An experimental and theoretical investigation of HCN production in the Hadean Earth atmosphere

Ben K. D. Pearce*,[1] Chao He,[1] and Sarah M. Hörst[1]

[1] *Department of Earth and Planetary Science, Johns Hopkins University, Baltimore, MD, 21218, USA**

SUPPORTING INFORMATION

In Table S1, we display the 53 chemical reactions added to the CRAHCN-O chemical network for our 0D chemical kinetics models of the Hadean Earth. CRAHCN-O was originally developed to accurately model HCN and H_2CO in atmospheres dominated by any of H_2, CH_4, H_2O, CO_2, and N_2. We added these new reactions in order to better estimate the production of hydrocarbons and a few other potential molecules of interest including NH_3 and NO.

Table S1. New two-body reactions added to CRAHCN-O for our Hadean Earth atmospheric models, and their experimental or theoretical Arrhenius coefficients. These reactions are added to better estimate the production of hydrocarbons and other potential species of interest such as NO and NH_3. For complete network, see tables in Pearce et al. (1, 2, 3). The Arrhenius expression is $k(T) = \alpha \left(\frac{T}{300}\right)^{\beta} e^{-\gamma/T}$.

Reaction Equation	α	β	γ	Source(s)
$C_2H + H_2 \longrightarrow C_2H_2 + H$	2.5×10^{-11}	0	1560	Baulch et al. (4)
$C_2H + OH \longrightarrow C_2H_2 + {}^3O$	3.0×10^{-11}	0	0	Tsang and Hampson (5)
$C_2H + OH \longrightarrow CO + {}^3CH_2$	3.0×10^{-11}	0	0	Tsang and Hampson (5)
$C_2H + HO_2 \longrightarrow OH + HCCO$	3.0×10^{-11}	0	0	Tsang and Hampson (5)
$C_2H + HCN \longrightarrow HC_3N + H$	5.3×10^{-12}	0	769	Hoobler and Leone (6), Hébrard et al. (7)
$C_2H_2 + {}^3O \longrightarrow CO + {}^3CH_2$	3.5×10^{-12}	1.5	850	Cvetanović (8)
$C_2H_2 + CN \longrightarrow HC_3N + H$	2.3×10^{-10}	0	0	Gannon et al. (9)
$C_2H_2 + CN \longrightarrow HCN + C_2H$	2.2×10^{-10}	0	0	Sayah et al. (10)
$C_2H_4 + {}^3O \longrightarrow HCO + CH_3$	8.9×10^{-13}	1.55	216	Tsang and Hampson (5)
$C_2H_4 + {}^3O \longrightarrow H_2CO + {}^3CH_2$	8.3×10^{-12}	0	754	Westenberg and DeHaas (11)
$C_2H_4 + {}^4N \longrightarrow HCN + CH_3$	2.1×10^{-13}	0	754	Avramenko and Krasnen'kov (12)
$C_2H_4 + OH \longrightarrow C_2H_3 + H_2O \longrightarrow C_2H_2 + H_2O + H$	1.7×10^{-13}	2.75	2100	Tsang and Hampson (5)
$C_2H_4 + CH_3 \longrightarrow C_2H_3 + CH_4 \longrightarrow C_2H_2 + CH_4 + H$	6.9×10^{-12}	0	5600	Baulch et al. (4)
$C_2H_4 + CN \longrightarrow CH_2CHCN + H$	3.2×10^{-10}	0	0	Gannon et al. (9)
$C_2H_4 + CN \longrightarrow HCN + C_2H_3 \longrightarrow HCN + C_2H_2 + H$	2.1×10^{-10}	0	0	Sayah et al. (10)
$C_2H_4 + {}^2N \longrightarrow CH_3CN + H$	2.2×10^{-10}	0	500	Hébrard et al. (7), Balucani et al. (13)
$C_2H_6 + {}^3CH_2 \longrightarrow C_2H_5 + CH_3 \longrightarrow C_2H_4 + CH_3 + H$	1.1×10^{-11}	0	3980	Böhland et al. (14)
$C_2H_6 + {}^3O \longrightarrow C_2H_5 + OH \longrightarrow C_2H_4 + OH + H$	8.6×10^{-12}	1.5	2920	Baulch et al. (4)
$C_2H_6 + H \longrightarrow C_2H_5 + H_2 \longrightarrow C_2H_4 + H_2 + H$	1.2×10^{-11}	1.5	3730	Baulch et al. (4)
$C_2H_6 + OH \longrightarrow C_2H_5 + H_2O \longrightarrow C_2H_4 + H_2O + H$	1.1×10^{-12}	2.0	435	Baulch et al. (4)
$C_2H_6 + CH \longrightarrow C_2H_4 + CH_3$	1.3×10^{-10}	0	0	Galland et al. (15)
$C_2H_6 + CH \longrightarrow CH_3CHCH_2 + H$	3.0×10^{-11}	0	0	Galland et al. (15)
$C_2H_6 + CH_3 \longrightarrow CH_4 + C_2H_5 \longrightarrow CH_4 + C_2H_4 + H$	1.8×10^{-16}	6.0	3040	Baulch et al. (4)
$C_2H_6 + C_2H \longrightarrow C_2H_2 + C_2H_5 \longrightarrow C_2H_2 + C_2H_4 + H$	6.0×10^{-12}	0	0	Baulch et al. (4)
$C_2H_6 + CN \longrightarrow HCN + C_2H_5 \longrightarrow HCN + C_2H_4 + H$	3.5×10^{-12}	2.16	624	Baulch et al. (4)
$C_2H_6 + {}^1O \longrightarrow C_2H_5 + OH \longrightarrow C_2H_4 + OH + H$	6.3×10^{-10}	0	0	Matsumi et al. (16)

* Corresponding author: bpearce6@jhu.edu

$C_2H_6 + {}^1O \longrightarrow C_2H_6 + {}^3O$	7.3×10^{-10}	0	0	Fletcher and Husain (17)
$CH_3CHCH_2 + CN \longrightarrow CH_3CN + C_2H_3 \longrightarrow CH_3CN + C_2H_2 + H$	1.7×10^{-10}	0	-51	Hébrard et al. (7)
$CH_3CHCH_2 + C_2H \longrightarrow CH_2CHCH_2 + C_2H_2$	6.0×10^{-12}	0	0	Tsang (18)
$CH_3OH + {}^4N \longrightarrow CH_3 + HNO$	4.0×10^{-10}	0	4330	Roscoe and Roscoe (19)
$CH_3OH + OH \longrightarrow H_2CO + H_2O + H$	1.1×10^{-12}	1.44	56	Srinivasan et al. (20)
$CH_3CHO + {}^4N \longrightarrow HCN + H_2 + HCO$	1.0×10^{-14}	0	0	Lambert et al. (21)
$CH_3CHO + H \longrightarrow CO + H_2 + CH_3$	5.0×10^{-13}	2.75	486	Sivaramakrishnan et al. (22)
$CH_3CHO + H \longrightarrow CH_4 + HCO$	8.8×10^{-14}	0	0	Lambert et al. (23)
$NH_2 + {}^3O \longrightarrow H + HNO$	7.5×10^{-11}	0	0	Cohen and Westberg (24)
$NH_2 + {}^3O \longrightarrow OH + NH$	1.2×10^{-11}	0	0	Cohen and Westberg (24)
$NH_2 + {}^3O \longrightarrow H_2 + NO$	8.3×10^{-12}	0	0	Cohen and Westberg (24)
$NH_2 + NO \longrightarrow N_2 + H_2O$	5.9×10^{-11}	-2.37	437	Song et al. (25)
$NH_2 + OH \longrightarrow H_2O + NH$	7.7×10^{-13}	1.5	230	Cohen and Westberg (24)
$NH_2 + OH \longrightarrow NH_3 + {}^3O$	5.0×10^{-15}	2.6	870	Cohen and Westberg (24)
$NH_2 + HO_2 \longrightarrow H_2O + HNO$	6.1×10^{-16}	0.55	265	Sumathi and Peyerimhoff (26)
$NH_2 + HO_2 \longrightarrow NH_3 + O_2$	1.9×10^{-16}	1.55	1020	Sumathi and Peyerimhoff (26)
$NH_2 + H_2 \longrightarrow NH_3 + H$	2.1×10^{-12}	0	4281	Demissy and Lesclaux (27)
$NH_2 + C_2H_6 \longrightarrow NH_3 + C_2H_5 \longrightarrow NH_3 + C_2H_4 + H$	6.1×10^{-13}	0	3600	Demissy and Lesclaux (27)
$NH_2 + CH_4 \longrightarrow NH_3 + CH_3$	7.8×10^{-12}	0	4680	Möller and Wagner (28)
$NH_3 + {}^3O \longrightarrow NH_2 + OH$	1.6×10^{-11}	0	3670	Baulch et al. (4)
$NH_3 + OH \longrightarrow NH_2 + H_2O$	3.5×10^{-12}	0	925	Atkinson et al. (29)
$NH_3 + CN \longrightarrow HCN + NH_2$	1.5×10^{-11}	0	181	Sims and Smith (30)
$HNO + H \longrightarrow H_2 + NO$	3.0×10^{-11}	0	500	Tsang and Herron (31)
$HNO + {}^3O \longrightarrow OH + NO$	3.8×10^{-11}	0	0	Inomata and Washida (32)
$HNO + OH \longrightarrow H_2O + NO$	8.0×10^{-11}	0	500	Tsang and Herron (31)
$HNO + CN \longrightarrow HCN + NO$	3.0×10^{-11}	0	0	Tsang and Hampson (5)
$HNO + HCO \longrightarrow H_2CO + NO$	1.0×10^{-12}	0	1000	Tsang and Herron (31)

In Figure S1, we plot Run 2 of Experiments 1–5. Run 1 data is displayed in the main text.

In Figure S2, we investigate the chemical kinetics models of Experiment 2 using a Maxwellian EEDF, for the three chemical networks in this study. These results do not greatly differ from the Druyvestyn EEDF results in Figure 5 in the main text.

REFERENCES

[1]Pearce, B. K. D.; Ayers, P. W.; Pudritz, R. E. CRAHCN-O: A consistent reduced atmospheric hybrid chemical network oxygen extension for hydrogen cyanide and formaldehyde chemistry in CO_2-, N_2-, H_2O-, CH_4-, and H_2-dominated atmospheres. *J. Phys. Chem A.* **2020**, *124*, 8594–8606.

[2]Pearce, B. K. D.; Molaverdikhani, K.; Pudritz, R. E.; Henning, T.; Hébrard, E. HCN production in Titan's Atmosphere: Coupling quantum chemistry and disequilibrium atmospheric modeling. *Astrophys. J* **2020**, *901*, 110.

[3]Pearce, B. K. D.; Molaverdikhani, K.; Pudritz, R. E.; Henning, T.; Cerrillo, K. E. Towards RNA life on Early Earth: From atmospheric HCN to biomolecule production in warm little ponds. *Astrophys. J., in press* **2022**,

[4]Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; et al., Evaluated kinetic data for combustion modelling. *J. Phys. Chem. Ref. Data* **1992**, *21*, 411–429.

[5]Tsang, W.; Hampson, R. F. Chemical Kinetic Data Base for Combustion Chemistry. Part I. Methane and Related Compounds. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1087–1279.

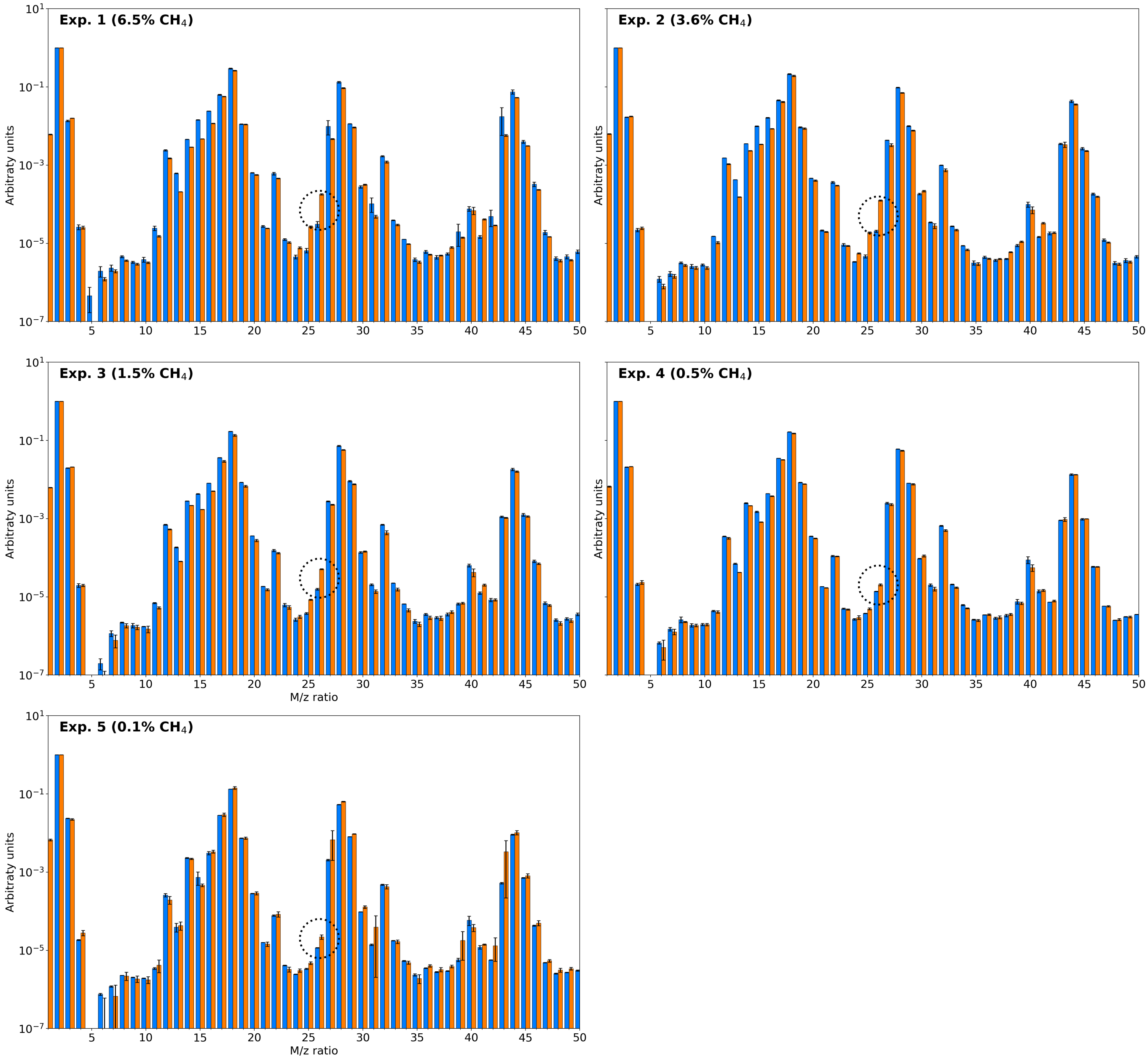

Figure S1. Histogram mass spectra for Run 2 of Experiments 1–5. The 26 peak is circled in each plot to direct the reader's eye to the location where HCN can be detected in our experiments.

[6]Hoobler, R. J.; Leone, S. R. Rate coefficients for reactions of ethyl radical (C_2H) with HCN and CH_3CN: implications for the formation of complex nitriles on titan. *J. Geophys. Res.* **1997**, *102*, 28717–28723.

[7]Hébrard, E.; Dobrijevic, M.; Pernot, P.; Carrasco, N.; Bergeat, A.; Hickson, K. M.; Canosa, A.; Le Picard, S. D.; Sims, I. R. How Measurements of Rate Coefficients at Low Temperature Increase the Predictivity of Photochemical Models of Titan's Atmosphere. *J. Phys. Chem. A* **2009**, *113*, 11227–11237.

[8]Cvetanović, R. J. Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen O(^{3}P) with Unsaturated Hydrocarbons. *J. Phys. Chem. Ref. Data* **1987**, *16*, 261–326.

[9]Gannon, K. L.; Glowacki, D. R.; Blitz, M. A.; Hughes, K. J.; Pilling, M. J.; Seakins, P. W. H atom yields from the reactions of CN radicals with C_2H_2, C_2H_4, C_3H_6, trans−2-C_4H_8, and iso−C_4H_8. *J. Phys. Chem. A* **2007**, *111*, 6679–6692.

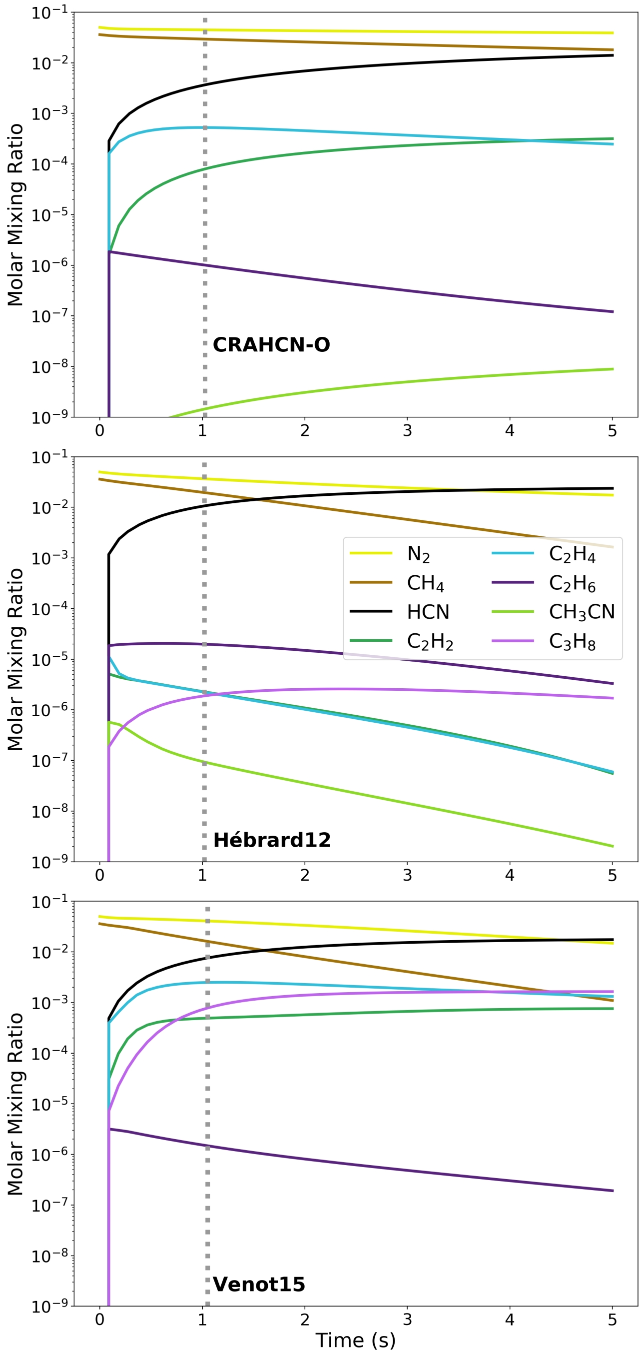

Figure S2. Chemical kinetics simulations of Experiment 2 using three different chemical networks and the Maxwellian EEDF. The grey vertical dotted line represents the time step closest to $t = 1$ second that is used to compare molecule concentrations across simulations.

[10]Sayah, N.; Li, X.; Caballero, J. F.; Jackson, W. M. Laser induced fluorescence studies of CN reactions with alkanes, alkenes and substituted aliphatic species. *J. Photochem. Photobiol. A* **1988**, *45*, 177–194.

[11]Westenberg, A. A.; DeHaas, N. Absolute measurements of the $O + C_2H_4$ rate coefficient. *Symp. Int. Combust. Proc.* **1969**, *12*, 289–299.

[12]Avramenko, L. I.; Krasnen'kov, V. M. Reactions of nitrogen atoms reaction 2. Rate constant and mechanism of the elementary reaction of nitrogen atoms with ethylene. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1964**, 563–566.

[13]Balucani, N.; Skouteris, D.; Leonori, F.; Petrucci, R.; Hamberg, M.; Geppert, W. D.; Casavecchia, P. Combined Crossed Beam and Theoretical Studies of the $N(^2D)$ + C_2H_4 Reaction and Implications for Atmospheric Models of Titan. *J. Phys. Chem. A* **2012**, *116*, 10467–10479.

[14]Böhland, T.; Dobẽ, S.; Temps, F.; Wagner, H. G. Kinetics of the Reactions between $CH_2(\tilde{X}^3B_1)$-Radicals and Saturated Hydrocarbons in the Temperature Range 296 K $\leq$ T $\leq$ 707 K. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 1110–1116.

[15]Galland, N.; Caralp, F.; Hannachi, Y.; Bergeat, A.; Loison, J.-C. Experimental and Theoretical Studies of the Methylidyne $CH(X^2\Pi)$ Radical Reaction with Ethane (C_2H_6): Overall Rate Constant and Product Channels. *J. Phys. Chem. A* **2003**, *107*, 5419–5426.

[16]Matsumi, Y.; Tonokura, K.; Inagaki, Y.; Kawasaki, M. Isotopic branching ratios and translational energy release of H and D atoms in reaction of $O(^1D)$ atoms with alkanes and alkyl chlorides. *J. Phys. Chem.* **1993**, *97*, 6816–6821.

[17]Fletcher, I. S.; Husain, D. The Collisional Quenching of Electronically excited Oxygen Atoms, $O(2^1D_2)$, by the Gases NH_3, H_2O_2, C_2H_6, C_3H_8, and $C(CH_3)_4$, using Time-resolved Attenuation of Atomic Resonance Radiation. *Can. J. Chem.* **1976**, *54*, 1765–1770.

[18]Tsang, W. Chemical kinetic data base for combustion chemistry. Part V. Propene. *J. Phys. Chem. Ref. Data* **1991**, *20*, 221–273.

[19]Roscoe, J. M.; Roscoe, S. G. The Reactions of Active Nitrogen with Simple Alcohols. *Can. J. Chem.* **1993**, *51*, 3671–3679.

[20]Srinivasan, N. K.; Su, M. C.; Michael, J. V. High-temperature rate constants for $CH_3OH + Kr \longrightarrow$ products, $OH + CH_3OH \longrightarrow$ products, $OH + (CH_3)CO \longrightarrow CH_2COCH_3 + H_2O$, and $OH + CH_3 \longrightarrow CH_2 + H_2O$. *J. Phys. Chem. A* **2007**, *111*, 3951–3958.

[21]Lambert, R. M.; Christie, M. I.; Golesworthy, R. C.; Linnett, J. W. Mass spectrometric study of the reaction of nitrogen atoms with acetaldehyde. *Proc. R. Soc. London A* **1968**, *302*, 167–183.

[22]Sivaramakrishnan, R.; Michael, J. V.; Klippenstein, S. J. Direct Observation of Roaming Radicals in the Thermal Decomposition of Acetaldehyde. *J. Phys. Chem. A* **2010**, *114*, 755–764.

[23]Lambert, R. M.; Christie, M. I.; Linnett, J. W. A novel reaction of hydrogen atoms. *Chem. Commun. (London)* **1967**, 388–389.

[24]Cohen, N.; Westberg, K. R. Chemical Kinetic Data Sheets for High-Temperature Reactions. Part II. *J. Phys. Chem. Ref. Data* **1991**, *20*, 1211–1311.

[25]Song, S.; Hanson, R. K.; Bowman, C. T.; Golden, D. M. Shock Tube Determination of the Overall Rate of $NH_2 + NO \longrightarrow$ Products in the Thermal De-NOx Temperature Window. *Int J. Chem. Kinet.* **2001**, *33*, 715–721.

[26]Sumathi, R.; Peyerimhoff, S. D. A quantum statistical analysis of the rate constant for the $HO_2 + NH_2$ reaction. *Chem. Phys. Lett.* **1996**, *263*, 742–748.

[27]Demissy, M.; Lesclaux, R. Kinetics of Hydrogen Abstraction by NH_2 Radicals from Alkanes in the Gas Phase. A Flash Photolysis-Laser Resonance Absorption Study. *J. Am. Chem. Soc.* **1980**, *102*, 2897–2902.

[28]Möller, W.; Wagner, H. G. Messung der geschwindigkeitskonstanten der reaktion $NH_2 + CH_4 \longrightarrow NH_3 + CH_3$ hinter einfallenden stosswellen. *Z. Naturforsch. A* **1984**, *39*, 846–852.

[29]Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOx and SOx species. *Atmos. Chem. Phys.* **2004**, *4*, 1461–1738.

[30]Sims, I. R.; Smith, I. W. M. Pulsed laser photolysis-laser-induced fluorescence measurements on the kinetics of CN(v = 0) and CN(v = 1) with O_2, NH_3 and NO between 294 and 761 K. *J. Chem. Soc. Faraday Trans. 2* **1988**, *84*, 527–539.

[31]Tsang, W.; Herron, J. T. Chemical kinetic data base for propellant combustion. I. Reactions involving NO, NO_2, HNO, HNO_2, HCN and N_2O. *J. Phys. Chem. Ref. Data* **1991**, *20*, 609–663.

[32]Inomata, S.; Washida, N. Rate Constants for the Reactions of NH_2 and HNO with Atomic Oxygen at Temperatures Between 242 and 473 K. *J. Phys. Chem. A* **1999**, *103*, 5023–5031.