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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
E-mail: Izadyar@um.ac.ir

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Abstract

Kinetic and mechanisms aspects of nitrogen elimination from 4-methyl-1-pyrazoline and it's deuterated derivatives have been investigated in the gas phase with the B3LYP, MPW1PW91 and PBEPBE methods, using the 6-311+G(d,p) basis sets. This reaction may proceeds through the three paths 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 accordance 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 cyclopropane.

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

1. Introduction

Experimental studies on the gas- phase elimination of pyrazoline demonstrated that olefines and corresponding cyclopropans are the products of this reaction [1]. The generally accepted mechanism for photolysis of azo-compounds involves the loss of nitrogen to produce hydrocarbons [2], generally believed to be formed via radical intermediates [3]. This intermediate is isobutyl-biradical [4]. The result for direct photolysis are consist with the scheme (1). The reaction has been observed by Strausz [5] to be analogous to that reported by Solomon, Thomas, and Steel [6]. Similarly Strausz has not observed any evidence for conversion for the pyrazoline singlet (py*) to a triplet. We propose this research to study magnitude and importance of isotope effect and gain insight into the mechanism pathway of this 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 characterization of the bond breaking at the transition state (TS) of the pyrolysis reactions. Four levels of the theoretical calculations have been utilized in the first attempt to gain insight into the mechanistic aspects of these reactions.

2. Computational method and models:

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 Function Theory (DFT) levels were made by using the Becke's three-parameter from the formation of Lee. Yang and PARR[B3LYP/6-311++G(d,p)][7-9], the Perdew-Wang 1991 correlation functional [B3PW91/6-311++G(d,p)][10], the Perdew, Burke, and Ernserhof [PBE/6-311++G(d,p)] and using Moller-Plesset [MP2/6-311++G(d,p)]. These calculations were performed by using Gaussian 09 program[12].

Thermodynamic quantities such as zero point vibrational energy [ZPV], Temperature correction E(T) and absolute entropies S(T) were obtained by frequency calculation.

The first order rate coefficient K(T) was calculated using the transition state theory (TST) [13] according to equation 1 and assuming that the transmission coefficient is equal to 1.

Where $\Delta G^{\#}$ is the Gibbs free energy change between the reactant and the transition state(TS) and K_B, h are the Boltzmann and Plank constant, respectively.

The activation energy,(E_a), and the Gibbs free energy,($\Delta G^{\#}$), were computed using the equations, (2) and (3), respectively, which have been derived from the TST, too [13]:

$$\boldsymbol{K(T) = \left(\frac{K_B T}{h}\right) \exp\left(-\frac{\Delta G^{\#}}{RT}\right)} \quad \textbf{Equation 1} \qquad \boldsymbol{E_a = \Delta H^{\#}(T) + \mathrm{RT}} \quad \textbf{Equation 2} \qquad \boldsymbol{\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}(T)} \quad \textbf{Equation 3}$$

The natural bond orbital (NBO) analysis, which was suggested by Reed et al. [14,15] was applied to determine the charge changes occurring in the pyrolysis processes.

The intrinsic reaction coordinate (IRC) method was also used to check the profiles connecting the TSs to the associated minima of the concerted mechanism.

The atom in molecule (AIM) calculation was considered. This method for better description of the changes were occurred through the reaction provides a rigorous and unambiguous criterion to determine which atoms are bonded and which ones are separated in the given system [16].

3. Result and discussion

3.1) Energy analysis

According to percentage of the products (methylcyclopropane =53% and 2-methylpropene =43%) in the experimental work [1], we consider four transition states for transition state for 4-methyl1-pyrazoline pyrolysis:

a) For formation of methyl cyclopropane maybe that one of C-N bonds is broken (Scheme 2), but because of its high activation energy (72 kcal.mol^{-1}) versa experimental activation energy (about 42 kcal mol^{-1}) [1] this pathway is rejected.

b) To form the methylcyclopropane another mechanism is the cleavage of two C-N bonds syncrounissity and reaction proceed through the four-membered cyclic transition state (Fig.1). the activation energy in this case obtained 40.62 kcal mol^{-1} l that is too closely to experimental results.

c) In the case of producing of 2-methylpropene the existence of six-membered cyclic transition state is seemed (Scheme 3). Where in this case the activation energy is obtained 36.94 kcal mol^{-1} but because of the percent of formed 2-methylpropene, this case is rejected.

d) Another possible mechanism for formation of 2-methylpropene is the four- membered cyclic transition state formed from cyclopropane that is produced in the stage of { a } (Fig.2). The activation energy in this case was obtained about 71 kcal mol^{-1}. That by attention to the percentage of methylcyclopropane, this mechanism is accepted.

Thermodynamic calculations for reaction 1, 2 and activation parameters are computed. The calculated values shows that the pyrolysis reaction is an exothermic process ($\Delta H < 0$), The global process is spontaneous ($\Delta G < 0$) and the entropy changes through the reaction is positive($\Delta S > 0$).

3.2) Structural analysis

Structural parameters of Fig.1 and Fig.2 are given in Tables 1-3. As the values shows N1-N2 bond length is decreased from reactant to TS1 and the product (N1-N2 bond length is 1.106 in N2 molecule) that shown triple bond is formed. C3-C4 and C4-C5 bond length from R1 to TS1 are increase and from TS1 to product is decrease (wich it shows that a biradical is formed).

The changes of C3-C5 bond length confirms existence of a biradical for TS1 and observing bond angle variation, for example between C3-C4-C5 atoms in the Fig.1 imply possibility of hybridation changes in the central atom of each angle(C4).

For Fig.2 . reducing of C3-C4 bond length from R2 to TS2 and then to product shows a change of bond order from 1 to 2 and increase in distance of H8 from C4 and approach to C5 suggests transmission of H8. In this mechanism, when C-N bond is elongated and N-N bond shorted, the new bond formation occurs between C3-C4 and its order increase as the reaction progresses. This process follows by a fast transition of H8 to the center of the C5 resulting in the production of 2-methyl propene instead of methylcyclopropane. The change in the C4-C5 bond length is not significant.

3.3) Charge analysis

NBO 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 two bonds of C-N are 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-N bond. From comparing the TS2 and R2 for Fig .2 the following results are achieved:

The charge value of C3 is became more positive and C4 became more negative and this occurs because of the transmission of H8 from C4 and also forming the double bond. Positive charge of C5 increases too and this change is for breaking C3-N5 bond and transmission of H8 to C5. Because of transmission of H8 from tert-carbon to primary carbon it's charge become more positive.

3.4) AIM analysis

The values of AIM calculation are reported in Table 5 and 6. From the result of the tables for Fig 1, charges density of C3-C4 and C4-C5 from R1 to TS1 is increased and in N1-C5 and N2-C3 is decrease. Also for Fig. 2 the Laplacian for N1-C5 and N2-C3 bonds than became negative, conforming the absence of electrons at this bond.

Electron density of C3-C4 increase and it occurs for formation of double bond. The value of 0.185 for Laplacian of this bond shows a concentration of electron on this bond and also increasing of C4-C6 Laplacian from 0.232 to 0.159 shows breaking in this bond.

3.5) Deuterium kinetic isotope effects analysis

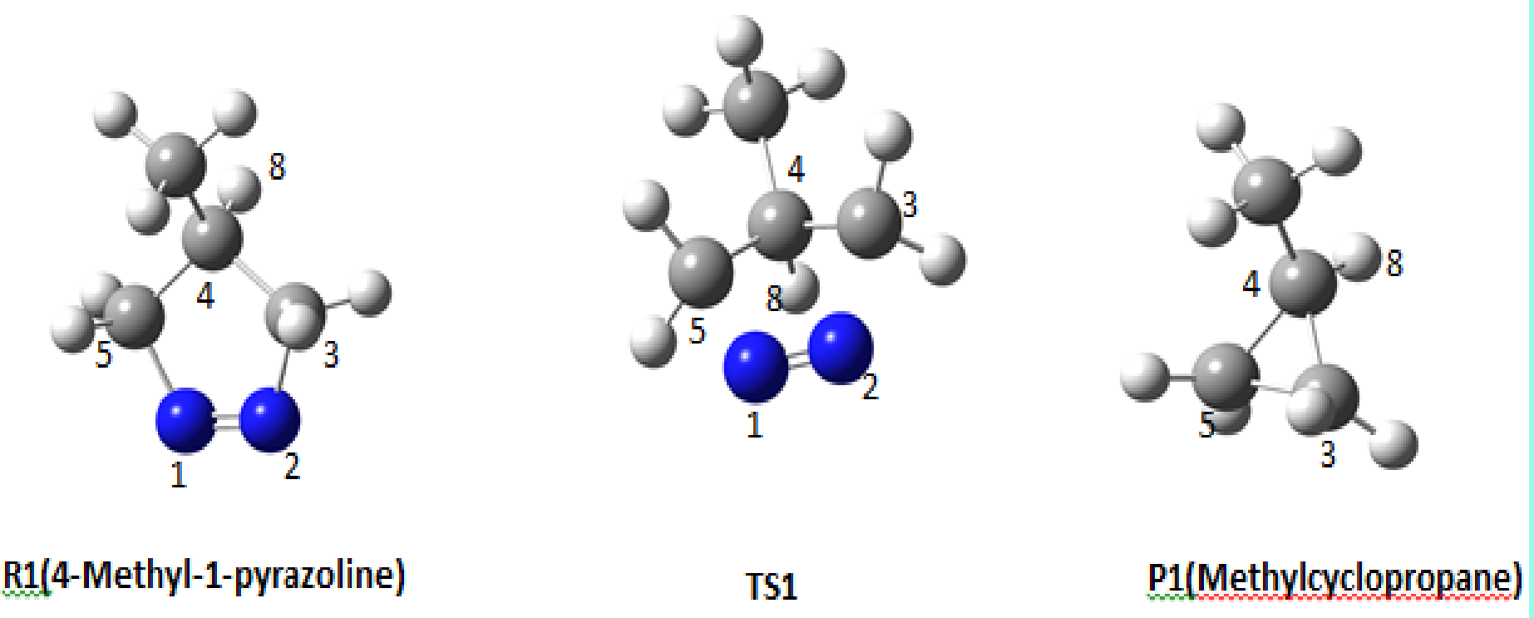
We estimated K_H/K_D values and kinetic isotope effects to find out the role of hydrogen atom transfer in mechanism of Fig.2 based on the following equation 4:

$$\boldsymbol{\log k_H/k_D = n\,\Delta(\Delta G^{\#})/(2.303RT)} \qquad \textbf{(4)}$$

where $\Delta(\Delta G^{\#})$ corresponds to the difference between Gibbs free energy of activation of the TSs and its deuterated structure and n is the number of α-deuterium atom which are substituted instead of hydrogen. Values of the secondary kinetic isotope effect per deuterium for mechanism of Fig. 2 shows the secondary kinetic isotope effects during the reaction.

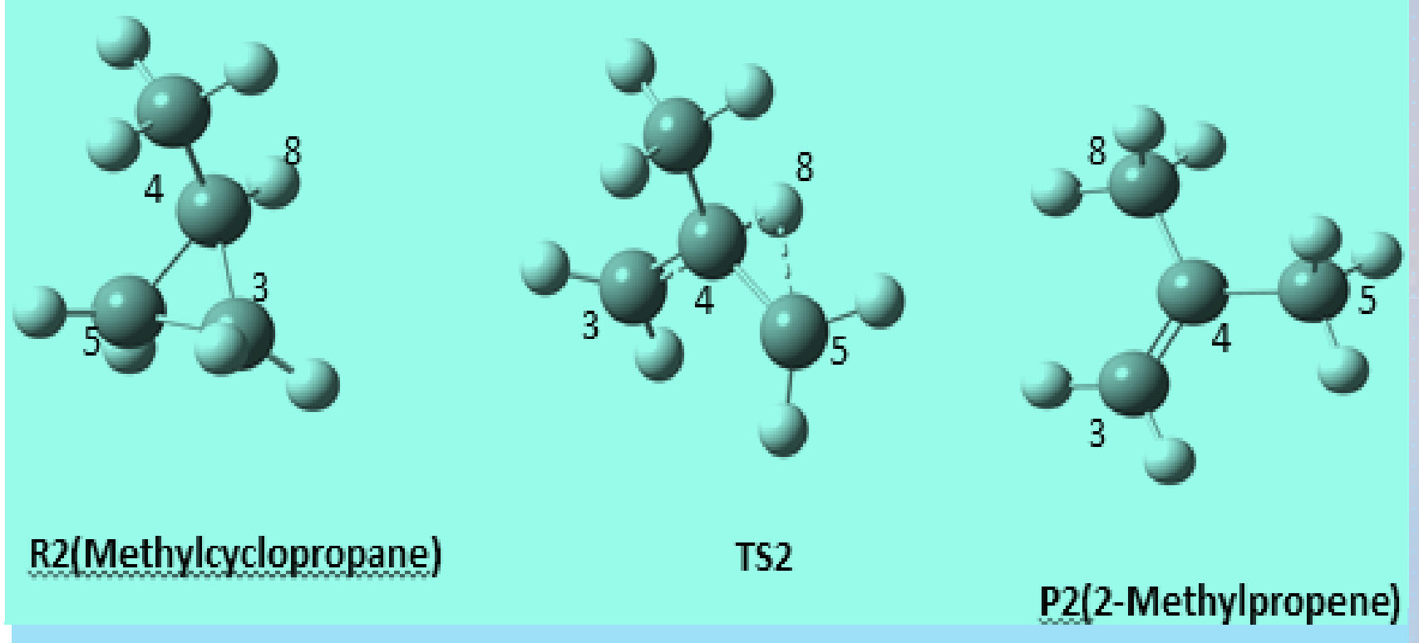
4. Conclusion

1) Due to evidences 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 the methyl cyclopropane is biradical.
3) Transition state for 2-methylpropene is a four membered cyclic.
4) Activation parameters are in good agreement with experimental values at B3LYP/6-311++g(d,p) level of theory.
5) The ratio of k_H/k_D for forming of the 2-methylpropene at B3LYP/6-311+G(d,p) obtained 2.22.



R1(4-Methyl-1-pyrazoline) TS1 P1(Methylcyclopropane)

Fig 1. Optimized structure for the reactant (R1=4-methyl-1-pyrazoline), ts1 and product(p1=methylcyclopropane) at the B3LYP/6-311++G(d,p) level.



R2(Methylcyclopropane) TS2 P2(2-Methylpropene)

Fig 2. Optimized structure for the reactant (R2= methylcyclopropane), ts1 and product(p2=2-methylpropene) at the B3LYP/6-311++G(d,p) level.

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$\mathrm{Py} + h\nu \rightarrow \mathrm{Py}^*$

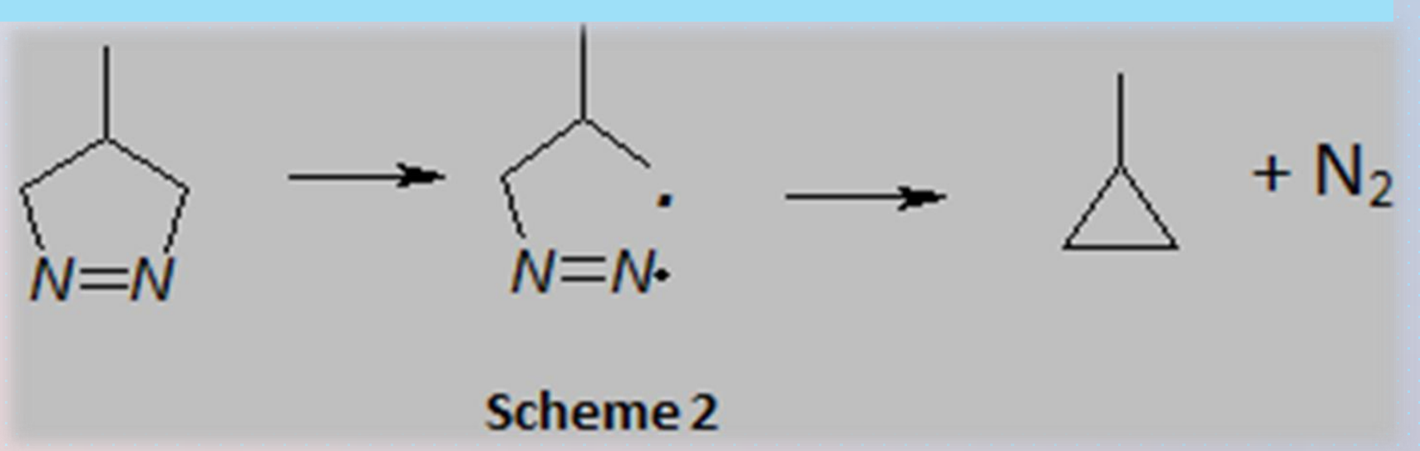
$\mathrm{Py}^* \rightarrow \mathrm{Int}^* + N_2$

$\mathrm{Py}^* \rightarrow \mathrm{Py} + \text{cleavage olefins} + N_2$

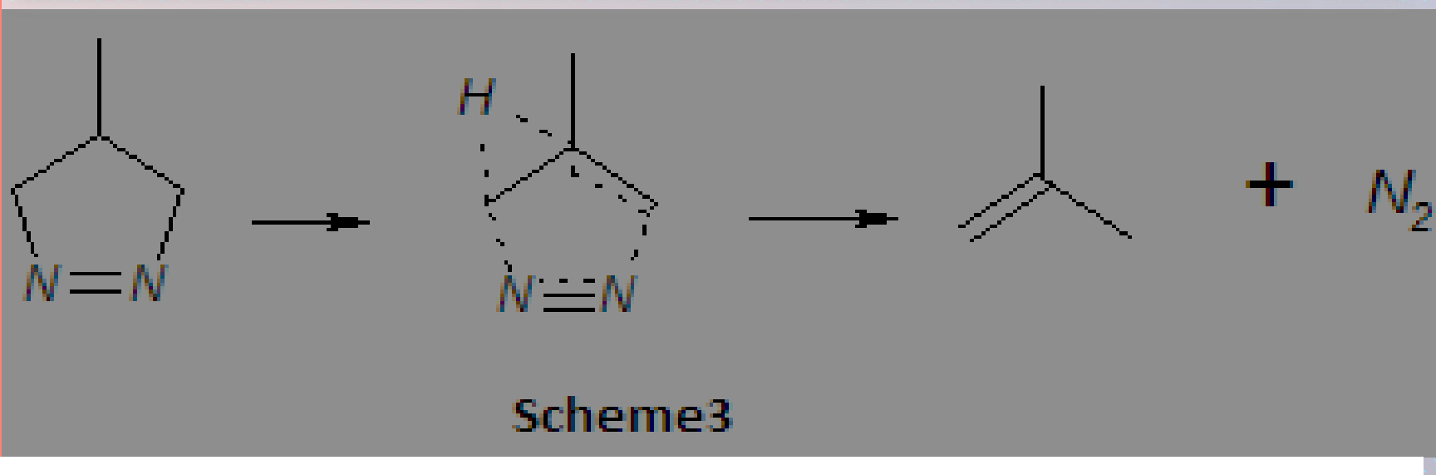
$\mathrm{Py}^* \rightarrow \mathrm{Py} + h\nu(\text{Flourescence})$

$\mathrm{Int} \rightarrow \text{cyclo propanes} + \text{olefins}$

Scheme 1



Scheme 2



Scheme3

Table 1.Strctural parameters for Fig.1(in angstrom) using the B3LYP/6-311++G(d,p) method.

	R_1	Ts1	Methyl cyclo propaan
N_1—N_2	1.241	1.120	---------
N_2—C_3	1.492	2.600	---------
C_3—C_4	1.542	1.454	1.510
C_4—C_5	1.542	1.454	1.510
C_5—N_1	1.492	2.600	--------
C_3—C_5	2.374	2.570	1.511

Table 2 .Strctural parameters for Fig.2(in angstrom) using the B3LYP/6-311++G(d,p) method.

	Methyl cyclo propan	Ts2	2-Methyl propene
C_3—C_4	1.510	1.433	1.337
C_4—C_5	1.510	1.496	1.509
C_3—C_5	1.511	2.507	2.491
C_5—H_8	2.208	1.851	1.099
C_4—H_8	1.089	1.135	2.162

Table 3. Angle parameters for Fig.1(in degree) using the B3LYP/6-311++G(d,p) method.

	R	TS1
N_1—N_2—C_3	112.320	106.118
N_2—C_3—C_4	106.322	87.313
C_3—C_4—C_5	100.678	124.129
C_4—C_5—N_1	106.322	87.313
N_1—N_2—C_3—C_4	-9.122	-24.864
N_2—C_3—C_4—C_5	13.284	59.538

Table 4. Distributed NBO charges on the R1, TS1, R2 and the TS2 at the B3LYP/6-311++G(d,p)level.

	R1	TS1	R2	TS2
N1	-0.148	-0.011	----	----
N2	-0.148	-0.011	----	----
C3	-0.250	-0.246	-0.400	-0.338
C4	-0.273	-0.424	-0.232	-0.386
C5	-0.250	-0.246	-0.400	-0.369
C6	-0.567	-0.539	-0.571	-0.562
H8	0.201	0.202	0.200	0.335

Table 5 . Topological properties (in a.u.) for the atoms involved in R1 and TS1 calculated at the B3LYP/6-311++G(d,p) .

	R1		TS1	
Bond point (3,-1)	ρ(r)	L(r)	ρ(r)	L(r)
C_3—C_4	0.243	0.135	0.280	0.179
C_4—C_5	0.243	0.135	0.280	0.179
C_5—N_1	0.263	0.165	0.020	-0.017
C_3—N_2	0.263	0.165	0.020	-0.017

Table 6 . Topological properties (in a.u.) for the atoms involved in R2 and TS2 calculated at the B3LYP/6-311++G(d,p) .

	R2		TS2	
Bond point (3,-1)	ρ(r)	L(r)	ρ(r)	L(r)
C_3—C_4	0.239	0.108	0.292	0.185
C_4—C_5	0.293	0.108	0.250	0.136
C_4—H_6	0.275	0.232	0.232	0.159