Kinetics and mechanism of propene elimination from allyl methyl amine pyrolysis in the gas phase

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1. Introduction

The mechanism of the retro-ene reaction has been the subject of the interesting controversies [1-3]. Both experimental and theoretical studies indicate that this type of reaction proceeds through a concerted mechanism, although in some cases, stepwise mechanism involving diradical intermediate is less favorable [4-8]. The most important molecular mechanisms that are involved in the gas phase pyrolysis of these compounds include the radical and concerted mechanisms. Martin et. al. studied the gas phase thermolysis of alkyl allyl amine at 673-773 K [9]. The rate equation is accordance to Eq. 1.

$$K(sec^{-1}) = 10^{11.4}\ Exp(-181.6\ kJ.mol^{-1}(RT)^{-1} \qquad (1)$$

Upon pyrolysis reaction, allyl methyl amine (AMN) eliminates propene and corresponding imine compounds via an intramolecular γ-hydrogen transfer (fig. 1).

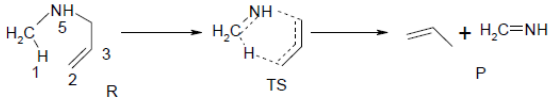

Fig 1. Atom numbering for the reactant, TS and products

The objective of this study is to provide a theoretical prediction of the kinetic and activation parameters. It is also important to elucidate the molecular mechanism associated with this retro-ene reaction in order to find out a precise idea of the reaction pathway.

2. Methods

The structures corresponding to the reactant, transition state and products for the studied reaction were optimized using the Gaussian 03 computational package. Optimized geometries of the stationary points on the potential energy surfaces (PES) were obtained using the Becke's-three parameter hybrid exchange functional with the correlation functional of Lee-Yang-Parr (B3LYP). In these calculations we used the 6-31G* basis set. The corresponding TSs were calculated using the STQN method.

Thermodynamic parameters (Enthalpy, Gibbs free energy and Entropy) for the stationary points along the pyrolysis reaction were calculated. In order to determine the atomic charges at the stationary points along the reaction paths, population analysis was applied.

3. Results and discussion

Propene elimination from the AMN may occur through the two probable mechanisms. The first one may be started by the cleavage of the C4-N5 bond followes by a step-wise mechanism. The second possibility is the interamolecular transfer of H-atom to an unsaturated center via six-centered cyclic TS, yielding propene and imine. This can proceed through the H1-C2 bond formation and C4-N5 bond cleavage.

The C4-N5 bond breaking is the rate-determining step in the former mechanism. Bond dissociation energy of the C4-N5 would be mainly the activation barrier of this process from the energy point of view. From the results it is obvious that the calculated activation energy is 288.55 kJ mol^{-1} for the AMN pyrolysis. The calculated Activation energy is much greater than the experimental one; hence the radical mechanism is rejected. So, we should focus on the later one and consequently, the concerted mechanism was fully investigated.

Optimized structures for the reactants and the TSs are shown in figure 1 and geometrical parameters for the stationary points along the reaction are given in table 1 (See figure 1 for atom labeling).

Table 1. Main geometric parameters for the AMN (R) and the TS in the gas phase, using the B3LYP/6-31G(d) method (Distances in angstrom and dihedrals in degree).

Parameter	R	TS
H1-C2	2.89	1.38
C2-C3	1.33	1.41
C3-C4	1.51	1.39
C4-N5	1.45	2.01
N5-C6	1.46	1.36

During the pyrolysis reaction of alkyl allyl amine, H1-C2, C3-C4 and N5-C6 bond lengths are decreased, while H1-C6, C4-N5 and C2-C3 bond lengths are increased.

Calculated activation energies, free energies and entropies for the pyrolysis reactions are given in Table 2. From table 2 we can see that the calculated potential energy barriers for the reactions at the B3LYP/6-31G(d) is 186.4 $kJmol^{-1}$, the usual range for the experimental activation energies of alkyl allyl amines.

Table 2. Calculated kinetic and activation parameters for the pyrolysis of AMN at 626.65 K, using the B3LYP/6-31G(d) methods (Ea, $\Delta H^{\neq}$ in kJ mol^{-1} and $\Delta S^{\neq}$ in J $mol^{-1}K^{-1}$).

Ea	$\Delta H^{\neq}$	log A	$-\Delta S^{\neq}$
186.35	181.15	12.80	14.31

Negative values for the activation entropy confirmed the concerted mechanism for the studied reactions (Table 2).

The reactivity of alkyl allyl amine can be explained in terms of the acidic character of the H1 atom. Charge distribution on the atoms for the reactants and the TSs was calculated using the NBO analysis at the B3LYP/6-31G(d) level. we can notice that the positive charge on C6 and H1 atoms increases .This positive character shows that acidic character for H1 atom increases. This makes the H1-C6 bond to break at the same time for C4-N5 bond. So the new bond formation of C6-N5 and C3-C4 is a synchronous phenomenon.

4. Conclusions

Kinetics and mechanism of alkyl allyl amine pyrolysis was studied theoretically in the gas phase and a valid reaction channel was established. The pyrolysis reaction is homogeneous, unimolecular and obeys the first-order rate law. Two probable mechanisms have been postulated, radical and concerted mechanisms, and the concerted one is preferred to other pathway.

An analysis of the atomic charges suggests that the initial migration of H1 atom with the extension of C4-N5 bond can be regarded as driving force for the pyrolysis reaction. Theoretical and experimental results are in good agreement, describing a synchronous six-center concerted mechanism Experimental verification for some of these predictions is available.

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