Theoretical study of acid acetylation of methylamine

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.
**scaglieri@quimica.frc.utn.edu.ar*

Abstract: A theoretical study of acid acetylation of methylamine 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 by the method at the DFT with B3LYP level of theory and was adopted the 3-21+G* basis set. Energies were calculated using the AM1. The energy of activation for the reaction was 8.85 kcal/mol.

Keywords: AM1, Acetylation, methylamine.

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.

Acetylation of amine is a nucleophilic substitution reaction. This reaction can be catalyzed by Brönsted acid. In the mechanism, the acetic anhydride first accepts a proton at the carbonyl oxygen and this change enhances the positive charge on the carbonyl carbon. This protonation facilitates the successive addition of amine at the position to form a tetrahedral intermediate, determining step of the rate of the reaction.

Computational method to study the reaction using acid catalysis[1] and an experimental work[2], agreed that this reaction takes place with the formation of a tetrahedral intermediate.

A theoretical study of acid acetylation of methylamine from the analysis of intermediate of the reaction was carried out. The reaction and the compounds studied are shown in Figure 1.

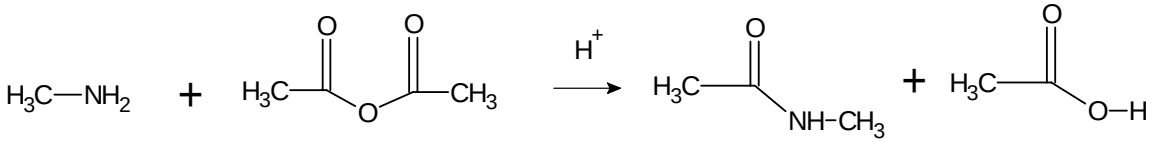

Figure 1. General Scheme of Acid Acetylation of Methylamine

2. Theoretical

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[3] with B3LYP level of theory and was adopted the 3-21+G* basis set. Energies of all reagents and products and the energy of activation for the reaction were calculated using the AM1- Austin Model 1[4] method. Following the same procedure it was identified the geometric parameters and energy of intermediate. All the calculations were executed using Gaussian 09[5] software package.

3. Results and discussion

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 23.76 kcal/mol of energy for the tetrahedral intermediate and the activation energy was 8.85 kcal/mol.

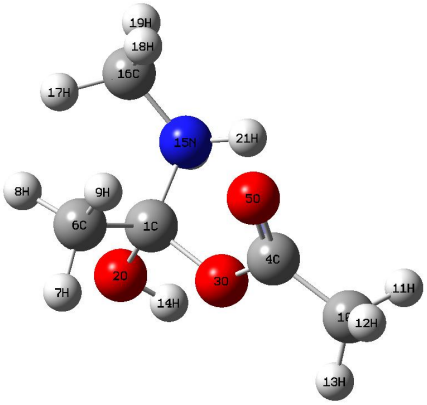

Figure 2. Tetrahedral Intermediate

Table 1. Geometric Parameters Intermediate

Lengths	**Å**	**Angles**	**º**
r (C_1-O_2)	1.42	θ (C_1-O_2-H_{14})	108.86
r (C_1-N)	1.48	θ (C_1-N-H_{20})	102.48
r (O_2-H_{14})	0.97	θ (N-C_1-O_2)	111.40
r (C_1-C_6)	1.53	θ (C_6-C_1-N)	117.68
r (C_1-O_3)	1.45	θ (C_1-N-C_{16})	112.87
r (N-H_{20})	1.01	θ (N-C_1-O_3)	109.53
r (C_{16}-N)	1.41	θ (N-C_{16}-H_{18})	109.06
r (C_6-H_7)	1.12	θ (H_7-C_6-C_1)	108.51

4. Conclusions

It was observed a marked consistency between the theoretical results and bibliographic data, which validates the use of theoretical methods DFT and AM1 as tools for kinetic studying the reaction of acetylation of methylamine.

References

1. H.G. Kruger, J. Mol. Struct. (Theochem) 577 (2002) 281.
2. H.S. Prasad, G.R. Srinivasa, D. Channe Gowda, Synth. Commun. 35 (2005)1189.
3. C. Lee, W. Yang, R.G. Parr, Phys.Rev.B 37 (1988) 785.
4. M.J.S. Dewar, E.G. Zoebisch, E.F.Healy, J.J.P.Stewart, J. Am.Chem.Soc.107 (1985) 3902.
5. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.