Further Evidence of the Relative Stability Evaluation of Lewis Acid Base Complexes

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Abstract

Through Lewis acid-base complexation concept, interaction between three types of Lewis acid (BCl٣, AlCl٣ and SiCl٤) as acceptors and many oxygen containing ether groups (such as dimethyl ether, ethyl methyl ether, cyclohexyl methyl ether, phenyl methyl ether, ١,٢ dioxane, ١,٣ dioxane and ١,٤ dioxane) as donor ligands were evaluated based on several parameters including chemical potential, Global softness, HOMO- LUMO shapes and interaction energy of formed complexes.

Theoretical computational Density Functional Theory (DFT) and Hatree-Fock (HF) were used in addition to some empirical equations from literature to calculate the above mentioned parameters. This work proved that cyclohexyl methyl ether formed the most stable complex with silicon tetrachloride and the least stable complex being BCl٣ bond to dimetyl ether. This work provides further evidence that the relative Lewis acidity depends on the groups attached to the doner atom, and do not depend on the central atom of acid molecule.

Keywords: Lewis acid, complexation, interaction energy, donor, global softness, chemical potential.

Introduction

Metal-ligand bond strength depends on the value of interaction energy (E$_{int}$). The bond strength and complexes stability increase as the value of interaction energy decreases (more negative value)[1-3].

Complexes formation and their relative stability can be estimated from the complex geometry. Bond shortening between ligand atom and vacant orbital acceptor reflects strong interaction with high stability of complex[4,5].

It is found that the relative strength of donors depends on the nature of acceptor and vice versa, but many other factors may be involved. Hard Soft Acid Base (HSAB) classification is often used to rationalize some of strength difference[6]. Hard acid prefer hard base and soft acid prefer soft base. Hard hard interaction is fast because of large columbic attraction while a soft soft is fast because of large orbital overlap between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital)[7].

The interaction of a hard base with hard acid involves a low energy HOMO and a high energy LUMO[8]. A hard acid is likely to be strongly solvated [9].

According to HSAB, hard acids are positively charged on small atoms and have large gap between HOMO and LUMO energy, while soft acids are vice versa[10].

The strength of Lewis acid is a measure of its ability to attract a pair of electrons on molecule that behaves as Lewis base[11]. The relative strength of the Lewis acid depends on the nature of the atom and the groups attached to that atom[12].

Density Functional Theory (DFT) considers the accurate computation theory between other methods which results in a good quality calculations for small and relatively large system, it demonstrates the relationship between the electron density and the total energy of the ground state, while Hartree Fock method (HF) provides only averaged correlation energy [13,14].

This work aims to study the relative reactivity of Lewis acid base and the stability of formed complexes to determine if the sequence of acid strength depend on the nature of donor molecule or the nature of the central atom of acid molecule due to the tow famous theories addressed this field and to provide evidence to one of them.

Calculation Methods

Using ChemBio٣D Ultra, HOMO, LUMO and optimization of Equilibrium Geometries of all studied molecules and their complexes have been calculated with two methods, density

functional theory (DFT) -B٣LYP at ٦-٣١١G (d) basis set and Hartree–Fock (HF) at ٣-٢١G (d).

Interaction energy is calculated by the following equations:

$$E_{int.} = \Delta E_v + \Delta E\mu \quad ....١$$

All factors such as: $E_{int.}$, ΔE_v, $\Delta E\mu$□□□ chemical potential (μ) for□ acid and base, global softness (S) for acid and base, electronegativity (χ), the relation between Ionization energy (I) and Е_{НОМО}, the relation between electron affinity (A) and E_{LUMO} and finally λ (as constant) where defined in references [١٥-١٩].

Result and discussions

Cyclohexyl methyl ether > ١,٣ dioxine > ١,٤ dioxine > Ethyl methyl ether > ١,٢ dioxine > Phenyl methyl ether (anisole) > Dimethyl ether.

and with DFT method, the following was obtained:

Cyclohexyl methyl ether > ١,٣ dioxine > ١,٤ dioxine > Ethyl methyl ether > Dimethyl ether > ١,٢ dioxine > Phenyl methyl ether (anisole)

Complexes of boron trichloride with the same donors have been determined too, by HF method, the order was determined as follows:

Cyclohexyl methyl ether > ١,٣ dioxine > ١,٤ dioxine > Phenyl methyl ether (anisole) > Ethyl methyl ether > ١,٢ dioxine > Dimethyl ether

and by DFT method, the order obey the following:

Cyclohexyl methyl ether > ١,٣ dioxine > ١,٤ dioxine > Phenyl methyl ether (anisole) > Ethyl methyl ether > ١,٢ dioxine > Dimethyl ether

Finally, the order of stability for silicon tetrachloride with ethers show another results especially in phenyl and dioxane derivatives, for HF the order being:

Cyclohexyl methyl ether > Phenyl methyl ether (anisole) > ١,٣ dioxine > ١,٢ dioxine > ١,٤ dioxine Ethyl methyl ether > Ethyl methyl ether >Dimethyl ether

and for DFT:
Cyclohexyl methyl ether > Phenyl methyl ether (anisole) > ١,٣ dioxine > ١,٢ dioxine > ١,٤ dioxine Ethyl methyl ether > Ethyl methyl ether >Dimethyl ether.

DFT and HF methods were used to determined HOMO, LUMO energy which represent the base line to calculate all other parameters studied in this work till the net values of interaction energy. It is known

In order to evaluate chemical reactivity and complexes stability between seven types of ethers (as Lewis bases) and three types of Lewis acids BCl٣, AlCl٣ and SiCl٤, different parameters were determined as a base line to calculate interaction energy which represents the important factor to establish the main goal of this work.

Complexation of all seven types of donors (ethers) with each one of acceptor were studied using both DFT and HF methods.

Table (١) shows the order of stability of these complexes, the following order of stability was obtained for complexes of aluminum trichloride and ethers using HF method:

that DFT is more accurate than HF (which provides only averaged correlation energy). A comparison between the two methods was carried out for further confidence to evaluate the relative strength of Lewis

acid base interaction. The obtained results in Tables (1-3) show good matching between them except one case in Table (1) that disturb the sequence with respect to the position of dimethyl ether and both (phenyl methyl ether and 1,2 dioxane), in any case DFT still the considerable method in such studies.

According to remarkably results obtained by DFT method due to the relative complexation ability between phenyl methyl ether as ligand with AlCl₃ or BCl₃ (both are approximately the same) and SiCl₄ as acceptors, it is clear that phenyl methyl ether occupies the last order in its ability to interact with AlCl₃ between the seven mentioned ligands, while with SiCl₄ it occupies the second order. The other possible explanation (in addition to interaction energy values) is the shape and size of HOMO lobe. HOMO shape is an indication of how the density of the electrons distributed in the molecule. It is clearly shown that the electron density (available on phenyl methyl ether Fig.(1a) transferred completely to SiCl₄ site Fig.(1b) while in the case of AlCl₃, partially shifting were appeared Fig.(1c), this reflects that the ability of vacant d orbitals available in the silicon atom has more tendency to accept electron cloud density in the phenyl group which behaves as pi – ligand toward silicon d orbitals, while AlCl₃ vacant d orbitals do not have the same ability. By the same way, 1,2 Dioxane also occupies the latest complexation order with respect to AlCl₃, but with SiCl₄, the case is on the contrary, despite the lack of pi – ligand, dioxane which contains two centers of electron density (2 oxygen atoms) can be able to behave as bidentate molecule toward silicon vacant d orbitals which able to recover the further electron density from the oxygen but less than phenyl, see (Fig.(2 a,b,c)). Increasing SiCl₄ ability to accept further electron density is matching with (G. Michelangelo) [20] who state that Lewis base coordination to SiCl₄ activates Lewis acid.

There are two theories govern the order of Lewis acidity, the first theory gives definite concepts, for example, BCl₃ is absolutely stronger acid than AlCl₃ with out exception [16,21], while the second theory refers that the relative orders of Lewis acidity will depend on the identify of the base used. According to this work, evidence has been provided to predominate the second theory and this conclusion clearly appears in Table (1&3), which indicates that BCl₃ is more acidic toward both phenyl methyl ether and 1,2 dioxane, while AlCl₃ is more acidic toward other donors, so we provide further evidence that the second theory consider the preference one and there is no definite concepts about this case.

Conclusion

Cyclohexyl methyl ether is the strongest Lewis base (between the seven ligands) toward different studied acid due to its high donating ability as big electron release group. This work provides further evidence that the relative Lewis acidity depend on the nature of donor molecule and there is no definite opinion about this subject (as some references show). Both Al and Si have vacant d orbital, but Si in silicon tetrachloride has good ability to accept additional electon density especially from pi ligand such as phenyl group. Relatively, both HF and DFT give the same order except one case mentioned above.
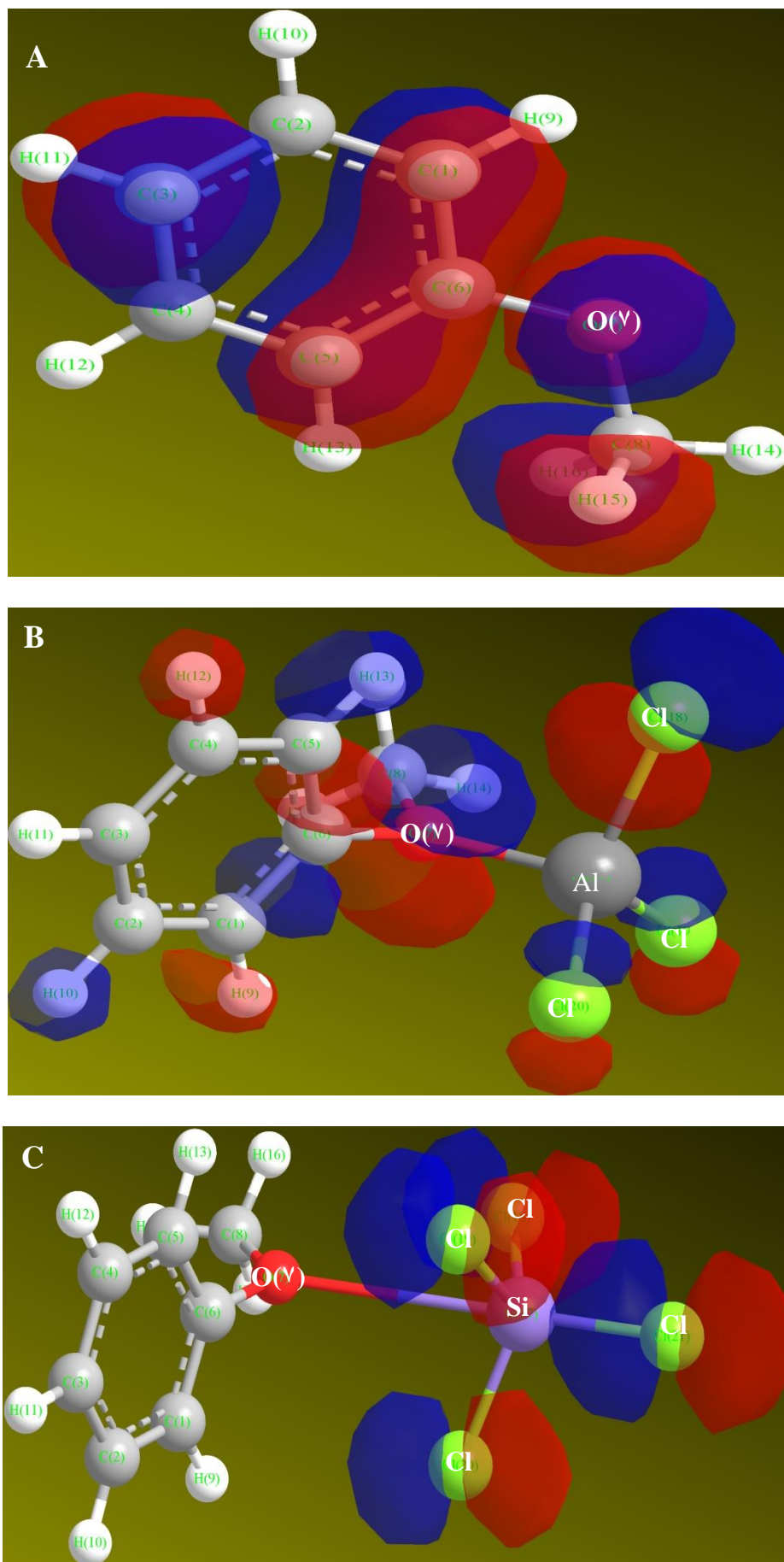
Fig.(¹) The shape of HOMO lobe A) phenyl ethyl ether, B) phenyl ethyl ether bind with AlCl٣, C) phenyl ethyl ether bind with SiCl٤.
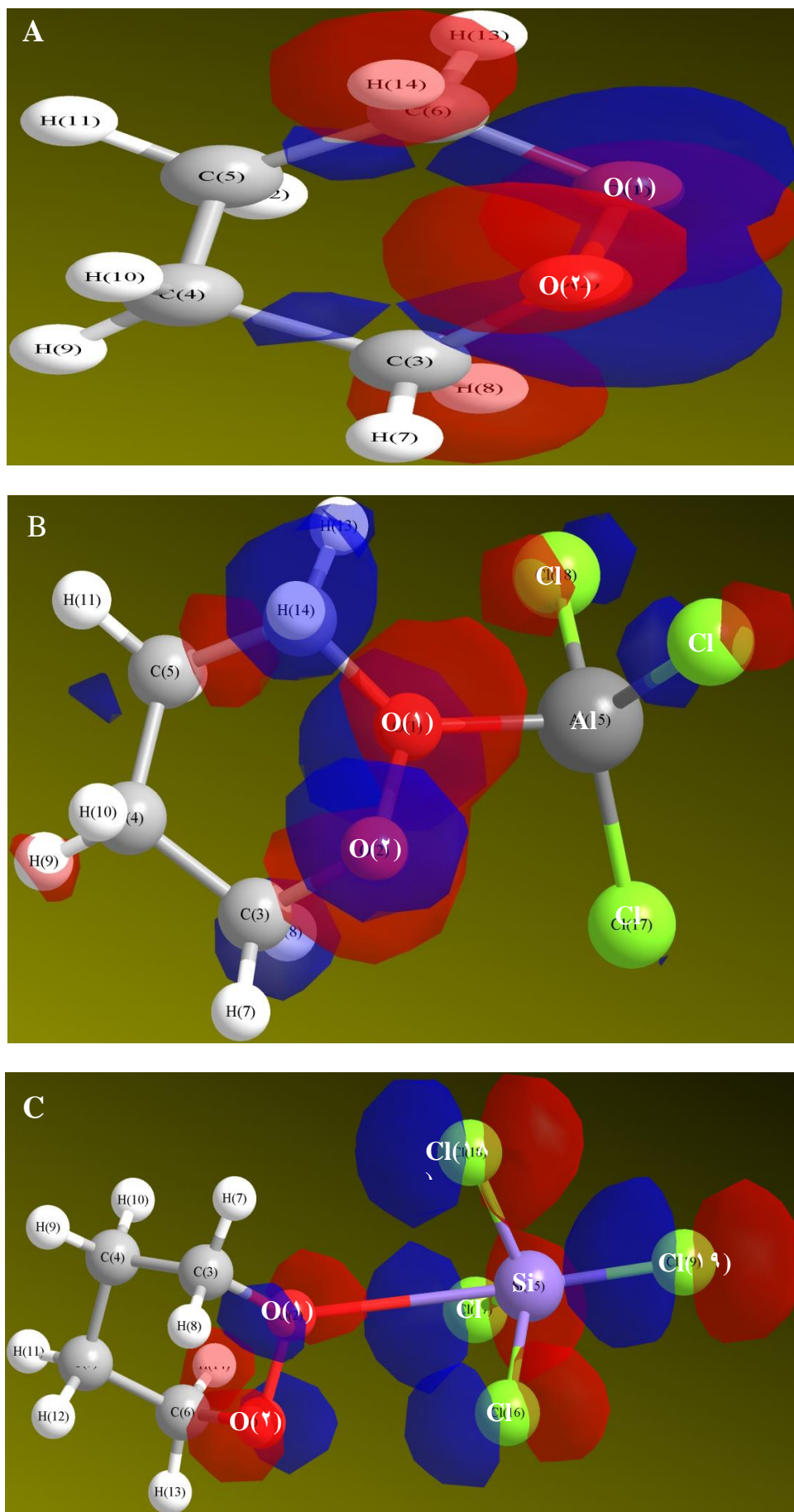
Fig.(٢) The shape of HOMO lobe A) ١،٢ Dioxane, B) ١،٢ Dioxane bind with AlCl٣,
C) ١،٢ Dioxane bind with SiCl٤.

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الخلاصة

وفقا لمفهـوم المعقـدات المتكونـة بـين حـوامض وقواعـد لويس، تم تقييم التأثرات الحاصلة بين مجموعة من حوامض لـويس (BCl₃ و AlCl₃ و SiCl₄) كمسـتقبلات وبعـض الايثرات الحاوية على الاوكسجين مثل (ثنائي مثيل ايثر واثيل مثيل ايثر وسايكلوهكسيل مثيل ايثر وفنيل مثيل ايثر و ۱-۲ دايوكسـان و ۱-۳ دايوكسان و ۱-٤ دايوكسـان) كليكانـدات مانحـة اعتمـادا على مجموعـة مـن المتغيرات والتي تتضمن الجهد الكيميـاوي، الليونـة، طاقة التفاعل واشكال HOMO، LUMO تم استخدام نظريـة دوال الكثافة DFT و هـارتري فوك HF اضـافة الـى المعـادلات التجريبيـة المسـتخرجة مـن الادبيـات ذات الصـلة بالموضوع. من خـلال هـذا البحـث تم التثبـت مـن الاسـتقرارية العاليـة للمعقـد المتكـون بـين السـايكلوهكسيل مثيـل ايثر ورابـع كلوريد السـليكون بينما كان المعقـد الاقل استقرارا هو المتكون بين ثنائـي مثيل ايثر وثالث كلوريد البـورون. تم في هذا البحث تقديم دليل اضـافي الـى النظريـة التي بموجبها يتم تقييم قوة حامض لويس على اسـاس المجـاميع التي تـرتبط بالـذرة المانحـة وليس علـى نـوع الـذرة المركزية لجزيئة الحامض.