Computational and Theoretical Chemistry 1093 (2016) 73–80

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Quantum chemical evaluation of the corrosion inhibition of novel aromatic hydrazide derivatives on mild steel in hydrochloric acid

Kazeem O. Sulaiman *, Abdulmujeeb T. Onawole

Department of Chemistry, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran 31261, Saudi Arabia

ARTICLE INFO

Article history:
Received 2 June 2016
Received in revised form 24 July 2016
Accepted 10 August 2016
Available online 13 August 2016

Keywords:
Quantum-chemical calculation
DFT
Mild steel
Acid inhibition
Acid corrosion

ABSTRACT

The theoretical evaluations of the corrosion inhibition efficiency of 2-(3,4,5-tri-R-benzylidene) hydrazinecarbothioamide, (R = —H, —CH_3, —OCH_3 and —NH_2), were done using RHF and DFT-B3LYP methods with 6-31G(d) basis set in gas phase, aqueous and acidic solutions. The correlation between the molecular structures of these compounds and their theoretically predicted inhibition effects was obtained from the quantum chemical evaluations, such that the structural parameters provided insights into the possible inhibition mechanism. 2-(3,4,5-triaminebenzylidene) hydrazinecarbothioamide showed a larger tendency of adsorption through chemisorption and physisorption and thus was identified to be the best potential candidate for excellent corrosion inhibition among the studied compounds.

1. Introduction

Corrosion is a notable challenging industrial problem in the modern society, owing to its destructive effect on the mechanical properties of metal based materials of different applications in various industries [1]. For instance, the industrial pickling process allows the direct contact of acid solution with an alloy (mild steel) and this alloy-acid interaction needs to be controlled to avert the economic losses due to corrosion of the mild steel [2]. Industries in the U.S.A. once estimated 170 billion dollars per year in controlling corrosion alone [3]. Besides designing more corrosion resistant alloy materials, the adoption of inhibitors is a considerable option in addressing the challenge.

Having proved to be an economical alternative in the corrosion control practices, the synthetic design and evaluation of organic corrosion inhibitors continually gain experimental and theoretical research interests [4,5]. A conjugated system of heteroatoms such as phosphorus, nitrogen, sulfur, and oxygen in organic compounds constitutes the vast number of such cheap corrosion inhibitors as they are capable of donating electron pairs and multiple bonds by adsorbing on the metal surface to prevent the corrosion attack [6,7]. Besides forming a protective film, these adsorptive inhibitors compete with the adsorption of other ions on the electrically charged metal surface, in preventing localized corrosion [8,9]. Several compounds with the —C=N— (azo methine) group and π-electron donating groups have been widely reported to show excellent inhibition of mild steel corrosion in acid medium [10–12]. The π or lone pair electrons present in the heteroatoms promote the nucleophilicity of the inhibitor molecule in binding to the electrophilic surface of the metal [13].

The constituents of the metal and its alloys, concentration and structure of the inhibitor, and the temperature of the metal environment, amongst other experimental conditions, are notable factors that determine the extent of the adsorption which in turns dictates the inhibition efficiency [14]. The molecular based properties of a compound, such as electron density around donor atoms in the molecular structure and its solubility, enable the required knowledge of inhibition mechanism that aids the selection of effective inhibitors among organic compounds [7,15]. For instance, the inhibition efficiency of azo dye derivatives was found to depend on the number of adsorption oxygen sites (OH and OMe groups), their charge density and π-electron clouds [16]. The quantum chemical calculations avail structural parameters like the charge distribution, the frontier molecular orbital energy (E_{HOMO} and E_{LUMO}), electrophilicity index (ω), the absolute electronegativity (χ) values, the fraction of electrons (ΔN) transfer from inhibitors to metals, and the back-donation ($\Delta E_{Back\text{-}donation}$) that have been well correlated with inhibition efficiencies of some organic compounds [17–20]. The establishment of these theoretical calculations promotes the scientific selection of inhibitors by comparing quantum chemical properties with the experimental data in most cases.

Specifically, the inhibition effect of a compound can be well associated to its adsorption via electronic interaction with the metal surface. For instance, the vacant d-orbitals in the iron atom

---

* Corresponding author.

http://dx.doi.org/10.1016/j.comptc.2016.08.014

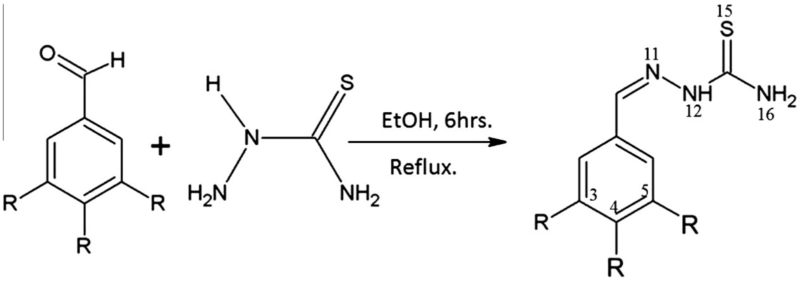

Fig. 1. Synthetic reaction scheme for the studied compounds.

(Fe = [Ar] $4s^2$ $3d^6$) can accept electrons from the HOMO of the inhibitor molecule while the metal atom back-donate its 4s electron to the LUMO of the inhibitor [21]. The higher E_{HOMO} suggests the greater tendency of electron donation by the molecule to the vacant orbital of the metal surface, while the higher E_{LUMO} suggests the better susceptibility to accept electrons. The $E_{HOMO\text{-}LUMO}$ gap affords crucial information about the possible stability of the inhibitor-metal complex formation, such that a low energy gap indicates softness and thus better reactivity. Corrosion system remarks bulk metals as soft acids such that only inhibitors that have better softness are more effective against the acidic corrosion of the metals [22]. With these in mind, one can theoretically predict and compare the corrosion inhibition potential of compounds.

Table 1
Chemical reactivity indices obtained for the studied compounds using DFT method.

Compound	Medium	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{L-H} (eV)	μ (Debye)	Energy (au)
A	Gas	−5.369	−1.487	3.882	7.144	−872.677
	Water	−5.937	−1.507	4.430	10.957	−872.699
	HCl	−5.935	−1.504	4.431	10.937	−872.686
B	Gas	−5.269	−1.328	3.941	8.227	−990.629
	Water	−5.908	−1.426	4.481	12.341	−990.651
	HCl	−5.905	−1.423	4.483	12.315	−990.636
C	Gas	−5.287	−1.399	3.888	8.288	−1216.230
	Water	−5.933	−1.524	4.409	12.081	−1216.254
	HCl	−5.930	−1.518	4.413	12.115	−1216.236
D	Gas	−5.144	−1.051	4.093	8.795	−1038.740
	Water	−5.212	−1.207	4.005	13.419	−1038.755
	HCl	−5.203	−1.245	3.958	13.549	−1038.755

Environmental concerns require corrosion inhibitors to be eco-friendly, non-toxic and acceptable. Besides their corrosion mitigation properties, the environmental implication of the hydrazide derivatives can be assured due to their biocompatibility nature. Hydrazide derivatives are of crucial interests in medicinal chemistry for their biological effects, such as analgesic and anti-inflammatory activities, are well established [23,24]. Specifically, isonicotinic acid hydrazide is applicable to tuberculosis treatment,

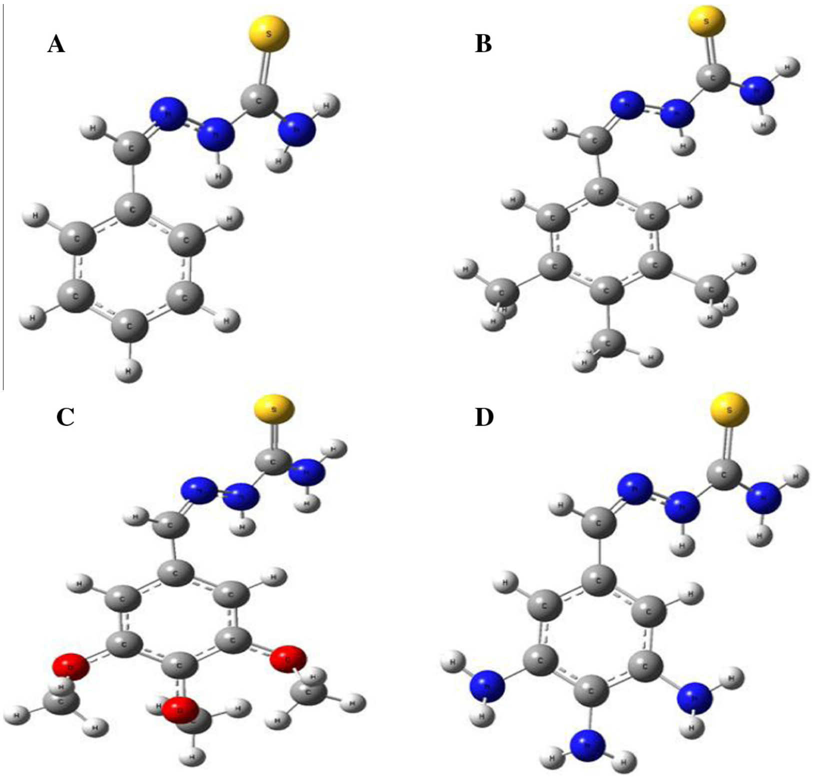

Fig. 2. Optimized geometries of the studied compounds.