
http://researchrepository.murdoch.edu.au/29212/
Accepted Manuscript

Computational Study for the Second-Stage Cracking of the Pyrolysis of Ethylamine: Decomposition of Methanimine, Ethenamine, and Ethanimine

Mansour H. Almatarneh, Lina Barhoumi, Ban Tayyem, Abd Al-Aziz A. Abu-Saleh, Marwa M. AL-A’qarbe, Faten Abuorabi, Ehab AlShamaileh, Mohammednoor Altarawneh, Ali Marashdeh

PII: S2210-271X(15)00438-7
DOI: http://dx.doi.org/10.1016/j.comptc.2015.10.032
Reference: COMPTC 1979

To appear in: Computational & Theoretical Chemistry

Received Date: 1 October 2015
Revised Date: 31 October 2015
Accepted Date: 31 October 2015

Please cite this article as: M.H. Almatarneh, L. Barhoumi, B. Tayyem, A.A-A. Abu-Saleh, M.M. AL-A’qarbe, F. Abuorabi, E. AlShamaileh, M. Altarawneh, A. Marashdeh, Computational Study for the Second-Stage Cracking of the Pyrolysis of Ethylamine: Decomposition of Methanimine, Ethenamine, and Ethanimine, Computational & Theoretical Chemistry (2015), doi: http://dx.doi.org/10.1016/j.comptc.2015.10.032

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Computational Study for the Second-Stage Cracking of the Pyrolysis of Ethylamine: Decomposition of Methanimine, Ethenamine, and Ethanamine

Mansour H. Almatarneh\textsuperscript{1*}, lina Barhoumi\textsuperscript{1}, Ban Tayyem\textsuperscript{1}, Abd Al-Aziz A. Abu-Saleh\textsuperscript{1}, Marwa M. AL-A'qarbeh\textsuperscript{1}, Faten Abuorabi\textsuperscript{1}, Ehab AlShamaileh\textsuperscript{1}, Mohammednoor Altarawneh\textsuperscript{2}, Ali Marashdeh\textsuperscript{3}

\textsuperscript{1}Department of Chemistry, University of Jordan, Amman 11942, Jordan.
\textsuperscript{2}School of Engineering and Information Technology, Murdoch University, Perth, Australia. Currently on leave from Chemical Engineering Department, Al-Hussein Bin Talal University, Ma’an, Jordan
\textsuperscript{3}Department of Chemistry, Al-Balqa Applied University, Al-Salt 19117, Jordan

\* Corresponding author: Mansour H. Almatarneh, m.almatarneh@ju.edu.jo, (+962) 65355000-Ext. 22177.
Abstract

The mechanism that accounts for the observed experimental activation energy for the decomposition of ethylamine (EA) is still unknown. This paper reports the first detailed study of possible mechanisms for the pyrolysis of second-stage cracking product of ethylamine: the decomposition reaction of methanimine, ethanimine, and aminoethylene. Investigated reactions characterise either H₂ elimination or 1,3-proton shift. These pathways result in the removal of H₂, CH₄, and NH₃; and the formation of hydrogen cyanide, acetylene, acetonitrile, ethynamine, and ketenimine. The IRC analysis was carried out for all transition state structures to obtain the complete reaction pathways. The stationary points were fully optimized at B3LYP and MP2 levels of theory using the 6-31G(d), 6-31G(2df,p), and 6-31++G(3df,3dp) basis sets. Based on comparing energetic requirements, we find 1,3-proton shift is the most probable pathway for the decomposition of ethanimine. The decomposition reaction of ethenamine was the most plausible reaction with an activation energy of 297 kJ mol⁻¹ calculated at the composite method of G4MP2.

Keywords: Decomposition reaction, Ethylamine, Methanimine, Ethenamine, Ethanimine, Transition state optimization, 1,3-Proton shift

Introduction

Ethylamine (EA), a primary aliphatic amine, is known to be a common starting material for many products including rubber latex, detergents, medicinal preparations, fibers, resins, and organic dyes. The decomposition reaction of EA has been extensively studied experimentally and theoretically [1-21]. This is due to its importance as a surrogate model compound for nitrogen amine contents in biomass [10] and for understanding of the constitution and the molecular evolution of interstellar matter, as being a component of interstellar gases [22]. The decomposition of EA was first investigated by Taylor [3]. It was found that decomposition of EA to be a homogeneous unimolecular reaction by finding no effects for adding the foreign gases hydrogen, nitrogen, and ammonia in temperature range 500-540 °C and at pressures of 50-
400 mmHg [3]. In a following work, Taylor and Ditman [4] reinvestigated the EA decomposition reaction at lighter conditions and concluded that the reaction to be heterogeneous and might go through a chain reaction mechanism at low pressure. In 1975, Lovas et al. [1] proposed a complex two stage cracking steps for EA pyrolysis. They stated that the decomposition reaction can produce nine polar species and three non-polar species, all of these species have been detected except for ethynylamine (CH≡CNH₂) and keteneimine (H₂C=C=NH) [1].

Methanimine Or methyleneimine (MI), ethenamine or vinylamine (VA), and its tautomer ethanimine or ethyleneimine (EI) are three of the polar products of the first crack routes that undergo further decomposition in the proposed second-crack route [1]. The aforementioned species were found to be major N-carriers during pyrolysis and decomposition of EA. Detailed kinetic models on decomposition of EA included these species [23,24]. (CH₂=NH) is the simplest imine compound, it has been observed in the pyrolysis of methylamine, ethylamine (amines in general), and azides as a reactive intermediate [25-33]. A great deal of research has been carried out to assign the microwave, infrared, and electronic spectrum of this moiety [25-43]. As a reactive species, MI can dissociate by 1,2-elimination of H₂ which has been studied both experimentally and theoretically [44-55]. Vinylamine and ethyleneimine are chemicals that widely used in industry; they were first detected as primary pyrolysis product of EA in the gas phase using microwave spectroscopic technique by Lovas et al. [1,2]. They characterized the microwave and infrared spectra of VA and EI two isomers, E- and Z- ethyleneimine in a temperature range from 150 to 900 °C and suggested a non-planar structure of vinylamine (CH₂=CHNH₂) [1,2]. Moreover, theoretical studies on VA structure produced the same result [16,18,20,56-60]. Traeger et. al. [12] reported using photoionization mass spectrometry and high-level Ab initio calculations to measure the heat of formation for ethyleneimmonium cation (CH₃CH=NH₂⁺) and derived an absolute proton affinity for cis (E) and trans (Z) ethyleneimine isomers (CH₃CH=NH). Stolkin et al. [7] obtained the first matrix spectra of EI produced by photolysis in low-temperature Argon matrix where EI molecule was produced by the pyrolysis of N-trimethylhexahydro-s-triazine (NTMT). They also reported a set of Ab initio SCF LCAO calculations for both the cis and trans isomer of EI [7]. On the other hand, the gas-phase infrared spectrum of EI produced by the pyrolysis of EA was first obtained by Hashiguchi et al. [11]. Ab initio MO method was used to calculate the force constants of both cis and trans isomers, and
from the microwave and infrared spectra combined with Ab initio MO calculations; they concluded that the \textit{cis} isomer to be the lower in energy than the \textit{trans} form by 2.5 kJ mol\(^{-1}\) [11].

Keteneimine is an unstable isomer of acetonitrile. It was firstly synthesized by Staudinger and Hauser in 1919 [61]; it has been assigned as one of the chemical components of the interstellar medium [62] and its spectrum has been obtained [63-70]. Moreover, theoretical studies to obtain the optimized geometries of ketenimines and the substituent effects on the stability of ketenimines have been reported [71-80]. Keteneimine is a transient tautomer of the stable acetonitrile and a reactive intermediate with sp-hybridized central carbon atom; it can undergo electrocyclic ring closure, nucleophilic addition, radical addition, and other reactions [81]. Ethynylamine is another unstable isomer of acetonitrile, its vibrational frequencies and rotational constants were firstly predicted by Saebø et al. [82] using Ab initio MO calculations in 1984. While the first experimental generation of ethynylamine was reported in 1986 by Baar et al. [83] and later in 1988 by Wentrup et al. [84]. Ab initio calculations predicted keteneimine to be more stable than ethynamine by by 25-67 kJ mol\(^{-1}\) [77,85].

Recently, Almatarneh et al. [21] reported a theoretical study for the mechanisms of the decomposition reaction of EA. They were interested in the first stage-cracking pattern postulated for the decomposition of EA. Four pathways were proposed for the decomposition of EA. The decomposition reaction involved the removal of H\(_2\), NH\(_3\), CH\(_4\), and the formation of methanimine (methyleneimine, MI), ethenamine (vinylamine, VA), and ethanimine (ethyleneimine, EI) by elimination and 1,3-proton shift. They found that the activation energy for the most favorable pathway is 281 KJ/mol which was higher than the expected experimental value. In this work, we focused on the second-stage cracking of the pyrolysis of EA that suggested by Lovas et al. [1]. Investigated pathways include either H\(_2\) elimination or 1,3-proton shift. These pathways lead to the formation of hydrogen cyanide, acetylene, acetonitrile, ethynamine, and ketenimine via the removal of H\(_2\), CH\(_4\), and NH\(_3\). Despite recent aforementioned progress, the underlying mechanism for the decomposition of ethylamine is still unknown. The most intriguing question is related to the extent in which the primary decomposition products of EA catalyse the degradation of the parent EA. In our previous work on the unimolecular decomposition of EA, we found that the initial decomposition channel corresponds to fission of the C-N bond. Out fitted pressure-dependent reaction rate constants
agrees well with analogous experimental measurements behind reflected shock tube [86]. To this end, we report in this study a detailed account of possible mechanisms for the parallel decomposition of MI, VA, and EI. Results obtained in this study will be instrumental to understand the overall decomposition of alkyl amines and the likelihood of the competitions between unimolecular- and bimolecular-derived routes.

2. Computational method
All calculations were performed using the program Gaussian09 [87] package. The geometries of all reactants, transition states, and products were fully optimized at B3LYP, M06-2X [88], and MP2 levels of theory using the 6-31G(d) basis set. Both extended 6-31G(2df,p) and 6-31++G(3df,3dp) basis sets at B3LYP level of theory have also been utilized to examine the effect of diffuse functions and to confirm the reliability of the 6-31G(d) basis set. Single point energies were determined using G4MP2 composite method. The principle reason for employing different levels of theory is to assure that the relative stabilities remain independent of the basis set. All reaction pathways have been verified using Intrinsic Reaction Coordinate (IRC) analysis of all proposed transition states. The last structures of the IRC in both directions were further optimized in order to positively identify their corresponding minima.

3. Results and Discussions
Scheme 1 depicts reactants, transition states, and products for second-stage decomposition reaction pathways of EA. The second-stage cracking of the pyrolysis of EA can follow seven possible pathways designated as denoted by pathways (A, B1→B3, C1→C3). Pathways B1 and C3 are initiated by 1,3-proton shifts while pathways A, B2, B3, C1, and C2 are initiated by 1,2 elimination were investigated. All pathways involved one-step mechanism. The activation energies, the enthalpies of activation and Gibbs free energies of activation for the proposed mechanisms at various levels of theory are listed in Tables 1, 3, and 5. The energies, the enthalpies, and Gibbs free energies for this reaction at various levels of theory are listed in Tables 2, 4, and 6. Optimized geometries for the reactants, transition states, and products involved in all investigated pathways (A, B1→B3, C1→C3) are shown in Fig. 1, and their relative energies are given in Figs. 2→4.
3.1. The Decomposition of Methanimine Intermediate

One possible pathway has been proposed for the decomposition of methanimine which is a one-step mechanism, see Scheme 1. The optimized geometries for the reactant, transition state, and product involved in pathway A along with their relative energies are given in Figs. 1 and 2. The reaction was initiated by 1,2-elimination to produce H₂ and a hydrogen cyanide. It is worth noting that there was a significant decrease in the ∠CNH angle from 125° in the reactant (Rₐ) to 55° in the transition state (Tₛₐ). The NH and CH bonds increased significantly in the transition state. The NH and CH bonds increased from 1.02Å and 1.09Å in the reactant to 1.41Å and 1.49Å in the transition state, respectively (with largest value of 1.55Å at MP2 level of theory).

As can be seen in Table 1, the activation energies for pathway A were 396 and 404 kJ mol⁻¹ at B3LYP/6-31++G(3df,3dp) and G4MP2 levels of theory, respectively. Table 2 shows the energies, enthalpies, and Gibbs free energies for the decomposition reaction of methanimine in kJ mol⁻¹ for pathway A. The values of enthalpies and Gibbs free energies indicate that the reaction is endothermic and endergonic (non-spontaneous) at all levels of theory, except at MP2 level of theory where the Gibbs free energies are slightly negative. From Table 1, the activation energies for the decomposition of methanimine at G4MP2 level differ by no more than 8 kJ mol⁻¹ from the B3LYP/6-31++G(3df,3dp) level of theory, and no more than 3 kJ mol⁻¹ from the less expensive method of B3LYP/6-31G(2df,p). The activation energies at the more modern functional, M06-2X [88], is 405 kJ mol⁻¹, and differ by no more than 2 and 4 kJ mol⁻¹ from G4MP2 and the B3LYP/6-31G(2df,p) levels of theory, respectively.

3.2. The Decomposition of Ethanimine Intermediate

Three decomposition pathways of ethanimine were investigated as shown in Scheme 1 and Fig. 1. In pathway B₁ (Fig. 3), the transfer occurred from the imino group to the methyl group to produce CH₄ and HCN (hydrogen cyanide) through 1,3-proton shift. The structure of ethanimine obtained from IRC calculations on the transition state was found to be Z-ethanimine conformer for pathway B₁ and E conformer for pathways B₂ and B₃. Comparing energies of the two conformers indicate that the E conformer is marginally more stable in the range of (1.2–4.8 kJ mol⁻¹). It is worth mentioning that there was a significant decrease in the ∠CNH angle from 111° in the reactant to 56.6° in the transition state (TSₐB₁) and for ∠CCN decreased from 128° to 118° in TSₐB₁. The CC single bond and NH bond increased significantly from 1.50Å to 1.96Å and
1.02Å to 1.39Å, respectively. Decreasing the $\angle CCN$ and $\angle CNH$ angles result in a significant angle strain of the transition state, and thus accounts for the high energy barrier. The activation energies for pathway $B_1$ were 392 and 402 kJ mol$^{-1}$ at B3LYP/6-31++G(3df,3dp) and G4MP2 levels of theory, respectively, see Table 3.

Meanwhile, pathways $B_2$ and $B_3$ involved a 1,2-elimination of hydrogen. In pathway $B_2$, the elimination step occurred at CN bond to afford CH$_3$CN (acetonitrile) and H$_2$. Transition state (TSB2) geometry showed significant decrease in the $\angle CNH$ angle from 111° in reactant to 58° in TSB2. The $\angle NCH$ angle is also decreased from 122° in the reactant ($R_{B_2}$) to 114° in the TSB2; in which it accounts in angle strain in the four-membered ring transition state. For pathway $B_3$, the 1,2-elimination of hydrogen occurred at the CC bond to form H$_2$C=C=NH (ketenimine) and H$_2$. The major changes in the geometry of the transition state (TSB3) were in $\angle CCN$, $\angle C_{(2)}C_{(1)}H$ and $\angle C_{(1)}C_{(2)}H$ angles (where C$_{(2)}$:Sp$^2$ carbon and C$_{(1)}$: Sp$^3$ carbon). The $\angle CCN$, $\angle C_{(2)}C_{(1)}H$ and $\angle C_{(1)}C_{(2)}H$ angles were changed from 122°, 116°, and 110° in the reactant to 139°, 100°, and 58° in the TSB3. The activation energies for pathway $B_2$ were 379 and 387 kJ mol$^{-1}$ at B3LYP/6-31++G(3df,3dp) and G4MP2 levels of theory, respectively. While for pathway $B_3$, the barrier was 381 kJ mol$^{-1}$ and 396 kJ mol$^{-1}$ at B3LYP/6-31++G(3df,3dp) and G4MP2 levels of theory, respectively, see Table 3.

Pathways $B_2$ and $B_3$ signify 1,2 hydrogen elimination. The energy barrier for pathway $B_2$ has a lower activation energy than Pathway $B_3$. Pathway $B_2$ is the most favorable among the other postulated pathways for the decomposition of ethanimine since it has the lowest activation energy at all calculated levels of theory. The activation energies for pathways $B_1$ and $B_2$ obtained at all level of theory were lower than theoretical values computed by Arenas et al. [89] (444 kJ mol$^{-1}$ for pathway $B_1$ and 431 kJ mol$^{-1}$ for pathway $B_2$). The relative energies for the decomposition pathways for ethanimine (B1→B3) at all studied levels of theory are shown in Fig.3. For pathways $B_2$ and $B_3$, it may be assumed that hydrogen abstraction from nitrogen and carbon sites should occur equally as CH and NH bond strengths are almost equal. The barriers for these proposed mechanisms were different depending on the site where the abstraction occurs.

Table 4 shows the enthalpies and Gibbs free energies for the decomposition reaction of ethanimine in kJ mol$^{-1}$ for pathways $B_1$, $B_2$ and $B_3$. It can be seen from Table 4 that the decomposition reaction of ethanimine is endothermic and endergonic (i.e. non-spontaneous
reaction) at all levels of theory for pathways B2 and B3, while endothermic (except for MP2/6-31G(d) and MP2/6-31+G(d) levels of theory) and exergonic (i.e. spontaneous) for pathway B1. Hydrogen elimination from CN bond is the most probable pathway in the proposed mechanism. It has a lower activation energy over the 1,3-proton shift step (pathway B1) and hydrogen elimination from CC bond. As we can see, hydrogen abstraction from C and N atoms (pathway B2) is the most probable primary step in the proposed mechanism for the decomposition reaction. The comparison of the relative energies for the three pathways at G4MP2 level of theory is given in Fig. 3. It is worth mentioning that the activation energies at G4MP2 level of theory differ by no more than 15 kJ mol\(^{-1}\) from the ones calculated at DFT functionals. While at M06-2X/6-31G(2df,P) level of theory is no more than 7 kJ mol\(^{-1}\) for the decomposition of ethanimine.

3.3. The Decomposition of Ethenamine Intermediate
The decomposition of ethenamine (aminoethylene) can follow several possible pathways designated as pathways C1→C3. The geometries for the reactants, intermediates, transition states, and products involved in pathways C1→C3 are shown in Fig. 1 and scheme 1, and their relative energies are given in Fig. 4. The structure of ethenamine obtained from IRC calculations on the transition state was found to involve two conformers; planer and pyramidal ethenamine. Planer ethenamine was the reactant for both pathways C1 and C3. However, pathway C2 was initiated by pyramidal ethenamine conformer. The value of energy of the two conformers obtained at B3LYP/6-31++G(3df,3dp) level of theory implied that the planer conformer is more stable by 27.4 kJ mol\(^{-1}\) in agreement with a previous study by Miranda et.al [60]. For pathways C1 and C2, 1,2-elimination of hydrogen was the initiating step. In pathway C1, the hydrogen elimination occurred at CN bond to produce H\(_2\)C=C=NH (ketenimine) and H\(_2\). Transition state (TS\(_{C1}\)) geometry showed significant difference at different levels of theory. NH bond increased from 1.01 Å in the reactant to 1.18 Å at B3LYP/6-31++G(3df,3dp), 1.36Å at G4MP2, and 1.53Å at MP2/6-31+G(d) in the transition state. Meanwhile, CH bond showed an increase from 1.08Å to 1.82Å at B3LYP/6-31++G(3df,3dp), 1.50Å at G4MP2, 1.33Å at MP2/6-31+G(d), and 1.94 Å at B3LYP/6-31+G(d) level of theory for the transition state. A similar variation was noticed for the bond angles. The \(\angle\)CNH and \(\angle\)NCH angles were decreased from 116° and 113° in the reactant to 92° and 81° at B3LYP/6-31++G(3df,3dp), 74° and 94° at MP2/6-31+G(d), and
97° and 79° at B3LYP/6-31+G(d) level of theory. The significant decrease in these angles account in the angle strain in the four membered ring transition state and high energy barrier for pathway C1 of 418 kJ mol⁻¹ at B3LYP/6-31++G(3df,3dp) level of theory (433 kJ mol⁻¹ at G4MP2 level of theory), see Table 5.

For pathway C2, the 1,2-elimination of hydrogen occurred at the CC bond to form HC≡C-NH₂ (ethynamine) and H₂. The major changes in the geometry of the transition state (TSₖ2) were in CCN, C(2)C(1)H and C(1)C(2)H angles. The ∠CCN, ∠C(2)C(1)H, and ∠C(1)C(2)H angles was changed from 122°, 120°, and 121° in reactant to 151°, 104°, and 61.4° in TSₖ2. Also, a significant increase in the bond length occurred for C(2)H and C(1)H. An increase from 1.08Å and 1.09Å in reactant to 1.50Å and 1.52Å for C(2)H and C(1)H, respectively, at B3LYP/6-31++G(3df,3dp) level of theory. The geometry of the transition state at MP2/6-31+G(d) level of theory has a noticeable difference in the bond angle and length values from other levels of theory. The values of ∠CCN, and ∠C(1)C(2)H angles were 145° and 38.4°; meanwhile the bond length values for C(2)H and C(1)H were 2.14Å and 1.37Å for the transition state at MP2/6-31+G(d) level of theory. As shown in Table 5, the activation energies for pathway C2 were 458 and 481 kJ mol⁻¹ at B3LYP/6-31++G(3df,3dp) and G4MP2 levels of theory, respectively, indicated an angle strain in the four membered ring transition state. Both pathways C1 and C2 initiated by 1,2 hydrogen elimination, and as CH and NH bond strengths are almost the same, it may be assumed that hydrogen abstraction from nitrogen and carbon sites should occur equally. Similar to what we mentioned earlier for the decomposition of ethanimine, the abstraction from NH bond (C1) has the lower activation energy compared to CH bond (C2).

For pathway C3, the ethenamine reactant was planar as revealed from IRC calculations. The reaction initiated by hydrogen transfer, via a 1,3-proton shift, from the methylene group to the amine group to produce acetylene and ammonia. A significant decrease occurred in the ∠C(1)C(2)H angle from 122° in the reactant to 71.8° in the transition state (TSₖ3). The ∠CCN angle decreased from 127° to 105° in the TSₖ3. The C(2)H and NH bonds increased significantly from 1.08Å and 1.39Å to 1.61Å and 1.51Å at B3LYP/6-31++G(3df,3dp) level, respectively. It is worth mentioning that the conformation of the reactant for pathway C3 differs at all the levels of theory used in this study. Planar ethenamine conformer was the optimized reactant at B3LYP/6-31G(d), B3LYP/6-31G(2df,p), and B3LYP/6-31++G(3df,3dp) levels of theory. Meanwhile, the pyramidal conformer was the optimized one at MP2/6-31G(d), MP2/6-31+G(d), and B3LYP/6-
10+G(d). This can be explained by the effect of the employed level of theory on the stability of the conformer, noting that the geometry of amnio group in the transition state is pyramidal at all levels of theory. The activation energies for pathway C3 were 301 and 297 kJ mol\(^{-1}\) at B3LYP/6-31++G(3df,3dp) and G4MP2 levels of theory, respectively. A comparison of the activation energies for the three pathways at G4MP2 level of theory can be seen in Fig. 4. As can be seen in Table 5 and Fig. 4, pathway C3 has the lowest energy barrier at all levels of theory and is the most favorable decomposition route for ethenamine over C1 and C2. The relative energies, enthalpies, and Gibbs free energies for the decomposition reaction of ethenamine in kJ mol\(^{-1}\) for pathways C1→C3 are given in Table 6. It can be seen that the decomposition of ethenamine is endothermic and endergonic (non-spontaneous reaction) at all levels of theory for the three proposed pathways.

As we can see, hydrogen elimination from C and N atoms is the most probable primary step in the proposed mechanism for the decomposition reaction. However, the barriers for these mechanisms were different depending on the site where the abstraction occurs. Our study found that the keteneimine to be more stable than ethynamine by 40 kJ mol\(^{-1}\) at B3LYP/6-31++G(3df,3dp) level of theory which is in an agreement to previous findings [77,85].

For the decomposition of ethenamine, the activation energies at G4MP2 level of theory differ by no more than 2-23 kJ mol\(^{-1}\) from the ones calculated at DFT functionals. While the difference in activation energy at M06-2X/6-31G(2df,p) from G4MP2 and B3LYP/6-31G(2df,p) levels of theory is no more than 13 and 16 kJ mol\(^{-1}\). It is worth noting that the activation energies at B3LYP/6-31G(2df,p) differ by no more than 1-8 kJ mol\(^{-1}\) from the values of B3LYP/6-31++G(3df,3dp) level of theory for the decomposition of methanimine, ethanimine, and ethenamine. Therefore, it is more convenient to use B3LYP/6-31G(2df,p) level of theory which is the least computationally expensive method for providing reliable energetics for such system.

**Conclusion**

The second-stage cracking mechanisms of ethylamine, decomposition of mathanimine, ethanimine, and ethenimine, were investigated using DFT calculations. Seven pathways for the decomposition reaction were investigated. The IRC analysis was carried out for all transition state structures to obtain the complete reaction pathways. We found that the hydrogen elimination from CN bond is the most probable pathway compared to the elimination from CC
bond. Pathway B2, where it involved a 1,3-proton shift, is the most favorable among the other postulated pathways for the decomposition of ethanimine since it has the lowest activation energy at all calculated levels of theory. For the decomposition reaction of ethanimine, C3 is the most plausible reaction with an activation energy of 303, 301, and 297 kJ mol\(^{-1}\) at B3LYP/6-31G(2df,p), B3LYP/6-31++G(3df,3dp), and G4MP2 levels of theory, respectively. A complete characterization of the overall decomposition mechanisms calls for a consideration of unimolecular fission of N-H fissions and bimolecular reactions with the title species with the O/H radical pool.

Acknowledgment
M. H. Almatarneh is grateful to the Atlantic Computational Excellence Network (ACENET) for computer time.

References:


54. Y. Tang, C.J. Nielsen, A Systematic Theoretical Study of Imines Formation From the Atmospheric Reactions of RₙNH₂ₙ with O₂ and NO₂ (R=CH₃ and CH₃CH₂, n=1 and 2), Atmos. Environ. 55 (2012) 185–189.
Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Inc., Wallingford CT, Gaussian 09, Revision D.01, 2013.  


Figures Captions:  

**Fig.1:** Optimized Geometries for the Reactants, Transition States, and Products Involved in all Investigated Pathways (A, B1→B3, C1→ C3).  

**Fig.2:** Optimized Structures for the Decomposition of Methanimine at B3LYP/6-31++G(3df,3dp) level of Theory and their Relative Energies at Different Levels of Theory for Pathway A.  

**Fig.3:** A Comparison of the Activation Energies for the Decomposition of Ethanimine (kJ mol⁻¹) at G4MP2 Level of Theory for Pathways B1→B3.  

**Fig.4:** A Comparison of the Activation Energies for the Decomposition of Ethenamine (in kJ mol⁻¹) at G4MP2 Level of Theory for Pathways C1→ C3.
Scheme 1: Possible mechanisms for the pyrolysis of second-stage cracking products of ethylamine: the decomposition reaction of methanimine, ethanimine and aminoethylene.
Fig. 1: Optimized Geometries for the Reactants, Transition States, and Products Involved in all Investigated Pathways (A, B1→B3, C1→C3).
Fig. 2: Optimized Structures for the Decomposition of Methanimine at B3LYP/6-31++G(3df,3dp) level of Theory and their Relative Energies at Different Levels of Theory for Pathway A.
Fig. 3: A Comparison of the Activation Energies for the Decomposition of Ethanimine (kJ mol$^{-1}$) at G4MP2 Level of Theory for Pathways B1→B3.
Fig. 4: A Comparison of the Activation Energies for the Decomposition of Ethenamine (in kJ mol\(^{-1}\)) at G4MP2 Level of Theory for Pathways C1→C3.
Table 1: Activation Energies, Enthalpies of Activation, and Gibbs Free Energies of Activation for the Decomposition of Methanimine (in kJ mol$^{-1}$) at 298.15 K (Pathway A)

<table>
<thead>
<tr>
<th></th>
<th>B3LYP/6-31G (d)</th>
<th>B3LYP/6-31+G (d)</th>
<th>B3LYP/6-31G (2df,p)</th>
<th>B3LYP/6-311++G (3df,3pd)</th>
<th>M06-2X/6-31G (d)</th>
<th>M06-2X/6-311++G (3df,3pd)</th>
<th>G4MP2</th>
<th>MP2/6-31G (d)</th>
<th>MP2/6-31+G (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E^h$, TSA</td>
<td>418</td>
<td>417</td>
<td>399</td>
<td>396</td>
<td>428</td>
<td>405</td>
<td>404</td>
<td>437</td>
<td>434</td>
</tr>
<tr>
<td>$\Delta H^h$, TSA</td>
<td>418</td>
<td>418</td>
<td>400</td>
<td>397</td>
<td>428</td>
<td>406</td>
<td>405</td>
<td>437</td>
<td>435</td>
</tr>
<tr>
<td>$\Delta G^h$, TSA</td>
<td>417</td>
<td>416</td>
<td>399</td>
<td>395</td>
<td>427</td>
<td>405</td>
<td>403</td>
<td>437</td>
<td>434</td>
</tr>
<tr>
<td>$\Delta S^h$, TSA</td>
<td>0.005</td>
<td>0.007</td>
<td>0.004</td>
<td>0.004</td>
<td>0.005</td>
<td>0.004</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Table 2: Relative Energies, Enthalpies, and Gibbs Free Energies for the Decomposition of Methanimine (in kJ mol$^{-1}$) at 298.15 K (Pathway A).

<table>
<thead>
<tr>
<th></th>
<th>B3LYP/6-31G (d)</th>
<th>B3LYP/6-31+G (d)</th>
<th>B3LYP/6-31G (2df,p)</th>
<th>B3LYP/6-311++G (3df,3pd)</th>
<th>M06-2X/6-31G (d)</th>
<th>M06-2X/6-311++G (3df,3pd)</th>
<th>G4MP2</th>
<th>MP2/6-31G (d)</th>
<th>MP2/6-31+G (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$, TSA</td>
<td>43</td>
<td>45</td>
<td>44</td>
<td>44</td>
<td>44</td>
<td>43</td>
<td>31</td>
<td>-4</td>
<td>16</td>
</tr>
<tr>
<td>$\Delta H$, TSA</td>
<td>51</td>
<td>53</td>
<td>52</td>
<td>51</td>
<td>49</td>
<td>47</td>
<td>39</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>$\Delta G$, TSA</td>
<td>32</td>
<td>33.1</td>
<td>33</td>
<td>32</td>
<td>37</td>
<td>36</td>
<td>20</td>
<td>-16</td>
<td>-5</td>
</tr>
<tr>
<td>$\Delta S$, TSA</td>
<td>0.064</td>
<td>0.065</td>
<td>0.062</td>
<td>0.064</td>
<td>0.038</td>
<td>0.037</td>
<td>0.063</td>
<td>0.062</td>
<td>0.046</td>
</tr>
</tbody>
</table>
Table 3: Activation Energies, Enthalpies of Activation, and Gibbs Free Energies of Activation for the Decomposition of Ethanimine (in kJ mol\(^{-1}\)) at 298.15 K (Pathways B1→B3).

<table>
<thead>
<tr>
<th></th>
<th>B3LYP/6-31G (d)</th>
<th>B3LYP/6-31+G (d)</th>
<th>B3LYP/6-31G (2df,p)</th>
<th>B3LYP/6-31+G (3df,3pd)</th>
<th>M06-2X/6-31G (d)</th>
<th>M06-2X/6-31G (2df,p)</th>
<th>G4MP2</th>
<th>MP2/6-31G (d)</th>
<th>MP2/6-31+G (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta E^\ddagger), TSB1</td>
<td>409</td>
<td>407</td>
<td>395</td>
<td>392</td>
<td>414</td>
<td>398</td>
<td>402</td>
<td>424</td>
<td>420</td>
</tr>
<tr>
<td>(\Delta H^\ddagger), TSB1</td>
<td>410</td>
<td>408</td>
<td>396</td>
<td>394</td>
<td>416</td>
<td>399</td>
<td>403</td>
<td>426</td>
<td>421</td>
</tr>
<tr>
<td>(\Delta G^\ddagger), TSB1</td>
<td>407</td>
<td>405</td>
<td>394</td>
<td>391</td>
<td>414</td>
<td>397</td>
<td>401</td>
<td>423</td>
<td>419</td>
</tr>
<tr>
<td>(\Delta S^\ddagger), TSB1</td>
<td>0.009</td>
<td>0.009</td>
<td>0.009</td>
<td>0.009</td>
<td>0.007</td>
<td>0.007</td>
<td>0.009</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>(\Delta E^\ddagger), TSB2</td>
<td>398</td>
<td>398</td>
<td>381</td>
<td>379</td>
<td>408</td>
<td>387</td>
<td>387</td>
<td>415</td>
<td>412</td>
</tr>
<tr>
<td>(\Delta H^\ddagger), TSB2</td>
<td>399</td>
<td>399</td>
<td>382</td>
<td>380</td>
<td>409</td>
<td>388</td>
<td>387</td>
<td>416</td>
<td>413</td>
</tr>
<tr>
<td>(\Delta G^\ddagger), TSB2</td>
<td>398</td>
<td>398</td>
<td>381</td>
<td>379</td>
<td>407</td>
<td>387</td>
<td>386</td>
<td>415</td>
<td>412</td>
</tr>
<tr>
<td>(\Delta S^\ddagger), TSB2</td>
<td>0.004</td>
<td>0.005</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
<td>0.003</td>
<td>0.004</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>(\Delta E^\ddagger), TSB3</td>
<td>409</td>
<td>405</td>
<td>389</td>
<td>381</td>
<td>425</td>
<td>403</td>
<td>396</td>
<td>442</td>
<td>433</td>
</tr>
<tr>
<td>(\Delta H^\ddagger), TSB3</td>
<td>408</td>
<td>404</td>
<td>389</td>
<td>381</td>
<td>425</td>
<td>402</td>
<td>396</td>
<td>441</td>
<td>432</td>
</tr>
<tr>
<td>(\Delta G^\ddagger), TSB3</td>
<td>410</td>
<td>406</td>
<td>390</td>
<td>382</td>
<td>426</td>
<td>404</td>
<td>397</td>
<td>443</td>
<td>434</td>
</tr>
<tr>
<td>(\Delta S^\ddagger), TSB3</td>
<td>-0.004</td>
<td>-0.004</td>
<td>-0.004</td>
<td>-0.003</td>
<td>-0.005</td>
<td>-0.005</td>
<td>-0.005</td>
<td>-0.005</td>
<td>-0.005</td>
</tr>
</tbody>
</table>
Table 4: Relative Energies, Enthalpies, and Gibbs Free Energies for the Decomposition of Ethanimine (in kJ mol$^{-1}$) at 298.15 K (Pathways B1→B3).

<table>
<thead>
<tr>
<th></th>
<th>B3LYP/6-31G (d)</th>
<th>B3LYP/6-31+G (d)</th>
<th>B3LYP/6-31G (2df,p)</th>
<th>B3LYP/6-311++G (3df,3pd)</th>
<th>M06-2X/6-31G (d)</th>
<th>M06-2X/6-31G (2df,p)</th>
<th>G4MP2</th>
<th>MP2/6-31G (d)</th>
<th>MP2/6-31+G (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$, TSB1</td>
<td>9</td>
<td>9</td>
<td>13</td>
<td>7</td>
<td>13</td>
<td>16</td>
<td>4</td>
<td>-26</td>
<td>-22</td>
</tr>
<tr>
<td>$\Delta H$, TSB1</td>
<td>18</td>
<td>18</td>
<td>20.8</td>
<td>16</td>
<td>21</td>
<td>24</td>
<td>12</td>
<td>-18</td>
<td>-13</td>
</tr>
<tr>
<td>$\Delta G$, TSB1</td>
<td>-15</td>
<td>-16</td>
<td>-8</td>
<td>-17</td>
<td>-2</td>
<td>-1</td>
<td>-17</td>
<td>-55</td>
<td>-54</td>
</tr>
<tr>
<td>$\Delta S$, TSB1</td>
<td>0.111</td>
<td>0.112</td>
<td>0.095</td>
<td>0.111</td>
<td>0.079</td>
<td>0.083</td>
<td>0.096</td>
<td>0.124</td>
<td>0.140</td>
</tr>
<tr>
<td>$\Delta E$, TSB2</td>
<td>25</td>
<td>30</td>
<td>27</td>
<td>122</td>
<td>35</td>
<td>33</td>
<td>23</td>
<td>-12</td>
<td>-4</td>
</tr>
<tr>
<td>$\Delta H$, TSB2</td>
<td>31</td>
<td>39</td>
<td>33</td>
<td>130</td>
<td>40</td>
<td>39</td>
<td>29</td>
<td>-4</td>
<td>4</td>
</tr>
<tr>
<td>$\Delta G$, TSB2</td>
<td>16</td>
<td>14</td>
<td>17.0</td>
<td>101</td>
<td>25</td>
<td>24</td>
<td>13</td>
<td>-33</td>
<td>-19</td>
</tr>
<tr>
<td>$\Delta S$, TSB2</td>
<td>0.051</td>
<td>0.084</td>
<td>0.052</td>
<td>0.098</td>
<td>0.052</td>
<td>0.050</td>
<td>0.053</td>
<td>0.096</td>
<td>0.078</td>
</tr>
<tr>
<td>$\Delta E$, TSB3</td>
<td>136</td>
<td>137</td>
<td>124</td>
<td>122</td>
<td>153</td>
<td>138</td>
<td>136.4</td>
<td>141</td>
<td>141</td>
</tr>
<tr>
<td>$\Delta H$, TSB3</td>
<td>144</td>
<td>145</td>
<td>131</td>
<td>130</td>
<td>159</td>
<td>143</td>
<td>143.8</td>
<td>148</td>
<td>147</td>
</tr>
<tr>
<td>$\Delta G$, TSB3</td>
<td>123</td>
<td>121</td>
<td>112</td>
<td>101</td>
<td>146</td>
<td>131</td>
<td>124.1</td>
<td>128</td>
<td>131</td>
</tr>
<tr>
<td>$\Delta S$, TSB3</td>
<td>0.070</td>
<td>0.081</td>
<td>0.066</td>
<td>0.098</td>
<td>0.044</td>
<td>0.043</td>
<td>0.066</td>
<td>0.069</td>
<td>0.054</td>
</tr>
</tbody>
</table>
Table 5: Activation Energies, Enthalpies of Activation, and Gibbs Free Energies of Activation for the Decomposition of Ethenamine (in kJ mol\(^{-1}\)) at 298.15 K (Pathways C1 → C3).

<table>
<thead>
<tr>
<th></th>
<th>B3LYP/6-31G (d)</th>
<th>B3LYP/6-31+G (d)</th>
<th>B3LYP/6-31+G (2df,p)</th>
<th>B3LYP/6-311++G (3df,3pd)</th>
<th>M06-2X/6-31G (d)</th>
<th>M06-2X/6-31G (2df,p)</th>
<th>G4MP2</th>
<th>MP2/6-31G (d)</th>
<th>MP2/6-31+G (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta E^\ddagger), TSC1</td>
<td>425</td>
<td>423</td>
<td>417</td>
<td>418</td>
<td>447</td>
<td>433</td>
<td>433</td>
<td>456</td>
<td>454</td>
</tr>
<tr>
<td>(\Delta H^\ddagger), TSC1</td>
<td>426</td>
<td>425</td>
<td>418</td>
<td>420</td>
<td>447</td>
<td>434</td>
<td>434</td>
<td>457</td>
<td>454</td>
</tr>
<tr>
<td>(\Delta G^\ddagger), TSC1</td>
<td>424</td>
<td>420</td>
<td>416</td>
<td>417</td>
<td>446</td>
<td>432</td>
<td>432</td>
<td>456</td>
<td>453</td>
</tr>
<tr>
<td>(\Delta S^\ddagger), TSC1</td>
<td>0.008</td>
<td>0.016</td>
<td>0.006</td>
<td>0.013</td>
<td>0.003</td>
<td>0.006</td>
<td>0.006</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>(\Delta E^\ddagger), TSC2</td>
<td>478</td>
<td>479</td>
<td>459</td>
<td>458</td>
<td>492</td>
<td>469</td>
<td>481</td>
<td>528</td>
<td>491</td>
</tr>
<tr>
<td>(\Delta H^\ddagger), TSC2</td>
<td>480</td>
<td>481</td>
<td>461</td>
<td>461</td>
<td>495</td>
<td>471</td>
<td>484</td>
<td>530</td>
<td>493</td>
</tr>
<tr>
<td>(\Delta G^\ddagger), TSC2</td>
<td>476</td>
<td>477</td>
<td>457</td>
<td>455</td>
<td>491</td>
<td>467</td>
<td>480</td>
<td>526</td>
<td>490</td>
</tr>
<tr>
<td>(\Delta S^\ddagger), TSC2</td>
<td>0.013</td>
<td>0.014</td>
<td>0.013</td>
<td>0.021</td>
<td>0.012</td>
<td>0.014</td>
<td>0.013</td>
<td>0.014</td>
<td>0.009</td>
</tr>
<tr>
<td>(\Delta E^\ddagger), TSC3</td>
<td>309</td>
<td>277</td>
<td>303</td>
<td>301</td>
<td>309</td>
<td>303</td>
<td>297</td>
<td>294</td>
<td>285</td>
</tr>
<tr>
<td>(\Delta H^\ddagger), TSC3</td>
<td>308</td>
<td>277</td>
<td>302</td>
<td>300</td>
<td>308</td>
<td>302</td>
<td>296</td>
<td>294</td>
<td>285</td>
</tr>
<tr>
<td>(\Delta G^\ddagger), TSC3</td>
<td>309</td>
<td>277</td>
<td>303</td>
<td>302</td>
<td>310</td>
<td>303</td>
<td>298</td>
<td>294</td>
<td>285</td>
</tr>
<tr>
<td>(\Delta S^\ddagger), TSC3</td>
<td>-0.005</td>
<td>0.001</td>
<td>-0.005</td>
<td>-0.005</td>
<td>-0.005</td>
<td>-0.005</td>
<td>-0.005</td>
<td>0.001</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Table 6: Relative Energies, Enthalpies, and Gibbs Free Energies for the Decomposition of Ethenamine (in kJ mol\(^{-1}\)) at 298.15 K (Pathways C1→C3).

<table>
<thead>
<tr>
<th></th>
<th>B3LYP/6-31G (d)</th>
<th>B3LYP/6-31+G (d)</th>
<th>B3LYP/6-31G (2df,p)</th>
<th>B3LYP/6-311++G (3df,3pd)</th>
<th>M06-2X/6-31G (d)</th>
<th>M06-2X/6-31G (2df,p)</th>
<th>G4MP2</th>
<th>MP2/6-31G (d)</th>
<th>MP2/6-31+G (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta E, \text{TSC1})</td>
<td>110</td>
<td>116</td>
<td>108</td>
<td>112</td>
<td>129</td>
<td>124</td>
<td>121</td>
<td>108</td>
<td>115</td>
</tr>
<tr>
<td>(\Delta H, \text{TSC1})</td>
<td>117</td>
<td>124</td>
<td>115</td>
<td>121</td>
<td>135</td>
<td>129</td>
<td>129</td>
<td>115</td>
<td>123</td>
</tr>
<tr>
<td>(\Delta G, \text{TSC1})</td>
<td>96</td>
<td>99</td>
<td>95</td>
<td>92.4</td>
<td>121</td>
<td>116</td>
<td>108</td>
<td>93</td>
<td>97</td>
</tr>
<tr>
<td>(\Delta S, \text{TSC1})</td>
<td>0.072</td>
<td>0.084</td>
<td>0.068</td>
<td>0.096</td>
<td>0.047</td>
<td>0.046</td>
<td>0.068</td>
<td>0.072</td>
<td>0.089</td>
</tr>
<tr>
<td>(\Delta E, \text{TSC2})</td>
<td>171</td>
<td>170</td>
<td>160</td>
<td>158</td>
<td>179</td>
<td>164</td>
<td>163</td>
<td>150</td>
<td>153</td>
</tr>
<tr>
<td>(\Delta H, \text{TSC2})</td>
<td>181</td>
<td>179</td>
<td>169</td>
<td>169</td>
<td>186</td>
<td>171</td>
<td>173</td>
<td>161</td>
<td>165</td>
</tr>
<tr>
<td>(\Delta G, \text{TSC2})</td>
<td>156</td>
<td>158</td>
<td>146</td>
<td>141</td>
<td>168</td>
<td>154</td>
<td>149</td>
<td>133</td>
<td>137</td>
</tr>
<tr>
<td>(\Delta S, \text{TSC2})</td>
<td>0.083</td>
<td>0.070</td>
<td>0.080</td>
<td>0.092</td>
<td>0.060</td>
<td>0.056</td>
<td>0.080</td>
<td>0.091</td>
<td>0.094</td>
</tr>
<tr>
<td>(\Delta E, \text{TSC3})</td>
<td>144</td>
<td>108</td>
<td>131</td>
<td>119</td>
<td>145</td>
<td>133</td>
<td>110</td>
<td>88</td>
<td>84</td>
</tr>
<tr>
<td>(\Delta H, \text{TSC3})</td>
<td>151</td>
<td>115</td>
<td>138</td>
<td>126</td>
<td>151.1</td>
<td>140</td>
<td>118</td>
<td>97</td>
<td>92</td>
</tr>
<tr>
<td>(\Delta G, \text{TSC3})</td>
<td>136</td>
<td>99.1</td>
<td>121</td>
<td>109</td>
<td>137.1</td>
<td>124</td>
<td>100</td>
<td>78</td>
<td>75</td>
</tr>
<tr>
<td>(\Delta S, \text{TSC3})</td>
<td>0.052</td>
<td>0.054</td>
<td>0.057</td>
<td>0.059</td>
<td>0.047</td>
<td>0.051</td>
<td>0.058</td>
<td>0.062</td>
<td>0.060</td>
</tr>
</tbody>
</table>
Graphical Abstract
Highlights

• The decomposition of methanimine, ethanimine, and ethenimine were investigated using several levels of theory.
• Investigated reactions characterise either H₂ elimination or 1,3-proton shift.
• The decomposition of ethanimine was the most plausible reaction with an activation energy of 302 kJ mol⁻¹ at G4MP2.