# Insights into nitromethane combustion from detailed kinetic modeling – Pyrolysis experiments in jet stirred and flow reactors

**Krishna Prasad Shrestha[1], NicolasVin[2], Olivier Herbinet[2], Lars Seidel[3*], Frédérique Battin-Leclerc[2], Thomas Zeuch[4] and Fabian Mauss[1]**

1. Thermodynamics and Thermal Process Engineering, Brandenburg University of Technology, Siemens-Halske-Ring 8, 03046 Cottbus, Germany

2. Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, BP 20451, 1 rue Grandville, 54000 Nancy, France.

3. LOGE Deutschland GmbH, Burger Chaussee 25, 03044 Cottbus, Germany

4. Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstraße 6, 37077 Göttingen, Germany

## Supplement Material

### 1. Flow reactor - pyrolysis

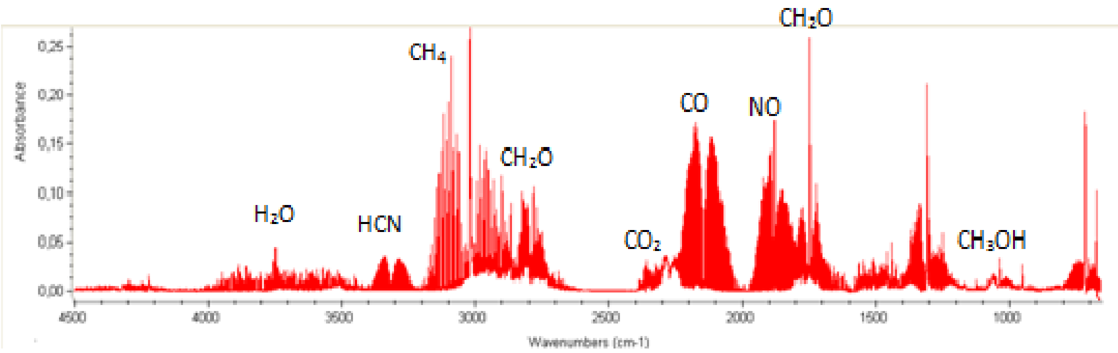


**Figure S1:** FTIR spectrum obtained during nitromethane pyrolysis.

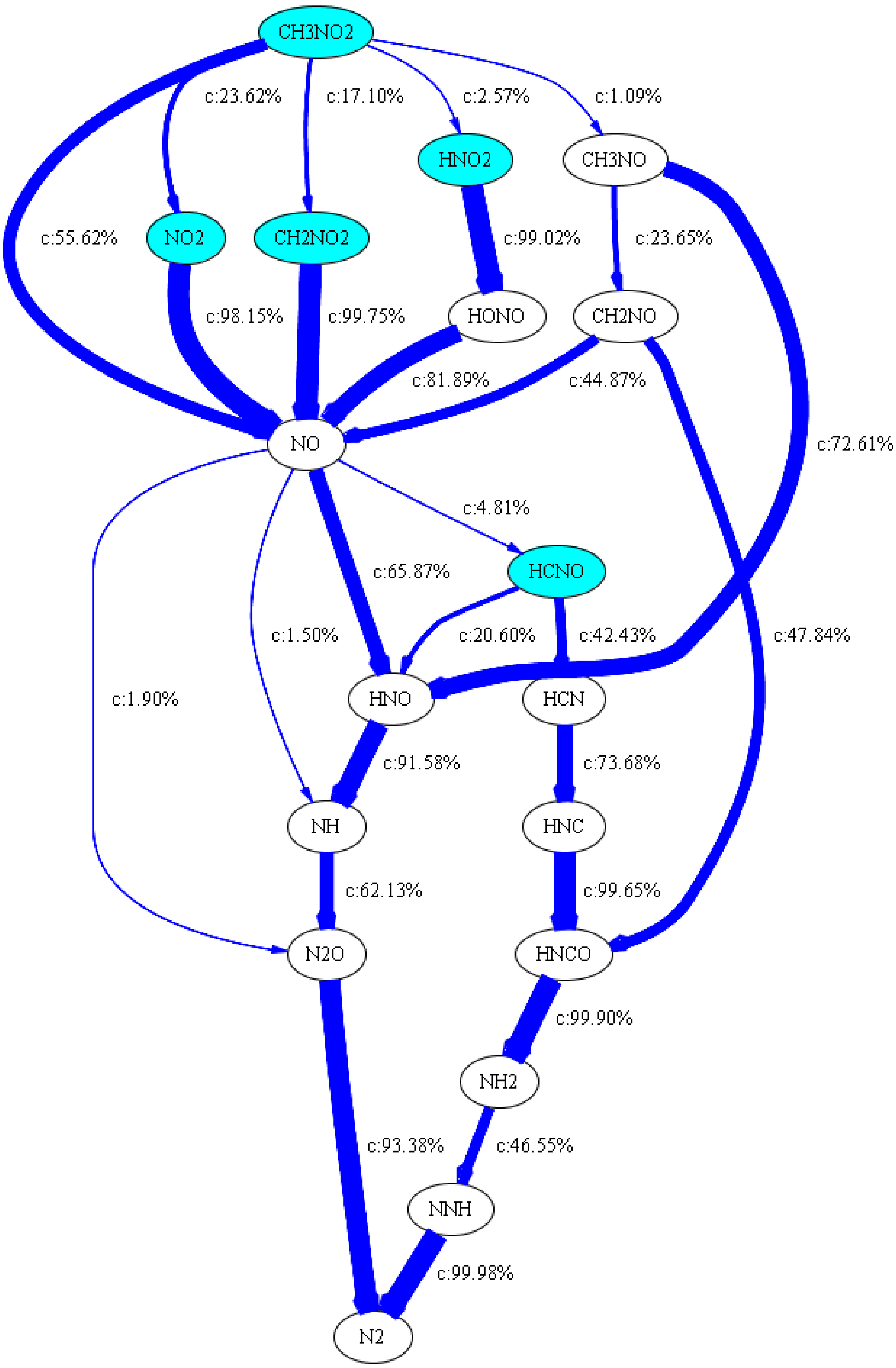


**Figure S2:** Integrated mass flux analysis for the pyrolysis of $CH_3NO_2$/Ar in flow reactor shown in Figure 7. Based on the N-atom. $CH_3NO_2$ 5 % / Ar 95 % (on a mole basis) at 5 Torr (= 0.666 kPa) ), 1200 K at 30 % $CH_3NO_2$ consumption.

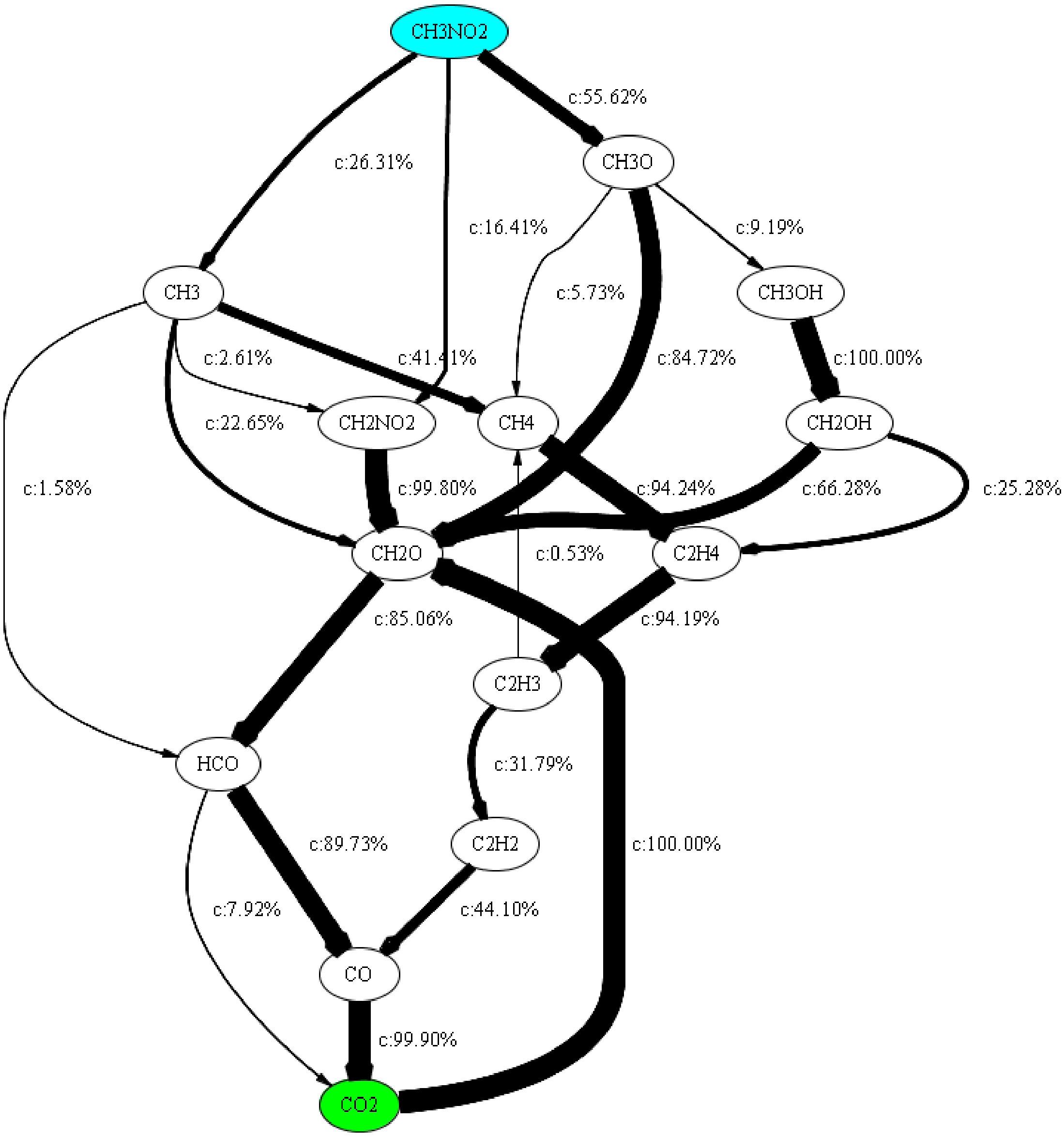


**Figure S3:** Integrated mass flux analysis for the pyrolysis $CH_3NO_2$/Ar in flow reactor shown in Figure 7. Based on the C-atom. $CH_3NO_2$ 5 % / Ar 95 % (on a mole basis) at 5 Torr (= 0.666 kPa), 1200 K at 30 % $CH_3NO_2$ consumption.

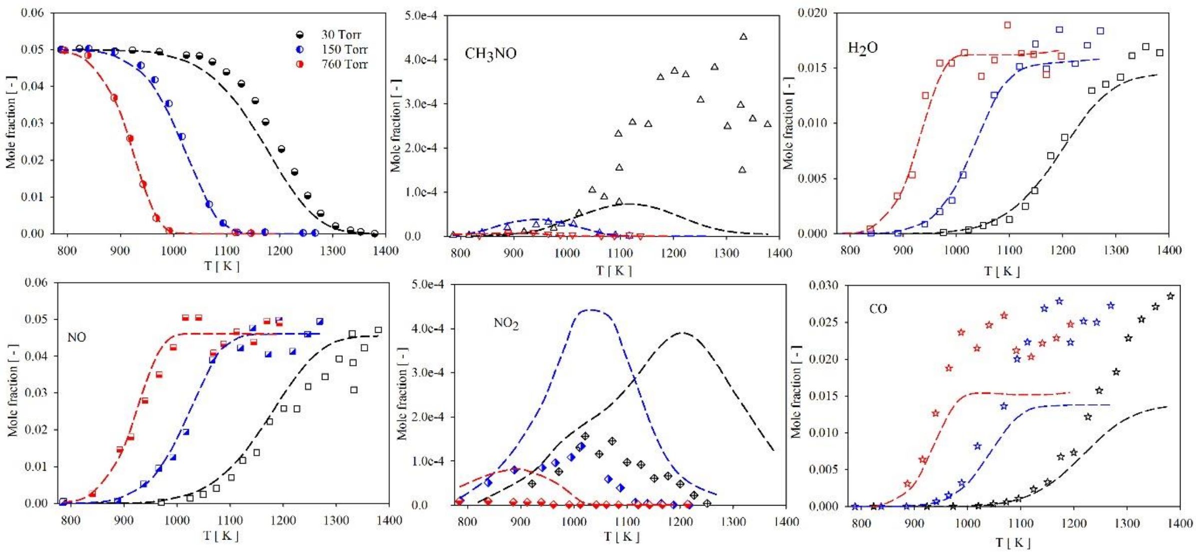


**Figure S4:** Pyrolysis of $CH_3NO_2$ 5 % / Ar 95 % in flow reactor at different pressures and residence times. Symbols: experimental data from [1], dashed lines: this model. Simulation are done using the temperature profile.

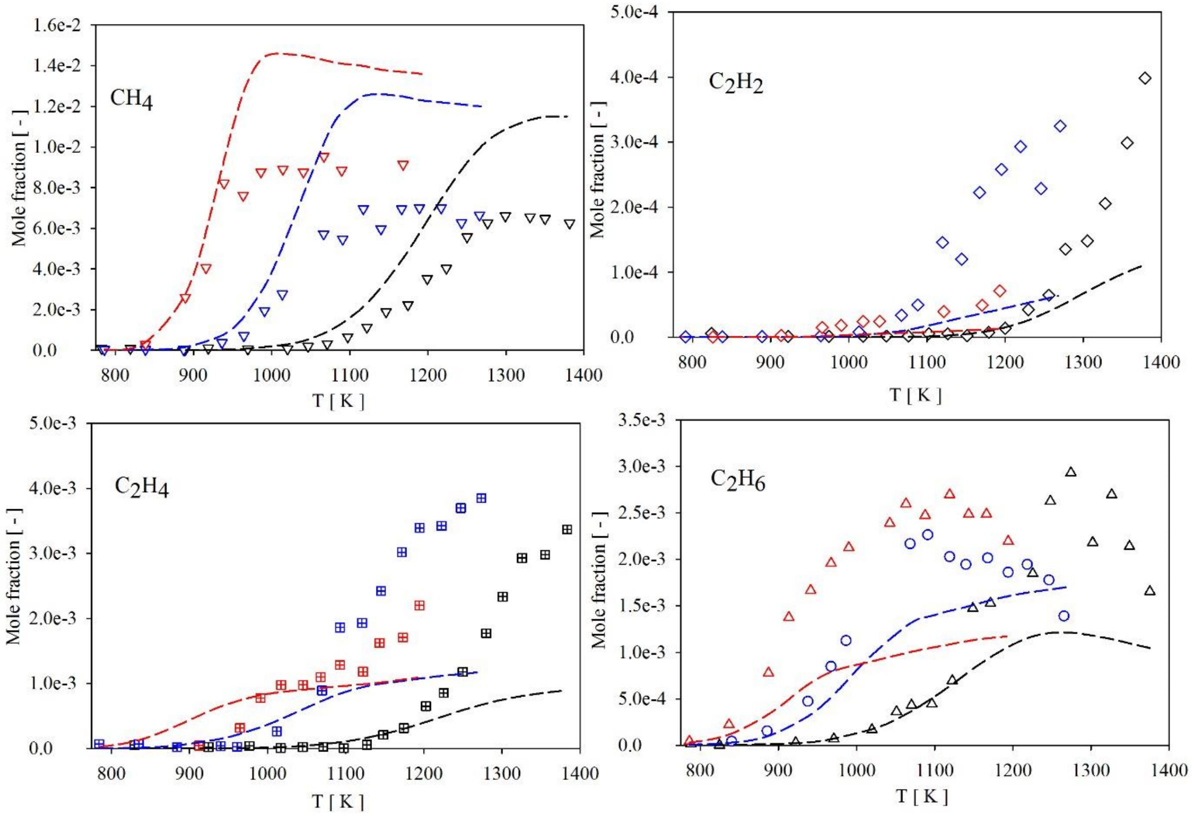

**Figure S5:** Pyrolysis of $CH_3NO_2$ 5 % / Ar 95 % in flow reactor at different pressures and residence times. Symbols: experimental data from [1], dashed lines: this model. Simulation are performed imposing the temperature profile. Legend information same as in Figure S4.

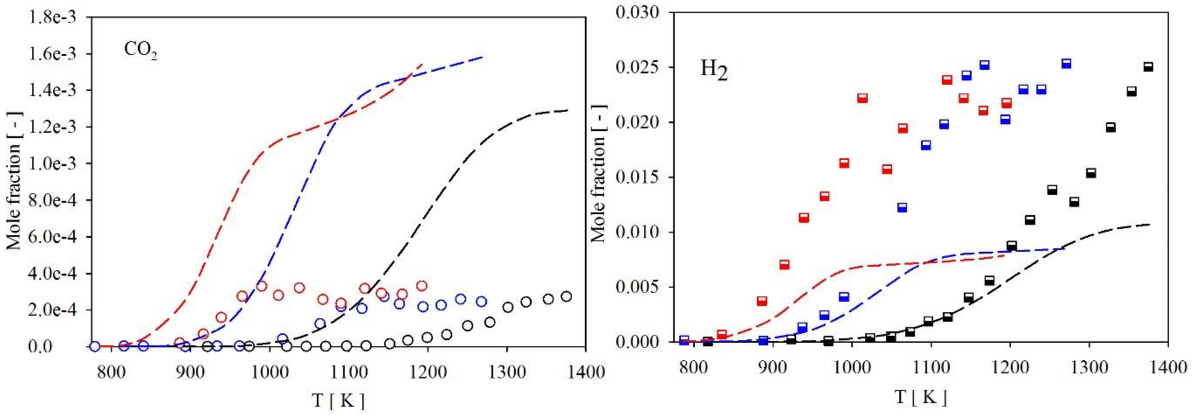


**Figure S6:** Pyrolysis of $CH_3NO_2$ 5 % / Ar 95 % in flow reactor at different pressures and residence times. Symbols: experimental data from [1], dashed lines: this model. Simulation are performed imposing the temperature profile. Legend information same as in Figure S4.

## 2. Jet stirred reactor

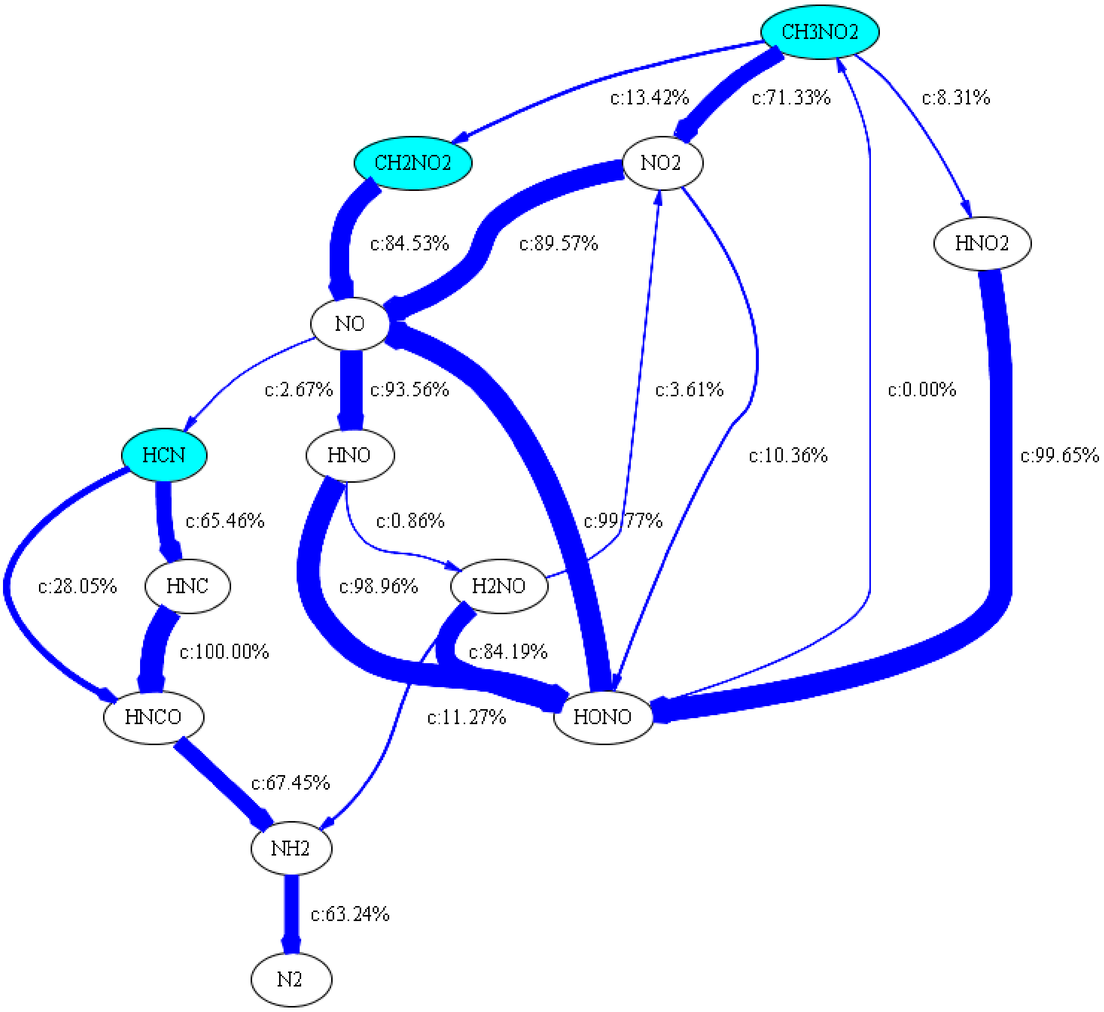


**Figure S7:** Integrated mass flux analysis during the pyrolysis of $CH_3NO_2$ 1 % /He 99 % in JSR at 1.07 bar, τ = 2.0 s for the condition shown in Figure 8. Based on N-atom.

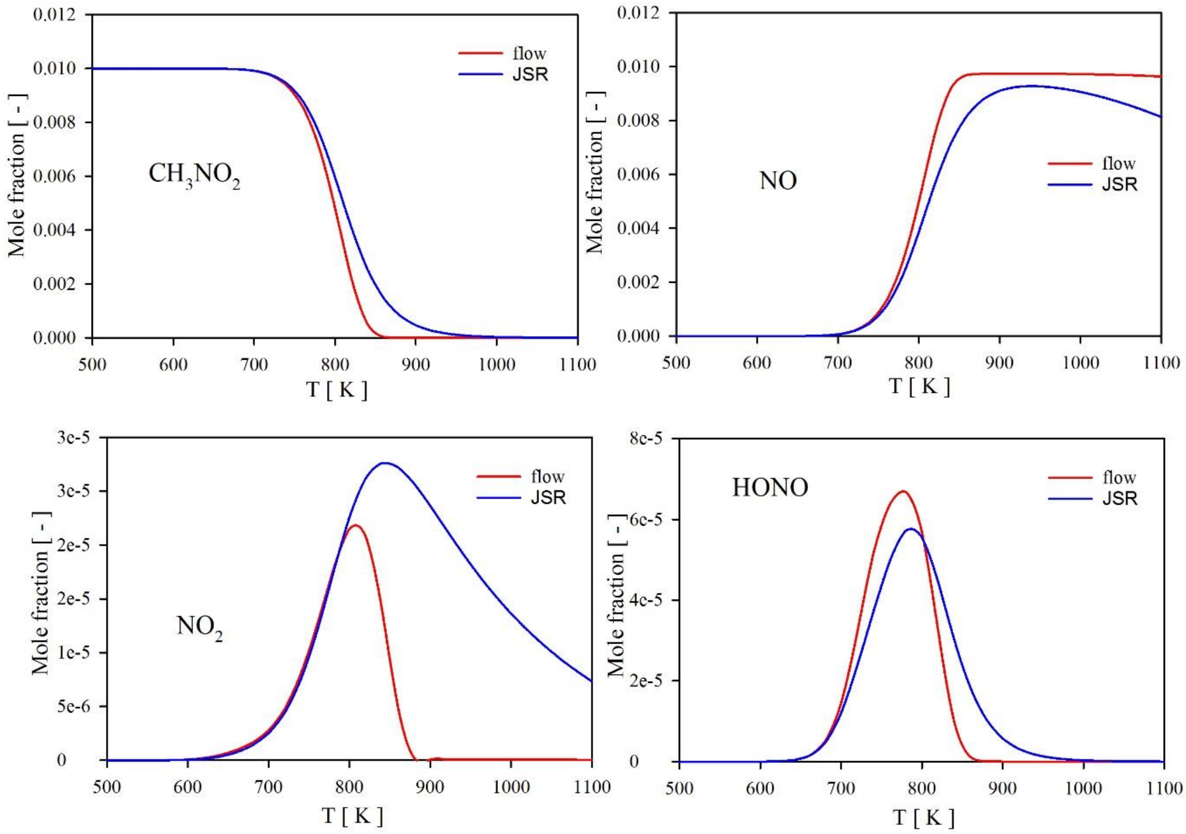


**Figure S8:** Species profile comparison during pyrolysis of $CH_3NO_2$ 1 % / He 99 % in flow reactor and JSR for the condition shown in Figure 3 and Figure 8 respectively. Red line: flow reactor, Blue line: JSR.

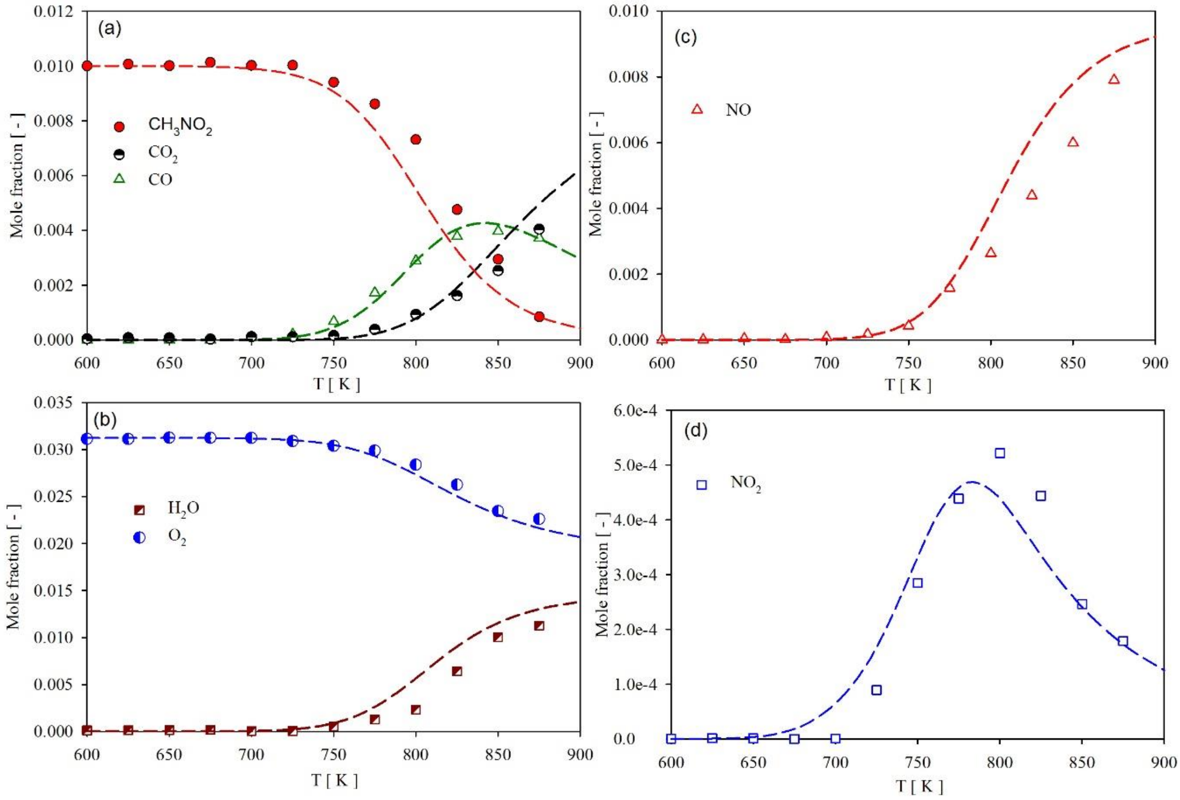


**Figure S9:** Oxidation of $CH_3NO_2$ 1 % / $O_2$ 3.125 % /Ar at 1 atm, $\phi = 0.4$, $\tau = 2.0$ s in a jet stirred reactor. Symbols: experimental data from Weng et al. [2]; dashed lines: this model.

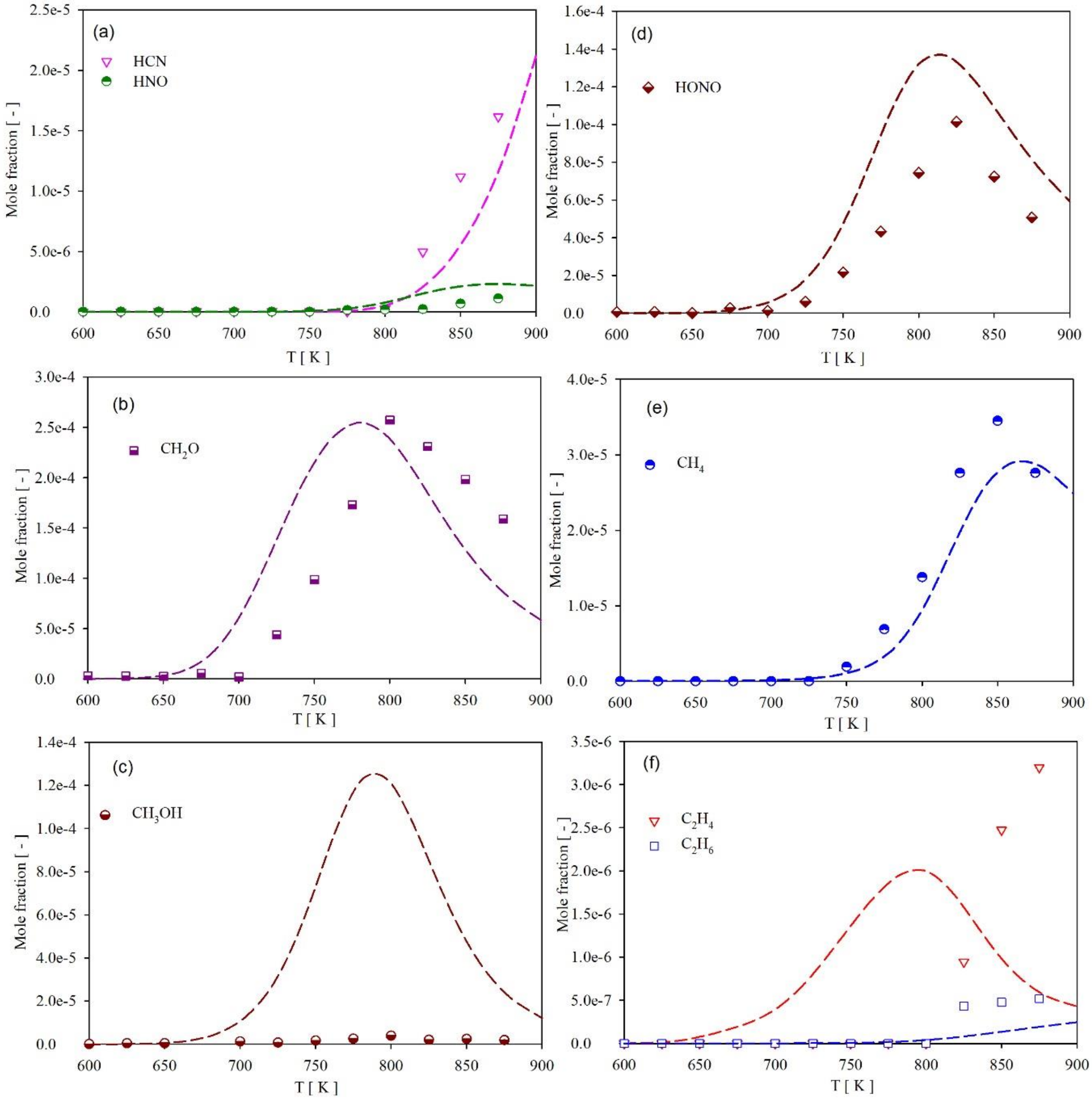


**Figure S10:** Oxidation of $CH_3NO_2$ 1 % / $O_2$ 3.125 % /Ar at 1 atm, $\phi = 0.4$, $\tau = 2.0$ s in a jet stirred reactor for condition in Figure S9. Symbols: experimental data from Weng et al. [2]; dashed lines: this model.

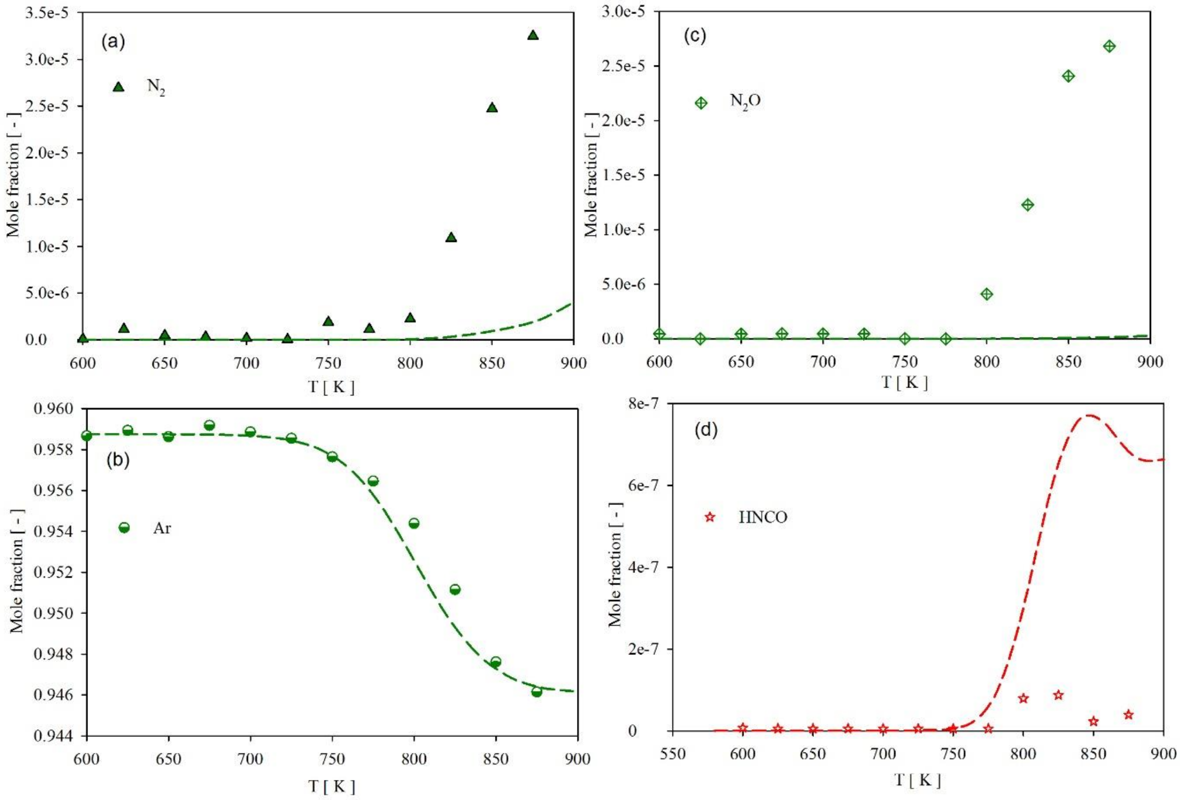


**Figure S11:** Oxidation of $CH_3NO_2$ 1 % / $O_2$ 3.125 % /Ar at 1 atm, $\phi = 0.4$, $\tau = 2.0$ s in a jet stirred reactor for condition in Figure S9. Symbols: experimental data from Weng et al. [2]; dashed lines: this model.

## 3. Burner stabilized flame

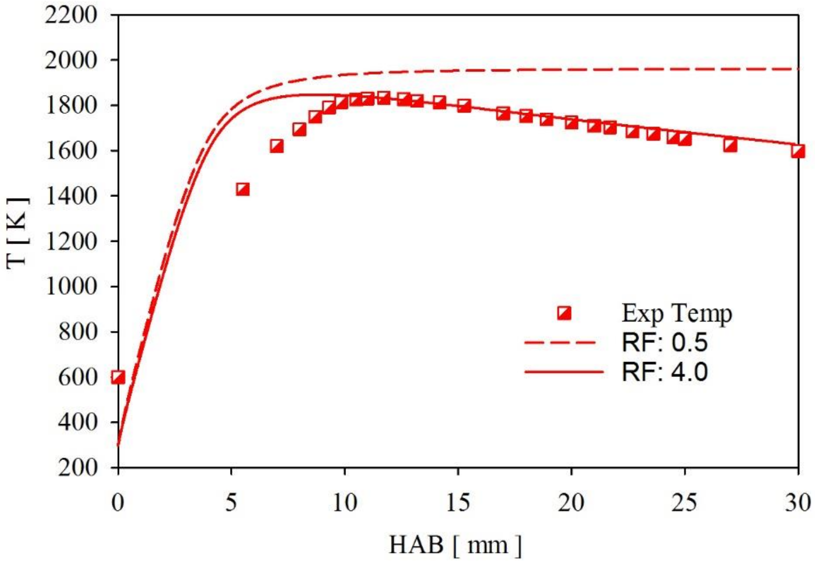


**Figure S12:** Temperature profile for the $CH_3NO_2/O_2/Ar$ premixed burner stabilized flame at 4.666 kPa, T = 298 K, ϕ = 1.5 shown in Figure 15. Symbols: experiment measurement from [3], lines: calculation solving the energy conservation equation. Dash lines: with radiation factor (RF) 0.5 (standard setting), solid lines: with radiation factor (RF) 4.0.

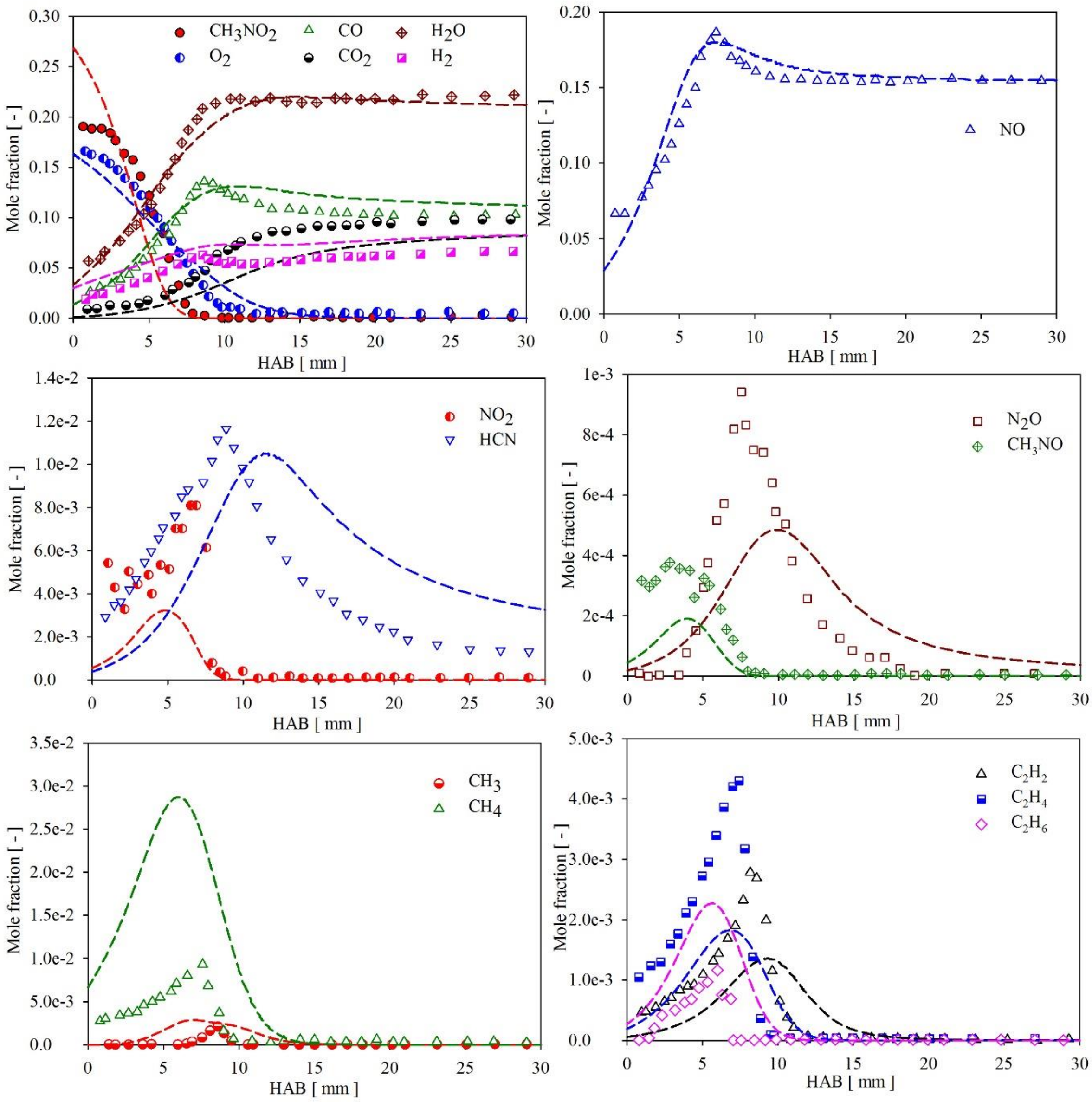


**Figure S13:** Speciation of premixed $CH_3NO_2/O_2/Ar$ burner stabilized flame at 4.666 kPa, T = 298 K, $\phi = 2.0$. Symbols: experiments from Zhang et al. [3]; dashed lines: prediction imposing the experimental temperature profile.

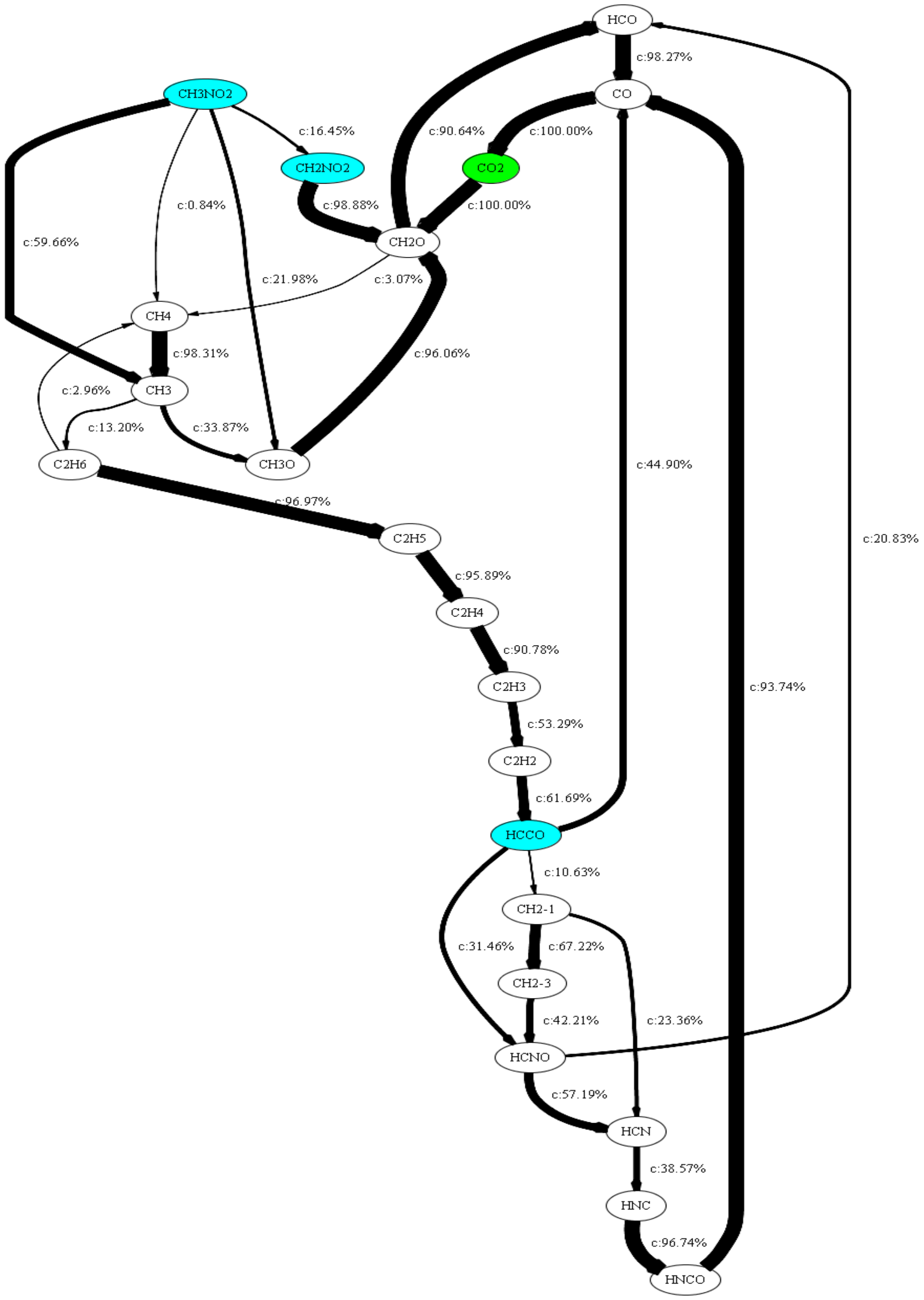


**Figure S14:** Integrated mass flux analysis for $CH_3NO_2/O_2/Ar$ burner stabilized flame at 4.666 kPa, T = 298 K, $\phi$ = 2.0 sown in Figure S13. Based on the C-atom.

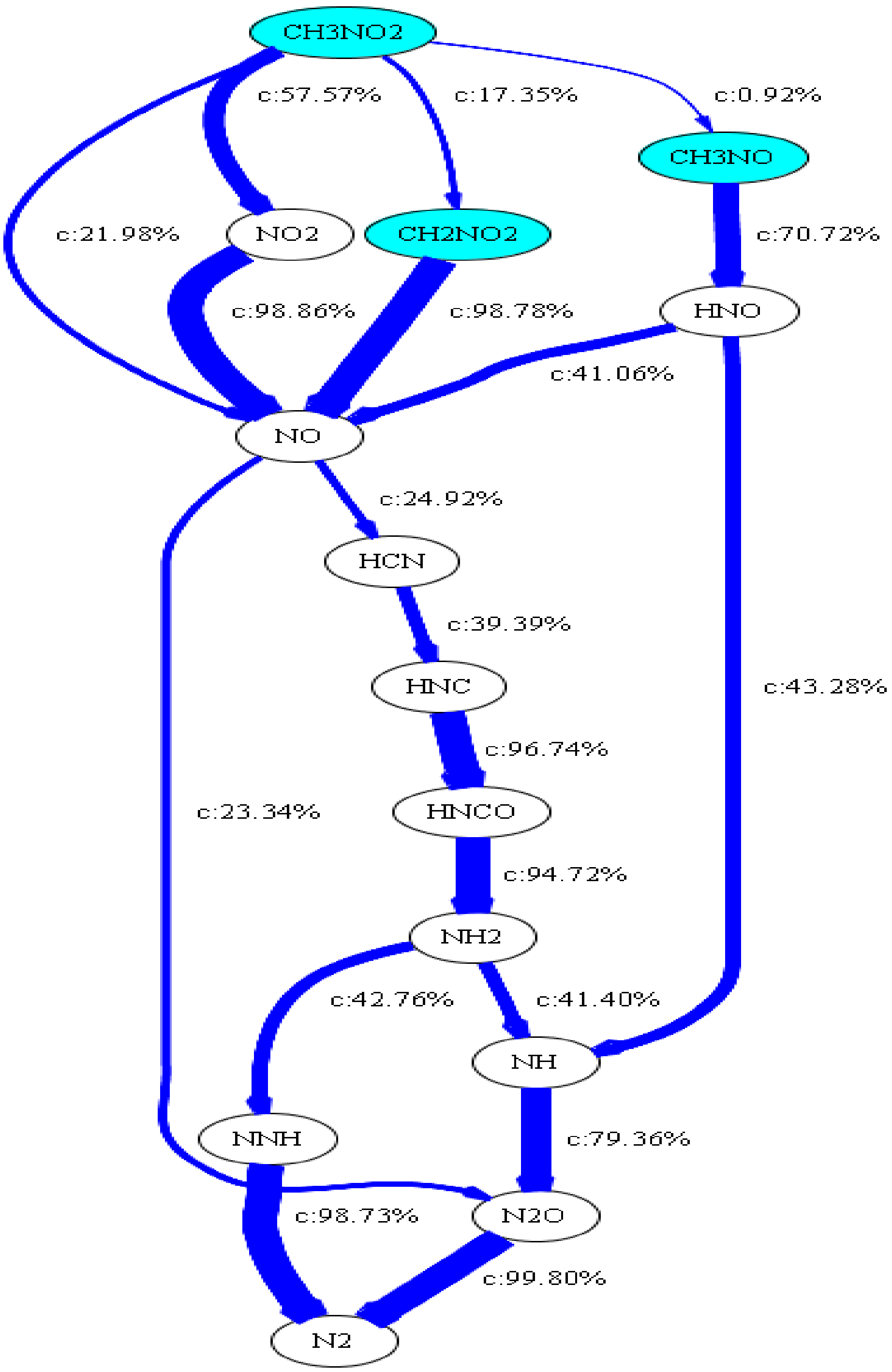


**Figure S15:** Integrated mass flux analysis for $CH_3NO_2/O_2/Ar$ burner stabilized flame at 4.666 kPa, T = 298 K, $\phi$ = 2.0 shown in Figure S13. Based on the N-atom.

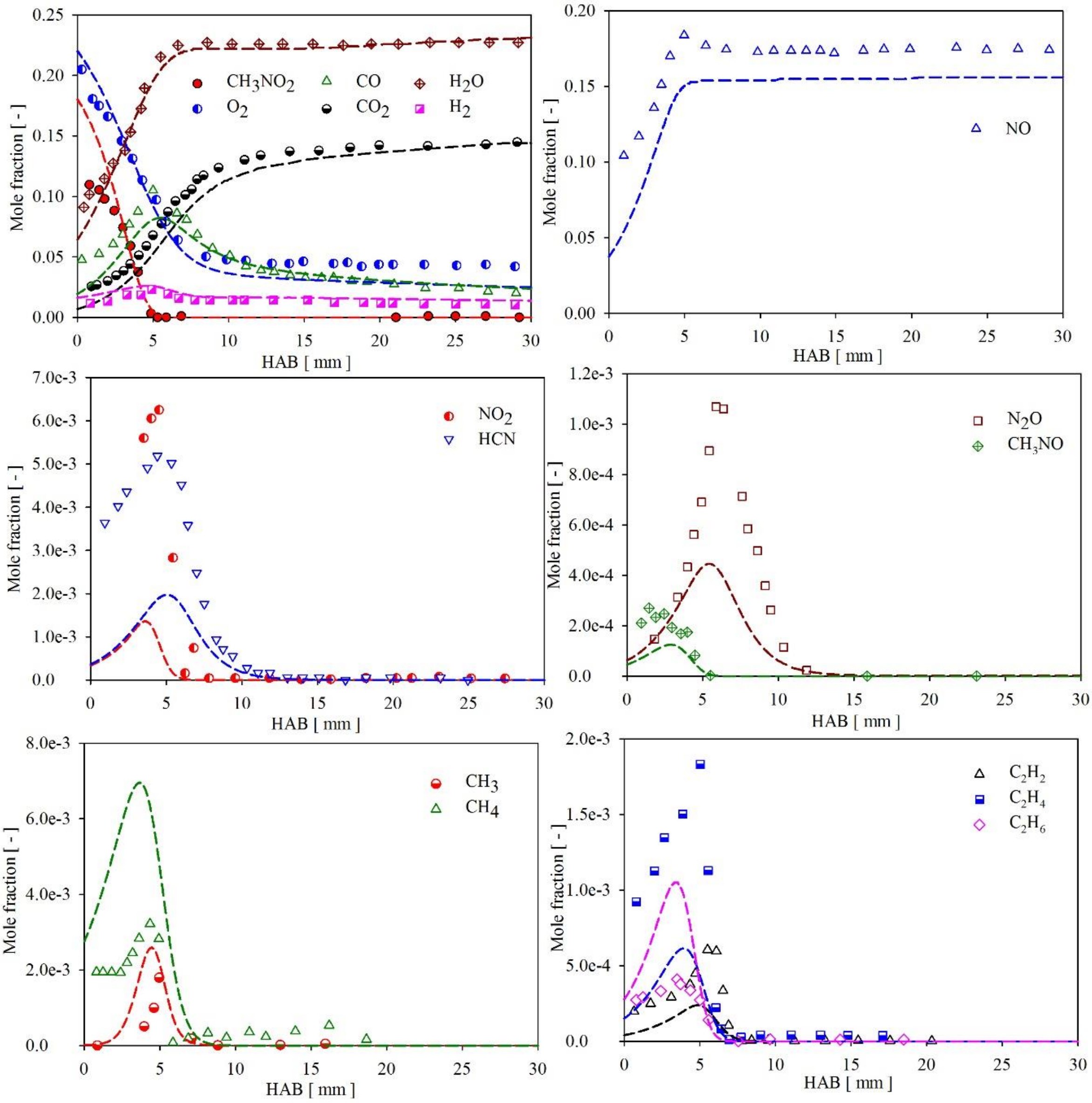


**Figure S16:** Speciation of premixed $CH_3NO_2/O_2/Ar$ burner stabilized flame at 4.666 kPa, T = 298 K, ϕ = 1.0. Symbols: experiments from Zhang et al. [3]; dashed lines: prediction imposing the experimental temperature profile.

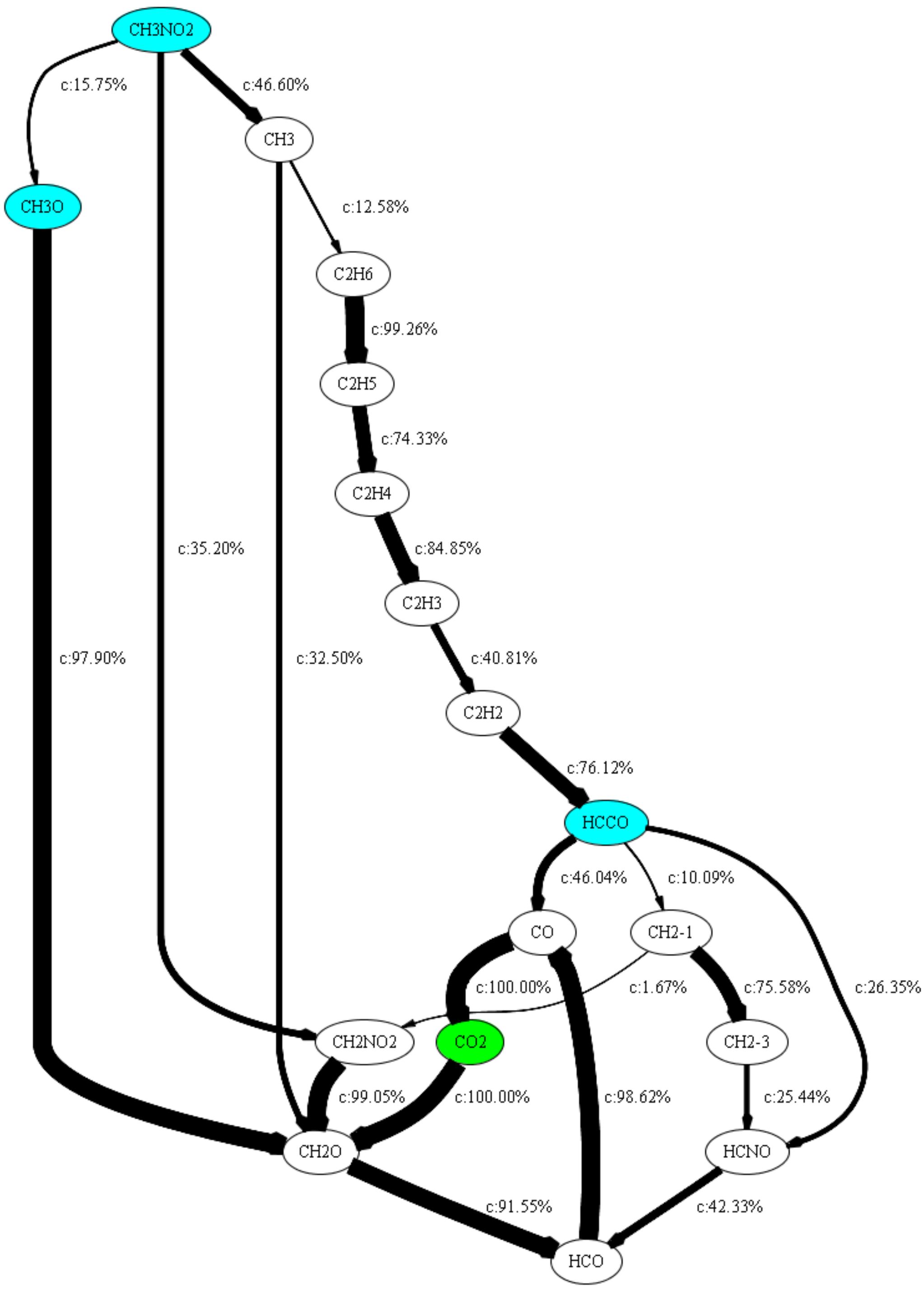


**Figure S17:** Integrated mass flux analysis for $CH_3NO_2/O_2/Ar$ burner stabilized flame at 4.666 kPa, T = 298 K, $\phi = 1.0$ shown in Figure S16. Based on the C-atom.

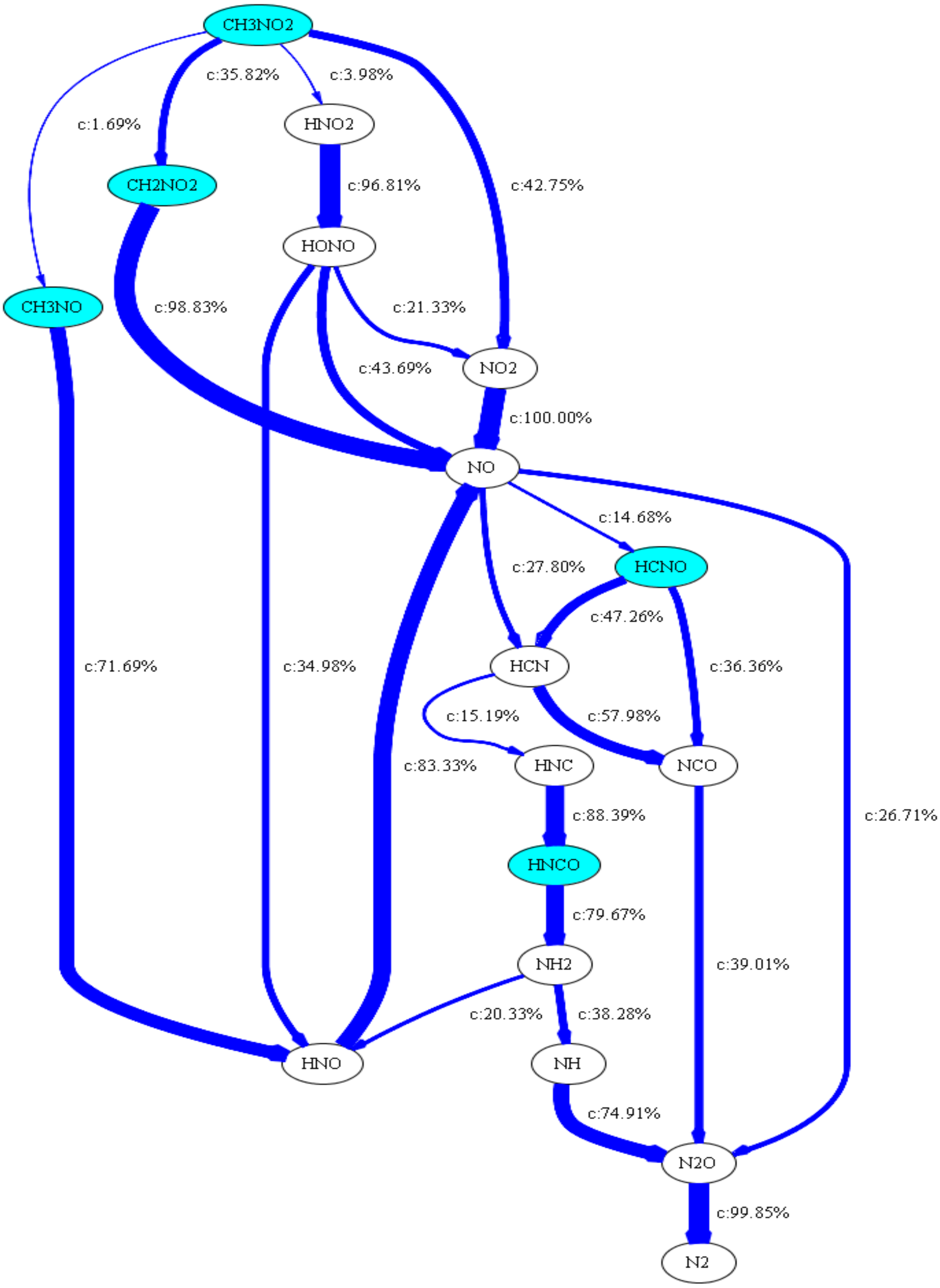


**Figure S18:** Integrated mass flux analysis for $CH_3NO_2/O_2/Ar$ burner stabilized flame at 4.666 kPa, T = 298 K, $\phi$ = 1.0 shown in Figure S16. Based on the N-atom.

## 4. Shock tube - Ignition delay time and pyrolysis

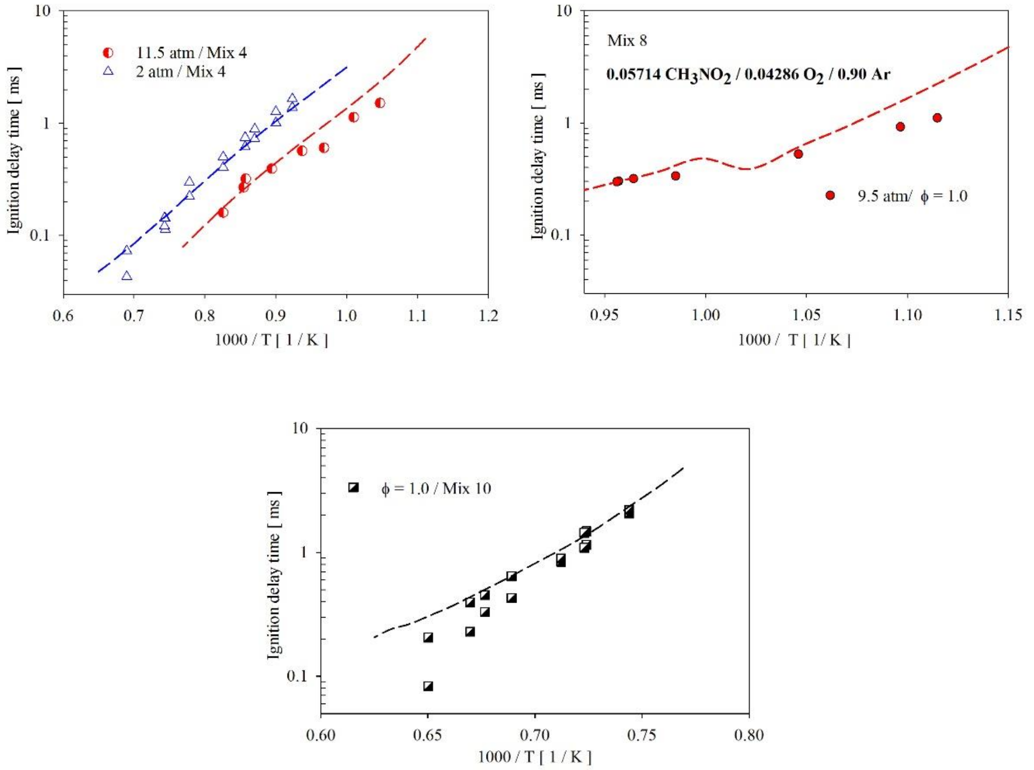


**Figure S19:** Ignition delay time of $CH_3NO_2/O_2/Ar$. Symbols: experiment from Mathieu et al. 2016 [4]; lines: this model. Mix: means mixture number, which is same as in [4].

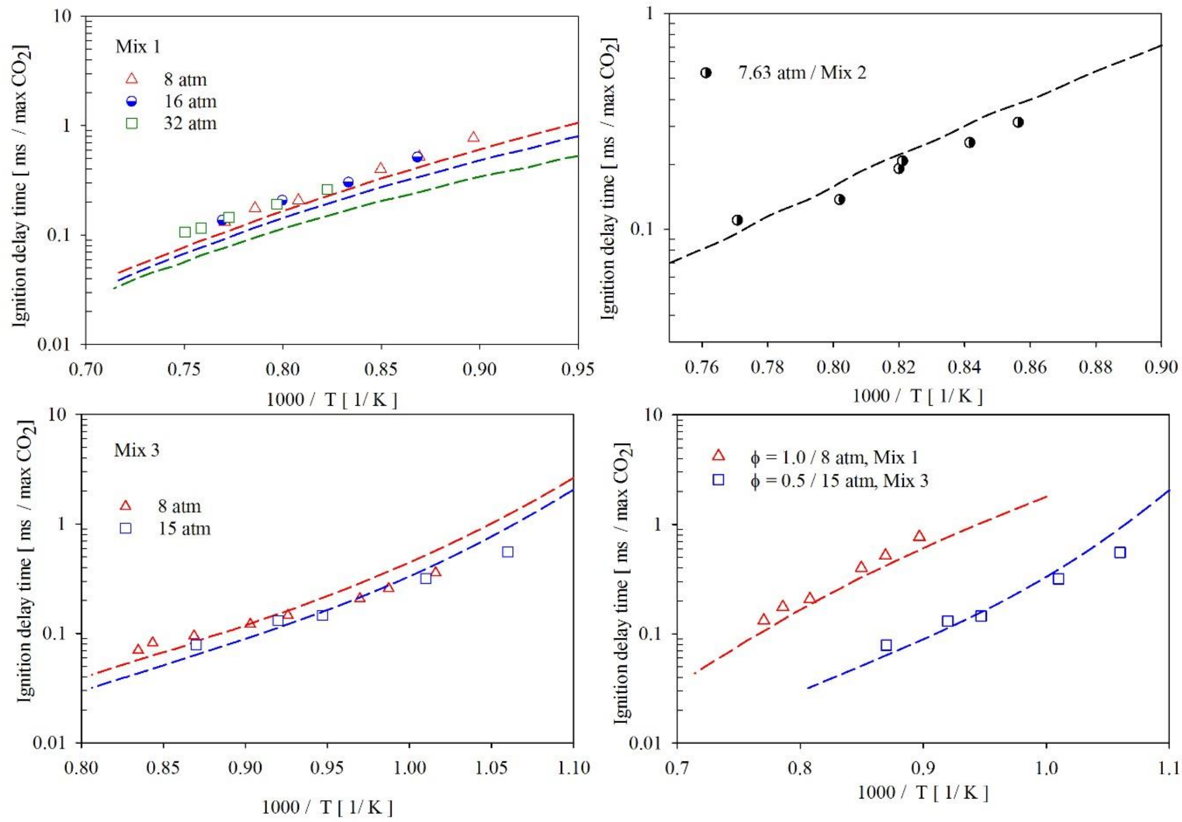


**Figure S20:** Ignition delay times of $CH_3NO_2/O_2/N_2$. Symbols: experiment from Nauclér et al. 2016 [5]; lines: this model. Mix: means mixture number, which is same as in [5].

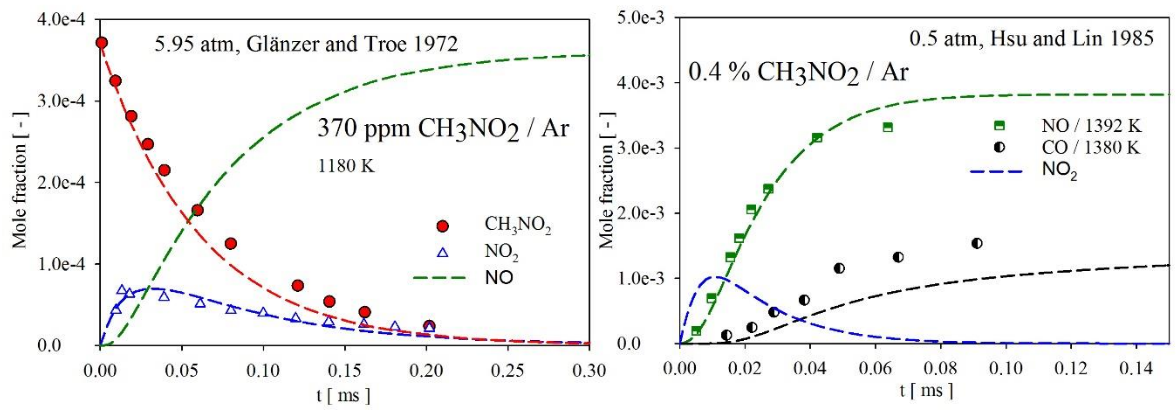


**Figure S21:** Speciation during the $CH_3NO_2$/Ar pyrolysis in shock tube, symbols: experiments from [6] (left), [7] (right); lines: this model.

### 5. Laminar flame speed

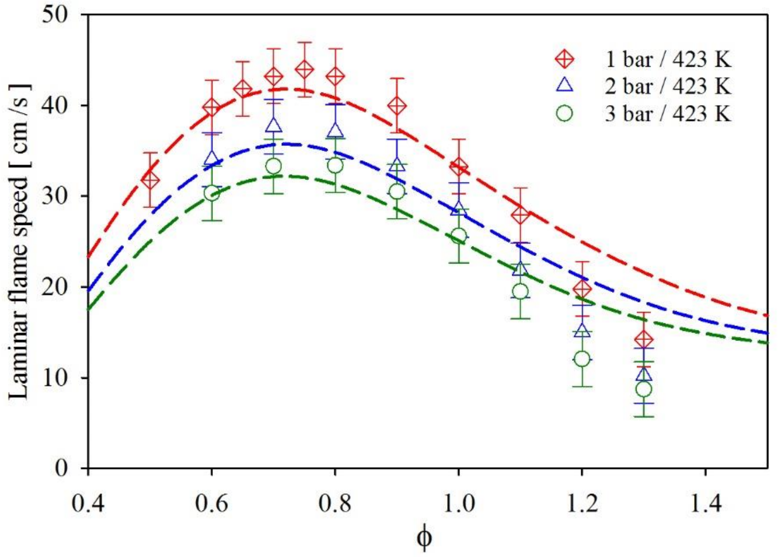


**Figure S22:** Laminar flame speeds of $CH_3NO_2$/air at 423 K and three different pressures (1−3 bar). Symbols: experiment from [8]; lines: this model.

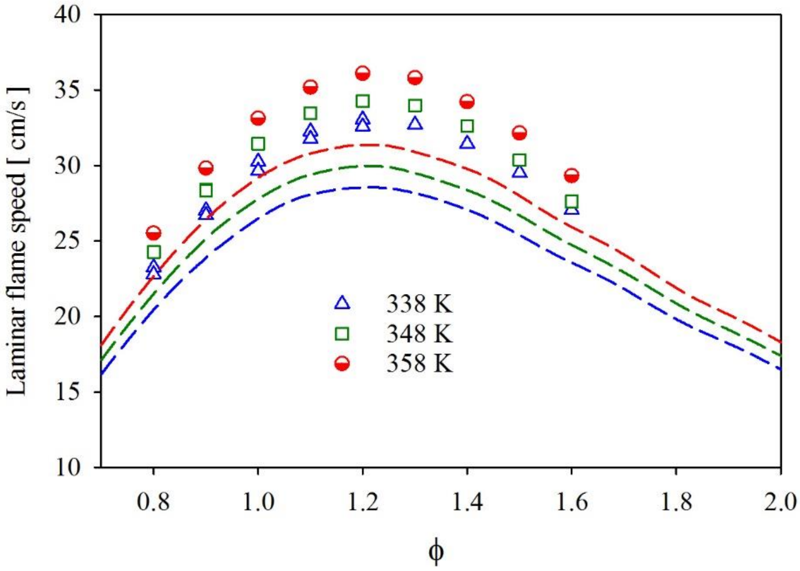


**Figure S23:** Laminar flame speed of $CH_3NO_2$/air at 1 atm and three different temperatures. Symbols: experiment from [9]; lines: this model.

## 6. $CH_3NO_2$(+M)⇋$CH_3$+$NO_2$(+M) rate constant comparison

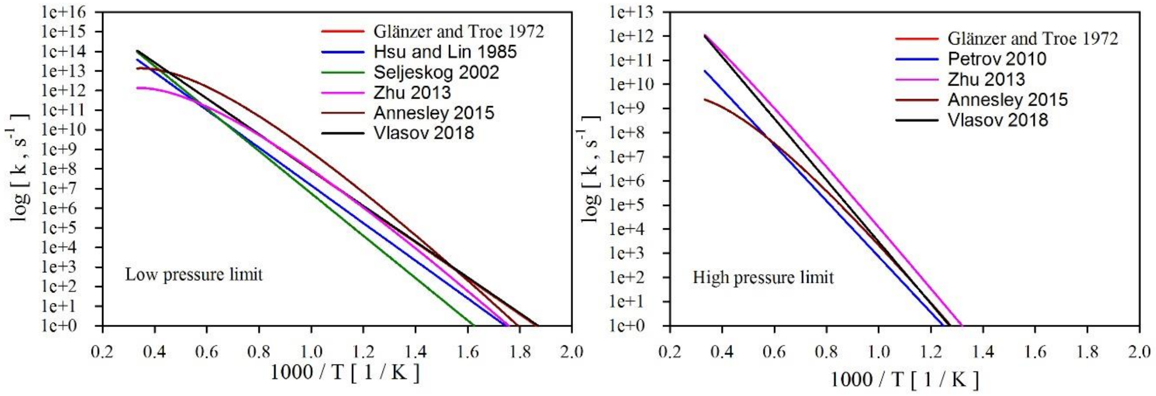


**Figure S24:** Rate constant comparison of reaction $CH_3NO_2$(+M)⇋$CH_3$+$NO_2$(+M) from different sources: Glänzer and Troe [6], Hsu and Lin [7], Seljeskog [10], Zhu et al. [11], Annesley et al. [12], Vlasov et al. [13], Petrov et al. [14].

## References


[1] Jia Z, Wang Z, Cheng Z, Zhou W. Experimental and modeling study on pyrolysis of n-decane initiated by nitromethane. Combust Flame 2016;165:246–58. doi:10.1016/J.COMBUSTFLAME.2015.12.010.

[2] Weng J-J, Tian Z-Y, Zhang K-W, Ye L-L, Liu Y-X, Wu L-N, et al. Experimental and kinetic investigation of pyrolysis and oxidation of nitromethane. Combust Flame 2019;203:247–54. doi:10.1016/J.COMBUSTFLAME.2019.01.033.

[3] Zhang K, Li Y, Yuan T, Cai J, Glarborg P, Qi F. An experimental and kinetic modeling study of premixed nitromethane flames at low pressure. Proc Combust Inst 2011;33:407–14. doi:10.1016/j.proci.2010.06.002.

[4] Mathieu O, Giri B, Agard AR, Adams TN, Mertens JD, Petersen EL. Nitromethane ignition behind reflected shock waves: Experimental and numerical study. Fuel 2016;182:597–612. doi:10.1016/j.fuel.2016.05.060.

[5] Nauclér JD, Li Y, Nilsson EJK, Curran HJ, Konnov AA. An experimental and modeling study of nitromethane + O2 + N2 ignition in a shock tube. Fuel 2016;186:629–38. doi:10.1016/j.fuel.2016.09.003.

[6] Glänzer K, Troe J. Thermische Zerfallsreaktionen von Nitroverbindungen I:

Dissoziation von Nitromethan. Helv Chim Acta 1972;55:2884–93. doi:10.1002/hlca.19720550821.

[7] Hsu DSY, Lin MC. Laser probing and kinetic modeling of NO and CO production in shock-wave decomposition of nitromethane under highly diluted conditions. J Energ Mater 1985;3:95–127. doi:10.1080/07370658508012337.

[8] Brequigny P, Dayma G, Halter F, Mounaïm-Rousselle C, Dubois T, Dagaut P. Laminar burning velocities of premixed nitromethane/air flames: An experimental and kinetic modeling study. Proc Combust Inst 2015;35:703–10. doi:10.1016/j.proci.2014.06.126.

[9] Nauclér JD, Nilsson EJK, Konnov AA. Laminar burning velocity of nitromethane + air flames: A comparison of flat and spherical flames. Combust Flame 2015;162:3803–9. doi:10.1016/J.COMBUSTFLAME.2015.07.017.

[10] Seljeskog M. Shock tube experiments on nitromethane and Promotion of chemical reactions by non- thermal plasma. The Norwegian University of Science and Technology, Ph.D Thesis, 2002.

[11] Zhu RS, Raghunath P, Lin MC. Effect of roaming transition states upon product branching in the thermal decomposition of CH3NO2. J Phys Chem A 2013;117:7308–13. doi:10.1021/jp401148q.

[12] Annesley CJ, Randazzo JB, Klippenstein SJ, Harding LB, Jasper AW, Georgievskii Y, et al. Thermal Dissociation and Roaming Isomerization of Nitromethane: Experiment and Theory. J Phys Chem A 2015;119:7872–93. doi:10.1021/acs.jpca.5b01563.

[13] Vlasov PA, Kuznetsov NM, Petrov YP, Turetskii S V. Nitromethane Isomerization during Its Thermal Decay. Kinet Catal 2018;59:6–10. doi:10.1134/S0023158418010147.

[14] Petrov YP, Karasevich YK, Turetskii S V. Decomposition of nitromethane in shock waves: The primary stage and the kinetics of decomposition at pressures of about 40 atm. Russ J Phys Chem B 2010;4:566–73. doi:10.1134/S1990793110040068.