

MECHANISMS OF THE REACTIONS OF NUCLEOPHILES WITH AROMATIC NITROCOMPOUNDS – A MASS SPECTROMETRY AND THEORETICAL STUDY

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The aim of this Ph.D. dissertation is to describe the exact mechanism of Nucleophilic Aromatic Substitution reactions between carbanions and aromatic nitrocompounds. Investigation of the kinetic and thermodynamic preferences of the S_NAr and S_NArH processes have been rationalized by the Density Functional Theory calculations and experimental measurements of the reactions in the gas phase using mass spectrometry techniques.

In the experimental section intramolecular gas-phase reactions of *N*-(2-*X*-5-nitrophenyl)-*N*-methylacetamide carbanions ($X = H, F, Cl$) have been examined to investigate the direct competition between the S_NAr and S_NArH reactions. In this section, for the first time it was proven that all three anions form cyclic σ^H -adducts and undergo elimination of water reaction to form nitroso ionic compounds.

Theoretical calculations of the reactions between different types of nucleophiles and *para*-substituted nitrobenzenes brought an important information about the dependence between the structure of the carbanions and energetic requirements of the addition reaction. Calculations of the potential energy surfaces of the nucleophilic substitution processes to the mono-, di- and trisubstituted aromatic rings lead to the establishment of the theoretical withdrawing effect scale of the substituents, from the weakest to the strongest: $t\text{-Bu} < \text{CH}_3 < \text{H} \approx \text{OCH}_3 < \text{F} < \text{Cl} < \text{Br} < \text{CF}_3 < \text{CN} < \text{NO}_2$. This scale is in full agreement with the experimental one.

In the other section the parameters of nucleophilicity, electrophilicity and aromaticity have been determined computationally using DFT method. By the calculation of these parameters for chosen groups of atoms of the reagents system it was possible to describe the nucleofugal character of the leaving groups. It was shown that the best leaving group in the case of aromatic substitution reaction is a fluorine atom. chlorine atom is a much weaker leaving group and the worst leaving group that is unable to departure spontaneously from the ring is a hydrogen atom.

Additionally, the influence of the solvent, temperature and isotopic kinetic effects have been also examined using theoretical methods.

Thus general picture of Nucleophilic Aromatic Substitution in halonitroarenes that emerges from described results is as follows: nucleophiles add initially at positions *ortho* or

para relative to the nitro group, occupied by hydrogen, to form σ^H -adducts. Providing that the structure of nucleophile and reactions conditions are favorable, fast further conversion of the σ^H -adducts, S_NArH reaction takes place. Otherwise σ^H -adducts dissociate and nucleophiles can add at positions occupied by halogens and S_NAr reaction takes place. Based on the theoretical results, two different mechanisms of the nucleophilic aromatic substitution reaction have been observed. First, two-step addition-elimination process has been proposed for reaction that proceed on the carbon atom occupied by hydrogen or fluorine. The first step leads to the stable intermediate products σ^H - or σ^F -adducts, which make this part of the mechanism reversible. From this point of potential energy surface in appropriate reaction condition the elimination of the leaving group is much faster than the addition step. The single step mechanism is observed for the nucleophilic substitution reaction of chlorine and bromine atoms in nitroaromatic derivatives. According to this mechanism the σ^X -adduct is also formed but it corresponds to the transition state rather than reaction intermediate, from which the spontaneous elimination of the halogen ion takes place. That is why the substitution of chlorine or bromine atoms are irreversible, one step reactions.