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Mechanism and kinetics for the reaction of fulminic acid, HCNO, with an amino radical, NH_2

Hue M.T. Nguyen[a,*], Trong N. Nguyen[b], Luc Vereecken[c]

[a] Faculty of Chemistry and Center for Computational Science, Hanoi National University of Education, Hanoi, Vietnam
[b] School of Chemical Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam
[c] Institute for Energy and Climate Research: IEK-8 Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

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ABSTRACT

The reaction of fulminic acid, HCNO, with NH_2 radicals was studied using quantum chemical and theoretical kinetic methodologies. B3LYP/6-311++G(3df,2p) calculations combined with CCSD(T) energy calculations at the basis set limit reveal a complex potential energy surface, where only two entrance channels contribute significantly to the product formation. Transition state theory and RRKM master equation calculations find a rate coefficient ranging from 7.2×10^{-12} cm^3 molecule^{-1} s^{-1} at room temperature, to $> 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 3000 K. Despite a reduced efficiency in product formation due to fast redissociation of the adducts to the reactants at high temperatures, the title reaction can thus be an efficient sink for HCNO at combustion temperatures in nitrogen-rich environments. At 1 bar and below, $H_2NCO + NO$ is the dominant product, with $H_2NCN + OH$ and $HCN + NHOH$ contributing weakly. This work presents rate coefficients and product distributions for the temperature range 300–3000 K, and pressure range of 10^{-3}–10^{3} bar; a brute-force error analysis examines the expected uncertainty interval for these predictions.

1. Introduction

The mitigation of NOx emissions from combustion systems is critical to improve air quality in many places on the globe. Several mitigation strategies have been proposed, with solutions that encompass fuel additives, reburning, or treatment of flue gases with catalytic converters, with or without further chemicals (e.g., AdBlue based on urea) [1–6]. The HCNO molecule, fulminic acid, is a critical intermediate in NOx reduction [3]. It is formed primarily from the reactions of HCCO and CH_2 with NO [3,7–13], as:

$$HCCO + NO \rightarrow HCNO + CO \tag{1}$$

$$HCCO + NO \rightarrow HCN + CO_2 \tag{2}$$

Boullart et al. [11], Eickhoff and Temps [12], and Rim and Hershberger [13] reported values for $k_1/(k_1+k_2)$ ranging from 0.64 ± 0.12 to 0.88 ± 0.04, using different experimental techniques. These results showed that channel (1), yielding HCNO, is the dominant pathway. HCNO is also formed by reactions of NO with $^3CH_2$ and $^1CH_2$ radicals in the flame [14–16]:

$$^3CH_2\ (^1CH_2) + NO \rightarrow HCNO + H \tag{3}$$

$$^3CH_2\ (^1CH_2) + NO \rightarrow HCN + OH \tag{4}$$

For the $^3CH_2 + NO$ reaction, Bauerle et al. [14] measured H, O, and OH production rates in shock waves over the temperature range from 1100 to 2600 K and concluded that (3) and (4) are major product channels, with both rate coefficients increasing with temperature. Later, Grußdorf et al. [16] reported that the dominant channel is HCNO + H, accounting for about 84%. The physicochemical properties of HCNO, and its reactions with various species present in hydrocarbon combustion such as H- and O-atoms, HO_x radicals, and other reactive species have been investigated [3,17–29]. Theoretical studies showed that there are two main mechanisms for the reactions of HCNO, i.e. direct H-abstraction and the association–elimination process, where the latter is typically more favorable. For example, in the HCNO + OH reaction, the H-abstraction occurs via an energy barrier of 8.7 kcal mol^{-1} while the channel of HO addition to the carbon of HCNO is a barrierless process leading to the major products [28].

The NH_2 radical is an interesting coreactant for HCNO, as nitrogen-containing species have been used extensively in NOx reduction strategies, where especially NH_3 and NH_3-sources such as urea are in use as active components of fuels or flue gas treatment systems. The NH_2 radical can be formed by dissociation of NH_3 or

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* Corresponding author.
E-mail address: hue.nguyen@hnue.edu.vn (H.M.T. Nguyen).

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by its reaction with radical species such as O-atoms, CH_3, OH, etc. [9,30]:

$$NH_3 + O \rightarrow NH_2 + OH \tag{5}$$

$$NH_3 + CH_3 \rightarrow NH_2 + CH_4 \tag{6}$$

$$NH_3 + OH \rightarrow NH_2 + H_2O, \tag{7}$$

where recommended rate coefficients are $k_5 = 1.6 \times 10^{-17}$ $T^{1.94}$ $\exp(-3250/T)\,cm^3$ molecule^{-1} s^{-1}, $k_6 = 1.8 \times 10^{-13}$ $\exp(-5100/T)\,cm^3$ molecule^{-1} s^{-1}, and $k_7 = 8.3 \times 10^{-17}$ $T^{1.6}$ $\exp(-480/T)\,cm^3$ molecule^{-1} s^{-1} [9,30].

The title reaction is also of some interest outside of combustion systems. Fulminic acid was detected recent along with its isomer, HNCO, in dark clouds by Marcelino et al. [31]; he also concluded that the reaction of NO with CH_2 radical is a key reaction for the formation of HCNO in these environments. The NH_2 radical has likewise been detected in the interstellar medium [32], is included in chemical models for Titan [e.g., 33], and plays a minor role in the removal of ammonia from earths' atmosphere [34]. Compared to combustion systems, these environments are characterized by lower temperatures and pressures, which may affect the reaction rate and product distribution.

To our knowledge, the cross-reaction of HCNO with NH_2 radicals has not been studied in detail before. In this work, we present a quantum chemical characterization of the potential energy surface (PES) of the $HCNO + NH_2$ reaction, based on which we determine the temperature- and pressure-dependent rate coefficient and product distribution, using theoretical kinetic methodologies. The results are expected to be directly useful for kinetic modeling studies containing the reactants.

2. Computational methods

The potential energy surface (PES) of the $HCNO + NH_2$ reaction was first characterized using the B3LYP/6-311++G(3df,2p) level of theory [35–37], obtaining the rovibrational characteristics of the reactants, products, intermediates and transition states. Vibrational wavenumbers were used scaled by 0.98 [38,39]. The relative energies were then improved by single point CCSD(T)/6-311++G(3df,2p) calculations on the B3LYP geometries [40,41]. The full PES is depicted in the supporting information (Fig. 2S). Many of the pathways and intermediates are only accessible through very high energy barriers, and play no role in the kinetics of the system. We have selected the kinetically relevant part of the PES, shown in Fig. 3, and further improved the relative energy of the critical points therein by extrapolation to the complete basis set limit (CBS) [42], based on CCSD(T)/aug-cc-pVxD calculations ($x = D,T,Q$) [43]. To assess the accuracy of such calculations, the heats of formation of main products at 298.15 K are compared against high-accuracy literature data (see Table 1). For most products, this results in deviations between the 6-311++G(3df,2p) basis set and the CBS limit of less than 1 kcal mol^{-1}, and differences of less than 0.5 kcal mol^{-1} against reference literature data [44], suggesting that the chosen level of theory is sufficiently accurate to describe the reaction kinetics of the title reaction. This is further corroborated by the low spin contamination in the DFT calculations, where S^2 for doublet states remains below 0.77 even before spin annihilation. Likewise, T1 diagnostic values are always below the upper limit of 0.044 proposed by Rienstra-Kiracofe et al. [45,46]: the highest value, $T1 = 0.042$, was found for the **T0P1** transition state, while all other structures have T1 diagnostics ≤ 0.040. The barrierless dissociation of H_2NCHNO (**IS1a**) to $H_2NCH + NO$ (**PR2**) was characterized by a set of constrained geometry optimizations at increasing C–N atom distances ranging up to 7 Å; the energies along this reaction path are further optimized by single point CCSD(T)/aug-cc-pVTZ calculations. At the kinetically relevant separations, S^2 values of the DFT wavefunction remain < 0.76 before annihilation, and T1 diagnostics < 0.025, though higher values are found at short separations below 2 Å. To investigate variational kinetic effects in the low **T0/1** entrance transition state, IRC calculations were performed using B3LYP, combined with B3LYP frequency calculations and single point CCSD(T) calculations on the obtained points along the reaction coordinate. These calculations showed increased T1 values reaching 0.044 at reactant separations shorter than the TS saddle point, which itself has a T1 diagnostic of 0.039; these higher values could indicate some multi-reference character in the wave function. All quantum chemical calculations were performed using Gaussian-09 [47].

The reaction of $HNCO + NH_2$ shows several entrance channels, many of which are not accessible kinetically in practical reaction conditions. For brevity, we only discuss the relevant pathways in this paper, relegating the less accessible pathways to the supporting information. The rate coefficient of the reaction is calculated using canonical transition state theory (CTST) [48,49] for temperatures ranging from 300 to 3000 K; variational effects on the **T0/1** entrance TS are studied using canonical variational TST (CVTST) [48,50]. Tunneling is accounted for by asymmetric Eckart tunneling [51,52]. The product distribution is then calculated using RRKM-based master equation analysis [53], based on a rigid rotor harmonic oscillator paradigm. The solution method used, CSSPI as implemented in our in-house software [53], is based on a stochastic description of the underlying Monte Carlo random walk of the nascent adducts, yielding product distributions valid at completion of the reaction (i.e. all chemically activated intermediates converted to products or stabilized adducts). This method does not assume steady-state of the intermediate concentrations, though the product yield is also directly valid in steady-state conditions as the concentrations of the intermediates then correspond to the probability distributions inherent in the random walk. It is assumed that the stabilized adducts react primarily with other reactants in the reaction mixture, i.e. unimolecular reactions are expected to be negligibly slow due to the ~40 kcal mol^{-1} dissociation barriers.

Redissociation of adducts to the free reactants becomes important at higher temperatures, such that the overall rate coefficient shows pressure dependence; the rate coefficient for the adduct formation channel needs to be corrected for this. Collisional energy transfer was described by the Troe biexponential model [54] using N_2 ($\varepsilon = 97.0\,K$, $\sigma = 3.617\,Å$) as a bath gas, and collisional transfer parameters for the [CH_2N_2O] adducts were estimated as $\varepsilon = 365.76\,K$, $\sigma = 3.58\,Å$, and $\Delta E_{down} = 400\,cm^{-1}$. The barrierless dissociation channel H_2NCHNO (**IS1a**) to $H_2NCH + NO$ (**PR2**) was treated by microvariational minimization of the RRKM energy-specific rate coefficients $k(E)$, based on a rigid rotor harmonic oscillator description of the structures, using the rovibrational and energetic properties obtained from the constrained geometries described above.

3. Results and discussion

3.1. PES and reaction mechanism

The optimized geometries of the reactants, and of key intermediates, products and transition states are shown in Figs. 1 and 2, with energetic data listed in Table 2. A simplified PES is depicted in Fig. 3, showing the kinetically relevant pathways; a more complete PES can be found in the supporting information (Figs. 1S and 2S). Two entrance channels for the $HCNO + NH_2$ reaction are kinetically relevant. The first is an H-abstraction reaction through transition state **T0P1** with a barrier of 10.4 kcal mol^{-1}, forming $CNO + NH_3$. The second pathway is the addition of the NH_2 radical onto the carbon of HCNO, forming $HC^{\bullet}(NH_2)NO$ through **T0/1** with an