

NOTE

AM1 and PM3 Studies in Corrosion of Mild Steel in Presence of Aniline and its Derivatives

H.C. TANDON*, SANJAY KUMAR and LAXMAN SINGH†
Department of Chemistry, Srivenkateshwara College
Dhaura Kuan, New Delhi-110 021, India

The effect of aniline and its derivatives *o*-nitroaniline, *p*-nitroaniline, *o*-toluidine, *p*-toluidine, *o*-chloroaniline and *p*-chloroaniline on the corrosion of mild steel in concentrated sulphuric acid has been investigated theoretically. The calculations are done by using semi-empirical methods like Austin Model 1 (AM1) and Parametric Method-3 (PM3) to study the effectiveness of these compounds as inhibitors. The present work shows similar observations to those that have been reported experimentally. The results have been discussed on the basis of dipole moments, heats of formation and net atomic charge on the N-atom of the compounds.

Key Words: AM1, PM3, Corrosion, Mild steel.

Mild steel is a vital building material of construction, extensively used in chemical and other related industries due to its versatility and low cost. Natesan *et al.* and others¹⁻³ have studied the mechanism of corrosion of mild steel in sulphuric acid solution. Electrochemical measurements using mild steel electrode in acidic medium suggested that both anodic and cathodic curves were affected by inhibitors. Organic compounds containing nitrogen, sulphur and oxygen atoms are widely known as efficient corrosion inhibitors in acid solutions⁴. The inhibitive action of these compounds may be due to the formation of a coordinate type of bond between the metal and the lone pair of electrons⁵⁻⁹.

Recently, with the above background, Desai and Oza¹⁰ investigated the effect of aniline and its derivatives on the corrosion behaviour of mild steel in sulphuric acid by weight-loss method electrochemical measurements. Their experimental results showed that *para*-substituted derivatives of aniline were better corrosion inhibitors than its *ortho*-isomers. Their experimental results prompted us to carry out molecular orbital study to find the answers at the electronic level.

We carried out the calculations by applying AM1 and PM3 methods using Hyperchem standard (5.1). The geometries were fully optimized at Molecular Mechanics Plus model (MM+) and AM1, PM3 levels. Heats of formation have been calculated for aniline and its *ortho*-, *para*-substituted nitro, chloro and methyl groups (Table-1). From Table-1 it appears that inhibition efficiency of the aniline

†Department of Chemistry, Lajpat Rai College, Sahibabad-201 005 (Ghaziabad), India.

derivatives cannot be concluded because some ortho-substituted and other para-substituted anilines are less exothermic in nature. But we can surely conclude that substituted anilines are more reactive than pure aniline.

TABLE-1
HEATS OF FORMATION (kcal mol^{-1}), NET ATOMIC CHARGE ON N-ATOM
AND DIPOLE MOMENTS (μ) OF ANILINE AND ITS DERIVATIVES

System	AM1	PM3	Net charge		(debye)	
			AM1	PM3	AM1	PM3
Aniline	21.3	25.6	-0.412	0.051	1.585	1.567
<i>o</i> -Chloro-aniline	81.6	81.6	-0.234 (-0.314)	0.507 (-0.502)	5.312	7.761
<i>p</i> -Chloro-aniline	86.8	14.2	-0.334 (-0.210)	0.077 (0.06)	7.290	1.957
<i>o</i> -Nitro-aniline	20.5	12.6	-0.370 (0.582*)	0.069 (1.326*)	5.292	4.877
<i>p</i> -Nitro-aniline	21.4	10.5	-0.357 (0.577*)	0.100 (1.316*)	7.276	6.658
<i>o</i> -Methyl-aniline	87.2	80.5	-0.315	0.086	1.480	1.316
<i>p</i> -Methyl-aniline	12.7	12.9	0.322	0.068	1.587	1.330

The values in parentheses are the net charges on the substituted atom.

The values indicated by asterisks are the net charges on substituted N-atoms in $-\text{NO}_2$ group.

The calculated net atomic charges on N-atom in the reported compounds are listed in Table-1. The net charges on N-atom in *para*-substituted are more than in ortho-substituted anilines with the exception of nitro-substituted showing that *p*-substituted anilines are more effective inhibitors than *ortho*- compounds. The calculated charges are more accurate in AM1 than in PM3. Earlier, it was mentioned by Steward in one of her papers that the PM3 method wrongly calculated the atomic charges. It is evident in our present results also. But we have reported this result for comparison.

Dipole moment becomes an important parameter, where corrosion inhibition efficiency is in question, because the asymmetry of the molecule leads to increase in the dipole moment (due to polarization), makes it more soft and highly reactive. We have reported these results in Table-1. The dipole moment values for *para*-substituted are more than for *ortho*-substituted. Hence *p*-substituted anilines are better corrosion inhibitors than its *ortho*- isomers. The presence of nitro group at *ortho*- position in aniline retards its protonation due to its electron-withdrawing tendency and steric hindrance. *p*-Nitroaniline, where steric hindrance is less pronounced, undergoes protonation relatively easily thereby neutralizing a greater amount of the acid than its *ortho*- isomer.

In the case of chlorine atom in aniline molecule, it increases its basic character, hence becomes an effective inhibitor. But it is more prominent in *para*-substituted than in *ortho*- isomer, due to increase in the dipole moment value of *p*-isomer over *o*-isomer (Table-1). Further, chlorine with its positive inductive effect enables the enhancement of electrodensity over the amino nitrogen atom of aniline, thereby increasing its basic character.

The different isomeric toluidines showed a similar trend to that observed for the corresponding nitro- and chloroanilines.

Conclusion

Aniline and its substituted derivatives are good corrosion inhibitors in acidic media. But among all, the *para*- isomers are found to be more effective inhibitors than *ortho*- isomers. More critical study in this case requires sophisticated and accurate methods like *ab-initio* method at different a basis set. This work is going on in our group, which will be reported elsewhere.

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Contact:

Dr. Ferdinand Wild

University of Zurich

Gruppa Berke, Winterthurerstr. 190, CH-8057, Zurich, Switzerland

Tel: +41 1 635 4646 Fax: +41 1 635 6802

E-mail: fwild@aci.unizh.ch