THEORETICAL STUDY OF ALKALINE ACETYLATION OF ANILINE

Caglieri[a],*, Macaño[a], Zanel[a]

[a] CIQA-Centro de Investigación y Transferencia en Ingeniería Química Ambiental. Universidad Tecnológica Nacional - Facultad Regional Córdoba. Avenida Cruz Roja Argentina esquina Maestro López. X5016ZAA. Córdoba, Argentina.

scaglieri@quimica.frc.utn.edu.ar

Abstract

A theoretical study of alkaline acetylation of aniline from the analysis of intermediate of the reaction was carried out. Geometries of all species involved in the reaction were made and identified. All of the geometry optimizations were performed and the energies were calculated by the method DFT with B3LYP level of theory and using the method MP2. The 6-31+G* basis set was adopted. The energy of activation for the reaction was 17.57 kcal/mol.

Keyword: Acetylation, Aniline, DFT, MP2, amide

1. Introduction

The acetylation of amines is one of the most frequently used transformations in organic synthesis as it provides an efficient and inexpensive means for protecting amino groups in a multistep synthetic process and the amide bond is found to be present in a large number of pharmacologically active molecules.

Acetylation of amine is a nucleophilic substitution reaction. This reaction is carried out with acetic anhydride in the presence of amine bases such as tertiary amine and pyridine. The nitrogen from the amine produces the nucleophilic attack on the carbonyl carbon of the anhydride to obtain tetrahedral intermediate, decisive step of the reaction rate. Subsequent loss of a proton will yield the amide and acetic acid as products.

Computational investigation (Tong et.al, 2012) and an experimental work (Yadav et.al, 2001), agreed that this reaction takes place with the formation of a tetrahedral intermediate.

A theoretical study of alkaline acetylation of aniline from the analysis of intermediate of the reaction was carried out. The reaction and the compounds studied are shown in Figure1.

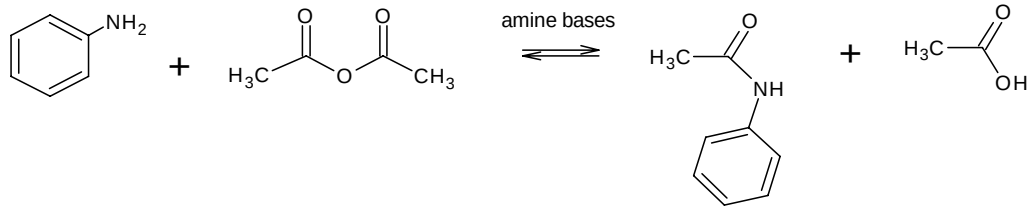

Fig. 1: General Scheme of Alkaline Acetylation of Aniline

2. Main Body

2.1 Figures and Tables

Geometries of all species involved in the acetylation were made and identified. All of the geometry optimizations were performed by the method at the DFT - Density Functional Theory with B3LYP level of theory and was adopted the 6-31+G* basis set.

Energies of all reagents and products and the energy of activation for the reaction were calculated using the MP2- 2nd order Mo/ller–Plesset method. Following the same procedure it was identified the geometric parameters and energy of intermediate. All the calculations were executed using Gaussian 09 (Frisch et.al, 2009) software package.

Figure 2 show the optimized structure of the intermediate and the Table 1 lists the geometric parameters, lengths and binding angles values, obtained. The calculations show 93.83 kcal/mol of energy for the tetrahedral intermediate and the activation energy was 17.57 kcal/mol.

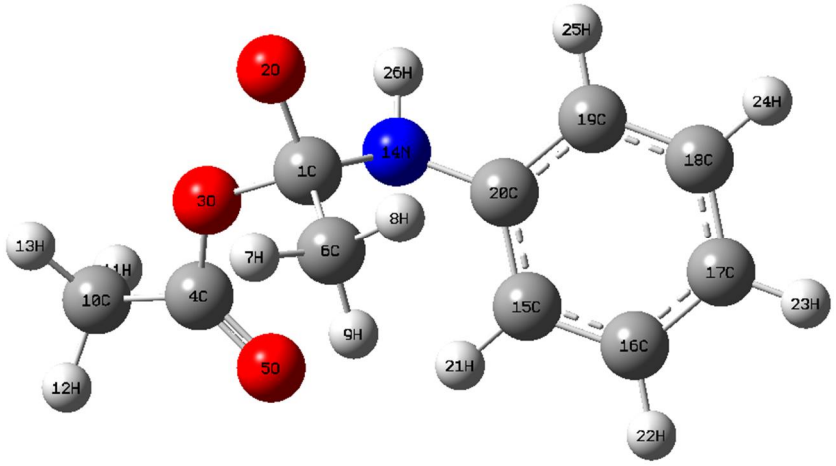

Fig. 2: Tetrahedral Intermediate

Table 1: Geometric Parameters Intermediate

Lengths	Å	Angles	º
r (C_1-O_2)	1.42	θ (C_6-C_1-O_2)	107.04
r (C_1-N)	1.46	θ (C_1-N-C_{20})	118.97
r (O_3-C_4)	1.37	θ (N-C_1-O_3)	108.66
r (C_1-C_6)	1.53	θ (C_6-C_1-N)	117.64
r (C_1-O_3)	1.46	θ (C_1-N-H_{26})	110.71
r (N-H_{26})	1.00	θ (N-C_1-O_2)	111.42
r (C_{20}-N)	1.42	θ (C_1-O_3-C_4)	121.68
r (C_6-H_8)	1.12	θ (H_7-C_6-C_1)	108.31

It was observed a marked consistency between the theoretical results and bibliographic data, which validates the use of theoretical methods DFT and MP2 as tools for studying the reaction of acetylation of aniline.

2.2 Acknowledgments and Legal Responsibility

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3. References

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