**CLAFQO-13**
**13ª Conferencia Latinoamericana de Físico-Química Orgánica**
**13th Latin American Conference on Physical Organic Chemistry**
**May 17-21, 2015, Carlos Paz, Argentina.**

# CONTRIBUTED PAPER

Presenter's Name: Silvana Claudia Caglieri

Mailing Address: 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.

Telephone: 351-4684317 E-mail: scaglieri@quimica.frc.utn.edu.ar

Title of the contribution: Solvent Effect on the Aniline Acetylation: Theoretical Study

Authors' names: Silvana Claudia Caglieri

Preferred mode of presentation is:

( ) Oral Presentation ( X ) Poster

Abstract

# SOLVENT EFFECT ON THE ANILINE ACETYLATION: THEORETICAL STUDY

Silvana C. Caglieri

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.

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 and 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 and an experimental work, agreed that this reaction takes place with the formation of a tetrahedral intermediate.

A theoretical study of aniline acetylation in several solvents from the analysis of intermediate of the reaction was carried out. 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 6-31G* basis set. Energies of all reagents and products and the energy of activation for the reaction were calculated using the MP2-2$^{nd}$ order Mo/ller–Plesset method. Following the same procedure it was identified the geometric parameters and energy of intermediate.

The nature of solvent has an important effect on the reaction. In order to investigate the solvent effect on the aniline acetylation, both aprotic solvents such as: acetonitrile and acetone and protic solvents such as: methanol and ethanol were used. The effect of the solvent was performed with IEFPCM o PCM (Polarizable Continuum Model) method. Values of activation energy are reported in Table. Acetonitrile (aprotic solvent with the highest dielectric constant showed in the table) reveals to be the best solvent in term of activity for the reaction. This behavior could be associated with greater stability of the intermediate of the reaction.

| Solvents | Dielectric Constant | Activation Energy (kcal.mol$^{-1}$) |
|---|---|---|
| **acetonitrile** | 37.5 | 19.32 |
| **acetone** | 20.7 | 20.86 |
| **methanol** | 33 | 19.56 |
| **ethanol** | 24 | 19.94 |