Probing Hydrogen-Nitrogen Chemistry: A Theoretical Study of Important Reactions in N_xH_y , HCN and HNCO Oxidation

Yang Li *, S. Mani Sarathy

King Abdullah University of Science and Technology, Clean Combustion Research Centre, Physical Sciences and Engineering Division, Thuwal 23955, Saudi Arabia

Abstract

As an indirect storage medium of hydrogen, ammonia (NH_3) has drawn significant attention from academia and industry. Understanding nitrogen combustion chemistry is a major challenge in applying ammonia for converting chemical energy to thermal energy. Diazene (N_2H_2), diazenyl radical (NNH), amidogen radical (NH_2), hydrogen cyanide (HCN) and isocyanic acid (HNCO) are the crucial intermediate species in the combustion of NH_3 or its mixtures with other hydrocarbons. In light of that, this study provides advanced theoretical treatment of 14 important reactions in the oxidation of these intermediates, including isomerization, dissociation and abstraction reactions. The rate constants of all these reactions, and the temperature-dependent thermochemistry of the species involved in the reactions, were calculated utilizing high level quantum chemical methods. Rotational-vibrational properties of the reactants, products and stationary points were determined at the M06-2X/6-311++G(d,p) level of theory. Coupled cluster (CCSD(T)) methods were employed, with two large basis sets (cc-pVTZ and cc-pVQZ), and complete basis set of extrapolation techniques to compute the energies of the resulting geometries. All calculated results were compared with experimental and theoretical results in the literature. Finally, the implications of this work for combustion modelling were investigated, and the simulated species' profiles of HCN and HNCO demonstrated the influence of the updated rate coefficients on kinetic model predictions.

Keywords: Hydrogen-Nitrogen chemistry; hydrogen cyanide; isocyanic acid; quantum chemistry; rate constants; thermochemistry

* Corresponding author: yang.li@kaust.edu.sa

1. Introduction

Ammonia (NH_3) is a carbon free energy carrier with an energy density higher than hydrogen, an easier and more widespread production and distribution capacity, and better commercial viability [1], however, its combustion produces nitrogen oxides (NO_x) and other harmful pollutants. Therefore, understanding its oxidation chemistry is necessary to develop its applications in industry. In the literature, review papers from Miller *et al.* [2], Dagaut *et al.* [3] and Glarborg *et al.* [4] have provided an overview of the combustion chemistry of NH_3 and nitrogen-containing fuel (Fuel-N), and noted some crucial intermediate species: diazene (N_2H_2), diazenyl radical (NNH), amidogen radical (NH_2), hydrogen cyanide (HCN) and isocyanic acid (HNCO), as shown in Figure 1. The importance of these species has also been emphasized in some recent experimental and modeling studies of nitrogen chemistry [5-11]. Most recently, Mei *et al.* [11] performed an experimental and kinetic modeling study on the laminar flame propagation of ammonia under oxygen enrichment and elevated pressure conditions; their sensitivity analysis reported the three top sensitive reactions: $\text{NNH} \leftrightarrow \text{N}_2 + \text{H}$, $\text{N}_2\text{H}_2 + \text{H} \leftrightarrow \text{NNH} + \text{H}_2$ and $\text{NH}_2 + \text{H} \leftrightarrow \text{NH} + \text{H}_2$.

Figure 1: Generalized reaction scheme of combustion chemistry of ammonia (NH_3) and nitrogen-containing fuel (Fuel-N).

In the present work, the various literature sources were initially compared for reaction rate constants in the above-mentioned system; several significant disagreements were discovered. In addition to these N_xH_y species (NNH , N_2H_2 and NH_2), few studies were found on HCN and HNCO , which are highly toxic compounds [4]. A sensitivity analysis was performed here, using the latest kinetic model from

Glarborg *et al.* [4]; the simulation conditions are summarized in Table 1. Simulations were performed using ANSYS CHEMKIN-PRO [12]; an HCN concentration was chosen as the sensitivity target. The reactant compositions for the simulation selected was as $\text{NH}_3 : \text{NO}_2 : \text{CH}_4 : \text{CO} : \text{H}_2 : \text{O}_2 : \text{N}_2 = 1 : 1 : 1 : 1 : 10 : 85$; in this way, the chemistry of ammonia, NO_x and simple hydrocarbons were all accounted for, since they represent important hydrogen carriers (NH_3 and CH_4), the major product gas (NO_2) of NH_3 combustion, and the major by-product (CO) of steam methane reforming.

Table 1: Sensitivity analysis simulation conditions

Reactor	Perfectly Stirred Reactor (PSR)
Reactants	$\text{NH}_3 / \text{NO}_2 / \text{CH}_4 / \text{CO} / \text{H}_2 / \text{O}_2 / \text{N}_2$
Mole ratio	1 : 1 : 1 : 1 : 10 : 85
Pressure / atm	10
Temperature / K	1000, 1100 and 1200
Residence time / s	10

Figure 2 shows the results of sensitivity analysis, in which the top ten sensitive reactions are illustrated, and the H-atom abstraction reactions: $\text{HCN} + \text{OH} \leftrightarrow \text{CN} + \text{H}_2\text{O}$ and $\text{HNCO} + \text{OH} \leftrightarrow \text{NCO} + \text{H}_2\text{O}$ were found to be sensitive; these are highlighted in red. These two reactions were important in decreasing HCN production.

Figure 2: Sensitivity analysis for speciation HCN profile

In addition to the sensitive reactions noted above, there are only a few experimental and modeling works of HCN and HNCO oxidation, and few fundamental studies were found regarding the rate coefficient determination of the key reactions for N_xH_y (N_2H_2 , NNH and NH_2), HCN and HNCO. Studies in the literature related to nitrogen chemistry are summarized in Table 2, most were conducted before 2000.

Table 2: Literature studies related to nitrogen chemistry.

NO.	Reference	Year	Research object
Review papers			
1	Miller <i>et al.</i> [2]	1989	Nitrogen chemistry
2	Dagaut <i>et al.</i> [3]	2008	Hydrogen cyanide chemistry
3	Valera-Medina <i>et al.</i> [1]	2018	Ammonia chemistry
4	Glarborg <i>et al.</i> [4]	2018	Nitrogen chemistry
Experimental and modeling studies of nitrogen chemistry			
5	Faravelli <i>et al.</i> [5]	2003	Nitrogen chemistry
6	Sivaramakrishnan <i>et al.</i> [6]	2007	Nitrogen chemistry
7	Rasmussen <i>et al.</i> [7]	2008	Nitrogen chemistry
8	Mathieu <i>et al.</i> [8]	2015	Nitrogen chemistry
9	Deng <i>et al.</i> [9]	2016	Nitrogen chemistry
10	Zhang <i>et al.</i> [10]	2017	Nitrogen chemistry
11	Mei <i>et al.</i> [11]	2019	Nitrogen chemistry
Experimental and theoretical studies of rate constants			
N_xH_y system			
12	Dove <i>et al.</i> [13]	1979	$NH_2 + H$
13	Yumura <i>et al.</i> [14]	1981	$NH_2 + H$
14	Bahng <i>et al.</i> [15]	1984	$NH_2 + H$
15	Davidson <i>et al.</i> [16]	1990	$NH_2 + H$
16	Rohrig <i>et al.</i> [17]	1994	$NH_2 + H$
17	Linder <i>et al.</i> [18]	1995	$NH_2 + H$
18	Mackie <i>et al.</i> [19]	2005	$NH_2 + H$
19	Fontijn <i>et al.</i> [20]	2006	$NH_2 + H$
20	Shrestha <i>et al.</i> [21]	2018	$NH_2 + H$
21	Samu <i>et al.</i> [22]	2018	$NH_2 + H$
22	Kimball-Linne <i>et al.</i> [23]	1986	$NH_2 + OH$

23	Cheskis <i>et al.</i> [24]	1979	$\text{NH}_2 + \text{OH}$
24	Cohen <i>et al.</i> [25]	1991	$\text{NH}_2 + \text{OH}$
25	Fagerstrom <i>et al.</i> [26]	1995	$\text{NH}_2 + \text{OH}$
26	Mousavipour <i>et al.</i> [27]	2009	$\text{NH}_2 + \text{OH}$
27	Klippenstein <i>et al.</i> [28]	2009	$\text{NH}_2 + \text{OH}$
28	Chuang <i>et al.</i> [29]	1997	$\text{N}_2\text{H}_2 + \text{H}$
29	Kobayashi <i>et al.</i> [30]	2000	$\text{N}_2\text{H}_2 + \text{H}$
30	Zheng <i>et al.</i> [31]	2012	$\text{N}_2\text{H}_2 + \text{H}$
31	Linder <i>et al.</i> [32]	1996	$\text{N}_2\text{H}_2 + \text{H}$ and OH
32	Walch <i>et al.</i> [33]	1989	NNH decomposition
33	Bozzelli <i>et al.</i> [34]	1995	NNH decomposition
34	Klippenstein <i>et al.</i> [35]	2011	NNH decomposition
<hr/>			
HCN system			
35	Boden <i>et al.</i> [36]	1968	$\text{HCN} + \text{H}$
36	Albers <i>et al.</i> [37]	1975	$\text{HCN} + \text{H}$
37	Schacke <i>et al.</i> [38]	1977	$\text{HCN} + \text{H}$
38	Szekely <i>et al.</i> [39]	1983	$\text{HCN} + \text{H}$
39	Li <i>et al.</i> [40]	1984	$\text{HCN} + \text{H}$
40	Bair <i>et al.</i> [41]	1985	$\text{HCN} + \text{H}$
41	Wagner <i>et al.</i> [42]	1986	$\text{HCN} + \text{H}$
42	Juan <i>et al.</i> [43]	1987	$\text{HCN} + \text{H}$
43	Balla <i>et al.</i> [44]	1987	$\text{HCN} + \text{H}$
44	Sims <i>et al.</i> [45]	1988	$\text{HCN} + \text{H}$
45	Natarajan <i>et al.</i> [46]	1988	$\text{HCN} + \text{H}$
46	Atakan <i>et al.</i> [47]	1989	$\text{HCN} + \text{H}$
47	Sun <i>et al.</i> [48]	1990	$\text{HCN} + \text{H}$
48	Lambert <i>et al.</i> [49]	1993	$\text{HCN} + \text{H}$
49	Wooldridge <i>et al.</i> [50]	1996	$\text{HCN} + \text{H}$
50	Sumathi <i>et al.</i> [51]	1998	$\text{HCN} + \text{H}$
51	He <i>et al.</i> [52]	1998	$\text{HCN} + \text{H}$
52	Jiang <i>et al.</i> [53]	2013	$\text{HCN} + \text{H}$
53	Davies <i>et al.</i> [54]	1968	$\text{HCN} + \text{O}$
54	Morley <i>et al.</i> [55]	1976	$\text{HCN} + \text{O}$
55	Haynes <i>et al.</i> [56]	1977	$\text{HCN} + \text{O}$
56	Perry <i>et al.</i> [57]	1985	$\text{HCN} + \text{O}$
57	Szekely <i>et al.</i> [58]	1985	$\text{HCN} + \text{O}$

58	Miller <i>et al.</i> [59]	1986	HCN + O
59	Roth <i>et al.</i> [60]	1980	HCN + OH
60	Cicerone <i>et al.</i> [61]	1983	HCN + OH
61	Szekely <i>et al.</i> [62]	1984	HCN + OH
62	Jacobs <i>et al.</i> [63]	1988	HCN + OH
63	Wooldridge <i>et al.</i> [64]	1995	HCN + OH
64	Wang <i>et al.</i> [65]	2002	HCN + OH
65	Galano <i>et al.</i> [66]	2007	HCN + OH
66	Miller <i>et al.</i> [67]	1984	HCN + H, O and OH
67	Lee <i>et al.</i> [68]	1991	HCN isomerization
68	Lin <i>et al.</i> [69]	1992	HCN isomerization
69	Abashkin <i>et al.</i> [70]	1994	HCN isomerization
70	Gazdy <i>et al.</i> [71]	1995	HCN isomerization
71	Bacalzo-Gladden <i>et al.</i> [72]	1999	HCN isomerization
72	Kumeda <i>et al.</i> [73]	1999	HCN isomerization
73	Maeda <i>et al.</i> [74]	2005	HCN isomerization
74	Isaacson <i>et al.</i> [75]	2006	HCN isomerization
75	Halpern <i>et al.</i> [76]	2006	HCN isomerization
76	Quapp <i>et al.</i> [77]	2010	HCN isomerization
77	Baraban <i>et al.</i> [78]	2015	HCN isomerization
78	Glarborg <i>et al.</i> [79]	2016	HCN isomerization
<hr/>			
		HNCO system	
79	Louge <i>et al.</i> [80]	1984	HNCO + H
80	Perry <i>et al.</i> [81]	1985	HNCO + H
81	Miller <i>et al.</i> [82]	1992	HNCO + H
82	Mertens <i>et al.</i> [83]	1996	HNCO + H
83	Nguyen <i>et al.</i> [84]	1996	HNCO + H
84	Liu <i>et al.</i> [85]	1991	HNCO + O
85	He <i>et al.</i> [86]	1992	HNCO + O
86	Wooldridge <i>et al.</i> [87]	1996	HNCO + OH
87	Sengupta <i>et al.</i> [88]	1997	HNCO + OH
88	Tully <i>et al.</i> [89]	1988	HNCO + O and OH
89	Mertens <i>et al.</i> [90]	1992	HNCO + O and OH
90	Baulch <i>et al.</i> [91]	2005	Multiple nitrogen-containing reactions
91	Dean and Bozzelli [92]	2015	Multiple nitrogen-containing reactions

The motivation for this work is summarized as follows: First, based on the above sensitivity analysis results, H-atom abstraction reactions ($\text{HCN} + \text{OH} \leftrightarrow \text{CN} + \text{H}_2\text{O}$ and $\text{HNCO} + \text{OH} \leftrightarrow \text{NCO} + \text{H}_2\text{O}$) were found to be important. Second, Mei *et al.* [11] performed the experimental and kinetic modelling study on the laminar flame propagation of ammonia under oxygen enrichment and elevated pressure conditions; their sensitivity analysis reported the three primary sensitive reactions: $\text{NNH} \leftrightarrow \text{N}_2 + \text{H}$, $\text{N}_2\text{H}_2 + \text{H} \leftrightarrow \text{NNH} + \text{H}_2$ and $\text{NH}_2 + \text{H} \leftrightarrow \text{NH} + \text{H}_2$. Third, review papers from Miller *et al.* [2], Dagaut *et al.* [3] and Glarborg *et al.* [4] also noted the importance of these reactions, as well as the isomerization reaction: $\text{HCN} \leftrightarrow \text{HNC}$. For this reason, the aim of this study was to systematically perform high level quantum chemical calculations for the rate constants of the above dissociation, isomerization and abstraction reactions, moreover, the abstractors have also been comprehensively included for the abstraction reactions H, OH, O and O_2 . In total, the targets were 14 reactions, divided into three systems: N_xH_y System, HCN System and HNCO System, as shown in Table 3.

Table 3: Important nitrogen related reactions targeted in this work

N_xH_y System	HCN System	HNCO System
$\text{NNH} \leftrightarrow \text{N}_2 + \text{H}$	$\text{HCN} \leftrightarrow \text{HNC}$	-
$\text{N}_2\text{H}_2 + \text{H} \leftrightarrow \text{NNH} + \text{H}_2$	$\text{HCN} + \text{H} \leftrightarrow \text{CN} + \text{H}_2$	$\text{HNCO} + \text{H} \leftrightarrow \text{NCO} + \text{H}_2$
$\text{N}_2\text{H}_2 + \text{O} \leftrightarrow \text{NNH} + \text{OH}$	$\text{HCN} + \text{O} \leftrightarrow \text{CN} + \text{OH}$	$\text{HNCO} + \text{O} \leftrightarrow \text{NCO} + \text{OH}$
$\text{NH}_2 + \text{H} \leftrightarrow \text{NH} + \text{H}_2$	$\text{HCN} + \text{OH} \leftrightarrow \text{CN} + \text{H}_2\text{O}$	$\text{HNCO} + \text{OH} \leftrightarrow \text{NCO} + \text{H}_2\text{O}$
$\text{NH}_2 + \text{OH} \leftrightarrow \text{NH} + \text{H}_2\text{O}$	$\text{HCN} + \text{HO}_2 \leftrightarrow \text{CN} + \text{H}_2\text{O}_2$	-
-	$\text{HCN} + \text{O}_2 \leftrightarrow \text{CN} + \text{HO}_2$	-

2. Computational Methods

Gaussian 09 [93] was used to perform all *ab initio* calculations. The density functional theory (DFT) method M06-2X [94], with the 6-311++G(d,p) [95, 96] basis set, was simultaneously used to calculate geometry optimization, vibrational frequency and intrinsic reaction coordinate (IRC). For the electronic single-point energies (SPEs) calculation, a coupled cluster theory CCSD(T) [97], with the

cc-pVTZ and cc-pVQZ [98] basis sets, was employed, followed by the complete basis set (CBS) extrapolation:

$$E_{CBS} = E_{CCSD(T)/cc-pVQZ} + (E_{CCSD(T)/cc-pVQZ} - E_{CCSD(T)/cc-pVTZ}) * 4^4 / (5^4 - 4^4) \quad (1)$$

Notably, for the SPE calculation of the transition state (TS) of reaction $\text{HCN} + \text{O}_2 \leftrightarrow \text{CN} + \text{HO}_2$, the CCSD(T)/cc-pVQZ method failed to obtain the result, therefore, the combined CCSD(T)/cc-pVXZ [97] and Møller–Plesset perturbation theory MP2/cc-pVXZ [99] (in which X = D, T and Q) [98] were used for this reaction independently, followed by the complete basis set (CBS) extrapolation:

$$E_{CBS} = E_{CCSD(T)/cc-pVTZ} + (E_{CCSD(T)/cc-pVTZ} - E_{CCSD(T)/cc-pVDZ}) * 3^4 / (4^4 - 3^4) + E_{MP2/cc-pVQZ} + (E_{MP2/cc-pVQZ} - E_{MP2/cc-pVTZ}) * 4^4 / (5^4 - 4^4) - E_{MP2/cc-pVTZ} + (E_{MP2/cc-pVTZ} - E_{MP2/cc-pVDZ}) * 3^4 / (4^4 - 3^4) \quad (2)$$

In addition, combined compound methods CBS-APNO/G3/G4 [100-102] were utilized to calculate the zero Kelvin energies (ZKEs), which were further used to derive the average atomization formation enthalpies for calculation of thermodynamic properties. The scale factors for the zero-point energies (ZPEs) and vibrational frequencies were 0.9698 and 0.983 respectively, recommended for the M06-2X functional by Zhao and Truhlar [94].

The MultiWell [103] program suite performed the kinetic calculations to obtain rate constants and thermochemistry, which were based on the canonical transition state theory (TST) [104] and statistical thermodynamics, respectively. In the rate constant calculations, quantum mechanical tunneling was taken into account; using an unsymmetrical Eckart barrier model [105], the rate coefficients were calculated by the Thermo module, and subsequently fitted to a modified Arrhenius expression as a function of temperature:

$$k = A(T/T_{ref})^n \exp(-E/RT) \quad (3)$$

where A was the frequency factor, T was the temperature in Kelvin, $T_{ref} = 1$ K, n was the temperature exponent at 1 K, and E was related to the activation energy (by $E_a = E + nRT$).

In the thermochemistry calculation, enthalpy of formation, entropy and heat capacity were calculated simultaneously as a function of temperature (298.15 – 2000 K), and were fitted to NASA polynomials [106] using the Fitdat utility in ANSYS CHEMKIN-PRO [12].

It is notable that the above calculation approach and methods proved to be effective for the rate coefficient calculations of isomerization, abstraction and dissociation reactions in references [107, 108], and the thermochemistry calculation of extensive C2–C7 hydrocarbon species in reference [109]. In addition, all calculated results are validated in the sections that follow.

3. Results and Discussion

3.1. Potential energy surface and barrier heights comparison

Intrinsic reaction coordinate (IRC) calculations were performed on the transition states (TSs) of all 14 reactions to ensure their connection to the desired reactants and products. Here, the reaction $\text{N}_2\text{H}_2 + \text{H} \leftrightarrow \text{NNH} + \text{H}_2$ is shown as a representative; Figure 3 shows the potential energy surface (PES) of this reaction. The forward and reverse barrier heights were predicted to be 1.95 and 42.56 kcal mol⁻¹ respectively at $T = 0$ K, indicating the strong exothermicity of this reaction ($\Delta H_{0K} = -40.61$ kcal mol⁻¹).

Figure 3: PES for reaction $\text{N}_2\text{H}_2 + \text{H} \leftrightarrow \text{NNH} + \text{H}_2$.

Table 4 summarizes the barrier height of all 14 reactions examined here, for both forward and reverse directions. In the N_xH_y system, all reactions were exothermic, both the dissociation reaction ($NNH \leftrightarrow N_2 + H$) and the other abstraction reactions showed relatively low forward barrier heights: $1.45 - 5.96 \text{ kcal mol}^{-1}$ ($6.07 - 24.94 \text{ kJ mol}^{-1}$). However, for the HCN system, all abstraction reactions were endothermic, with relatively high barrier heights: $15.74 - 88.83 \text{ kcal mol}^{-1}$ ($65.86 - 371.66 \text{ kJ mol}^{-1}$). Of all the reactions, the H-atom abstraction by OH radical displayed the lowest barrier heights in each system, due to its high reactivity.

Table 4: Barrier height of all reactions (unit: kcal mol^{-1}).

Reaction	Forward barrier	Reverse barrier
N_xH_y system		
$NNH \leftrightarrow N_2 + H$	6.52	14.99
$N_2H_2 + H \leftrightarrow NNH + H_2$	1.95	42.56
$N_2H_2 + O \leftrightarrow NNH + OH$	1.99	41.21
$NH_2 + H \leftrightarrow NH + H_2$	5.96	17.01
$NH_2 + OH \leftrightarrow NH + H_2O$	1.45	27.07
HCN system		
$HCN \leftrightarrow HNC$	43.97	29.61
$HCN + H \leftrightarrow NC + H_2$	26.81	3.78
$HCN + O \leftrightarrow NC + OH$	28.68	4.26
$HCN + OH \leftrightarrow NC + H_2O$	15.74	7.29
$HCN + HO_2 \leftrightarrow NC + H_2O_2$	42.81	2.66
$HCN + O_2 \leftrightarrow NC + HO_2$	88.83	10.46
HNCO system		
$HNCO + H \leftrightarrow NCO + H_2$	16.67	9.47
$HNCO + O \leftrightarrow NCO + OH$	13.64	5.05
$HNCO + OH \leftrightarrow NCO + H_2O$	6.13	13.51

To validate the calculated barrier heights, these results were compared with results in the available literature, as summarized in Table 5, where, comparisons were made in three dimensions: (1) dissociation, isomerization and abstraction reactions; (2) N_xH_y , HCN and HNCO systems; (3) forward ($HCN + H \leftrightarrow CN + H_2$) and reverse ($CN + H_2 \leftrightarrow HCN + H$) directions. Excellent agreement was obtained from these comparisons, which exhibited less than 1 kcal mol⁻¹ difference between current results and data from the literature.

Table 5: Comparison of barrier heights (unit: kcal mol⁻¹).

Reaction	Current Study	Literature Study	Reference
N_xH_y system			
$NNH \leftrightarrow N_2 + H$	6.52	5.0 – 7.4	Bozzelli <i>et al.</i> 1995 [34]
$NH_2 + H \leftrightarrow NH + H_2$	5.96	5.72	Mackie <i>et al.</i> 2005 [19]
$NH_2 + OH \leftrightarrow NH + H_2O$	1.45	1.70	Klippenstein <i>et al.</i> 2009 [28]
HCN system			
$HCN \leftrightarrow HNC$	43.97	44.60	Lee <i>et al.</i> 1991 [68]
$HCN + H \leftrightarrow CN + H_2$	26.55	24.5 – 27.4	Jiang <i>et al.</i> 2013 [53]
$CN + H_2 \leftrightarrow HCN + H$	3.52	4.10	Wagner <i>et al.</i> 1986 [42]
$HCN + OH \leftrightarrow CN + H_2O$	15.74	15.95	Wang <i>et al.</i> 2002 [65]
HNCO system			
$HNCO + H \leftrightarrow NCO + H_2$	16.67	15.63	Nguyen <i>et al.</i> 1996 [84]
$HNCO + OH \leftrightarrow NCO + H_2O$	6.13	5.80	Sengupta <i>et al.</i> 1997 [88]

3.2. Rate constant comparisons

All calculated rate coefficients in this study were fitted by modified Arrhenius expressions, and summarized in Table 6; these were directly incorporated into chemical kinetic models. Notably, the input files used for the rate constants calculation by MultiWell code have all been provided in the Supplementary Material 2.

Table 6: Rate coefficients calculated here

Reaction	A (s^{-1})	n	Ea ($cal\ mol^{-1}$)
N_xH_y system			
NNH $\leftrightarrow$ N ₂ + H	7.68E+07	1.73	4282
N ₂ H ₂ + H $\leftrightarrow$ NNH + H ₂	4.82E+08	1.76	739
N ₂ H ₂ + O $\leftrightarrow$ NNH + OH	1.11E+08	1.62	805
NH ₂ + H $\leftrightarrow$ NH + H ₂	1.09E+05	2.59	1812
NH ₂ + OH $\leftrightarrow$ NH + H ₂ O	4.04E+04	2.52	-616
HCN system			
HCN $\leftrightarrow$ HNC	8.98E+10	0.92	42512
HCN + H $\leftrightarrow$ CN + H ₂	2.09E+09	1.92	26229
HCN + O $\leftrightarrow$ CN + OH	1.57E+08	1.82	27825
HCN + OH $\leftrightarrow$ CN + H ₂ O	7.69E+03	2.78	13054
HCN + HO ₂ $\leftrightarrow$ CN + H ₂ O ₂	4.61E+04	2.54	41604
HCN + O ₂ $\leftrightarrow$ CN + HO ₂	4.56E+08	2.29	88454
HNCO system			
HNCO + H $\leftrightarrow$ NCO + H ₂	1.46E+05	2.53	12941
HNCO + O $\leftrightarrow$ NCO + OH	3.63E+03	2.88	10107
HNCO + OH $\leftrightarrow$ NCO + H ₂ O	1.15E+00	3.64	1182

Based on the extensive literature review shown in Table 1, the rate constants of the following reactions were validated through comprehensive comparisons:

- N_xH_y System:

- HCN System:

- HNCO System:

To maintain consistency in the figures below, all experimental data is plotted as symbols in various shapes, and theoretical results are plotted as lines in different colors.

3.2.1. N_xH_y system

Figure 4 shows the rate constant comparison for the reaction: $\text{NH}_2 + \text{H} \leftrightarrow \text{NH} + \text{H}_2$. In the figure, experimental data was taken from Bahng *et al.* [15], which is only a single data point: $(7.7 \pm 14) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 293 K. Calculation results from Davidson *et al.* [16], Linder *et al.* [18], Samu *et al.* [22] and Baulch *et al.* [91] were also obtained for the comparison. Among them, the theoretical results obtained from Samu *et al.* [22], Baulch *et al.* [91] and current study, all matched with the experimental data at room temperature. At combustion relevant temperatures ($T > 1000 \text{ K}$), the maximum discrepancy between the three predicted results were found to be a factor of two--acceptable given the uncertainty of quantum chemical calculations.

Figure 5 shows rate constant comparisons for the reaction: $\text{NH} + \text{H}_2 \leftrightarrow \text{NH}_2 + \text{H}$, considered to be the reverse reaction of the H-atom abstraction from the NH_2 radical. Experimental data in the figure was taken from Fontijn *et al.* [20] and Rohrig *et al.* [17], studies which covered the temperature range between 800 – 1700 K. Calculated results from this study are compared with the theoretical results from Mackie *et al.* [19] and Linder *et al.* [18], in which the G3//B3LYP/6-31G(d) and CASSCF/ccpVDZ//MRCI/cc-pVTZ level of theories were employed, respectively. Different levels of theories resulted in slightly different barrier heights for this reaction: 17.01 kcal mol⁻¹ (current study), 18.72 kcal mol⁻¹ (Mackie *et al.* [19]) and 18.66 kcal mol⁻¹ (Linder *et al.* [18]). With a slightly lower barrier height, the current study predicted a faster rate than calculations in the two studies cited, by a factor of about two to four; results from this study matched well with the experimental data.

Figure 6 shows rate constant comparisons for the reaction: $\text{NH}_2 + \text{OH} \leftrightarrow \text{NH} + \text{H}_2\text{O}$. The experimental data were obtained from Klippenstein *et al.* [28] and Kimball-Linne *et al.* [23].

Klippenstein *et al.* [28] also performed high-level quantum chemical calculations, and the predicted barrier height is compared with this study in Table 5. Moreover, reaction exothermicity predicted in the two studies were also in excellent agreement at -25.62 and -25.43 kcal mol⁻¹ respectively. However, the rate constants predicted in both studies showed significantly lower value than in the experimental data. Some other calculations from Dean and Bozzelli [110], Mackie *et al.* [19] and Cohen *et al.* [25] showed the same trend. Given the expected uncertainty in barrier height prediction, Klippenstein *et al.* [28] lowered the barrier height by 2 kcal mol⁻¹, resulting in relatively good agreement when compared with the experimental data. With a similar level of theory (CCSD(T)/CBS) used for the energy calculation, the barrier height in this study was reduced by 2 kcal mol⁻¹, leading to a larger rate constant by a factor of 1.5 – 3.0 at 800 – 2000 K. The updated rate constant lay between the two experimental data sets. This is the only case of modifying the reaction barrier height manually in the current study. For all other reactions examined in this paper, the results were original, made without adjustment.

Figure 4: Rate constant comparison for reaction: $\text{NH}_2 + \text{H} \leftrightarrow \text{NH} + \text{H}_2$. Literature source: Experimental data from Bahng *et al.* [15]. Calculation results from Davidson *et al.* [16], Linder *et al.* [18], Samu *et al.* [22] and Baulch *et al.* [91].

Figure 5: Rate constant comparison for reaction: $\text{NH} + \text{H}_2 \leftrightarrow \text{NH}_2 + \text{H}$. Literature source: Experimental data from Fontijn *et al.* [20] and Rohrig *et al.* [17]. Calculation results from Mackie *et al.* [19] and Linder *et al.* [18].

Figure 6: Rate constant comparison for reaction: $\text{NH}_2 + \text{OH} \leftrightarrow \text{NH} + \text{H}_2\text{O}$. Literature source: Experimental data from Klippenstein *et al.* [28] and Kimball-Linne *et al.* [23]. Calculation results from Dean and Bozzelli [110], Mackie *et al.* [19] and Cohen *et al.* [25].

3.2.2. HCN system

Figure 7 shows rate constant comparison for the isomerization reaction: $\text{HCN} \leftrightarrow \text{HNC}$. Various theoretical studies were collected from the literature (Isaacson *et al.* [75], Dean and Bozzelli [110], Lin *et al.* [69], Glarborg *et al.* [79] and Quapp *et al.* [77]), in which the different levels of theories used in the calculations resulted in different rate coefficients by about one order of magnitude. Predictions from the current study lay between the literature values across the entire temperature range.

Figure 8 shows the H-atom abstraction reaction from HCN by the O-atom. Experimental data was obtained from Szekely *et al.* [58], in which the rate constant at high temperature (2000 – 2500 K) was measured in a shock tube by monitoring the absolute concentration time-profiles of CN radical (broad-band absorption near 388 nm). The rate constant of the current study was plotted together with theoretical predictions from Perry *et al.* [57] and Miller *et al.* [59]; the current study showed good agreement with Miller *et al.* [59] (the difference was less than a factor of two), and both results were in excellent agreement with the experimental data.

Figure 9 and Figure 10 show H-atom abstraction reactions from HCN by the OH radical in forward and reverse directions respectively. The rate constants calculated in the current study were compared with calculation results from Wang *et al.* [65] for both directions of the reactions. In Wang's study, the QCISD(T)/6-311+G(2df, 2p)//QCISD/6-311G(d, p) method was used for the *ab initio* calculation; rate constant calculations were performed via (1) conventional transition state theory (TST), and (2) canonical variational TST (CVT); (3) CVT with a small-curvature tunneling (SCT) correction. Results from all three approaches are plotted in Figure 9 and Figure 10, together with the rate constant calculated here. For the rate constant comparison of the forward direction, experimental data from Wooldridge *et al.* [64] and Roth *et al.* [60] were used for the validation. The rate constant calculated from the current study showed excellent agreement with experimental data at a wide range of temperatures: 1050 – 2200 K, while Wang's calculation predicted a faster rate. For the rate constant comparison of the reverse direction shown in Figure 10, experimental data obtained from Jacobs *et al.* [63], Szekely *et al.* [62] and Jacobs *et al.* [63] measured the total rate of this reaction: $\text{CN} + \text{H}_2\text{O} \leftrightarrow \text{HCN} + \text{OH}$ at relatively low pressure (10 – 60 Torr) and low temperature (518 – 1027 K). Under such

conditions, the chemically activated reaction channel could be a major contributor, compared with the direct abstraction channel, therefore, the calculated rate from this study is shown to be slightly slower than the experimental data. Szekely *et al.* [62] investigated the rate coefficient of this reaction in the temperature range of 2460 - 2840 K, using a shock tube technique. Compared to this data set, the theoretical calculations from the current study, and from Wang *et al.* [65], both over predicted the rate constant by a factor of about five to seven, quantitatively. Further investigation may be required into this reaction in the future, while--notably--such conditions (2460 - 2840 K) are not encountered in typical combustors.

Figure 7: Rate constant comparison for reaction: $\text{HCN} \leftrightarrow \text{HNC}$. Literature source: Calculation results from Isaacson *et al.* [75], Dean and Bozzelli [110], Lin *et al.* [69], Glarborg *et al.* [79] and Quapp *et al.* [77].

Figure 8: Rate constant comparison for reaction: $\text{HCN} + \text{O} \leftrightarrow \text{CN} + \text{OH}$. Literature source: Experimental data from Szekely *et al.* [58]. Calculation results from Perry *et al.* [57] and Miller *et al.* [59].

Figure 9: Rate constant comparison for reaction: $\text{HCN} + \text{OH} \leftrightarrow \text{CN} + \text{H}_2\text{O}$. Literature source: Experimental data from Wooldridge *et al.* [64], Roth *et al.* [60]. Calculation result from Wang *et al.* [65].

Figure 10: Rate constant comparison for reaction: $\text{CN} + \text{H}_2\text{O} \leftrightarrow \text{HCN} + \text{OH}$. Literature source: Experimental data from Jacobs *et al.* [63], Szekely *et al.* [62]. Calculation result from Wang *et al.* [65].

3.2.3. HNCO system

Figure 11 and Figure 12 show rate constant comparisons for the H-atom abstraction from HNCO by H-atom in forward and reverse directions, respectively. For forward direction, experimental data was obtained from Mertens *et al.* [83], whose experiment was performed behind the reflected shock waves in a shock tube at a relatively high temperature range (2200 – 3400 K). Nguyen *et al.* [84] and Miller *et al.* [82] performed quantum chemistry calculation using QCISD//6-311++G(2df,-2pd)//PUMP4/6-311++G(d,p) and BAC-MP4/6-31G(d,p)//UHF/6-31G(d,p) methods, respectively. Ultimately, these two calculations predicted nearly identical rate constants compared with those from the current study. Moreover, theoretical predictions were in excellent agreement with the experimental data. For the reverse direction, Perry *et al.* [81] and Louge *et al.* [80] monitored the concentration profile of NCO radical at a relatively low temperature range (600 – 1500 K) to conduct the experiments.

Reasonably good agreement was obtained between the calculation result and experimental data, with a slight over prediction in the low temperature range (600 – 900 K).

Figure 13 shows a rate constant comparison for the reaction: $\text{HNCO} + \text{O} \leftrightarrow \text{NCO} + \text{OH}$. The high- and low-temperature experimental data was obtained from Mertens *et al.* [90] and Tully *et al.* [89], respectively. Later a photolysis/chemiluminescence technique was used in both experiments. However, the two experimental points obtained in Tully’s experiment at 679 and 741 K were the total rates of the $\text{HNCO} + \text{O} \leftrightarrow \text{products}$ reaction. The chemically activated reaction channel was dominant over the direct abstraction channel at this temperature and pressure condition ($p = 750$ Torr). Therefore, the theoretical results from the current study and from He *et al.* [86] showed excellent agreement with Mertens’s data at high temperatures, and they were lower than the total rate constant measured in Tully’s experiment at low temperatures.

Figure 11: Rate constant comparison for reaction: $\text{HNCO} + \text{H} \leftrightarrow \text{NCO} + \text{H}_2$. Literature source: Experimental data from Mertens *et al.* [83]. Calculation results from Nguyen *et al.* [84] and Miller *et al.* [82].

Figure 12: Rate constant comparison for reaction: $\text{NCO} + \text{H}_2 \leftrightarrow \text{HNCO} + \text{H}$. Literature source: Experimental data from Perry *et al.* [81] and Louge *et al.* [80].

Figure 13: Rate constant comparison for reaction: $\text{HNCO} + \text{O} \leftrightarrow \text{NCO} + \text{OH}$. Literature source: Experimental data from Mertens *et al.* [90] and Tully *et al.* [89]. Calculation result from He *et al.* [86].

3.3. Thermochemistry comparison

Three sources were selected to validate the calculated thermochemical properties in this study:

- Current study: CBS-APNO/G3/G4//M06-2X/6-311++G(d,p)
- References [111-113]: Active thermochemical tables (ATcT)
- Glarborg *et al.* [4]: Review paper
- Bugler *et al.* [114]: CBS-APNO/G3/G4//B3LYP/cc-pVTZ

Of these sources, Bugler *et al.* [114] performed quantum chemical calculations at a similar level of theory as the current study for the gas-phase thermochemistry of 60 nitrogenous compounds; they were comprehensively validated with the existing literature data.

Table 7 shows thermochemistry comparison for all nine nitrogen-containing species calculated in this study: N₂H₂, NNH, NH₂, NH, HCN, HNC, HNCO, CN and NCO. Excellent agreement was obtained for the 298 K enthalpies of formation ($\Delta_f H^\theta$), 298 K entropies (S^θ) and heat capacities (C_p) at selected temperatures (differences were within 0.9 kcal mol⁻¹ and 0.4 cal K⁻¹ mol⁻¹, respectively). This comparison indicated the reliability of the method and approach adopted for computing thermochemical values in this work.

Table 7: Thermochemistry comparison for all nitrogen containing species. (Units: kcal mol⁻¹ for $\Delta_f H_\theta$, cal K⁻¹ mol⁻¹ for S_θ and C_p)

Species	Source	H_f	S	C_p						
		298 K	298 K	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
N ₂ H ₂	Current study	48.6	52.1	8.3	9.1	10.1	11.1	12.9	14.3	16.5
	ATcT	47.8	-	-	-	-	-	-	-	-
	Bugler <i>et al.</i>	48.6	52.1	8.3	9.2	10.2	11.2	13.1	14.6	16.9
NNH	Current study	60.3	53.6	8.3	8.7	9.2	9.7	10.5	11.2	12.4
	ATcT and Glarborg <i>et al.</i>	59.6	53.7	8.2	8.6	9.1	9.6	10.5	11.3	12.4
	Bugler <i>et al.</i>	60.3	53.6	8.3	8.7	9.3	9.8	10.8	11.6	13.0
NH ₂	Current study	44.6	46.5	8.0	8.2	8.5	8.8	9.4	10.1	11.4
	ATcT and Glarborg <i>et al.</i>	44.5	46.6	8.1	8.2	8.5	8.8	9.5	10.2	11.6
	Bugler <i>et al.</i>	44.6	46.5	8.0	8.2	8.5	8.8	9.5	10.2	11.6
NH	Current study	85.1	43.3	7.0	7.0	7.0	7.0	7.2	7.4	7.9

	ATcT and Glarborg <i>et al.</i>	85.8	43.3	7.0	7.0	7.0	7.0	7.2	7.5	8.1
	Bugler <i>et al.</i>	85.1	43.3	7.0	7.0	7.0	7.0	7.2	7.4	8.0
HCN	Current study	31.3	48.1	8.4	9.2	9.8	10.3	11.1	11.8	13.0
	ATcT and Glarborg <i>et al.</i>	30.9	48.2	8.6	9.4	10.0	10.5	11.3	12.0	13.2
	Bugler <i>et al.</i>	31.3	47.9	8.1	8.8	9.4	9.9	10.6	11.2	12.3
HNC	Current study	46.0	48.7	9.3	9.9	10.4	10.8	11.4	12.0	13.0
	ATcT and Glarborg <i>et al.</i>	46.0	49.1	9.6	10.2	10.6	10.9	11.6	12.1	13.1
	Bugler <i>et al.</i>	45.8	47.7	7.6	8.2	8.8	9.3	10.0	10.7	11.7
HNCO	Current study	-28.7	57.1	11.0	12.3	13.2	14.0	15.2	16.1	17.6
	ATcT	-28.4	-	-	-	-	-	-	-	-
	Bugler <i>et al.</i>	-28.7	57.0	10.8	12.2	13.3	14.1	15.5	16.5	18.3
CN	Current study	106.2	48.3	7.0	7.0	7.1	7.2	7.6	7.9	8.3
	ATcT and Glarborg <i>et al.</i>	105.2	48.4	7.0	7.0	7.2	7.3	7.7	8.0	8.5
	Bugler <i>et al.</i>	105.3	48.4	7.0	7.0	7.1	7.3	7.6	7.9	8.4
NCO	Current study	29.6	54.1	9.4	10.3	11.1	11.7	12.6	13.3	14.1
	ATcT	30.5	-	-	-	-	-	-	-	-
	Bugler <i>et al.</i>	29.6	54.1	9.4	10.3	11.1	11.7	12.7	13.3	14.1

3.4. Implications for kinetic model development

One of the major applications of accurate rate constants and thermochemistry is for the development of detailed chemical kinetic models. Based on the extensive literature review shown in Table 1, two recently developed kinetic models (ammonia/C0-C2 oxidation) from Deng *et al.* [9] and Glarborg *et al.* [4] were selected for examining the effects of inclusion of the newly calculated rate constants on the speciation predictions.

Figure 14 shows the rate constant comparison between the current study and those obtained from the above two literature models. First, rates from the models of Deng and Glarborg overlapped for all reactions shown in the figure. Second, H-atom abstraction by the OH radical was the dominant channel, while the abstraction by molecular oxygen in the HCN system showed the slowest rate across the entire temperature range ($k < 1\text{E}+06 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Third, the rate constants for all these abstraction channels converged towards the high temperatures, and fourth, the biggest discrepancies between the theoretical results from the current study and the rates obtained from the two models were found for the reaction:

$\text{HCN} + \text{O} \leftrightarrow \text{CN} + \text{OH}$ and $\text{HNCO} + \text{OH} \leftrightarrow \text{NCO} + \text{H}_2\text{O}$, quantitatively. At 1300 K, the differences were a factor of about six and three, respectively.

All calculated rate coefficients were incorporated into the two kinetic models, resulting in two *modified model*, speciation simulations for HCN and HNCO, which were performed under the conditions shown in Table 1. The pressure, temperature range and residence time were set to be ten atm, 600 – 2000 K and 10 s respectively. Figure 15 shows the simulated speciation profiles for HCN and HNCO. Using both Deng and Glarborg's models as the original model, the modified model predicted higher concentrations of both HCN and HNCO, at the point of peak concentration; the differences were a factor of about 1.3 and 3.5 for HCN and HNCO respectively. This result indicates that further investigation to improve the kinetic model is necessary, which is beyond the scope of this paper.

(a) HCN system

(b) HNCO system

Figure 14: Rate constant comparisons between current study and rates from the Deng *et al.* [9] and Glarborg *et al.* [4].

Figure 15: Simulated speciation profiles of HCN and HNCO.

4. Conclusions

This study presented systematic quantum chemical calculations for important reactions in gas-phase nitrogen chemistry. Temperature-dependent rate coefficients for 14 reactions of the N_xH_y , HCN and HNCO systems were calculated based on the transition state theory (TST). These reactions included isomerization, dissociation, and abstraction reaction types. Thermodynamic properties of the nitrogenous species in these reactions were also carried out based on statistic thermodynamics. Calculated barrier heights, rate constants and thermochemistry (enthalpy, entropy and heat capacity) were comprehensively compared against both experimental and theoretical results in the literature. Overall, excellent agreements were obtained. Viewed from the application, all calculated rate coefficients were implemented into the two recently developed kinetic models; results from the simulation showed the influences of the updated rates on the concentration profiles of the intermediates, HCN and HNCO, demonstrating that further investigation is necessary for improvement and development of the kinetic model.

Supplementary Material 1: Additional information

Supplementary Material 2: All input files for the MultiWell solver

Acknowledgements

The authors gratefully acknowledge the KAUST Super-computing Laboratory (KSL) for providing computing re-sources and technical support. Research performed by the Clean Combustion Research Center was supported by King Abdullah University of Science and Technology (KAUST) and Saudi Aramco.

References

- [1] Valera-Medina A, Xiao H, Owen-Jones M, David WIF, Bowen PJ. Ammonia for power. *Progress in Energy and Combustion Science*. 2018;69:63-102.
- [2] Miller JA, Bowman CT. Mechanism and modeling of nitrogen chemistry in combustion. *Progress in Energy and Combustion Science*. 1989;15:287-338.
- [3] Dagaut P, Glarborg P, Alzueta MU. The oxidation of hydrogen cyanide and related chemistry. *Progress in Energy and Combustion Science*. 2008;34:1-46.

- [4] Glarborg P, Miller JA, Ruscic B, Klippenstein SJ. Modeling nitrogen chemistry in combustion. *Progress in Energy and Combustion Science*. 2018;67:31-68.
- [5] Faravelli T, Frassoldati A, Ranzi E. Kinetic modeling of the interactions between NO and hydrocarbons in the oxidation of hydrocarbons at low temperatures. *Combustion and Flame*. 2003;132:188-207.
- [6] Sivaramakrishnan R, Brezinsky K, Dayma G, Dagaut P. High pressure effects on the mutual sensitization of the oxidation of NO and CH₄–C₂H₆ blends. *Physical Chemistry Chemical Physics*. 2007;9:4230-44.
- [7] Rasmussen CL, Rasmussen AE, Glarborg P. Sensitizing effects of NO_x on CH₄ oxidation at high pressure. *Combustion and Flame*. 2008;154:529-45.
- [8] Mathieu O, Pemelton JM, Bourque G, Petersen EL. Shock-induced ignition of methane sensitized by NO₂ and N₂O. *Combustion and Flame*. 2015;162:3053-70.
- [9] Deng F, Yang F, Zhang P, Pan Y, Bugler J, Curran HJ, *et al.* Towards a kinetic understanding of the NO_x promoting-effect on ignition of coalbed methane: A case study of methane/nitrogen dioxide mixtures. *Fuel*. 2016;181:188-98.
- [10] Zhang Y, Mathieu O, Petersen EL, Bourque G, Curran HJ. Assessing the predictions of a NO_x kinetic mechanism on recent hydrogen and syngas experimental data. *Combustion and Flame*. 2017;182:122-41.
- [11] Mei B, Zhang X, Ma S, Cui M, Guo H, Cao Z, *et al.* Experimental and kinetic modeling investigation on the laminar flame propagation of ammonia under oxygen enrichment and elevated pressure conditions. *Combustion and Flame*. 2019;210:236-46.
- [12] ANSYS Chemkin-Pro 172, ANSYS, Inc: San Diego. 2016.
- [13] Dove JE, Nip WS. A shock-tube study of ammonia pyrolysis. *Canadian Journal of Chemistry*. 1979;57:689-701.
- [14] Yumura M, Asaba T. Rate constants of chemical reactions in the high temperature pyrolysis of ammonia. *Symposium (International) on Combustion*. 1981;18:863-72.
- [15] Bahng M-K, Macdonald RG. Determination of the rate constants for the radical–radical reactions NH₂($\tilde{X}2B1$) + NH($X3\Sigma^-$) and NH₂($\tilde{X}2B1$) + H($2S$) at 293 K. *The Journal of Physical Chemistry A*. 2009;113:2415-23.
- [16] Davidson DF, Kohse-Höinghaus K, Chang AY, Hanson RK. A pyrolysis mechanism for ammonia. *International Journal of Chemical Kinetics*. 1990;22:513-35.
- [17] Röhrig M, Wagner HG. The reactions of NH($X3\Sigma^-$) with the water gas components CO₂, H₂O, and H₂. *Symposium (International) on Combustion*. 1994;25:975-81.
- [18] Linder DP, Duan X, Page M. *Ab Initio* variational transition state theory calculations for the H + NH₂ .tautm. H₂ + NH hydrogen abstraction reaction on the triplet potential energy surface. *The Journal of Physical Chemistry*. 1995;99:11458-63.
- [19] Mackie JC, Bacskey GB. Quantum chemical study of the mechanism of reaction between NH ($X3\Sigma^-$) and H₂, H₂O, and CO₂ under combustion conditions. *The Journal of Physical Chemistry A*. 2005;109:11967-74.
- [20] Fontijn A, Shamsuddin SM, Crammond D, Marshall P, Anderson WR. Kinetics of the NH reaction with H₂ and reassessment of HNO formation from NH + CO₂, H₂O. *Combustion and Flame*. 2006;145:543-51.
- [21] Shrestha KP, Seidel L, Zeuch T, Mauss F. Detailed kinetic mechanism for the oxidation of ammonia including the formation and reduction of nitrogen oxides. *Energy & Fuels*. 2018;32:10202-17.
- [22] Samu V, Varga T, Rahinov I, Cheskis S, Turányi T. Determination of rate parameters based on NH₂ concentration profiles measured in ammonia-doped methane–air flames. *Fuel*. 2018;212:679-83.
- [23] Kimball-Linne MA, Hanson RK. Combustion-driven flow reactor studies of thermal DeNO_x reaction kinetics. *Combustion and Flame*. 1986;64:337-51.
- [24] Cheskis SG, Sarkisov OM. Flash photolysis of ammonia in the presence of oxygen. *Chemical Physics Letters*. 1979;62:72-6.
- [25] Cohen N, Westberg KR. Chemical kinetic data sheets for high - temperature reactions. Part II. *Journal of Physical and Chemical Reference Data*. 1991;20:1211-311.
- [26] Fagerström K, Jodkowski JT, Lund A, Ratajczak E. Kinetics of the self-reaction and the reaction with OH of the amidogen radical. *Chemical Physics Letters*. 1995;236:103-10.
- [27] Mousavipour SH, Pirhadi F, HabibAgahi A. A theoretical investigation on the kinetics and mechanism of the reaction of amidogen with hydroxyl radical. *The Journal of Physical Chemistry A*. 2009;113:12961-71.
- [28] Klippenstein SJ, Harding LB, Ruscic B, Sivaramakrishnan R, Srinivasan NK, Su MC, *et al.* Thermal decomposition of NH₂OH and subsequent reactions: *Ab initio* transition state theory and reflected shock tube experiments. *The Journal of Physical Chemistry A*. 2009;113:10241-59.
- [29] Chuang Y-Y, Truhlar DG. Improved dual-level direct dynamics method for reaction rate calculations with inclusion of multidimensional tunneling effects and validation for the reaction of H with trans-N₂H₂. *The Journal of Physical Chemistry A*. 1997;101:3808-14.
- [30] Kobayashi Y, Kamiya M, Hirao K. The hydrogen abstraction reactions: A multireference Møller–Plesset perturbation (MRMP) theory study. *Chemical Physics Letters*. 2000;319:695-700.
- [31] Zheng J, Rocha RJ, Pelegrini M, Ferrão LFA, Carvalho EFV, Roberto-Neto O, *et al.* A product branching ratio controlled by vibrational adiabaticity and variational effects: Kinetics of the H + trans-N₂H₂ reactions. *The Journal of Chemical Physics*. 2012;136:184310.

- [32] Linder DP, Duan X, Page M. Thermal rate constants for $R+N_2H_2 \rightarrow RH+N_2H$ ($R=H, OH, NH_2$) determined from multireference configuration interaction and variational transition state theory calculations. *The Journal of Chemical Physics*. 1996;104:6298-307.
- [33] Walch SP. Theoretical characterization of selected regions of the ground state potential surface of N_2H_2 . *The Journal of Chemical Physics*. 1989;91:389-94.
- [34] Bozzelli JW, Dean AM. $O + NNH$: A possible new route for NOX formation in flames. *International Journal of Chemical Kinetics*. 1995;27:1097-109.
- [35] Klippenstein SJ, Harding LB, Glarborg P, Miller JA. The role of NNH in NO formation and control. *Combustion and Flame*. 2011;158:774-89.
- [36] Boden JC, Thrush BA, Norrish RGW. Kinetics of reactions involving CN emission IV. Study of the reactions of CN by electronic absorption spectroscopy. *Proceedings of the Royal Society of London Series A Mathematical and Physical Sciences*. 1968;305:107-23.
- [37] Albers EA, Hoyermann K, Schacke H, Schmatjko KJ, Wagner HG, Wolfrum J. Absolute rate coefficients for the reaction of H-atoms with N_2O and some reactions of CN radicals. *Symposium (International) on Combustion*. 1975;15:765-73.
- [38] Schacke H, Wagner HG, Wolfrum J. Reaktionen von Molekülen in definierten Schwingungszuständen (IV). Reaktionen schwingungsangeregter Cyan-Radikale mit Wasserstoff und einfachen Kohlenwasserstoffen. *Berichte der Bunsengesellschaft für physikalische Chemie*. 1977;81:670-6.
- [39] Szekely A, Hanson RK, Bowman CT. High-temperature determination of the rate coefficient for the reaction $H_2 + CN \rightarrow H + HCN$. *International Journal of Chemical Kinetics*. 1983;15:915-23.
- [40] Li X, Sayah N, Jackson WM. Laser measurements of the effects of vibrational energy on the reactions of CN. *The Journal of Chemical Physics*. 1984;81:833-40.
- [41] Bair RA, Jr. THD. Theoretical studies of the reactions of HCN with atomic hydrogen. *The Journal of Chemical Physics*. 1985;82:2280-94.
- [42] Wagner AF, Bair RA. An *ab initio* determination of the rate constant for $H_2 + CN \rightarrow H + HCN$. *International Journal of Chemical Kinetics*. 1986;18:473-86.
- [43] De Juan J, Smith IWM, Veyret B. Pulsed photolysis-laser-induced fluorescence measurements of the rate constants for reactions of the cyanogen radical with hydrogen, oxygen, ammonia, hydrogen chloride, hydrogen bromide, and hydrogen iodide. *The Journal of Physical Chemistry*. 1987;91:69-72.
- [44] Balla RJ, Pasternack L. Kinetics of gas-phase cyanogen by diode laser absorption. *The Journal of Physical Chemistry*. 1987;91:73-8.
- [45] Sims IR, Smith IWM. Rate constants for the reactions $CN(\nu=0)$, $CN(\nu=1)+H_2$, $D_2 \rightarrow HCN$, $DCN+H$, D between 295 and 768 K, and comparisons with transition state theory calculations. *Chemical Physics Letters*. 1988;149:565-71.
- [46] Natarajan K, Roth P. A shock tube study of CN radical reactions with H_2 and NO verified by H, N and O atom measurements. *Symposium (International) on Combustion*. 1988;21:729-37.
- [47] Atakan B, Jacobs A, Wahl M, Weller R, Wolfrum J. Kinetic studies of the gas-phase reactions of CN with O_2 and H_2 from 294 to 1000 K. *Chemical Physics Letters*. 1989;154:449-53.
- [48] Sun Q, Yang DL, Wang NS, Bowman JM, Lin MC. Experimental and reduced dimensionality quantum rate coefficients for $H_2(D_2)+CN \rightarrow H(D)CN+H(D)$. *The Journal of Chemical Physics*. 1990;93:4730-9.
- [49] Lambert HM, Carrington T, Filseth SV, Sadowski CM. Cross sections and energy disposal for cyanogen(X) produced in the hydrogen atom + hydrogen cyanide reaction at 53 and 58 kcal mol⁻¹ collision energies. *The Journal of Physical Chemistry*. 1993;97:128-33.
- [50] Wooldridge ST, Hanson RK, Bowman CT. A shock tube study of reactions of CN with HCN, OH, and H_2 using CN and OH laser absorption. *International Journal of Chemical Kinetics*. 1996;28:245-58.
- [51] Sumathi R, Nguyen MT. A theoretical study of the CH_2N system: Reactions in both lowest lying doublet and quartet states. *The Journal of Physical Chemistry A*. 1998;102:8013-20.
- [52] He G, Tokue I, Macdonald RG. Thermal rate constant for $CN + H_2/D_2 \rightarrow HCN/DCN + H/D$ reaction from $T = 293$ to 380 K. *The Journal of Physical Chemistry A*. 1998;102:4585-91.
- [53] Jiang B, Guo H. Competition between abstraction and exchange channels in $H + HCN$ reaction: Full-dimensional quantum dynamics. *The Journal of Chemical Physics*. 2013;139:224310.
- [54] Davies PB, Thrush BA. Reactions of oxygen atoms with hydrogen cyanide, cyanogen chloride and cyanogen bromide. *Transactions of the Faraday Society*. 1968;64:1836-43.
- [55] Morley C. The formation and destruction of hydrogen cyanide from atmospheric and fuel nitrogen in rich atmospheric-pressure flames. *Combustion and Flame*. 1976;27:189-204.
- [56] Haynes BS. The oxidation of hydrogen cyanide in fuel-rich flames. *Combustion and Flame*. 1977;28:113-21.
- [57] Perry RA, Melius CF. The rate and mechanism of the reaction of HCN with oxygen atoms over the temperature range 540–900 K. *Symposium (International) on Combustion*. 1985;20:639-46.
- [58] Szekely A, Hanson RK, Bowman CT. Shock tube study of the reaction between hydrogen cyanide and atomic oxygen. *Symposium (International) on Combustion*. 1985;20:647-54.

- [59] Miller JA, Parrish C, Brown NJ. A statistical-theoretical investigation of the thermal rate coefficient and branching ratio for the reaction atomic oxygen + hydrogen cyanide .fwdarw. products. The Journal of Physical Chemistry. 1986;90:3339-45.
- [60] Roth P, Löhner R, Hermanns HD. Stoßwellenmessungen zur Kinetik der Reaktion HCN + O. Berichte der Bunsengesellschaft für physikalische Chemie. 1980;84:835-40.
- [61] Cicerone RJ, Zellner R. The atmospheric chemistry of hydrogen cyanide (HCN). Journal of Geophysical Research: Oceans. 1983;88:10689-96.
- [62] Szekely A, Hanson RK, Bowman CT. High temperature determination of the rate coefficient for the reaction $\text{H}_2\text{O} + \text{CN} \rightarrow \text{HCN} + \text{OH}$. International Journal of Chemical Kinetics. 1984;16:1609-21.
- [63] Jacobs A, Wahl M, Weller R, Wolfrum J. Kinetic studies of the reaction of CN with H_2O from 518 to 1027 K. Chemical Physics Letters. 1988;144:203-7.
- [64] Wooldridge ST, Hanson RK, Bowman CT. Simultaneous laser absorption measurements of CN and OH in a shock tube study of $\text{HCN} + \text{OH} \rightarrow$ products. International Journal of Chemical Kinetics. 1995;27:1075-87.
- [65] Wang CY, Zhang S, Li QS. *Ab initio* study of rate constants of the reaction: $\text{HCN} + \text{OH} \rightarrow \text{CN} + \text{H}_2\text{O}$. Theoretical Chemistry Accounts. 2002;108:341-6.
- [66] Galano A. Mechanism of OH radical reactions with HCN and CH_3CN : OH regeneration in the presence of O_2 . The Journal of Physical Chemistry A. 2007;111:5086-91.
- [67] Miller JA, Branch MC, McLean WJ, Chandler DW, Smooke MD, Kee RJ. The conversion of HCN to NO and N_2 in $\text{H}_2\text{-O}_2\text{-HCN-Ar}$ flames at low pressure. Symposium (International) on Combustion. 1985;20:673-84.
- [68] Lee TJ, Rendell AP. The structure and energetics of the $\text{HCN} \rightarrow \text{HNC}$ transition state. Chemical Physics Letters. 1991;177:491-7.
- [69] Lin MC, He Y, Melius CF. Implications of the $\text{HCN} \rightarrow \text{HNC}$ process to high-temperature nitrogen-containing fuel chemistry. International Journal of Chemical Kinetics. 1992;24:1103-7.
- [70] Abashkin Y, Russo N, Toscano M. Transition states and energy barriers from density functional studies: Representative isomerization reactions. International Journal of Quantum Chemistry. 1994;52:695-704.
- [71] Gazdy B, Musaev DG, Bowman JM, Morokuma K. An *ab initio* study of the ground and first excited state of $\text{HCN} \leftrightarrow \text{HNC}$ isomerization and a calculation of the $\text{HNC A} \rightarrow \text{X}$ fluorescence spectrum. Chemical Physics Letters. 1995;237:27-32.
- [72] Bacalzo-Gladden F, Musaev DG, Lin MC. A model calculation for the isomerization and decomposition of chemisorbed HCN on the $\text{Si}(100)\text{-}2\times 1$ surface. Journal of the Chinese Chemical Society. 1999;46:395-402.
- [73] Kumeda Y, Minami Y, Takano K, Taketsugu T, Tsuneto H. *Ab initio* molecular orbital dynamic reaction path simulations of $\text{HNC} \rightleftharpoons \text{HCN}$ isomerization reaction: Election of the reaction mode in a thermally excited system. Journal of Molecular Structure: THEOCHEM. 1999;458:285-91.
- [74] Maeda S, Ohno K. A new approach for finding a transition state connecting a reactant and a product without initial guess: Applications of the scaled hypersphere search method to isomerization reactions of HCN, $(\text{H}_2\text{O})_2$, and alanine dipeptide. Chemical Physics Letters. 2005;404:95-9.
- [75] Isaacson AD. Including anharmonicity in the calculation of rate constants. 1. The HCN/HNC isomerization reaction. The Journal of Physical Chemistry A. 2006;110:379-88.
- [76] Halpern AM. Computational studies of chemical reactions: The HNC-HCN and $\text{CH}_3\text{NC-CH}_3\text{CN}$ isomerizations. Journal of Chemical Education. 2006;83:69.
- [77] Quapp W, Zech A. Transition state theory with Tsallis statistics. Journal of Computational Chemistry. 2010;31:573-85.
- [78] Baraban JH, Changala PB, Mellau GC, Stanton JF, Merer AJ, Field RW. Spectroscopic characterization of isomerization transition states. Science. 2015;350:1338-42.
- [79] Glarborg P, Marshall P. Importance of the hydrogen isocyanide isomer in modeling hydrogen cyanide oxidation in combustion. Energy & Fuels. 2017;31:2156-63.
- [80] Louge MY, Hanson RK. High temperature kinetics of NCO. Combustion and Flame. 1984;58:291-300.
- [81] Perry RA. Kinetics of the reactions of NCO radicals with H_2 and NO using laser photolysis-laser induced fluorescence. The Journal of Chemical Physics. 1985;82:5485-8.
- [82] Miller JA, Melius CF. A theoretical analysis of the reaction between hydrogen atoms and isocyanic acid. International Journal of Chemical Kinetics. 1992;24:421-32.
- [83] Mertens JD, Hanson RK. A shock tube study of $\text{H+HNCO} \rightarrow \text{H}_2\text{+NCO}$ and the thermal decomposition of NCO. Symposium (International) on Combustion. 1996;26:551-5.
- [84] Nguyen MT, Sengupta D, Vereecken L, Peeters J, Vanquickenborne LG. Reaction of isocyanic acid and hydrogen atom ($\text{H} + \text{HNCO}$): Theoretical characterization. The Journal of Physical Chemistry. 1996;100:1615-21.
- [85] Liu X, Machara NP, Coombe RD. Dynamics of the atomic oxygen(1D) + isocyanic acid reaction. The Journal of Physical Chemistry. 1991;95:4983-8.
- [86] He Y, Lin MC, Wu CH, Melius CF. The reaction of HNCO with NO_2 in shock waves. Symposium (International) on Combustion. 1992;24:711-7.

- [87] Wooldridge MS, Hanson RK, Bowman CT. A shock tube study of $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ and $\text{HNCO} + \text{OH} \rightarrow$ products via simultaneous laser absorption measurements of OH and CO_2 . *International Journal of Chemical Kinetics*. 1996;28:361-72.
- [88] Sengupta D, Nguyen MT. Mechanism of $\text{NH}_2 + \text{CO}_2$ formation in $\text{OH} + \text{HNCO}$ reaction: Rate constant evaluation via *ab initio* calculations and statistical theory. *The Journal of Chemical Physics*. 1997;106:9703-7.
- [89] Tully FP, Perry RA, Thorne LR, Allendorf MD. Free-radical oxidation of isocyanic acid. *Symposium (International) on Combustion*. 1989;22:1101-6.
- [90] Mertens JD, Chang AY, Hanson RK, Bowman CT. A shock tube study of reactions of atomic oxygen with isocyanic acid. *International Journal of Chemical Kinetics*. 1992;24:279-95.
- [91] Baulch DL, Bowman CT, Cobos CJ, Cox RA, Just T, Kerr JA, *et al.* Evaluated kinetic data for combustion modeling: Supplement II. *Journal of Physical and Chemical Reference Data*. 2005;34:757-1397.
- [92] Dean AM, Bozzelli JW. Combustion Chemistry of Nitrogen. In: Gardiner WC, editor. *Gas-Phase Combustion Chemistry*. New York, NY: Springer New York; 2000. p. 125-341.
- [93] Foresman J, Ortiz J, Cioslowski J, Fox D. *Gaussian 09, Revision D. 01*; Gaussian, Inc. Wallingford, CT. 2009.
- [94] Zhao Y, Truhlar DG. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor Chem Acc*. 2008;120:215-41.
- [95] McLean AD, Chandler GS. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, $Z=11-18$. *The Journal of Chemical Physics*. 1980;72:5639-48.
- [96] Krishnan R, Binkley JS, Seeger R, Pople JA. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *The Journal of Chemical Physics*. 1980;72:650-4.
- [97] III GDP, Bartlett RJ. A full coupled-cluster singles and doubles model: The inclusion of disconnected triples. *The Journal of Chemical Physics*. 1982;76:1910-8.
- [98] Jr. THD. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *The Journal of Chemical Physics*. 1989;90:1007-23.
- [99] Møller C, Plesset MS. Note on an approximation treatment for many-electron systems. *Physical Review*. 1934;46:618-22.
- [100] Ochterski JW, Petersson GA, Jr. JAM. A complete basis set model chemistry. V. Extensions to six or more heavy atoms. *The Journal of Chemical Physics*. 1996;104:2598-619.
- [101] Curtiss LA, Raghavachari K, Redfern PC, Rassolov V, Pople JA. Gaussian-3 (G3) theory for molecules containing first and second-row atoms. *The Journal of Chemical Physics*. 1998;109:7764-76.
- [102] Curtiss LA, Redfern PC, Raghavachari K. Gaussian-4 theory. *The Journal of Chemical Physics*. 2007;126:084108.
- [103] Barker JR, Nguyen TL, Stanton JF, C. Aieta MC, Gabas F, Kuma TJD, *et al.* *MultiWell-2016 Software Suite*; J. R. Barker, University of Michigan, Ann Arbor, Michigan, USA. 2016.
- [104] Eyring H. The activated complex in chemical reactions. *The Journal of Chemical Physics*. 1935;3:107-15.
- [105] Eckart C. The penetration of a potential barrier by electrons. *Physical Review*. 1930;35:1303-9.
- [106] Gordon S, McBride BJ. Computer program for calculation of complex chemical equilibrium compositions, rocket performance, incident and reflected shocks, and Chapman-Jouguet detonations. *NASA STI*. 1976.
- [107] Li Y, Klippenstein SJ, Zhou C-W, Curran HJ. Theoretical kinetics analysis for H atom addition to 1,3-butadiene and related reactions on the $\dot{\text{C}}_4\text{H}_7$ potential energy surface. *The Journal of Physical Chemistry A*. 2017;121:7433-45.
- [108] Bugler J, Power J, Curran HJ. A theoretical study of cyclic ether formation reactions. *Proceedings of the Combustion Institute*. 2017;36:161-7.
- [109] Li Y, Curran HJ. Extensive theoretical study of the thermochemical properties of unsaturated hydrocarbons and allylic and super-allylic radicals: The development and optimization of group additivity values. *The Journal of Physical Chemistry A*. 2018;122:4736-49.
- [110] W. C. JG. *Gas-Phase Combustion Chemistry*: Springer New York; 2012.
- [111] Ruscic B, Pinzon RE, Morton ML, von Laszewski G, Bittner SJ, Nijssure SG, *et al.* Introduction to active thermochemical tables: Several “key” enthalpies of formation revisited. *The Journal of Physical Chemistry A*. 2004;108:9979-97.
- [112] Branko R, Reinhardt EP, Gregor von L, Deepti K, Alexander B, David L, *et al.* Active thermochemical tables: Thermochemistry for the 21st century. *Journal of Physics: Conference Series*. 2005;16:561.
- [113] Ruscic B, Feller D, Peterson KA. Active thermochemical tables: Dissociation energies of several homonuclear first-row diatomics and related thermochemical values. *Theor Chem Acc*. 2013;133:1415.
- [114] Bugler J, Somers KP, Simmie JM, Güthe F, Curran HJ. Modeling nitrogen species as pollutants: Thermochemical influences. *The Journal of Physical Chemistry A*. 2016;120:7192-7.