Chemical Physics Letters 664 (2016) 149–153

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

First-principle based modeling of urea decomposition kinetics in aqueous solutions

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ARTICLE INFO

Article history:
Received 27 September 2016
In final form 10 October 2016
Available online 11 October 2016

Keywords:
Urea
Decomposition
Multiscale modeling
Kinetics
Ab initio
Water cooperation

ABSTRACT

This study aims at validating a multi-scale modeling methodology based on an implicit solvent model for urea thermal decomposition pathways in aqueous solutions. The influence of the number of cooperative water molecules on kinetics was highlighted. The obtained kinetic model is able to accurately reproduce urea decomposition in aqueous phase under a variety of experimental conditions from different research groups. The model also highlights the competition between HNCO desorption to gas phase and hydrolysis in aqueous phase, which may influence SCR depollution process operation.

1. Introduction

Urea decomposition kinetics is important for a vast variety of applications, including agriculture [1], medical technologies [2] and energy [3]. In lean-burn automotive exhaust aftertreatment systems, a urea-water solution is injected upstream of the deNOx catalyst to generate ammonia for the selective catalytic reduction (SCR) process. Previous studies showed that urea aqueous phase decomposition can compete effectively with water evaporation rate [4] and urea polymerization [5]. While a number of recent studies [6,7] contributed to the elucidation of main urea decomposition pathways in aqueous solution, the mechanism of ammonia and isocyanic acid release remains insufficiently understood, although a molecular mechanism for the homolytic breaking of C—N bond seems more plausible than an ionic one [8]. Among the homolytic decomposition channels identified (ammonia elimination, hydrolysis and tautomerization), Alexandrova and Jorgensen [6] found the first path to have the lowest activation energy, partly resulting from the resonance stabilization in the first transition state. However, their study mainly focused on the solvent effects on the potential energy surface (PES), but not on the corresponding kinetic rate constants. These authors did not investigate the subsequent hydrolysis of isocyanic acid leading to an additional ammonia production. In the present study, we demonstrated the feasibility of a multiscale first-principle based kinetic modeling of urea decomposition in aqueous solution. We performed a high-level electronic structure study on the main ammonia production paths from urea decomposition including an implicit solvent model. Based on these new results, we herein derived the corresponding phenomenological rate constants and thermokinetic data to build a macrokinetic mechanism, which was subsequently validated against experimental data, allowing rate-of-production studies of urea decomposition under realistic operating conditions.

2. Methodology

The electronic structure calculations were performed with the Gaussian 09 suite of programs [9]. All geometry optimizations were performed at the M06-2X/6-311++G(d,p) level of theory to correctly describe long-range hydrogen bonding [10]. Systematic conformational searches were performed to identify the most stable structures. The T1 diagnostic for all species involved in this work was less than 0.02, supporting the appropriateness of single-reference methods in describing the wave function. Frequency calculations confirmed the desired character of the stationary points and IRC calculations effectively ensured the connection between the reactants and products. In DFT calculations, we used the SMD

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http://dx.doi.org/10.1016/j.cplett.2016.10.032
0009-2614/

implicit solvent model [11], which is known to produce errors for solvation energies typically lower than 1 kcal/mol for neutral molecules. Post Hartree-Fock energies were determined for the most important reaction steps by performing CCSD(T)/aug-cc-pVTZ evaluations using Molpro 2015 program [12] on the geometries previously optimized at the DFT level. The ZPE-corrected Gibbs free energy was evaluated using the following formula:

$$G = \mathrm{E}(CCSD(T)//DFT) + G_{corr}(DFT) + \Delta E_{solvation,DFT,0K}$$

In this equation E refers to the electronic energy and G_{corr} to the thermal corrections to the Gibbs Free energy, which envelopes the ZPE correction together with the translational, rotational and vibrational enthalpic and entropic corrections, calculated using M06-2X at the desired pressure and temperature. $\Delta E_{solvation}$ corresponds to the gas-to-water solvation energy, calculated at the M06-2X level without any thermal correction.

The harmonic transition state theory was selected to compute the corresponding phenomenological rate constants. Wigner correction factors [13] were computed to account for tunneling effects. Free activation energies were computed over the 300–600 K temperature range to get phenomenological rate constants in the Arrhenius-Kooij form $k = A\left(\frac{T}{1\,\mathrm{K}}\right)^n \exp\left(-\frac{E}{RT}\right)$. Macrokinetic modeling was carried out using the homogeneous (CSTR) reactor model implemented in Chemkin software package [14]. The same condensed-phase mean-field macrokinetic formalism was used as in our previous work [4]. The reverse rate constants were computed from the corresponding forward ones and reaction Gibbs free energies. The Weizmann-1 (W1) theory [15] was used to determine the enthalpies of the energetic minima of the PES over the 300–600 K range and the obtained thermochemical data were implemented in the mechanism using the NASA formalism [16]. As can be seen in Table S1 (Supplementary material), W1 theory coupled to SMD solvation model accurately predicts the available experimental thermochemical data, demonstrating its suitability for the present bottom-up kinetic modeling approach. Desorption rates were modeled from recommended [17] sticking coefficients (0.1 for NH_3, HNCO and CO_2) using Hertz-Knudsen equation and equilibrium constants evaluated from thermochemical data.

3. Results and discussion

Our electronic structure calculations confirm, referring to the work of Jorgensen [6], that water-assisted NH_3 elimination has a lower free energy of activation than hydrolysis (Fig. S1 in Supplementary material). As shown in Table 1, the Gibbs free energy barriers at 300 K and 1 atm for NH_3CONH (Int 2) formation through water-assisted H-shuttling lie at 30.9 and 30.3 kcal/mol for respectively one and two H_2O molecules involved, in good agreement with the values obtained by Tsipis and Karipidis [23], Alexandrova and Jorgensen [6] and Yao et al. [7] (respectively 29.5, 26.4 and 25.3 kcal/mol). The Free energy barrier associated to nucleophilic attack of water on carbonyl is much higher than this value, favoring NH_3 elimination over urea hydrolysis. It is important to note that relative DFT energies can differ from post-HF values by up to 10 kcal/mol (Fig. 2), which highlights the importance of a fine description of the electron correlation to get accurate energetic barriers (see Fig. 1).

The subsequent hydrolysis of HNCO (Fig. 2) proceeds through the formation of carbamic acid, which can in turn decompose through either intramolecular or assisted mechanism. In the present study, we focused on the addition of water across the C=N bond of HNCO, as it is energetically more favorable [24] than addition across the C=O bond due to the extended concentration of the electron density on nitrogen [25]. Although a competitive bicarbonate mechanism could also be considered in this study, it is

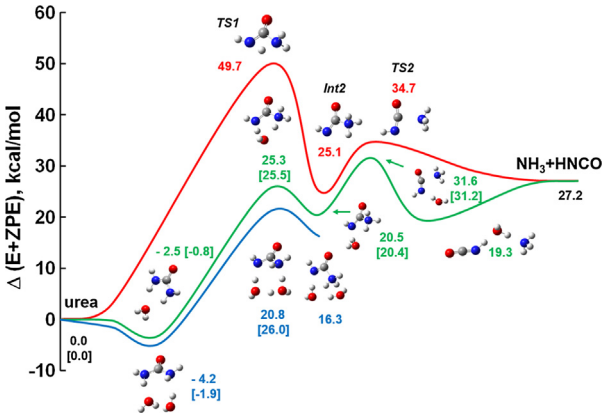

Fig. 1. Relative ZPE-corrected electronic energies (in kcal/mol) obtained at the M06-2X and CCSD(T)//M06-2X levels (in brackets) for unimolecular and water-assisted NH_3 elimination. Red, green and blue curves correspond respectively to zero, one and two assisting water molecules. Since the energy potential for C—N bond fission is weakly dependent on water involvement, this step was not studied in presence of 2 H_2O molecules. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

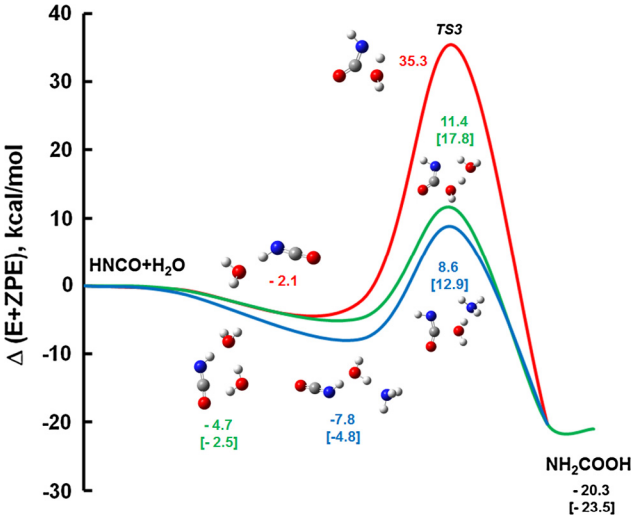

Fig. 2. Relative ZPE-corrected electronic energies (in kcal/mol) obtained at the M06-2X and CCSD(T)//M06-2X levels (in brackets) for HNCO hydrolysis. Red, green and blue curves correspond respectively to zero, one water and one ammonia assisting molecules. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Relative Gibbs Free energies at 300 K and 1 atm with respect to the reactants.

Urea + H_2O → NH_3 + HNCO + H_2O				Urea + 2 H_2O → NH_3 + HNCO + 2 H_2O		HNCO + H_2O + NH_3 → NH_2COOH + NH_3		HNCO + 2 H_2O → NH_2COOH + H_2O	
Complex	TS1	Int2	TS2	Complex	TS1	Complex	TS3	Complex	TS3
4.1	35.0	28.2	38.2	14.5	44.8	11.0	30.6	12.2	36.0