PM3 Calculations on Corrosion Inhibition of Aluminum by phosphonium compounds

Zohor M . Elshawi[1,*] , Salim M. Khalil[3], Manal Ali. Erteeb[4]

1- Department of lab medicine, Higher Institute for Medical Profession – Elzahra
Email [*]; zohorshawe.82@yahoo.com
2- Department of Chemistry and Chemical Technology,Faculty of Science, Tafila Technical University.
3- Department of Chemistry and Higher Institute Of Sciences And Technology-Azizia
Email [*] : Manal.rateeb8503@gmail.com

ABSTRACT

We have performed a PM3 calculations on phosphonium as corrosion inhibitors of aluminum with complete optimization of geometries using B3LYP/6-31 G level (d, p) to find a relation between the molecular structure and corrosion inhibition. The electronic properties such as the energy of the highest occupied molecular orbital (HOMO), the energy of lowest unoccupied orbital (LUMO), the energy gap (LUMO–HOMO), quantum chemical parameters such as hardness, softness, the fraction of the electron transferred, and the electrophilicity index. the inhibition efficiency of the investigated phosphonium compounds follows the trend allyl triphenyl phosphonium iodide < allyl triphenyl phosphonium bromide < allyl triphenyl phosphonium chloride < allyl triphenyl phosphonium .

Keywords: aluminum, PM3, Phophonium compounds, inhibitors, corrosion.

1-INTRODUCTION

Corrosion concern for industry, may cause reduced service life or complete failure of manufactured parts and finished goods. These issues directly impact the cost efficiency of the manufacturing process and cost of the finished goods, Corrosion inhibitors can be used to prevent the problems associated with corrosion. Corrosion is the destructive attack to metal by a chemical or electrochemical reaction with its environment. The terms corrosion and rusting are often used interchangeably The term "rust" typically is applicable to ferrous materials, iron and steel. Resistance of corrosion Some metals are more intrinsically resistant to corrosion than others (for some examples, see galvanic series). There are various ways of protecting metals from corrosion including painting, hot dip galvanizing, and combinations of these [1] .

1.1. Corrosion inhibitor

A corrosion inhibitor is a material that attaches or coats the metal surface, providing a protective barrier film, which in turn stops the corrosive reaction from developing. Temporary coatings are often used to prevent corrosion during storage and shipment, and between machining or processing operations. The most effective corrosion inhibitor coatings, at one time, were oil or solvent-based materials.

1.2 PM3(parametric model 3)

PM3 (parametric model 3) is a variation of AM1 [2] differing mainly in how the parameterization is done. The power of semi-empirical methods lies not in their theoretical rigor, but in the fact that adjustable parameters within the methods are optimized to reproduce important chemical properties. Any semi-empirical method is composed of a theoretical framework and a set of parameters. Ideally, these parameters should be fully optimized using an over determined reference set of molecules, but hitherto this has not proven possible. In the limit, when fully optimized parameters are used, the quality of a method depends solely on the nature of the approximations used, and more sophisticated methods will be the more accurate. This is exemplified by comparison between MNDO and CNDO (complete neglect of differential overlap). MNDO is a more sophisticated method than CNDO, taking into account lone-pair /lone-pair repulsions; therefore, a properly parameterized MNDO model should perform better than an equivalent CNDO model.The theoretical framework for AM1 is similar to that of MNDO, the only difference being the presence in AM1 of radial Gaussians which modify the core-core repulsion term. As there have been two earlier parameterizations of the MNDO-type model, in order to facilitate discussion, the resulting method, namely, the combined theoretical framework and optimized parameter set, is best described as a modified neglect of differential overlap, parametric method3, or MNDO-PM3. Within this parameterization method three types of reference functions are used [3].

1.3 The aim of the work

This work is aimed to give more theoretical insight to the effect of phosphonium compound as inhibitor corrosion of metal such as allyl triphenyl phosphonium, allyl triphenyl phosphonium bromide, allyl triphenyl phosphonium chloride and allyl triphenyl phosphonium iodide, using quantum mechanics methods such as ab intio and semiemperical calculations. Calculations will include HOMO and LUMO energies and energy gap. Calculating the quantum global parameters such as softness, hardness, fraction of electron transferred, and electrophylicity index are also reported .

1- RESULTS AND DISCUSSION

The calculated phosphonium compounds are allyl triphenyl phosphouinm, allyl triphenyl phosphonium chloride, allyl triphenyl phosphonium bromide and allyl triphenyl phosphonium iodide under investigation and there structures are shown in Scheme.1 . Frontier Molecular orbital's (HOMO and LUMO), energy gap (ΔE), hardness (η) softness (σ), the fraction of the electron trandferred (ΔN), and electrophililcity index (ω), were calculated for these compounds according to molecular orbital theory[8],the EHOMO and ELUMO of the inhibitor molecule are related to the ionization potential (I) and the electron affinity (A) respectively, by the following relation:

$I = - E_{HOMO}$ ……..…..(1)

$A = - E_{LUMO}$. ….…….(2)

The absolute electronegativity (X), the absolute hardness (η) of the inhibitor, the softness (σ) and the electrophilicity index (ω) are given by [9]:

$X = (\frac{I+A}{2})$ ……………….(3)

$\eta = (\frac{I-A}{2})$ ………………...(4)

$\sigma = \frac{1}{\eta}$ …………………...(5)

$\omega = \frac{\mu^2}{2\eta}$ …………………...(6)

where (η) represent the chemical potential and is assumed to be equal to the negative of electronegativity (X) [4]. ω is the electrophilicity index, which was proposed by Parr [4] as a measure of the electrophilic power of a molecule. When two systems, metal and inhibitor, are brought together, electrons will flow from lower X (inhibitor) to higher X (metal) until the chemical potentials become equal. The obtained values of X and η are used to calculate the fraction of the electron transferred, (ΔN), from the inhibitor to metallic surface as follow [5]:

$$\Delta N = \frac{X_{metal} - X_{inh}}{2(\eta_{metal} + \eta_{inh})} \text{ …………(7)}$$

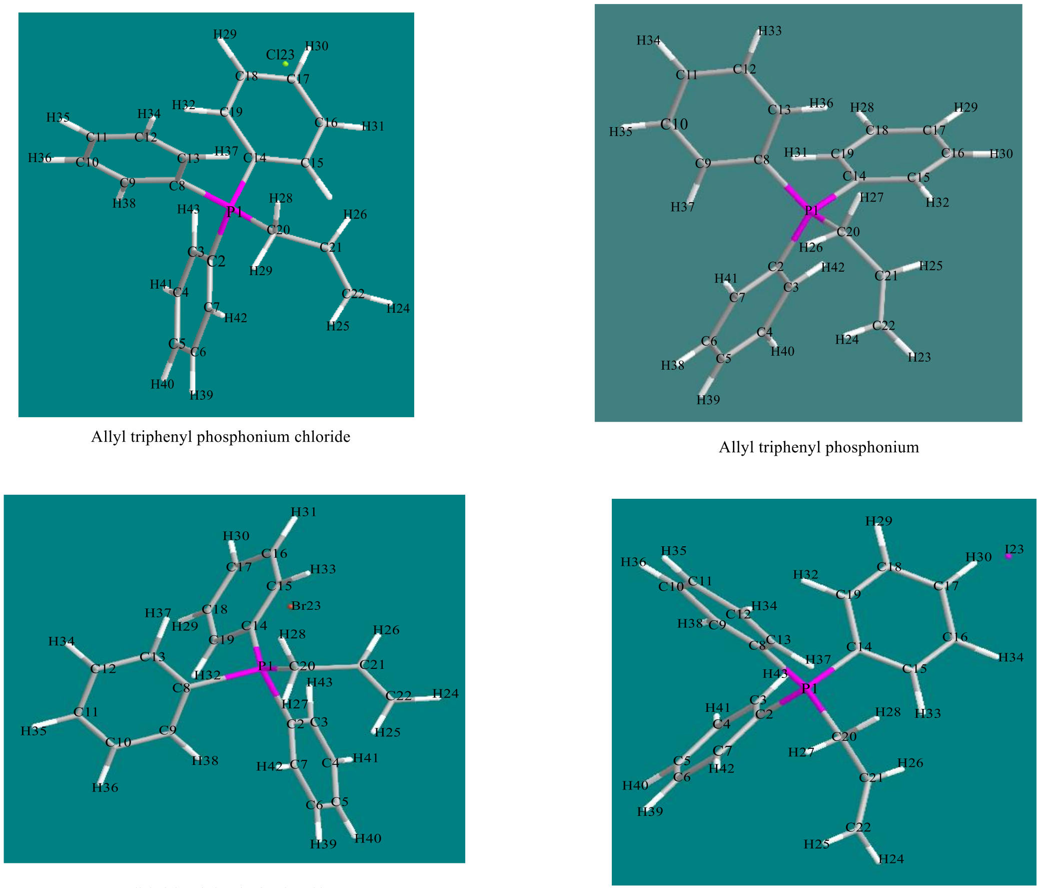
where X_{metal} and X_{inh} denote the absolute electronegativity of metal and the inhibitor, respectively, η metal and η inh denote the absolute hardness of metal and the inhibitor, respectively. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as resistance [4]. The calculated results of the energies of frontier molecular orbital's for the inhibitors are given in Tabl

Table 1 Calculated HOMO-LUMO energies of the inhibitor phosphonium compounds and electronic charge density on phosphorus atom.

Compounds	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**Atomic electron density**
Al	**-5.9857**	**-0.4328**	
C_3H_5 $(C_6H_5)_3P^+$	**-10.0242**	**-0.4398**	**3.0044**
C_3H_5 $(C_6H_5)_3P^+Cl^-$	**-10.0293**	**-0.4047**	**3.0320**
C_3H_5 $(C_6H_5)_3P^+Br$	**-9.9666**	**-0.3774**	**3.0299**
C_3H_5 $(C_6H_5)_3P^+I^-$ -	**-7.7369**	**-0.3613**	**2.9976**

[a]From Ref [6]

The electronic charge density on the phosphorus atom changes slightly when comparing with the inhibitors, similar to the results of the effect of organophosphorus compounds on the corrosion behavior of aluminum [7]. According to the frontier molecular orbital (FMO) theory, the chemical reactivity is a function of interaction between HOMO and LUMO levels of reacting species [8]. E_{HOMO} is quantum chemical parameter which is associated with the electron donating ability of the molecule. High energy value of E_{HOMO} is likely to indicate a tendency of the molecule to donate electrons to the appropriate acceptor molecule of low empty molecular orbital energy [9].



Allyl triphenyl phosphonium chloride

Allyl triphenyl phosphonium

Allyl triphenyl phosphonium bromide

Allyl triphenyl phosphonium iodide

. Figure 1. Optimized geometry of the phosphonium compounds

Therefore, the energy of the lowest unoccupied molecular orbital, E_{LUMO}, indicates the ability of the molecule to accept electron [10]. So the lower the value of E_{LUMO}, the more the molecule would accept electrons. Thus the binding ability of the inhibitor to metal surface increases with increasing $HOMO_{Al}$ and decreasing of the $LUMO_{inh}$ energy values. The energies of HOMO and LUMO of aluminum were compared to the values calculated for phosphonium compounds to determine the appropriate type of the interaction are given in Table 2

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The interactions of the LUMO-HOMO gap of Al-inhibitor are given in Table 2.

Table 2. HOMO-LUMO gap interaction of Aluminum-inhibitor .

Inhibitors	**$(LUMO)_{inhib}$ – $(HOMO)_{Al}$(eV)**	**$(LUMO)_{Al}$– $(HOMO)_{inhib}$(eV)**
C_3H_5 $(C_6H_5)_3P^+$	**5.5459**	**9.5914**
C_3H_5 $(C_6H_5)_3P^+$ Cl^-	**5.5810**	**9.5965**
C_3H_5 $(C_6H_5)_3P^+$ Br^-	**5. 6083**	**9.5338**
C_3H_5 $(C_6H_5)_3P^+$ I^-	**5.6244**	**9.5363**

Table 2 shows the $LUMO_{inh}$ – $HOMO_{Al}$ gap for interaction aluminum - inhibitor. Aluminum will act as a Lewis base while the inhibitors phosphonium compounds act as a Lewis acids. So luminum will utilize the HOMO orbital to initiate the interaction with LUMO orbital of the phosphonium compounds. The interaction will have certain amount of ionic character because the values of $LUMO_{inh}$ – $HOMO_{Al}$ gap fall about 5 eV. Strong covalent bond can be expected only if $LUMO_{inh}$ – $HOMO_{Al}$ gap is approximately zero EV(11,12)

Table 3. Calculated quantum chemical parameters for phosphonium compounds with aluminum

Quantum parameter	$C_3H_5(C_6H_5)_3P^+$	$C_3H_5(C_6H_5)_3P^+Cl^-$	$C_3H_5(C_6H_5)_3P^+Br^-$	$C_3H_5(C_6H_5)_3P^+I^-$
$E_{HOMO(ev)}$	-10.0242	-10.0293	-9.9666	-7.7369
$E_{LUMO(ev)}$	-0.4398	-0.4047	-0.3774	-0.3613
ΔEgap	9.5844	9.6246	9.5892	7.3756
I(eV)	10.0242	10.0293	9.9666	7.7369
A(eV)	0.4398	0.4047	0.3774	0.3613
X(eV)	5.2320	5.2170	5.1720	4.0491
η (eV)	4.7922	4.8123	4.7946	3.6878
σ	0.2086	0.2078	0.2085	0.2711
ΔN	0.0978	0.0968	0.0948	0.0649
ω (eV)	2.8560	2.8278	2.7896	2.2228
ΔG	-2.0230	-2.0080	-1.9630	-0.4800

$X_{Al} = 3.2092$ $\eta_{Al} = 2.7764$

The calculated electron transferred (Δ**N)** and the elctrophilicity (**ω**) values are in the order:- allyl triphenyl phosphonium > allyl triphenyl phosphonium chloride > allyl triphenyl phosphonium bromide > allyl triphenyl phosphonium iodide which agrees with the interaction gaps in the Table 3. That is to say, the decrease in the energy of interaction gaps, the values of donation and back-donation ω result in an increase in the values of donation (Δ**N)** and back-donation. These donation and back-donation (**ω**) processes strengthen the adsorption of phosphonium compounds on to aluminum surface [13]. Table 3.Shows a negative in ΔG values in going from allyl triphenyl phosphonium to allyl triphenyl phosphonium iodide, which suggests that the adsorption is spontaneous follows the trend : allyl triphenyl phosphonium iodide < allyl

triphenyl phosphonium bromide < allyl triphenyl phosphonium chloride < allyl triphenyl phosphonium .

3.3 Structural details

`All geometrical parameters (bond lengths and bond angles) for the compounds under investigation are reported. as can be seen from the calculated geometrical parameters, that Cl atom (allyl triphenyl phosphonium chloride) causes changes in the adjacent bond lengths, while Br (allyle triphenyl phosphonium bromide) and I (allyl triphenyl phosphonium iodide) show almost no change in bond lengths. For the effect on bond angle Cl, Br and I show a slight changes in the bond angles at which they attached on phosphorus atom. This agrees with theoretical calculations of Khalil [14] and Al-Halasah and Khalil [15].

3.4 Electron densities

The electron density on every atom in the compounds under investigation are calculated.

It can be seen from calculated electron distribution that Cl substituent in allyl triphenyl phosphonium chloride increases the electron density on phosphorus atom, i.e. acts as electron withdrawing, while Br (allyl triphenyl phosphonium bromide) acts as a weak electron withdrawing. For I substituent (allyl triphenyl phosphonium iodide), the electron density decreases slightly on phosphorus atom, acts as weak electron releasing [16,17]. This may be due to the low electronegativity of iodide compared to other halogens. Also the positive charge on the phosphorus atom has tendency to attract electrons to itself. i.e. depends on electron demand [18].

5 - CONCLUSIONS

1. It can be concluded that allyl triphenyl phosphonium and allyl triphenyl phosphonium chloride can be a good inhibitors for aluminum while allyl triphenyl phosphonium bromide and allyl triphenyl phosphonium iodide are inhibitors to Al to a lesser extent .
2. The adsorption of the inhibitor on the metal surface is spontaneous. This study, thus displays a good correlation between theoretical and experimental data which confirm the reliability of the PM3 method to study the inhibition corrosion of metal surface.

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