Determination of Relative Reactivity of HSAB Complexes Using DFT Theory

Salah Aldin Jassim Humadi*
Department of Chemistry, College of Science, University of Diyala. Diyala, Iraq.

Abstract

Based on the density functional theory (DFT) , the stability of molecular complexes has been predicted according to hard-soft acid base (HSAB) theory. Relative stability of products and reactivity of soft base sulfide derivatives with halogens (Iodine , Bromine , Chlorine) as soft acid was studied to determine the relative ability of these reactants causing the reaction to be more spontaneous.
DFT at the levels of B3LYP/3-21G and B3LYP/3-21G (d) was used to study HOMO LUMO energy gaps , bonds length and total energy to calculate the softness sequence of each type of acid or base mentioned in this work. All cases studied prove that iodine can be considered as the most softness acid and ethyl methyl sulfide≈ dimethyl sulfide the most softness bases.

Key words : DFT , HSAB , stability, reactivity , halogens

تحديد الفعالية النسبية لبعض معقدات HSAB باستخدام نظرية الدوال المكثفة

صلاح الدين جاسم حمادي
قسم الكيمياء، كلية العلوم، جامعة ديالى، ديالى‘العراق

الخلاصة

باستخدام نظرية الدوال المكثفة DFT تم متابعة استقرارية المعقدات المتكونة وفق مفهوم حامض قاعدة صلب لين HSAB . تم دراسة الاستقرارية النسبية للنواتج وفعالية القاعدة اللينة كبريتيد ثنائي المثيل R2S وبعض مشتقاتها مع الهالوجينات (اليود البروم والكلور) كحامض لويس لتشخيص القدرة النسبية لهذه المتفاعلات على انجاز التفاعل بشكل اكثر تلقائية تم استخدام نظرية DFT وبمستوى B3LYP/3-21Gومستوى اخر B3LYP/3-21G(d) لدراسة الفرق في مستوى الطاقة بين HOMO و LUMO واطوال الاواصر والطاقة الكلية لانجاز التفاعل لغرض ترتيب الليونة النسبية لكل من النماذج المدروسة سواء كانت حامض او قاعدة وتبين من خلال الحالات المدروسة ان اليود I_2 يمثل الحامض الاكثر ليونة وان كبريتيد الاثيل مثيل ≈ ثنائي مثيل كبريتيد يعتبر القاعدة الاكثر ليونة

Introduction

HSAB theory is one of the most important guidance to predict the reaction path way and the stability of the products . Its principle conclude the following equation:
[hard acid (:soft base)$_n$] + [soft acid (:hard base)$_n$] $\longrightarrow$ [hard acid (:hard base)$_n$] + [soft acid (:soft base)$_n$].
that means : hard acids prefer hard bases and soft acids prefer soft bases[1].

Theoretical calculation used widely in the applications of HSAB such as the quantitative explanation of the differences in reactivity toward nucleophilic attack[2,3]. HSAB applications is very important in chemistry , it is useful in the quantitative analysis for metals ions , in redox chemistry by

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*Email:drsalahalmula@gmail.com.

explanation of reduction potential values , classification of geochemical minerals due to expection ore types and their components , in medicinal chemistry and toxicology of the elements [4].

Based on the density functional theory (DFT) investigation, the quantitative relationship between nucleophilicity / basicity and HSAB theory based properties of compounds with lonepair electrons can also be done[5]. The chemical reactivity descriptors calculated using DFT are; total energy (E), chemical hardness (η), electronic chemical potential (μ), and electrophilicity (ω). Chemical hardness corresponds to the gap between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO)[6].

The determination of possible reaction pathways is related to variable parameters including total energy , HOMO LUMO energy gap and others . For different reaction pathways between reactants and products , path of lower energy will be the pathway , also when the frontier orbitals are closest energy , hence the most favorable pathway [7,8].

The HSAB can be restated as follows:

A hard – hard interaction is fast because of a large columbic attraction.

A soft – soft interaction is fast because of a large orbital interaction between the HOMO of nucleophile (base) and the LUMO of electrophile (acid) [9].

A Higher value of EHOMO is likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy. Increasing values of EHOMO facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer [10]. Total energy represents the importance gaudiness of the ease of chemical reaction , it means the sum of kinetic and potential energy[11].

The negative total energy also indicates that the product is a very stable molecule and is less prone to be split or broken [12,13]. The governing principle of DFT involves solving the Schrödinger equation in terms of the electron density[14] .DFT is also able to describe site selectivity or reactivity of an atom in a molecule[3].

Calculation method:

ChemBio3D Ultra 11. was used as acalculation program .Geometry optimizations of all the structures leading to energy minima were carried out using molecular mechanics method (MM) , then density functional theory method DFT , B3LYP at the basis set 3-21G were used after the first method MM to reach the final minimization . Also, another method DFT / B3LYP- 3-21G (d) was used in this study For comparison purpose.

Results and discussion :

Selection of the suitable method is required in such studies and matching between theoretical and experimental data [15-18] to obtain real results is so important. Based on the available results in the literature ,geometrical optimization including bond lengths of intramolecular diatomic halogens is considered one of the important

factors that give good confidence of the accuracy .Results shown in table-1

confirm that there is considerable convergence between experimental and calculated values from B3LYP- 3-21G (d) method

Table 1- Calculated and experimental halogens bond lengths

	DFT/B3LYP/3-21G	**DFT/B3LYP/3-21G(d)**	**Experimental**
	Bond length A^{o}		
I2	2.900	2.719	2.66 ref.15 2.67 ref.16
Br2	2.475	2.396	2.284 ref.17
Cl2	2.204	2.047	1.988 ref.18

HOMO and LUMO energies :

According to the values of Energy Gap (E) between HOMO and LUMO , smaller values of the energy difference indicates high reactivity of the reactants species , for different studied species , table-2 shown EHOMO and ELUMO values and the gaps between each type . in addition , fig-1,2 refers to the ease of chemical reactions between higher HOMO energy of both soft base $(C_2H_5)CH_3S$ and $(CH_3)_2S$ **(**which they 'have equal opportunities**)** with smaller LUMO energy of soft acid iodine , while fig-3 shows the size of LUMO shape of halogens which represents LUMO energy levels.

Table 2- HOMO and LUMO energies at different calculation levels

Compound	DFT B3LYP 3-21G			DFT B3LYP 3-21G (d)		
	HOMO eV	LUMO eV	GAP eV	HOMO eV	LUMO eV	GAP eV
Soft acid						
I_2	-9.047	5.776	14.823	-8.250	14.329	22.58
Br_2	-9.921	8.247	18.168	-8.789	20.186	28.97
Cl_2	-10.759	10.383	21.142	-9.304	25.771	35.07
Soft base						
$(CH_3)_2S$	-9.498	20.744	30.242	-9.024	25.426	34.45
H_2S	-11.601	29.122	40.723	-11.60	30.936	42.53
CH_3HS	-10.509	22.283	32.792	-10.25	26.889	37.48
$(C_2H_5)CH_3S$	-9.481	20.093	29.574	-9.026	24.912	33.93

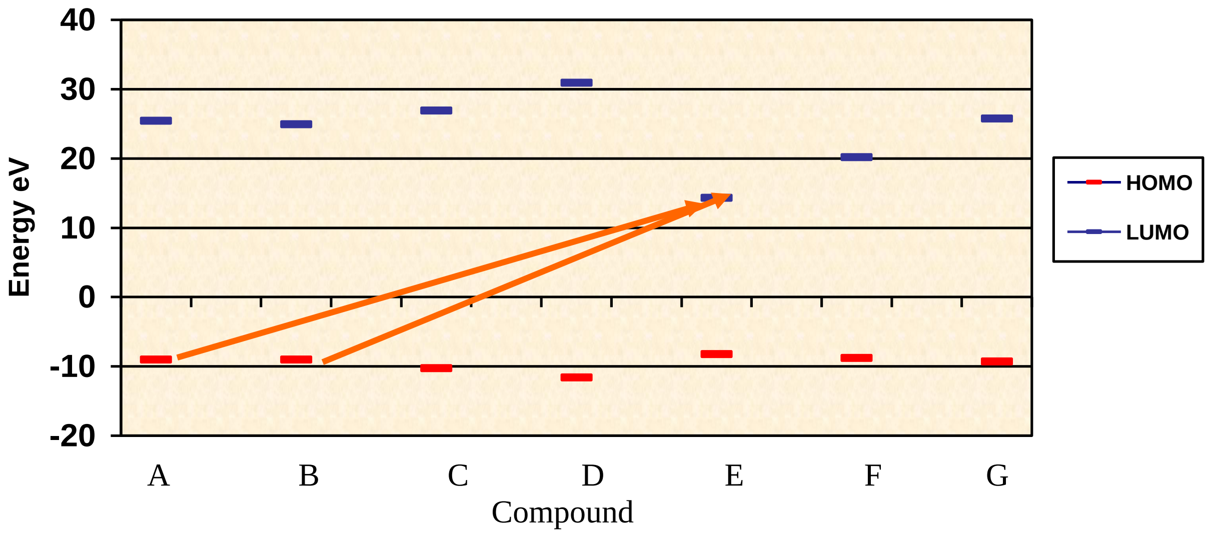

Figure 1- HOMO and LUMO energies calculated by DFT B3LYP 3-21G (d)

A= $(CH_3)_2S$
B=$C_2H_5CH_3S$
C=CH_3HS
D= H_2S
E=I_2
F=Br_2
G=Cl_2

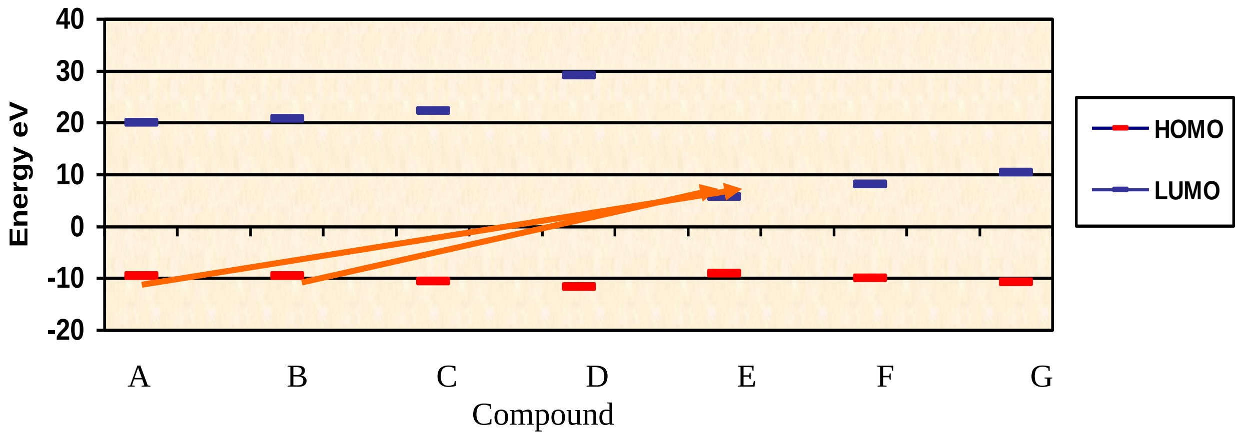

Figure 2- HOMO and LUMO energies calculated by DFT B3LYP 3-21G

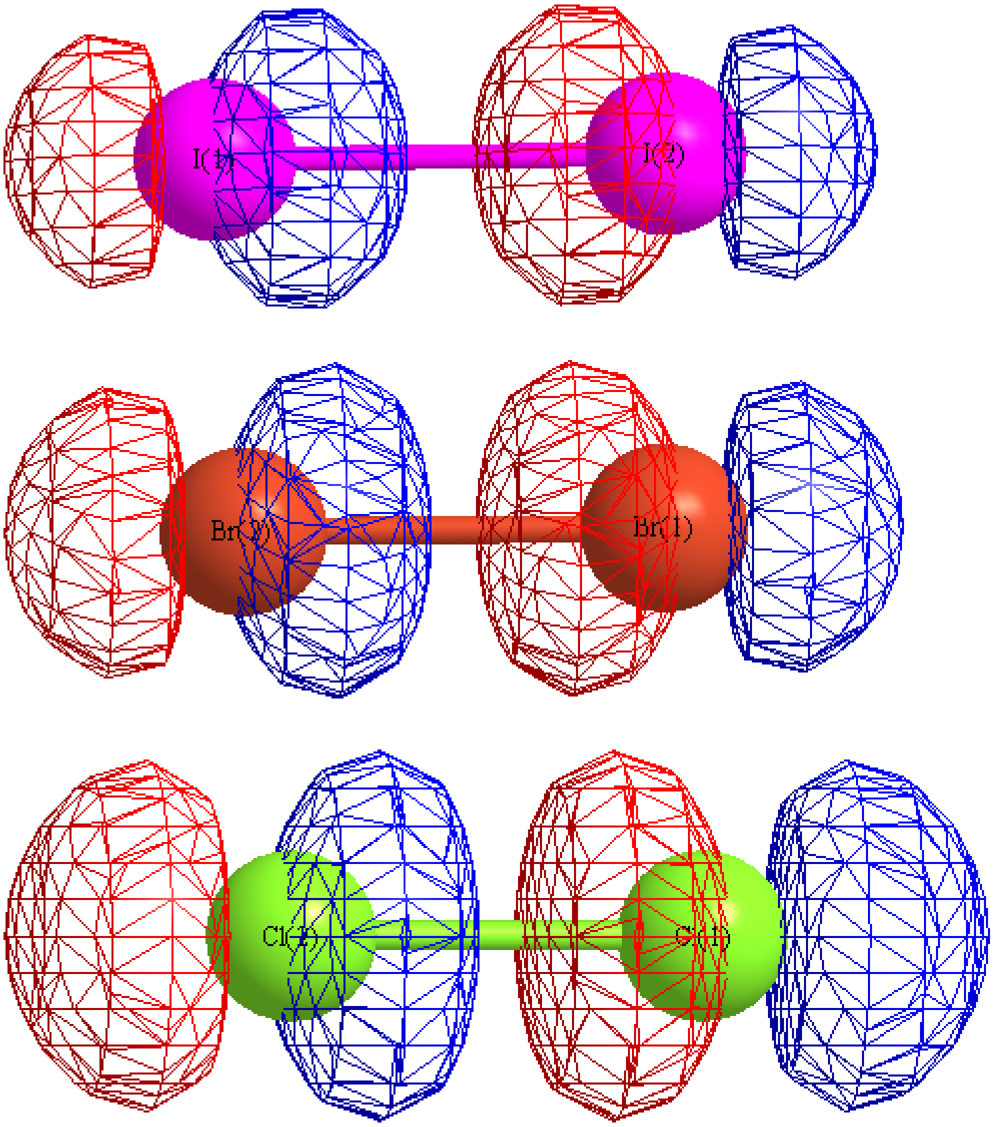

Figure 3- LUMO size energies of halogens

Total energy:

Total energy calculated in this work play an important role in governing the stability **of** complex , table-3 shown the data corresponding to the calculated values of total energy , more negative value means the complex is more stable, so due to this idea $(CH_3)_2(CH_3)S\ I_2$ can be considered more stable than the others , ethyl methyl sulfide represents the softness base toward the softness acid iodine

Geometrical analysis:

Intramolecular diatomic halogen bond length should elongate if an interaction is occurred[19].the sequence of elongation refers to the ease of interaction and the ability of complexation , the more elongation means the more interaction , so according to the table-4 ,dimethyl sulfide and ethyl metyl sulfide consider the softness base at DFT/B3LYP-3-21G (d) which is more accurate.

Table 3- Total energy (eV) of different complexes

Complex	Total energy eV	
	DFT/B3LYP-3-21G	DFT/B3LYP-3-21G (d)
$(CH_3)_2S$	-475	-475
$(CH_3)_2SI_2$	-14256	-14256
$(CH_3)_2SBr_2$	-5598	-5599
$(CH_3)_2SCl_2$	-1391	-1391
H_2SI_2	-14178	-14178
$(CH_3)HSI_2$	-14217	-14217
$(CH_3)_2S\ I_2$	-14256	-14256
$(C_2H_5CH_3)S\ I_2$	-14295	-14295

Table 4- I—I bond length in different complexes at different calculation levels

complex	Bond length of I-I A^o	
	DFT/B3LYP/3-21G	DFT/B3LYP/3-21G(d)
I_2	2.900	2.719
H_2S-I-I	2.943	2.726
$(CH_3)HS$-I-I	2.958	2.773
$(CH_3)_2S$-I-I	2.979	2.796
$(C_2H_5CH_3)S\ I_2$	2.9944	2.799

Conclusion :

The present study reflects the following points :

1- A comparative study between DFT B3LYP/3–21+G and DFT B3LYP/3–21+G(d) levels in chemical softness principles has been accomplished and results obtained shown that DFT B3LYP/3–21+G(d) method was more accurate for studied species.

2-In computational chemistry, Estimating the Credibility of the results is very important by using experimental data to compare between different method .

3-Due to obtained result from this study , the sequence of softness base are :

$\mathbf{C_2H_5(CH_3)S \approx (CH_3)_2S > CH_3HS > H_2S}$,and the sequence of softness acid **are :** $\mathbf{I_2 > Br_2 > Cl_2}$

4-polarization function (d) is very necessary in treatment such molecules to obtain accurate results .

5- although the difference in the accuracy between the two method used , both methods relatively resulted in the same sequence of softness order of calculated molecules.

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