Kinetics and Mechanism of 4-Methyl-1- Pyrazoline Pyrolysis in the Gas Phase, A Computational Study
M. Izadyar, A. Mansuri
Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, I.R. Iran

Eighteenth Iranian of Organic Chemistry 2012 March 7-9

Abstract
Kinetic and mechanistic aspects of nitrolysis elimination from 4-methyl-1-pyrazoline and its deuterated derivatives have been investigated in the gas phase with the B3LYP, MPW1PW91 and PBE0 methods which include one step size radical and two concerted mechanisms. Theoretical calculations show that the radical mechanism is suitable from the activation energy point of view. Although calculated kinetic parameters and kinetic isotope effects for the first mechanism are in agreement to experimental results but the second mechanism from the kinetic isotope effects point of view can be used for propene formation as a product which competes with the major product of cyclopentane.

Keywords: Mechanism, Computational, Secondary Kinetic isotope effects, Pyrazolines, Transition State, Deuterium, Radicals.

1. Introduction

The investigation of the kinetic and mechanism for the gas-phase elimination reaction of 4-methyl-1-pyrazoline was carried out using electronic structure methods. The calculation of Density Functional Theory (DFT) was made by using the Becke's three parameter from the formation of Lee, Yang and Parr (B3LYP) and GGA (GGA) [7,9], the Perdew-Wang 91 correlation functional (BP86) [8,10], the Perdue, Berlin, and Ehrensof [PBE] [6,11] and using Muller-Plesset (MP2) and Goldstone (G) [11,12]. The activation energy for the first mechanism and for the second mechanism (py) is to a triplet. We propose this research to study the isotope effect and gain insight into the mechanism pathway this of the reaction. The presented research employs the deuterium isotope instead of hydrogen atoms on some specific situations of the reactants because the secondary deuterium kinetic isotope effect offers a powerful method for calculations for reaction 1 and 2 and activation parameters are computed. The calculated values show that the pyrolysis reaction is an exothermic process (ΔH < 0) and the entropy changes through the reaction is positive (ΔS > 0).

2. Computational method and models

The calculated values show that the pyrolysis reaction is an exothermic process (ΔH < 0) and the entropy changes through the reaction is positive (ΔS > 0).

3. Result and discussion

According to the percentage of the products (methylcyclopentane +35% and 2-methylcyclopentane +43%) in the experimental work [1], we consider four transition states for transition state for 4-methylpyrazoline pyrolysis.

For formation of methylcyclopentane maybe of C-N bonds is broken (Scheme 2), but because of its high activation energy (72 kcal/mol) versus experimental activation energy (about 42 kcal mol⁻¹) this pathway is rejected.

To form the methylcyclopentane mechanism is the cleavage of two C-N bonds synchronicity and reaction proceeds through the four-membered cyclic transition state (Fig. 1), the activation energy is 72 kcal/mol that is too close to the experimental result.

In the case of producing of 2-methylcyclopentane the existence of six-membered cyclic transition state is seemed (Scheme 3). Where in this case the activation energy is obtained 16.94 kcal mol⁻¹ but because of the importance of this compound the activation energy is 17.17 kcal mol⁻¹.

Another possible mechanism for formation of 2-methylcyclopentane is the four-membered cyclic transition state formed from cyclopentane that is produced in the stage of a pyrazoline (Fig. 2). The activation energy in this was obtained about 71 kcal mol⁻¹. That by attention to the percentage of methylcyclopentane, this mechanism is accepted.

The 4-methylpyrazoline reaction is an exothermic process (ΔH < 0) and the entropy changes through the reaction is positive (ΔS > 0).

2.2 Structural analysis

Structural parameters of Fig. 1 and Fig. 2 are given in Tables 1-3. As the values shows H1-N2 bond length is decreased from reactant to TS1 and the product (N1-N2 bond length is 1.106 in N2 molecule) is increased from TS1 to TS2. The C4-C5 bond length from TS2 to TS1 and then to product shows a change of bond order from 1 to 2 and increase in distance of HB from C4 and approach to C5 suggests transmission of HB. In this mechanism, when C=N bond is elaginated and N-N bond is shortened, the new bond formation occurs between C4-C5 and its order increase as the reaction progresses. This process follows by a fast transition of HB to the center of the resulting in the production of 2-methylcyclopentane. The change in the C4-C5 bond length is not significant.

2.3 AIM analysis

The AIM calculation data are listed in Table 4. Comparing the TS1 and R1 for Fig. 1, the following results are obtained:

Change in N1 and N2 charges and also in C3 and C4 shows that C-N bond of C is broken simultaneously. Changes in C3 and C5 charges are small and can be concluded that as forming the bond, breaking occurs too.

Increasing in negative charge of C4 shows that electron density of that is increasing. Furthermore, from the table data result that breaking of C-N bond is faster than the formation of N-O bond. From comparing the TS2 and R2 for Fig. 2 the following results are achieved:

The charge value of C3 is become more positive and C4 become more negative and this occurs because of the transmission of HB from C4 and also forming the double bond. Positive charge of C3 increases for breaking C-N bond and formation of HB to C5. Because of transmission of HB from tert-carbon to primary carbon its change become more positive.

The values of AIM calculation are reported in Table 5 and 6. From the result of the tables for Fig. 2, charges density of C3-C4 and C4-C5 from R1 to TS1 is increased and in N1-C5 and N2-C3 is also. As seen, for both the Laplacian for C5 and C2-N3 bond becomes negative, confirming the absence of electrons at this bond.

3.4 Reactions kinematic isotopes effects analysis

We estimated kD/kH values and kinetic isotope effects to find out the role of hydrogen atom transfer in mechanism of Fig. 2 based on the following equation:

\[ k_D/k_H = \exp\left(\frac{-\Delta H}{RT}\right) \]

Where ΔH(I) corresponds to the difference between Gibbes free energy of activation of the TSs and its deuterated structure and n is the number of o-deuterium atom which are substituted instead of hydrogen atoms. Values of secondary kinetic isotope effect for deuteration of mechanism of Fig. 2 shows the kinetic isotope effects during the pyrolysis process.

4. Conclusion

Due to situations such as simultaneous cleavage of two C-N bonds increase from R1 to TS1 and then decrease in product.

2. From AIM calculations, it can be concluded that the transition state for forming of methylcyclopentane is biradical.

3. Transition state for 2-methylcyclopentane is a four-membered cyclic transition state.

The calculated values show that the pyrolysis reaction is an exothermic process (ΔH < 0) and the entropy changes through the reaction is positive (ΔS > 0).

References:

Table 4. AIM Analysis of TS1 and TS2

<table>
<thead>
<tr>
<th>Bond</th>
<th>u</th>
<th>r'</th>
<th>r''</th>
<th>r'</th>
<th>r''</th>
<th>r'</th>
<th>r''</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
</tr>
<tr>
<td>C-H</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
</tr>
<tr>
<td>C-H</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
</tr>
</tbody>
</table>

Table 5. AIM Analysis of R1 and TS3

<table>
<thead>
<tr>
<th>Bond</th>
<th>u</th>
<th>r'</th>
<th>r''</th>
<th>r'</th>
<th>r''</th>
<th>r'</th>
<th>r''</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
</tr>
<tr>
<td>C-H</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
</tr>
<tr>
<td>C-H</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
</tr>
</tbody>
</table>

Table 6. AIM Analysis of R2 and TS4

<table>
<thead>
<tr>
<th>Bond</th>
<th>u</th>
<th>r'</th>
<th>r''</th>
<th>r'</th>
<th>r''</th>
<th>r'</th>
<th>r''</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
<td>1.095</td>
</tr>
<tr>
<td>C-H</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
<td>1.106</td>
</tr>
<tr>
<td>C-H</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
<td>1.117</td>
</tr>
</tbody>
</table>