Effect of acceptor and donor substituents in the *ortho, meta,* and *para* positions in the nitrobenzene molecule on the reaction of interaction with ethylene

Yuri V. Minasyan, Anastasia I. Degtyarenko, Karina D. Кosmacheva Sergei D. Plechovich, Sergei V. Zelentsov

Nizhnii Novgorod State University

Russia, 603950, Nizhnii Novgorod, Gagarin Ave., 23. NNGU. Chemical Department

Abstract: The uB3LYP/6-311g++(d,p) method in the gas phase was used to simulate the reaction of ethylene with *ortho*, *meta*, *para:* methylnitrobenzene, chloronitrobenzene, $(CCl_3)PhNO_2$, $(CF_3)PhNO_2$ in the T_1 state, as well as determined the influence of the position of donor and acceptor substituents in the benzene ring on the activation energy of the reaction under study. It is established that during the reaction ethylene oxide and nitroso compound are formed.

Keywords: uB3LYP, reaction mechanism, the triplet state, transitional state, nitrobenzene.

INTRODUCTION

Ethylene oxide is one of the target oxidation products of the olefin. It is widely used as a fumigant and are intermediates in the synthesis of solvents, lubricants, hydraulic liquids, emulsifiers. Therefore, the researches in the field of the olefin oxidations to oxygenated compounds are relevant. Especially important is the development of new methods of the low-temperature oxidation. An interesting photochemical oxidants of olefins are aromatic nitro compounds. Buchi [1] reported that under irradiation a mixture of nitrobenzene and 2-methyl-2-butene by UV light a complex mixture of products with low yields forms. In the study of the qualitative composition of the reaction products it has become clear that the ethylene bond is susceptible to the nitrobenzene induced photochemical oxidation. These authors suggested that cyclic compounds are formed as intermediates. The proof of the hypothesis is given in [2].

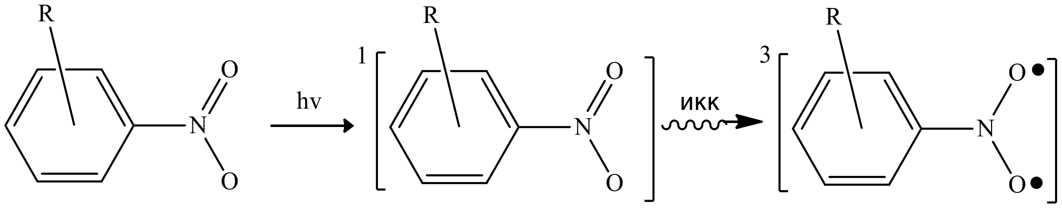
The aim of our work was a quantum chemical simulation of the interaction of ethylene with methyl nitrobenzene, 3-chlorine nitrobenzene, 3-fluorine nitrobenzene and chloronitrobenzene in the T_1 state, as well as to reveal the influence of the position of donor and acceptor substituents in the benzene ring on the activation energy of the reaction under study.

EXPERIMENTAL TECHNIQUE

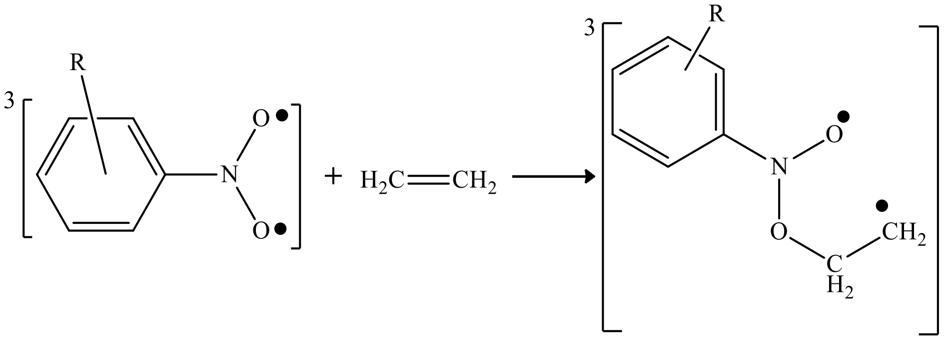
Quantum-chemical modeling of the systems under study was performed using the Gaussian 03 program, DFT method with uB3LYP / 6-311g ++ (d, p) basic set. The selection of the method and basis is based on the works [3,4]. To achieve this goal, they optimized the geometry of the systems under study, calculated transition states and determined their geometrical parameters. The activation energy is determined taking into account the energy of zero point.

RESULTS AND ITS DISCUSSION

The mechanism of the reaction of the interaction of aromatic nitro compounds with ethylene is similar to the mechanism discussed in [5]. At the first stage, UV light is exposed to the aromatic nitro compound with its transition to the excited S_1 state, then it undergoes ISC (intersystem crossing) with the transition to the T_1 state. Such a transition becomes possible due to the close location of the S_1 and T_1 levels in aromatic nitro compounds. For example, the energy difference between the S_1 and Tn levels in nitronaphthalene is 0.1–0.2 eV [6].



The next reaction is the addition of NA in the T_1 state on the olefin double bond.



In the third reaction, the resulting adduct is decomposed into oxide and nitrosomethane, which is in the triplet state (Scheme 3).

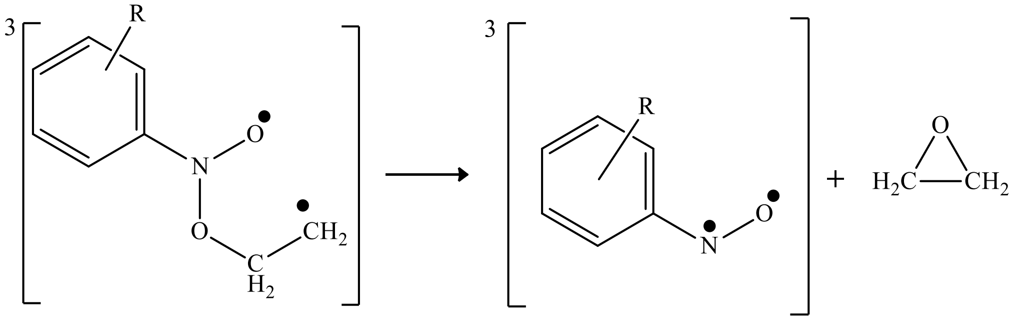
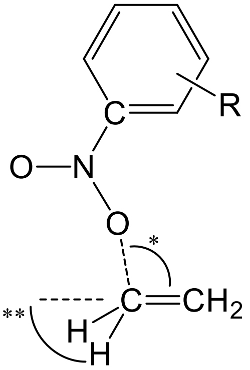


Table 1 presents the geometry of the transition state of the first reaction stage. For the first stage of the reaction, the key parameters are: the C–O bond distance, angle of attack, and pyramidal angle. Based on the obtained calculations, it is possible to identify the following patterns:

- with an increase in the length of the C–O bond in the transition state, the activation energy decreases

- with an increase in the angle of attack, an increase in the activation energy occurs

Table.1. Geometry of the transition state and reaction kinetics 1

nitrobenzene			
r(C-O)=2.27 $\varphi_{attack}=97.9$ $\varphi_{pyramidal}=67.9$ $E_a=2.7$ $\Delta_r H = -15.0$			
R	***ortho***	***meta***	***para***
CH_3	r(C-O)=2.14 $*\varphi_{attack}=100.8$ $**\varphi_{pyramidal}=67.9$ $E_a= 3.7$ $\Delta_r H = -13.4$	r(C-O)=2.26 $*\varphi_{attack}=97.78$ $**\varphi_{pyramidal}=67.9$ $E_a= 2.8$ $\Delta_r H = -14.9$	r(C-O)=2.26 $*\varphi_{attack}=97.85$ $**\varphi_{pyramidal}=67.9$ $E_a= 3.0$ $\Delta_r H = -14.8$
CCl_3	r(C-O)=2.16 $*\varphi_{attack}=100.42$ $**\varphi_{pyramidal}=67.8$ $E_a= 3.0$ $\Delta_r H = -12.7$	r(C-O)=2.43 $*\varphi_{attack}=97.10$ $**\varphi_{pyramidal}=67.8$ $E_a= 1.7$ $\Delta_r H = -15.9$	r(C-O)=2.52 $*\varphi_{attack}=98.6$ $**\varphi_{pyramidal}=67.8$ $E_a= 1.7$ $\Delta_r H = -15.9$
CF_3	r(C-O)=2.23 $*\varphi_{attack}=98.9$ $**\varphi_{pyramidal}=67.8$ $E_a= 1.8$ $\Delta_r H = -14.6$	r(C-O)=2.51 $*\varphi_{attack}=97.9$ $**\varphi_{pyramidal}=67.8$ $E_a= 1.4$ $\Delta_r H = -16.1$	r(C-O)=2.56 $*\varphi_{attack}=99.73$ $**\varphi_{pyramidal}=67.7$ $E_a= 1.3$ $\Delta_r H = -16.1$
Cl	r(C-O)=2.14 $*\varphi_{attack}=100.85$ $**\varphi_{pyramidal}=67.9$ $E_a= 3.4$ $\Delta_r H = -12.6$	r(C-O)=2.38 $*\varphi_{attack}=97.03$ $**\varphi_{pyramidal}=67.81$ $E_a= 1.9$ $\Delta_r H = -15.7$	r(C-O)=2.33 $*\varphi_{attack}=97.25$ $**\varphi_{pyramidal}=67.8$ $E_a= 2.2$ $\Delta_r H = -15.5$

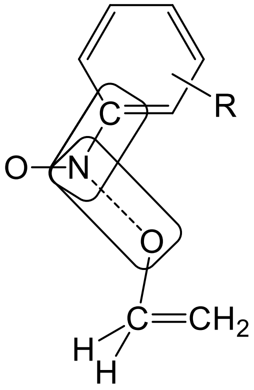
, where r(C-O) - is the C-O bond length, $*\varphi_{attack}$ - is the angle of attack, $**\varphi_{pyramidal}$ - is the pyramidal angle, Ea - is the activation energy, ΔrH - is the reaction enthalpy. E_a,kkal/mol, $\Delta_r H$, kkal/mol.

It is also clear from the results obtained that with an increase in the activation energy, the enthalpy of the reaction increases.

When considering the second stage of the reaction, we single out such parameters as the N – O bond distance, the difference in charges on the N and C atoms.

Compared with the first stage, the length of the N-O bond does not change when the position of the substituent changes. However, there is a significant increase in the difference in the magnitudes of the charges on the N and C atoms located in the reaction center. In the case where the substituent at the *ortho* position a decrease in the activation energy of decay is observed in comparison with the *meta* and *para* positions.

Table. 2. Geometry of the transition state and kinetics of the reaction 2

nitrobenzene			
r(N-O)=2.14 Δμ(N-O)=0.082 Δμ(N-C)=1.204 E_a=13.5 Δ_rH = -24.0			
R	***ortho***	***meta***	***para***
CH_3	r(N-O)=2.14 Δμ(N-O)=0.082 Δμ(N-C)=1.204 E_a=13.5 Δ_rH = -24.0	r(N-O)=1.87 Δμ(N-O)=0.08 Δμ(N-C)=0.587 E_a=14.9 Δ_rH = -20.2	r(N-O)=1.88 Δμ(N-O)=0.07 Δμ(N-C)=0.307 E_a=14.9 Δ_rH = -19.3
CCl_3	r(N-O)=1.86 Δμ(N-O)=0.299 Δμ(N-C)=0.404 E_a=12.4 Δ_rH = -29.9	r(N-O)=1.86 Δμ(N-O)=0.302 Δμ(N-C)=0.302 E_a=14.9 Δ_rH = -20.3	r(N-O)=1.85 Δμ(N-O)=0.203 Δμ(N-C)=0.095 E_a=14.9 Δ_rH = -19.8
CF_3	r(N-O)=1.86 Δμ(N-O)=0.195 Δμ(N-C)=0.939 E_a=12.9 Δ_rH = -26.1	r(N-O)=1.86 Δμ(N-O)=0.113 Δμ(N-C)=0.548 E_a=14.9 Δ_rH = -20.3	r(N-O)=1.85 Δμ(N-O)=0.141 Δμ(N-C)=0.334 E_a=14.9 Δ_rH = -19.9
Cl	r(N-O)=1.87 Δμ(N-O)=0.043 Δμ(N-C)=1.5 E_a=12.4 Δ_rH = -26.2	r(N-O)=1.86 Δμ(N-O)=0.096 Δμ(N-C)=0.575 E_a=14.9 Δ_rH = -20.2	r(N-O)=1.87 Δμ(N-O)=0.876 Δμ(N-C)=0.510 E_a=14.9 Δ_rH = -19.9

, where r(N–O) is the N–O bond length, Δμ(N–O) is the difference in charge values on N and O atoms, Δμ(N–C) is the difference in charge values on N and C., E_a,,kkal/mol, Δ_rH, kkal/mol.

CONCLUSION

The effect of acceptor and donor substituents in the *ortho*, *meta*, and *para* positions in the nitrobenzene molecule on the reaction of interaction with ethylene was determined:

1) with an increase in the length of the C–O bond in the transition state, the activation energy decreases.

2) with an increase in the angle of attack, an increase in the activation energy occurs.

3) with an increase in the activation energy, the enthalpy of the reaction increases.

4) It was found that ethylene oxide and a nitroso compound are formed during the reaction.

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