784	-291.195
F^-	------	36.145	2.981	0.889	-99.365
SiH_3F	1.6	56.726	8.763	20.354	-390.130
SiH_2F_2	1.601	62.384	10.486	17.648	-489.066
$SiHF_3$	1.60	65.985	12.782	14.595	-588.009
Cl^-	-------	36.586	2.981	0.889	-459.537
SiH_3Cl	2.10	59.608	9.665	19.737	-750.156
SiH_2Cl_2	2.05	68.069	12.333	16.371	-1209.117
$SiHCl_3$	2.037	74.347	15.613	12.710	-1668.077

The reaction between a nucleophile X^- (F^-, Cl^-) and the substrate SiH_4 leads to loss of a proton. Silyl radicals are more polarized than silanes, possibly due to the effect of the substituents. For polarization of fluorosilane in the gaseous phase at 298 K°, the values of entropy S (cal/mol.K) of the compounds SiH_4, SiH_3F, SiH_2F_2 and $SiHF_3$ are respectively 48.658, 56.726, 62.384 and 65.985. This increase indicates that interactions between fluorine atoms lead to increased polarity [15]. For chlorosilanes, the effects of the substituents are greater. The values of entropy S (cal/mol.K) for the compounds SiH_4, SiH_3Cl, SiH_2Cl_2 and $SiHCl_3$ are respectively 59.608, 68.069 and 74.347. When a chlorine atom replaces a fluorine atom in the fluorosilanes, the polarity of the silane increases by 3 Cal/mol, leading to stabilization of the silane.

2.4 CALCULATION OF ELECTRON AFFINITY

Electron affinity and the energy of the nucleophil X^- (X=F^- and Cl^-) and the atoms F and Cl are shown in Table 4.

Table 4. Electron affinity of atomic species

Species	Energy (a.u.) HF/6-31G* (d, p)	Energy (a.u.) DFT/3-21G* (d, p)
Cl^-	-459.539	-458.057
Cl	-459.448	-457.945
Electron affinity (eV)	2.74	2.29
F^-	-99.418	-99.150
F	-99.371	-99.182
Electron affinity (eV)	3.28	1.33

We see that the configuration interaction stabilizes Cl and Cl-by 0.1 a.u. Electron affinities calculated using HF/6-31G*(d,p) and DFT/3-21G(d,p) are 2.74 eV and 2.29 eV respectively. This latter value is not in good agreement with that obtained experimentally, namely 3.61 eV. Electron affinities previously obtained by O'Neil et al [16] and Meyer [17] are 3.32 eV and 3.48 eV respectively. This difference is certainly due to the small size of the base used for the study of the chlorine atom.

For the species F and F^-, electron affinity is 1.33eV calculated using DFT/3-21G (d,p) and 2.93 eV using HF/6-31G*(d,p). These two values are not in good agreement with the value obtained experimentally, namely 3.43eV. Using a Gaussian base of type 4s4ps4d, we calculated an electron affinity of 3.28 eV, which is closer to the experimental value.

3 CONCLUSION

In this study, we looked at the ability of the HF and DFT *ab initio* methods to calculate equilibrium distances of Si-F and Si-Cl bonds in silanes and silyl radicals, thermodynamic values (entropy S, heat capacity Cv, total energy and enthalpy ΔHr) and electron affinities of the fluoride and chlorine nucleophiles. Results obtained were in good agreement with experimental and theoretical data obtained using other *ab initio* methods. The HF/6-31G* method appears to give the best results.

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