

Detailed Kinetic Model for Combustion of NH_3/H_2 Blends

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1. O(³P) + HNO

1.1. Quantum Chemistry

The O(³P) + HNO reaction was investigated with both coupled-cluster methods and complete-active-space perturbation theory. The CASPT2 [1], ROHF-CCSD(T) [2], and ROHF-CCSDT(Q) [3] calculations were run with the ORCA 6.0.1 [4], Gaussian 16 [5], and MRCC [6, 7] software packages, respectively. Stationary-point geometries were first sought and optimized at the CASPT2(14,11)/aug-cc-pVTZ level of theory. This level of theory was also used to determine harmonic frequencies. To partially capture anharmonic effects, the computed zero-point energies and harmonic frequencies were multiplied by 0.957 [8]. For the ³HNO₂ intermediate, the (14,11) active space consisted of three bonding and anti-bonding sigma orbitals (6,6), the oxygen and nitrogen lone-pair orbitals (6,3), and the radical orbitals on the oxygens (2,2). The corresponding orbitals were selected for all other species. Single-point energies were then calculated with the CASPT2(14,11) method using the aug-cc-pVTZ and aug-cc-pVQZ basis sets [9], and the relative-energy differences were extrapolated to the complete-basis-set (CBS) limit with the relation[10]

$$\Delta E_{\infty} = \Delta E_{\text{QZ}} - (\Delta E_{\text{TZ}} - \Delta E_{\text{QZ}}) \frac{4^4}{5^4 - 4^4} . \quad (1)$$

Single-point energies were also calculated with the ROHF-CCSD(T) method using the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets. Here the CBS limit was determined separately for the Hartree-Fock (HF) and the slower-converging correlation energies. The CBS formula for the HF energy was [11]

$$E_{\text{HF}}(X) = E_{\text{HF},\infty} + B_{\text{HF}} e^{-\alpha_{\text{HF}} X} , \quad (2)$$

whilst the formula [12]

$$E_{\text{corr}}(X) = E_{\text{corr},\infty} + B_{\text{corr}} X^{-\alpha_{\text{corr}}} \quad (3)$$

was used for the correlation-energy extrapolation. In both cases, $X = 2$, $X = 3$, and $X = 4$ correspond to the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets, respectively. A system of three equations was solved to determine α , B , and E_{∞} . We refined the ROHF-CCSD(T)/CBS//CASPT2(14,11)/aug-cc-pVTZ relative energies by computing an additive correction term,

$$\Delta T(Q) = \Delta E[\text{CCSDT}(Q) - \text{CCSD}(T)] . \quad (4)$$

In these calculations, the aug-cc-pVDZ basis set was used. Over the course of the coupled-cluster calculations, we found that Gaussian and MRCC did not always find the same HF wave function for a given transition structure when the default wave-function guess was used. Given that multi-reference effects are significant for these structures, this was not a surprising finding. Thus, particular care was taken to ensure that, for a given species, Gaussian and MRCC found the HF wave function that yielded the lowest ROHF-CCSD(T) energy, and then this reference was consistently used in both the ROHF-CCSD(T) and ROHF-CCSDT(Q) evaluations. Note that a wave-function that yielded the lowest HF energy did not necessarily yield the lowest ROHF-CCSD(T) energy.

Table S1: Stationary-point energies for species on the $\text{O}(^3\text{P}) + \text{HNO}$ potential-energy surface. The energies are in kJ mol^{-1} . The tabulated CASPT2(14,11) and ROHF-CCSD(T) values are zero-point-energy corrected. Also listed are the electronic partition functions and symmetry numbers for the species. Spin-orbit effects were accounted for by reducing the energies of the $\text{O}(^3\text{P}) + \text{HNO}$ and $^2\text{NO} + ^2\text{OH}$ wells by 0.933 and 1.55 kJ mol^{-1} , respectively.

Species	$q_{\text{elec}}^{\text{a}}$	$\sigma_{\text{ext}}/m_{\text{opt}}^{\text{b}}$	ΔZPE	CASPT2(14,11)/CBS	ROHF-CCSD(T)/CBS ^c	$\Delta\text{T}(\text{Q})^{\text{d}}$	ATcT ^e	Fitted
$\text{O}(^3\text{P}) + \text{HNO}$	$q_{\text{O}}, 1$	1/1, 1/1	0.0	0.0	0.0 (0.016, 0.016)	0	0	-
$^2\text{NO} + ^2\text{OH}$	$q_{\text{NO}}, q_{\text{OH}}$	1/1, 1/1	-2.3	-239.0	-232.5 (0.024, 0.014)	-0.3	-228.9	-
$^2\text{NO}_2 + ^2\text{H}$	2,2	2/1,1/1	-12.6	-127.3	-108.8 (0.027)	-2.6	-103.9	-
$^3\text{HNO}_2$	3	1/1 ^f	12.8	-144.3	-120.1 (0.059)	-7.2	-	-
VdW1(T1)	3 (-2)	1/1	4.4	-0.8	-1.2 (0.018)	-0.2	-	-
VdW1(T2)	-	-	-	2.9	-	-	-	-
VdW1(T3)	-	-	-	11.8	-	-	-	-
VdW2(T1)	3 (-2)	1/2	2.7	1.3	0.4 (0.017)	-0.2	-	-
VdW2(T2)	-	-	-	1.5	-	-	-	-
VdW2(T3)	-	-	-	14.4	-	-	-	-
TS1(T1)	3 (-2)	1/1	-1.0	1.9	0.5 (0.029)	-2.4	-	-4.3 \pm 0.2
TS1(T2)	-	-	-	3.4	-	-	-	-
TS1(T3)	-	-	-	15.0	-	-	-	-
TS2(T1)	3	1/2	3.4	5.0	4.4 (0.043)	-7.3	-	-5.3 \pm 0.2
TS2(T2)	-	-	-	7.9	-	-	-	-
TS2(T3)	-	-	-	65	-	-	-	-
TS3	3	1/1	-9.9	14.5	29.0 (0.11)	-8.8	-	-

^a $q_{\text{O}} = 5 + 3e^{-228 \text{ K}/T} + e^{-326 \text{ K}/T}$, $q_{\text{NO}} = 2 + 2e^{-172 \text{ K}/T}$, $q_{\text{OH}} = 2 + 2e^{-201 \text{ K}/T}$.

^b Here $\sigma_{\text{ext}}/m_{\text{opt}}$ is the ratio of rotational (external) and optical symmetry numbers.

^c The values in the parentheses are T1 diagnostics [13].

^d Approximate CCSDT(Q) correction: variant B [3].

^e ATcT stands for Active Thermochemical Tables [14].

^f The inversion motion is explicitly considered, and an internal symmetry number of 2 is applied for this motion.

1.2. Master Equation

Rate-coefficient calculations were run with the master-equation (ME) solver MESMER 7.1 [15–17]. MESMER is a one-dimensional ME code that treats the total rovibrational energy as the only independent variable; angular-momentum effects are not explicitly considered. For all reactions with saddle-points, the transition state (TS) was placed there. In the $\text{O}(^3\text{P}) + \text{HNO}$ reaction, the fragments form van der Waals (VdW) complexes before passing over the saddle-points that lead to the $^3\text{HNO}_2$ or $^2\text{NO} + ^2\text{OH}$ products. However, the VdW wells are very shallow, and after applying zero-point-energy corrections, only VdW1 was found to be below the reactant asymptote. The reaction that forms VdW1 is barrierless, and to compute the TS state sum for this reaction, we performed energy- and angular-momentum resolved VRC-TST [18] calculations with the Gaussrate package [19]. The level of theory used in the VRC-TST calculations was wB97XD/cc-pVDZ [20], and the reaction coordinate was defined as the distance (scanned in the range 3–20 Å) between the nitrogen atom in HNO and the approaching $\text{O}(^3\text{P})$ atom. The total VdW-complex forming rate coefficient is well reproduced by the expression

$$k(T) = 4.32 \cdot 10^{-10} \left(\frac{T}{300 \text{ K}} \right)^{-0.371} \text{ cm}^3 \text{ s}^{-1}. \quad (5)$$

The two lowest-lying electronic states for the VdW complexes and TS1 are nearly degenerate, and to take this into account in rate-coefficient calculations, we multiplied their electronic partition functions by two ($3 \cdot 2 = 6$). Six of the nine potential-energy surfaces originating from the reactants form ground-state products for the $\text{O}(^3\text{P}) + \text{HNO} \longrightarrow ^2\text{NO} + ^2\text{OH}$ reaction, but only three of the potential-energy

surfaces are reactive for the $\text{O}(^3\text{P}) + \text{HNO} \longrightarrow ^3\text{HNO}_2$ reaction. We list in Table S2 the rotational symmetry numbers, optical symmetry numbers, and electronic partition functions for all species S2.

The inclusion of shallow wells (the VdW well in the present case) in ME models is typically undesirable because this leads to the overlapping of chemically-significant eigenvalues (CSEs) and internal-relaxation eigenvalues (IEREs). MESMER uses Bartis-Widom analysis [16, 17] to compute phenomenological rate coefficients, and this approach relies on CSEs and IEREs to be well-separated in magnitude. Thus, to omit the VdW complex from the final ME model, we determined “effective” TS state sums for the overall $\text{O}(^3\text{P}) + \text{HNO} \longrightarrow ^2\text{NO} + ^2\text{OH}$ and $\text{O}(^3\text{P}) + \text{HNO} \longrightarrow ^3\text{HNO}_2$ reactions,

$$N^\ddagger(\text{O}(^3\text{P}) + \text{HNO} \rightleftharpoons ^2\text{NO} + ^2\text{OH}) = \frac{N_{\text{loose}}^\ddagger N_{\text{TS1}}^\ddagger}{N_{\text{loose}}^\ddagger + N_{\text{TS1}}^\ddagger + N_{\text{TS2}}^\ddagger} \text{ and} \quad (6)$$

$$N^\ddagger(\text{O}(^3\text{P}) + \text{HNO} \rightleftharpoons ^3\text{HNO}_2) = \frac{N_{\text{loose}}^\ddagger N_{\text{TS2}}^\ddagger}{N_{\text{loose}}^\ddagger + N_{\text{TS1}}^\ddagger + N_{\text{TS2}}^\ddagger}. \quad (7)$$

At lower energies/temperatures ($T < 100$ K), the outer TS is the kinetic bottleneck, whereas at higher temperatures ($T > 100$ K) the TS1 and TS2 saddle-point determine the overall kinetics.

In general, multi-reference effects are significant for the inner TSs (see TS1 and TS2 in Table S1), and the relative-energy uncertainties of these saddle-points are at least several kJ mol^{-1} . Thus, we adjusted the heights of these barriers so that we could reproduce the experimental results of Inomata and Washida [21]. The fitting was done so that the energy difference between TS1 and TS2 was fixed to the ROHF-CCSD(T)/CBS + $\Delta\text{T}(\text{Q})$ value. In the end, we found that the energies of the inner TSs had to be reduced by about 2–3 kJ mol^{-1} from their ROHF-CCSD(T)/CBS + $\Delta\text{T}(\text{Q})$ values—an adjustment well within computational uncertainties. We further note that variational effects were not investigated for the inner TSs, although such effects could be important at elevated temperatures.

The traditional single-exponential-down model was used to treat collisional-energy transfer. The temperature-dependent parameter utilized in this work,

$$\langle \Delta E \rangle_{\text{down}}^{N_2} = 300 \text{ cm}^{-1} \left(\frac{T}{300\text{K}} \right)^{0.85}, \quad (8)$$

was taken from the work of Chen et al. [22], who found that with the above expression they could reproduce experimental fall-off curves for the $^2\text{NO} + ^2\text{OH} \longrightarrow \text{HONO}$ reaction. Pressure effects are weak for the studied system, and so the present results are not very sensitive to this parameter. Lennard-Jones (LJ) collision frequencies were calculated using tabulated LJ parameters [23]. For the $^3\text{HNO}_2$ intermediate, we chose to use the LJ parameters of N_2O ($\sigma = 3.828 \text{ \AA}$ and $\epsilon = 232.4 \text{ K}$). For N_2 and He , these parameters are $\sigma = 2.551 \text{ \AA}$ and $\epsilon = 10.22 \text{ K}$ and $\sigma = 71.4 \text{ \AA}$ and $\epsilon = 3.798 \text{ K}$, respectively.

Eckart tunnelling corrections were computed for the $^3\text{HNO}_2 \longrightarrow ^2\text{NO}_2 + ^2\text{H}$ reaction. For the direct $\text{O}(^3\text{P}) + \text{HNO} \longrightarrow ^2\text{NO} + ^2\text{OH}$ abstraction reaction, tunnelling corrections were not computed as the barrier for this appears to be submerged below the reactant asymptote. We used an energy-grain size of 25 cm^{-1} and a cut-off energy of $25 k_{\text{B}}T$ in the simulations.

2. $^2\text{H} + ^2\text{H}_2\text{NO}$

2.1. Quantum Chemistry

The $^2\text{H} + ^2\text{H}_2\text{NO}$ reaction was investigated with both coupled-cluster methods and complete-active-space perturbation theory. The CASPT2 and CCSD(T) calculations were run with Molpro 2024.3.0 [24–26]. Stationary-point geometries were sought and optimized at the CCSD(T)/aug-cc-pVTZ level of theory. This level of theory was also used to determine harmonic frequencies. The final single point energies were extrapolated by applying equation 1. To explore the interaction potential between ^2H and $^2\text{H}_2\text{NO}$, we computed 20100 single-point energies at the CASPT2(12,10)/aug-cc-pVDZ (does

molpro have a CASPT2 reference?) level of theory. The active space consisted of the single radical orbitals of ^2H and $^2\text{H}_2\text{NO}$ (2,2), the three bonding and anti-bonding sigma orbitals of $^2\text{H}_2\text{NO}$ (6,6), and the lone-pair orbitals on the oxygen and nitrogen atoms (4,2) (**check active-space definition!**). In these calculations, the center-of-mass distance was scanned in the range 1.5–10 Å, and at each distance increment, single-point energies were computed at randomly selected fragment orientations.

Table S2:

Species	aug-cc-pVTZ (Hartree)	aug-cc-pVQZ (Hartree)	CBS (kJ/mol)	ΔZPE (Hartree)	Frequencies (cm^{-1})	Reference
$^2\text{H} + ^2\text{H}_2\text{NO}$	-0.49982 + -130.91817	-0.49995 + -130.95175				
$^2\text{NH}_2 + ^2\text{OH}$	-55.79985 + -75.64559					
$\text{H}_2 + \text{HNO}$	-1.17264 + -130.30975	-1.17387 + -130.34260				
NH_2OH	-131.55260	-131.58727				
NH_3O	-131.51311	-131.54799				
$\text{TS}(\text{NH}_2\text{OH} \rightleftharpoons \text{NH}_3\text{O})$						
$\text{TS}(\text{NH}_3\text{O} \rightleftharpoons \text{H}_2 + \text{HNO})$	-131.42306	-131.45729				

Table S3: Stationary-point energies for species on the $\text{O}(^3\text{P}) + \text{HNO}$ potential-energy surface. The energies are in kJ mol^{-1} . The tabulated ROHF-CCSD(T) values are zero-point-energy corrected. Also listed are the electronic partition functions and symmetry numbers for the species. Spin-orbit effects were accounted for by reducing the energy of the $^2\text{NH}_2 + ^2\text{OH}$ well by ??? kJ mol^{-1} .

Species	$q_{\text{elec}}^{\text{a}}$	$\sigma_{\text{ext}}/m_{\text{opt}}^{\text{b}}$	ΔZPE	ROHF-CCSD(T)/CBS ^c	$\Delta\text{T}(\text{Q})^{\text{d}}$	ATcT ^e
$^2\text{H} + ^2\text{H}_2\text{NO}$	2, 2	1/1, 1/1 ^f	0.0	0.0 (T1)	0.0	0
$^2\text{NH}_2 + ^2\text{OH}$	q_{NO} , 2	2/1, 1/1	0.0	0.0 (T1)	0.0	-60.49 ± 0.62
$\text{H}_2 + \text{HNO}$	1, 1	1/1, 1/1	0.0	0.0 (T1)	0.0	-176.75 ± 0.62
NH_2OH	1	1/1	0.0	0.0 (T1)	0.0	-319.74 ± 0.68
NH_3O	1	3/1	0.0	0.0 (T1)	0.0	-214.5 ± 1.3
$\text{TS}(\text{NH}_2\text{OH} \rightleftharpoons \text{NH}_3\text{O})$	1, 1	1/1	0.0	0.0 (T1)	0.0	0
$\text{TS}(\text{NH}_3\text{O} \rightleftharpoons \text{H}_2 + \text{HNO})$	1, 1	1/1	0.0	0.0 (T1)	0.0	0

^a $q_{\text{OH}} = 2 + 2e^{-201 \text{ K}/T}$.

^b Here $\sigma_{\text{ext}}/m_{\text{opt}}$ is the ratio of rotational (external) and optical symmetry numbers.

^c The values in the parentheses are T1 diagnostics [13].

^d Approximate CCSDT(Q) correction: variant B [3].

^e ATcT stands for Active Thermochemical Tables [14].

^f The inversion motion is explicitly considered, and an internal symmetry number of 2 is applied for this motion.

2.2. Flexible Transition State Theory

For the barrierless $^2\text{H} + ^2\text{H}_2\text{NO} \longrightarrow \text{NH}_2\text{OH}$ and $^2\text{H} + ^2\text{H}_2\text{NO} \longrightarrow \text{NH}_3\text{OH}$ reactions, we computed the TS state sums using the Flexible-Transition-State-Theory (FTST) expressions derived by Robertson et al. [27]. The optimal location of the TS was determined as a function of energy and angular momentum. Four pivot points were used. $^2\text{H}_2\text{NO}$ is approximately planar, and two pivot points were placed $0.5a_0$ below and above the nitrogen and oxygen atoms. **I'll need to finish this.**

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