Study of the mechanism of interaction of acetylene with nitro compounds

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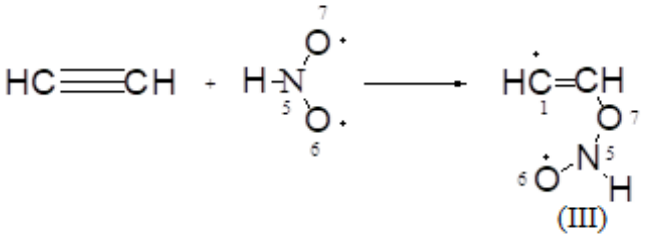
DFT/B3PW91/6-31+G(d) method was used to study the reaction mechanism of alkynes with nitro compounds by the example of acetylene with HNO_2, CH_3NO_2, and $C_2H_5NO_2$.

At the first stage, the interaction of HNO_2 in the T_1 state with acetylene 5takes place in the S_0 state.



As a result of the reaction, a biradical compound (III) is formed. The spin density is concentrated at atoms O(6) and C(1), being 0.4759 and 0.9661, resp. The corresponding transition state is determined and shown in fig. (1).

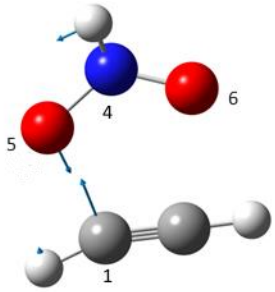


Fig.1 Transition state of the reaction $^{3}HNO_2$ with $^{1}H_2C_2$ having an imaginary frequency value of *i*239.67 cm $^{-1}$ (T_1)

In the transition state, a redistribution of the spin density at the O(7), O(6) and C(1) atoms is observed. The spin density at the O(7) atom decreases from 0.746 in the reagents down to 0.086 in the reaction product. At the O(6) atom, there is a slight decrease from 0.792 down to 0.463. At the atom C(1) spin density increases from 0 up to 1.291.

The interaction of nitro compounds with acetylene occurs along a straight line connecting O(5) and C(1) atoms. The direction of the displacement of atoms is shown in Fig. 1 by vectors. The transition state is characterized by the presence of the single imaginary frequency, the value of which is *i*239.67 cm $^{-1}$ (T_1).

The activation energy of this stage is 8.1 kcal / mol. (Fig.2)

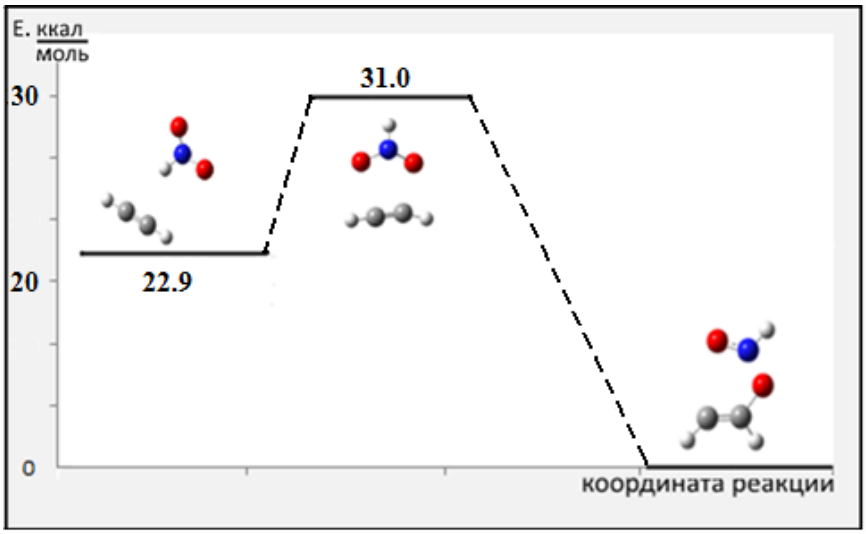
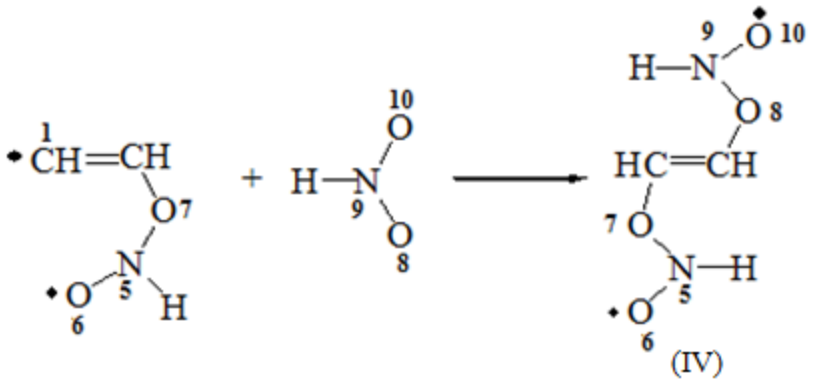


Fig. 2 Energy diagram of the oxidation of acetylene by HNO_2 in the triplet state

In the second stage, the second molecule of HNO_2 joins to the product of the first reaction stage to form the compound (IV)



The spin density is concentrated at O(6) and being 0.454 and 0.458, resp. As the reaction progresses, the spin density decreases at C(1) atom down to 0, at N(5) atom it remains constant, at O(7) atom it decreases from 0.3229 down to 0, at O(10) atom it increases from 0 up to 0.458. The product of the second stage is also of the biradical type.

The transition state at this stage was also determined (Fig. 3).

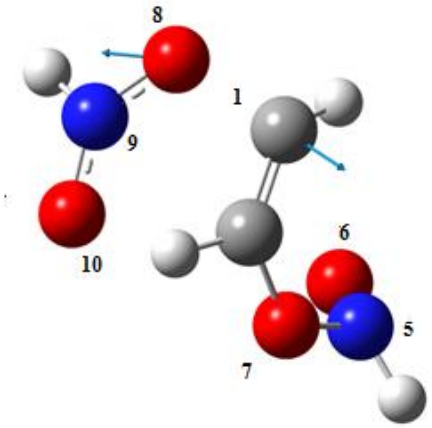


Fig.3 The transition of the fird state of the reaction under study with imaginary frequency of 1083.39 *i*cm^{-1} (T_1)

The interaction of nitro compounds with acetylene occurs along to straight line connecting O(8) and C(1) atoms. The transition state is characterized by imaginary frequency of 1083.39 *i*cm^{-1} (T_1). The activation energy of this stage is 7.3 kcal / mol. (Fig.4)

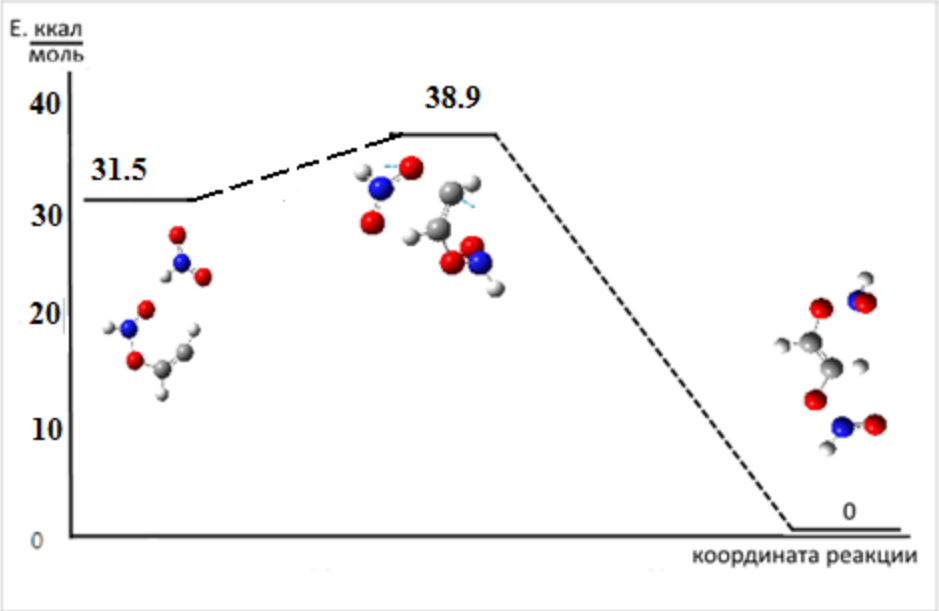
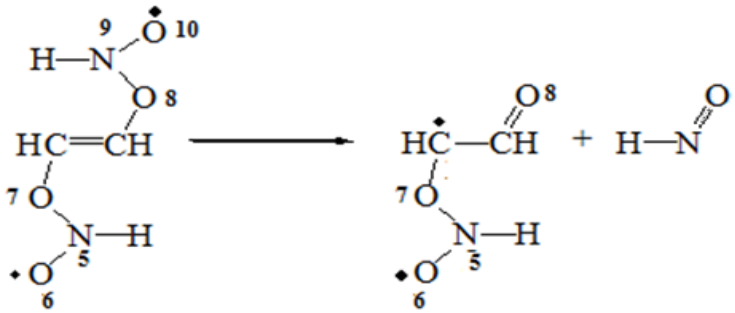


Fig. 4 Energy diagram of the reaction of the interaction of the reaction product 1 with HNO_2 in the triplet state

In the third stage, the reaction product of stage two decomposes into a nitroso compound and compound (V).



(V)

The spin density is localized at C(1) and O(6) being 0.631 and 0.528, respectfully. As the reaction proceeds, the spin density remains constant at N(5), at O(7) atom it increases from 0 up to 0.135, at C(1) atom it increases from 0 up to 0.631. During this stage, a nitroso compound in the singlet state and a diradical are formed. The transition state of this stage is shown in fig.5

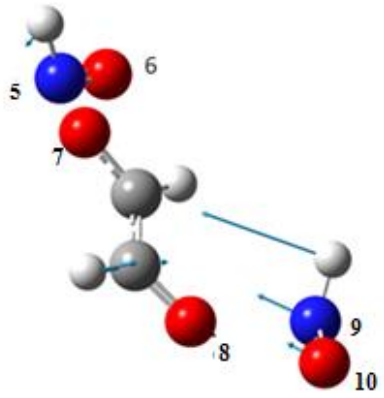


Fig.5 Transition state with an imaginary frequency value of 126.59 *i*cm^{-1} (T_1)

The decomposition of the reaction product of stage two occurs in a straight line connecting N(9) and O(8) atoms. The transition state is characterized by an imaginary frequency value of 126.59 *i*cm^{-1} (T^1). The direction of the displacement of atoms is shown in fig.6 by vectors.

The activation energy of this stage is 4.8 kcal /mol.

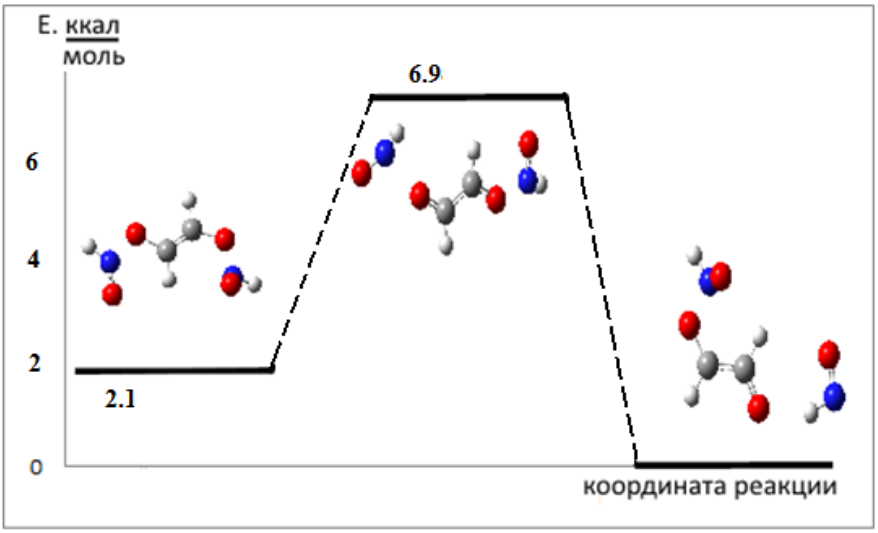
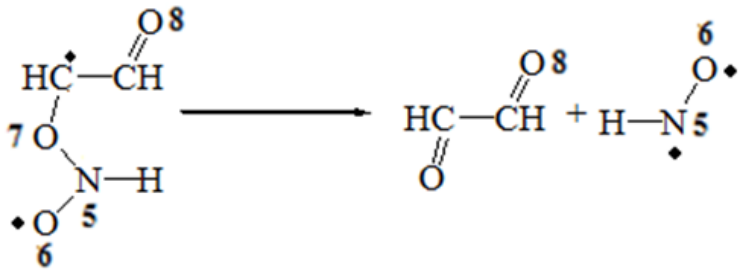


Fig.6 Energy diagram of the decomposition of the reaction product 2

At the fourth stage, the final decomposition of the product from the third stage into glyoxal and the nitroso compound takes place in the triplet state.



At this stage, in the case of decomposition products, the spin density is localized on nitroso oxide atoms, namely, at N(5) 1.081 and at O(6) 0.843. Also, during the course of the reaction, the spin density is stored at O(8) atom being 0.236 and at C(2) being 0.5911. Subsequently, the nitroso compound undergoes isc with subsequent return to the singlet state. The transition state of this stage is described in fig.7, indicating the value of the imaginary frequency 480.05 *i*cm $^{-1}$ (T_1).

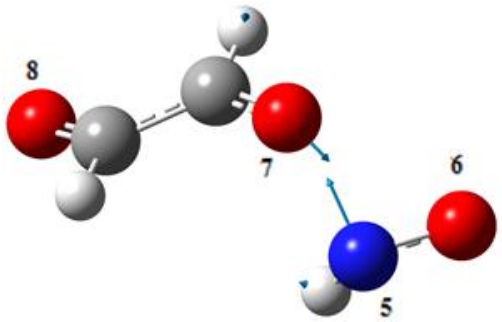


Fig.7. Transition state with imaginary frequency value 480.05 *i*cm^{-1} (T_1)

The decomposition of the reaction product occurs in a straight line, indicated in the figure by vectors and connecting the atoms O(7) and N(5). The activation energy of this stage is 0.4 kcal /mol. The activation energies are shown in Tabl. 1.

Table 1. The activation energy of the reaction of interaction of acetylene with nitro compounds

Ea,kcal /mol	Stage 1	Stage 2	Stage 3	Stage 4
HNO_2+C_2H_2	8.1	7.3	4.8	0.4
CH_3NO_2+C_2H_2	8.6	6.2	4	0.3
$C_2H_5NO_2$+C_2H_2	8.1	8.4	3.4	0.4

Conclusions

1. The activation energies of the reactions of acetylene with HNO_2, CH_3NO_2, $C_2H_5NO_2$ are calculated.

2. The reaction mechanism is proposed, which consists in the stepwise addition of two molecules of the nitro compound via the acetylene triple bond, followed by a two-step decomposition to glyoxal.

3. The addition reactions of HNO_2, CH_3NO_2, $C_2H_5NO_2$ with acetylene are exothermic.