

Paula do Nascimento Goulart, Glauco Favilla Bauerfeldt, Arthur Eugen Kummerle,

Renata Barbosa Lacerda

Rodovia BR 465, Km 07, s/n - Zona Rural, Seropédica - RJ, 23890-000

IBX (o-iodoxybenzoic acid) has gained popularity as a soft oxidant for the conversion of alcohols to aldehydes or ketones [1]. According to the literature, IBX promotes the oxidation of certain aliphatic primary alcohols to the corresponding aldehydes with excellent yield, but when this reaction is applied to aromatic alcohols, the oxidation product is a carboxylic acid [2]. Because of these differences, it is desired to study the oxidation reactions of some alcohols, evaluating the effect of the substituent group change in the proposed routes for the reaction mechanism. For this study, the GAUSSIAN software was used with the aid of the GaussView program through the semi-empirical method PM6 for calculations of geometry optimization, obtaining transition states and evaluation of the reaction paths Therefore, in this work, a mechanism is proposed, considering the electron transfers, in two steps, as shown in figures 1 and 2 below. From the calculated data from theoretical study of this reaction, we expected to comprehend the different yields obtained for these oxidations, as well as to suggest the most probable product. Experiments show that the oxidation reactions of most of the investigated alcohols converts to the corresponding carbonyl compound with yields greater than 90%, besides presenting the product free of impurities and a good insulation. However, exceptions are noted with respect to some aromatic compounds, which showed oxidation to the corresponding carboxylic compound under similar reaction conditions[3]. Table 1 shows that the oxidation reactions of the primary alcohols are thermodynamically allowed taking into account the different radicals proposed.



Figure 1-Mechanism for the first step.



Figure 2- Mechanism for the second step.

Table 1 Variation of the free energy for the reaction of each alcohol being oxidized to its aldehyde, step 1 of the proposed mechanism.

R(-CH ₂ OH)	$\Delta Gr_1(kcal/mol)$
benzila	-94,66
Etila(-C ₂ H ₅)	-92,62
Metila(-CH ₃)	-92,65
Etilfmoc(-C ₂ H ₄ O ₂ Cl)	-104,82
fenil	-91,46
propfenil	-83,03
ftalimidanitrom	-92,41
ftalimidanitroo	-91,40
ftalimidametoxim	-91,88
ftalimidametoxio	-93,06
ftalimida	-83,86
ftalato	-91,63



12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

It can be observed, for the saddle point of the first stage, that the alcohol oncoming occurs through the interaction between the isolated pair of electrons of oxygen and iodine, making the latter hypervalent. There is also the transfer of a proton to the hydroxyl group of the ibx, causing the departure of a water molecule. An optimized structure was obtained as a pre-barrier intermediate. In this intermediate, the hypervalence of the iodine atom is observed. A transition state was also obtained for the first stage of the mechanism. The chart below, in figure 3, illustrates such results that have been achieved so far.



Figure 3-Free energy surface for the first stage of the proposed reaction mechanism.

It is also desired to investigate the transition states obtained from the optimization of structures, considering the assitance of an explicit water molecule in the system studied, since it is suspected that this explicit solvent molecule is important for the system and that, from of it, the reaction progresses towards the proposed mechanism.

Key-words: oxidations, ibx, hypervalent, PM6 **Support:** This work has been supported by CAPES **References:**

[1] Frigerio, M.; Santagostino, M. Tetrahedron Lett. 1994, 35

- [2] Julius T. Su and William A. Goddard III J. AM. CHEM. SOC. 2005, 127
- [3] Leonard, N. J.; Carraway, K. L. J. Heterocycl. Chem. 1966, 3, 485