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THERMO-KINETIC PARAMETERS GOVERNING DECOMPOSITION OF AMINO ACIDS: A COMPUTATIONAL STUDY

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Abstract

Amino acid model compounds are important nitrogenated species that in various categories of biomass. These compounds exhibit unique fragmentation pathways because of their adjacent amino and hydroxyl groups. Comprehending the decomposition chemistry of amino acids is essential to reduce harmful nitrogen emissions during biomass thermal treatment. This research reports the kinetic and thermodynamic properties of amino acids, and sulfur-containing amino acid, based on accurate density functional theory calculations coupled with kinetic modelling. The first part of the thesis provides comprehensive thermochemical parameters for the complete set of amino acids in the gas phase. The optimized geometries of amino acid compounds display both similarities and notable variations, which are contingent upon the individual amino acid and its surrounding atomic environment. Across most amino acids, the backbone, which includes the amino group (-NH₂), the carboxyl group (-COOH), and the α -carbon, generally maintains a consistent geometry. Isodesmic reactions were utilized to compute standard enthalpies of formation of amino acids in the gas phase; $\Delta_f H_o^{298}$. Bond dissociation enthalpies (BDHs) for all plausible H-X (X = C, O, N, and S) bond fissions were computed for the complete set of amino acids. It is found that the fission of α C-H bonds in these compounds systematically entails lower BDH value in reference to other bonds. Internal rotations in these compounds were treated as hindered rotors in computations of standard entropies and heat capacities. Comparison of $\Delta_f H_o^{298}$ values with limited available literature values disclose a reasonable agreement. The second part of the thesis ensues to provide a comprehensive data set of kinetic parameters for H abstraction by important radicals from all plausible abstractable sites in the complete set of amino acids. Considered radicals include H, CH₃, NH₂, OH, HO₂, and HS; the most prevailing radicals under pyrolytic and oxidative conditions. Computed Arrhenius parameters and plotted branching ratios portray a similar trend in regard to preference for abstraction from the α C-H sites by the six radicals. For this reason, we have computed kinetic parameters for H subtraction from the α C-H in the other amino acids (glycine, leucine, proline, phenylalanine, tryptophan, tyrosine, serine, threonine and asparagine). The study also examines the individual effects of different substituents (COOH, NH₂, HS, and CH₂) and uncovers significant insights. Notably, the presence of the COOH group introduces polar effects that counterintuitively deactivate the thermodynamically favoured α -abstraction pathway. The last part of the thesis explores in detail governing decomposition mechanisms of the Serine (Ser) amino Thermo-kinetic parameters are computed for a large set of reactions and involved species in both gas and condensed media. Initial decomposition of Ser is solely controlled by a dehydration channel that leads to the formation of a dehydroalanine molecule. Decarboxylation and deamination routes are likely to be of a negligible importance. The Fall-off window of the dehydration channel extends till the atmospheric pressure. Bimolecular reactions between two Ser compounds simulate the widely discussed cross-linking reactions that prevail in the condensed medium. It is demonstrated that formation of the key experimentally observed products (NH₃, CO₂, and CO) may originate from direct bond fissions in the melted phase of Ser prior to evaporation. A constructed kinetic model (with 24 reactions) accounts for the primary steps in the degradation of Ser molecule in the gas phase. Overall, Outcomes presented herein shall provide an atomic-based insight into the very complex nitrogen transformation chemistry pertinent to amino acids in strategic applications pertinent to thermal as well as biological domains.

Keywords: Amino acids; Biomass; DFT; Thermochemistry; Arrhenius parameters; Mechanisms