



Theoretical study on the unimolecular decomposition of proline



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ABSTRACT

As a representative model compound for cyclic amino acids in biomass, initial reactions in the decomposition of proline are thoroughly investigated herein. The weakest bond in the proline molecule is found to be the H atom gem to the carboxylic group with a bond dissociation enthalpy of 75.0 kcal/mol. Carboxylation and dehydration channels are found to incur enthalpies of activations at 71.0 kcal/mol and 72.8 kcal/mol; respectively. Calculated pressure-dependent reaction rate constants, i.e.; $k(P,T)$ values, indicates that water elimination and H elimination from the carbon bearing the carboxylic group dominates the unimolecular decomposition of proline at all temperatures and pressures.

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1. Introduction

As combustion of biomass is associated with a CO₂-emission neutrality, it has attracted a mounted interest during the last few years. However, thermal treatment of biomass results in the emission of a wide spectra of trace pollutants. In particular, emission of nitrogen-containing species pose serious environmental and health problems. It is believed that these compounds are released during the course of devolatilisation and char burning [1]. In addition to inorganic nitrates and ammonium ions, heterocyclic nitrogenated compounds represents a significant fraction of the total N-content in biomass [2]. These compounds include purines, pyrimidines and pyrroles. Pyrolysis of N-cyclic compounds emits NH₃, HCN and HCNO and NO_x [3]. Chemistry of nitrogen conversion during combustion of biomass has been investigated by utilising simplified models of surrogate compounds; including pyrrole, pyridine and nitromethane [4]. As demonstrated by Lucassen et al. [5] an accurate description of nitrogen transformation and fate requires considering a nitrogen–oxygen cyclic compound such as morpholine. Our recent theoretical analysis supports experimental findings with regard to the dominance of unimolecular-decomposition pathways even under pure oxidative conditions [6].

While morpholine serves as a good representative model for cyclic oxygen–nitrogen containing, proline in particular accounts for the presence of a carboxylic group as in amino acids. Carbocyclic

groups often result from the rupture of ether linkages in cellulose and lignin; common structural entities in biomass. Proline is a major amino acids in various types of biomass such as tobacco [7]. Accordingly, pyrolysis of proline has been extensively studied [8]. Degradation of proline was postulated to follow general mechanisms encountered in self-decomposition of amino acids; namely, decarboxylation, dehydration and homolysis of the aliphatic side [9]. Pyrolysis of proline was found to produce numerous poly aromatic hydrocarbons (PAHs) and nitrogenated-PAHs such as 2,5-diketopiperazine, benzonitrile and pyrrole [8]. Thermal behaviour of the decomposition of proline was investigated with the aid of a thermogravimetry [10]. An overall rate of unimolecular decomposition was determined to be $1.54 \times 10^{14} T^{1.1} \exp(-20200/T) \text{ s}^{-1}$. A robust kinetic model for the pyrolysis of proline, as a model representative of cyclic α -amino acids in biomass, necessitates detailed mechanistic pathways that govern its initial decomposition. To this end, we report in this study a theoretical investigation into primary exit channels involved in the pyrolysis of proline. It is hoped that this study will provide useful information in the pursuit of better understanding of nitrogen behaviour upon thermal utilisation of biomass.

2. Computational details

Gaussian03 suite of programs [11] was used to perform all structural and energy calculations were carried out at the composite chemistry model of CBS-QB3 [12] as implemented in the Gaussian03 suite of programmes. The CBS-QB3 performs initial optimisation and frequency estimations at the B3LYP/6-311G(2d,p) level of theory. This is followed by successive single point energy calculations at very accurate theoretical levels. Thermochemical

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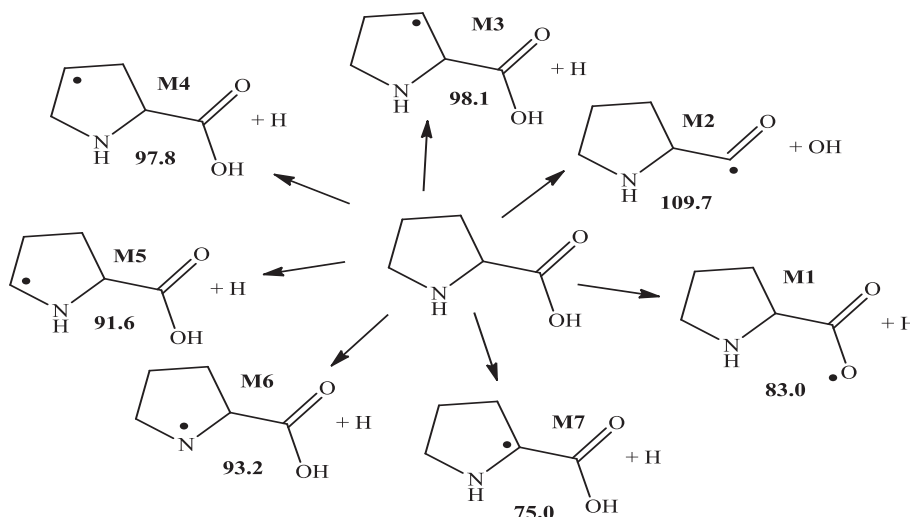


Fig. 1. Bond dissociation enthalpies for direct C–H, O–H and C–OH bond fission ($\Delta_r H_{298.15}^\circ$ values) in the proline molecule. All values are in kcal/mol at 298.15 K.

and kinetics parameters were derived with the aid of the Chemrate code [13]. Master equation analysis from RRMK theory [14] was utilised to compute pressure-dependent reaction rate constants for key reactions. In order to simulate a moderate collision environment, ΔE_{down} was set to 500 cm^{-1} in the energy transfer model. Deployed Lennard–Jones parameters for proline were adopted from corresponding values of pyrazine at $\sigma = 5.350 \text{ \AA}$ and $k/\epsilon_b = 307.0 \text{ K}$ [15]. These parameters serve to describe physical interaction between pairs of proline molecules. Detailed descriptions of pressure-dependent kinetics in general and physical significance of parameters deployed in the Chemrate code are given by Carstensen and Dean [16].

3. Results and discussions

3.1. Stationary point determinations

Fig. 1 depicts plausible channels for direct fissions of C–H, N–H, O–H and C–H bonds. As shown in Fig. 1, the proline molecule

posses four distinct C–H bonds. An H atom loss from the C atom gem to the C(O)OH group represents the lowest enthalpy demanding pathway. Formation of M7 radical via this route is associated with an endothermicity of 75.0 kcal/mol (298.15 K). Reaction enthalpies for fission of the other three C–H bonds are significantly larger and in the range of 91.6–98.1 kcal/mol. Calculated $\Delta_r H_{298.15}^\circ$ for these C–H bonds are very similar to corresponding values of the morpholine molecule. Unimolecular loss of an H atom from the NH group requires a sizable enthalpy reaction at 93.2 kcal/mol. Fission of the O–H hydroxyl bond is found to be endothermic by 83.0 kcal/mol and produces the M1 radical. Concluded from Fig. 1 is that reaction of the proline molecule with the O/H radical pool will most likely result in the formation of the M7 as a major intermediate. Initial oxidation of the proline molecule will further proceed via addition of oxygen molecule to the M7 and subsequent transformation of the resulted M7–OO moiety.

Fig. 2 shows closed-shell elimination pathways encountered in the initial decomposition of proline. These pathways features

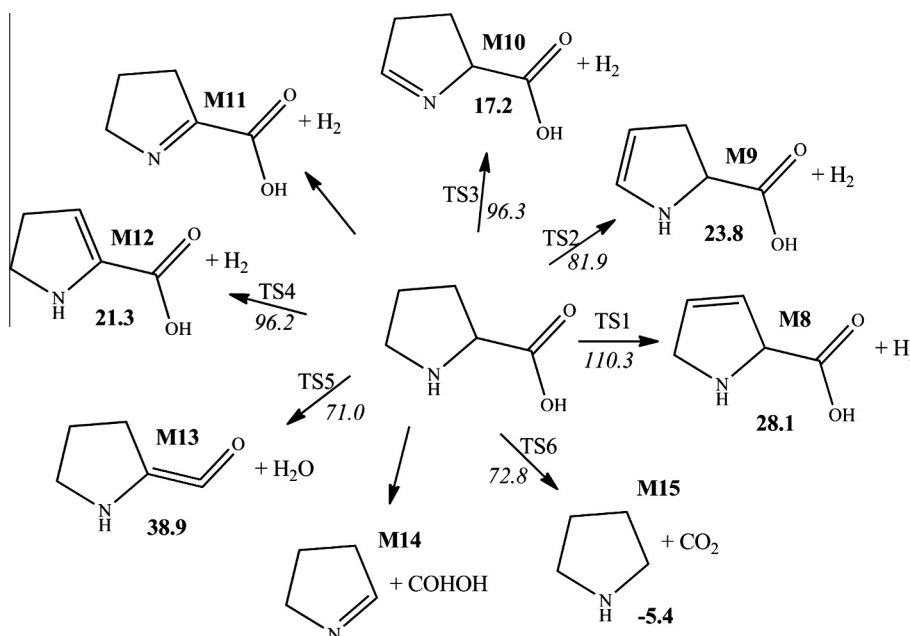


Fig. 2. Stationary point determinations in the unimolecular decomposition of proline. All values are in kcal/mol at 298.15 K.

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