Rate coefficients for fuel + NO₂:
predictive kinetics for HONO and HNO₂ formation

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ABSTRACT

High-accuracy electronic structure calculations and transition state theory are used to predict the rate coefficients for the H-abstraction reactions $\text{H}_2 + \text{NO}_2$ and $\text{CH}_4 + \text{NO}_2$. In each case, three different HNO_2 isomers are formed: cis-HONO, trans-HONO, and HNO_2 . These results are used as benchmarks to test different combinations of density functionals and basis sets. The performance of these DFT methods are evaluated both with and without the use of subsequent CCSD(T)-F12a single-point energy corrections. The compound method CCSD(T)-F12a/cc-pVTZ-f12//B2PLYPD3/cc-pVTZ is used to predict the rate coefficients for C_2 - C_4 alkanes and alkenes + NO_2 , and the resulting activation energies are generalized into rate rules. These new rules will enable accurate rate coefficients for $\text{RH} + \text{NO}_2$ reactions for larger hydrocarbons. In all cases, the dominant product for $\text{RH} + \text{NO}_2$ is $\text{R} + \text{cis-HONO}$, followed by $\text{R} + \text{HNO}_2$. Although trans-HONO is the most stable HNO_2 isomer, the rate constants leading to its formation are roughly an order of magnitude smaller.

KEYWORDS: NO_2 , HONO, exhaust gas recirculation, alkyl-nitrates, transition state theory

1. Introduction

In conventional internal combustion engines, NO_2 is formed after the oxidation of the fuel; consequently, fuel and NO_2 are seldom at appreciable concentrations in the same place at the same time. However, two recent trends in low-temperature combustion introduce large concentrations of NO_2 to the fuel-air mixture prior to ignition: exhaust gas recirculation (EGR), and the addition of alkyl-nitrates. In EGR, a portion of the exhaust gas is retained in the cylinder, thereby diluting the fuel-air mixture with H_2O , CO_2 , CO , NO_x , and unburned hydrocarbons. EGR is used primarily as a means of controlling the in-cylinder temperature prior to combustion through a combination of increased heat capacity and dilution of the fuel-air mixture.[1, 2] The effects of EGR on kinetics are less well understood. Alkyl-nitrates in general, and 2-ethylhexyl-nitrate (EHN) in particular, have been used for decades as cetane enhancers in diesel fuels.[3-7] More recently, EHN has been used as an additive in low-temperature compression-ignition engines to increase the reactivity of high-octane gasoline under low-load conditions.[8-12] As demonstrated in Ref. [7], adding 1% EHN to stoichiometric n-heptane/air decreased the ignition delay by a factor of 2 to 3 in the low-temperature regime. Following the cleavage of the RO-NO_2 bond, the resulting 2-ethylhexyloxy radical dissociates to form CH_2O and 3- C_7H_{15} . The main boost to ignition comes not from the NO_2 but from the heptyl radical, which rapidly undergoes first- and second-oxygen addition to form three radicals.[13]

Whether from EGR or EHN, the primary kinetic effect of NO_2 on low-temperature auto-ignition is through radical-radical reactions.[14-23] At high pressures, NO_2 combines with alkyl radicals to form nitro-alkanes, RNO_2 , *e.g.* Stein et al. measured nitrohexane as a major product at intermediate temperatures in the pyrolysis of EHN.[3] Under engine-relevant conditions, however, the RNO_2 dissociates back to $\text{R} + \text{NO}_2$, and the primary contribution of NO_x to the reactivity is through sequence of reactions in which NO and NO_2 convert less reactive peroxy radicals into more reactive OH and alkyloxy radicals:

Fuel + NO₂ reactions, in contrast, are less well characterized. The main reaction for fuel + NO₂ is abstraction to form one of three HNO₂ isomers:

Owing to the unusually high stability of the NO₂ radical, rate constants for H-abstraction via NO₂ are expected to be small, *i.e.* similar to H-abstraction from other resonantly stabilized radicals. However, due either to EGR or to alkyl-nitrate doping, the concentration of NO₂ prior to ignition can be several 100's of ppm; consequently, the rate of fuel + NO₂ still could be significant. Ignition parameters are sensitive to these reactions, since the HONO/HNO₂ isomers rapidly dissociate to NO + OH. Thus, the net effect of R6 is chain branching: $\text{RH} + \text{NO}_2 \rightarrow \text{R} + \text{OH} + \text{NO}$.

It remains an open question as to whether or not it is essential to include all three HNO₂ isomers in NO_x submechanisms. As will be demonstrated shortly, the rate constants for Reactions (R6a-b) can differ by orders of magnitude. Furthermore, Chan et al reported that secondary reactions involving HNO₂ isomers in general, and $\text{O}_2 + \text{HONO/HNO}_2 \rightarrow \text{HO}_2 + \text{NO}_2$ in particular, can have markedly different rate coefficients.[24] For these reasons, it is worth considering their rates of formation as distinct. A detailed investigation of HONO/HNO₂ unimolecular reactions is the subject of a forthcoming manuscript.

Slack and Grillo conducted shock tube studies on $\text{H}_2 + \text{NO}_2$ and $\text{CH}_4 + \text{NO}_2$. [25-27] Park et al performed low-pressure experiments on NO₂/H₂/CO/Ar mixtures.[28] They found that the

recommended rate constants of Tsang and Herron for $\text{H}_2 + \text{NO}_2$, which were based on Slack and Grillo's measurements, led to NO_2 reduction that was much faster than observed experimentally.[29] As part of a broader study on the $\text{H}_2/\text{O}_2/\text{NO}_x$ submechanism, Mueller et al reported that the model of Park et al. was able to reproduce their flow-tube data adequately, whereas the model from Slack and Grillo was not.[30] The authors speculated that the large over-prediction of Slack and Grillo could be due to gas dynamic effects resulting from the use of undiluted mixtures in the shock tube.

Yamaguchi and coworkers combined electronic structure calculations with flow-tube oxidation experiments to predict the rate constants for $\text{CH}_4 + \text{NO}_2$. Their rate constants for $\text{CH}_4 + \text{NO}_2$ were several orders of magnitude smaller than the work of Slack and Grillo.[31, 32] The authors did not consider cis-HONO as a distinct channel from trans-HONO. More recently, Chan et al. used density functional theory (DFT) to predict the rate coefficients for $\text{NO}_2 + \text{CH}_4$, C_2H_6 , C_3H_8 , and C_4H_{10} . [24] Based upon the authors' prior experience with their functional of choice, BHandHLYP, the activation energies needed to be reduced systematically by 5 kcal/mol.

More recent experimental and modeling work has highlighted the need for improved kinetics for fuel + NO_2 abstraction reactions. Mathieu et al. investigated the effects of NO_2 addition to H_2/O_2 ignition delays in a shock tube.[33] The rate constants used in Ref. [33] were adapted from the NO_x mechanism of Dayma and Dagaut.[34] OH^* sensitivity analysis was used en lieu of brute force ignition-delay sensitivity, and these results indicated a strong sensitivity to $\text{H}_2 + \text{NO}_2 = \text{H} + \text{HONO}$. Importantly, the modeling component in Ref. [33] did not distinguish between the three HNO_2 isomers as products from $\text{H}_2 + \text{NO}_2$. Rasmussen et al studied the effects of $\text{CH}_4 + \text{NO}_2$ in a high-pressure flow reactor.[19] They used the recommended rates of Yamaguchi, which treated cis- and trans-HONO as a single species.[31, 32] The authors found that the initiation temperature was highly sensitive to the rate constants for $\text{CH}_4 + \text{NO}_2$. Chan et al. noted that $\text{CH}_4 + \text{NO}_2 = \text{CH}_3 + \text{HONO}$ had the highest sensitivity coefficient for CH_4 in CH_4/air mixtures with 100 ppm NO_2 at 923 K.[22] Gokulakrishnan et al studied the effects of NO_x on

propane ignition delay times in a flow reactor.[21] The rate coefficients were adapted from Chan et al.[24] As with the Rasmussen study, the authors treated cis- and trans-HONO as a single channel. Principal Component Analysis revealed that the four possible $\text{C}_3\text{H}_8 + \text{NO}_2$ reactions were among the most sensitive reactions for stoichiometric propane/air oxidation doped with 100 ppm NO at 875 K.

Based upon the reported sensitivity of key ignition parameters to fuel + NO_2 kinetics, as well as the lack of consensus regarding the rate coefficients for the three HNO_2 isomers, the current work investigates the rate constants and branching fractions for a broad range of fuels with NO_2 .

2. Computational Methods

For $\text{H}_2 + \text{NO}_2$ and $\text{CH}_4 + \text{NO}_2$, high-accuracy post-coupled-cluster calculations are performed to calculate the stationary points on the H_2NO_2 and CH_4NO_2 potential energy surfaces (PES), respectively. The stationary points were computed using the same method as in Goldsmith et al.,[35] so only a brief summary is provided here. Geometry optimization and normal mode analysis were performed using UCCSD(T)/cc-pVTZ with an RHF reference wave function. Five post-CCSD(T) corrections were applied to the electronic energy: the complete basis-set limit, ΔE_{CBS} , was extrapolated from aug-cc-pVQZ and aug-cc-pV5Z basis set calculations; corrections for higher-level cluster excitations, $\Delta E_{\text{T/Q}}$, were computed from the difference between CCSDT(Q)/cc-pVDZ and CCSD(T)/cc-pVDZ energies; core-valence correlations, ΔE_{CV} , were determined from the difference in the CCSD(T)/cc-pcV ∞ Z energies where the core electrons are frozen (uncorrelated) or not; Relativistic effects, ΔE_{rel} , are approximated from the difference in CI energy with and without using the Douglas-Kroll one-electron integrals; and corrections for anharmonicity, ΔE_{anh} , were approximated from the difference in the B3LYP/6-311++G(d,p) zero-point energy using a second-order perturbative anharmonic analysis. Based upon a detailed comparison with reference data, the uncertainty at two standard deviations is expected to be ± 0.3 kcal/mol for the local minima and slightly higher for the saddle points (*personal*

communication: S.J. Klippenstein, L.B. Harding, B. Ruscic). All wave-function calculations were performed in MOLPRO;[36] the higher-level excitations were computed using the MRCC package of Kállay and coworkers;[37] the density functional theory calculations were performed in Gaussian09.[38]

For larger potential energy surfaces, the wavefunction methodology becomes prohibitively expensive. To find an appropriate balance between accuracy and affordability, three modern DFT methods were considered: M062X,[39] M11,[40] and B2PLYPD3.[41-43] For each density functional, four different triple-zeta basis sets were tested: 6-311++G(d,p), MG3S, cc-pVTZ, and jun-cc-pVTZ. Additionally, owing to its continued popularity, the compound method CBS-QB3 also was considered.[44] For each density functional / basis set combination, single-point calculations were performed using UCCSD(T)-F12a/cc-pVTZ-f12.[45-47]

The temperature dependent rate coefficients were computed using canonical transition state theory, as implemented in the code PAPER.[48] In the calculation of the partition functions, non-torsional modes were assumed to behave as harmonic oscillators. The torsional modes were treated as one-dimensional hindered internal rotors, and the rotational potential was computed in 10° increments using M11/jun-cc-pVTZ. The hindered-rotor partition function was computed via direct summation of the energy levels from the solution of the corresponding 1D Schrodinger equation. Tunneling was approximated via an asymmetric Eckhart model.

3. Results

3.1 $\text{H}_2 + \text{NO}_2$

The results of the compound coupled-cluster calculations for the stationary points on the H_2NO_2 PES are listed in Table 1. Table 1 includes the van der Waals (vdW) complexes on the $\text{H} + \text{HONO}/\text{HNO}_2$ side of the saddle point. The energies of the vdW complexes were used in the Eckhart tunneling

calculation; stabilization of these wells is of no kinetic relevance to this reaction. Also included is the CCSD(T)/cc-pVTZ T1 diagnostic. Note that the transition states for the formation of cis-HONO and trans-HONO have T1 diagnostics of 0.039 and thus have modest multi-reference character. To quantify the importance of these multi-reference effects, additional multi-reference calculations were performed. The transition state and van der Waals complex geometries were reoptimized using CASPT2(15e,12o)/cc-pVTZ. The active space consisted of the 3 lone pair, the NO π , π^* , the 2 NO σ , σ^* , and the radical in NO₂, as well as the σ , σ^* in H₂. [49, 50] The basis set limit was extrapolated from subsequent CASPT2(15e,12o)/cc-pVQZ single-point calculations. From the results in Table 1, the sum of the contributions from ΔE_{CBS} and $\Delta E_{\text{T/Q}}$ to the barrier height relative to the van der Waals complex is 17.8 kcal/mol. The CASPT2(15e,12o)/cc-pV ∞ Z value is 18.3 kcal/mol. Thus, we conclude that the multi-reference effects are not significant for this transition state.

Table 1: Stationary points on the H₂NO₂ Potential Energy Surface. All values are in kcal/mol, relative to H₂ + NO₂.

name	total	CBS	T/Q	CV	rel	anh	ZPE	T1
H ₂ + NO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.006
								0.025
H + cis-HONO	26.05	24.47	0.49	0.15	0.00	-0.05	0.99	0.021
H + trans-HONO	25.60	24.15	0.37	0.14	-0.01	-0.04	0.98	0.021
H + HNO ₂	34.34	31.92	0.45	-0.14	0.12	-0.06	2.05	0.020
ts: cis-HONO	32.35	33.89	-0.78	0.17	-0.02	-0.47	-0.44	0.039
ts: trans-HONO	41.01	42.23	-0.21	0.34	-0.13	0.03	-1.25	0.039
ts: HNO ₂	36.31	35.99	0.11	-0.09	0.10	-0.22	0.41	0.032
vdW: cis-HONO	25.81	24.21	0.49	0.15	0.00	-0.16	1.13	0.021
vdW: trans-HONO	25.43	23.85	0.37	0.14	-0.01	-0.12	1.19	0.021
vdW: HNO ₂	34.15	31.57	0.45	-0.14	0.11	-0.14	2.31	0.020

The rate coefficients for $\text{H}_2 + \text{NO}_2$ are illustrated in Figure 1 and listed in Table 2. The total rate constant of Park et al. (black dash) is in excellent agreement with our rate constant for $\text{H} + \text{cis-HONO}$ (solid red).

Figure 1: Rate constants for $\text{H}_2 + \text{NO}_2$.

Table 2: Rate coefficients for $\text{H}_2 + \text{NO}_2$. The rate coefficients are of the form $k(T) = A (T/T_0)^n \exp[-E_a/RT]$, with A in $\text{cm}^3/\text{mol-s}$, $T_0 = 1 \text{ K}$, and E_a in kcal/mole .

product	A	n	E_a	$k(1000\text{K})$
H + cis-HONO	1.79×10^1	3.51	26.3	1.06×10^6
H + trans-HONO	2.40×10^1	3.62	35.8	2.55×10^4
H + HNO_2	2.39×10^2	3.15	31.1	1.09×10^5
H + HONO (total), Tsang [29]	2.41×10^{13}	0.0	28.8	1.22×10^7
H + HONO (total), Park [28]	1.30×10^4	2.80	29.8	1.02×10^6

3.2 $\text{CH}_4 + \text{NO}_2$

The results of the compound coupled-cluster calculations for the stationary points on the CH_4NO_2 PES are listed in Table 3. The resulting rate coefficients are summarized in Table 4.

Table 3: Stationary points on the CH_4NO_2 Potential Energy Surface. All values are in kcal/mol, relative to $\text{CH}_4 + \text{NO}_2$.

name	total	CBS	T/Q	CV	rel	anh	ZPE	T1
$\text{CH}_4 + \text{NO}_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.006
								0.025
$\text{CH}_3 + \text{cis-HONO}$	26.10	27.34	0.50	0.33	-0.02	0.09	-2.14	0.005
								0.021
$\text{CH}_3 + \text{trans-HONO}$	25.65	27.03	0.38	0.31	-0.03	0.10	-2.15	0.005
								0.021
$\text{CH}_3 + \text{HNO}_2$	34.38	34.79	0.46	0.03	0.09	0.08	-1.08	0.005
								0.020
ts: cis-HONO	31.52	34.86	-0.60	0.33	-0.02	-0.30	-2.76	0.039
ts: trans-HONO	37.53	40.97	-0.13	0.41	-0.09	-0.30	-3.34	0.039
ts: HNO_2	34.06	36.26	0.08	0.09	0.10	-0.30	-2.17	0.032
vdW: cis-HONO	23.45	24.78	-0.40	0.00	0.32	-0.03	-1.22	0.018
vdW: trans-HONO	23.93	24.78	0.07	0.00	0.32	-0.03	-1.22	0.018
vdW: HNO_2	32.14	31.63	0.28	0.11	0.03	-0.03	0.11	0.018

Figure 2: Rate constants for $\text{CH}_4 + \text{NO}_2$.

The rate constants are plotted in Figure 2. The earlier results from Yamaguchi (dotted lines) and Chan (dashed lines) both suggest that the rate constant for $\text{CH}_3 + \text{HNO}_2$ is the largest; the two models

disagree, however, on the rate constants for HONO formation, with Chan showing $\text{CH}_3 + \text{cis-HONO}$ being roughly equal to $\text{CH}_3 + \text{HNO}_2$, whereas Yamaguchi has the rate constant for $\text{CH}_3 + \text{cis-HONO}$ being several orders of magnitude smaller than $\text{CH}_3 + \text{HNO}_2$. The present work shows a different trend: $\text{CH}_3 + \text{cis-HONO}$ is the largest, $\text{CH}_3 + \text{trans-HONO}$ is the smallest, and $\text{CH}_3 + \text{HNO}_2$ is roughly in between.

The data in Table 1 and Table 3 show what at first appears to be a curious trend. As noted by Chan et al, although trans-HONO is the most stable HNO_2 isomer, followed by cis-HONO then HNO_2 , the barrier heights for $\text{RH} + \text{NO}_2 \rightarrow \text{products}$ are highest for trans-HONO, followed by HNO_2 , then cis-HONO. Chan et al. attributed this behavior to the stabilizing effect of a five-member ring in the transition state for cis-HONO formation.

This apparent contra-thermodynamic behavior is a consequence of looking at the potential energy surface in the endothermic direction. If the reactions are considered in the exothermic direction, with the zero of energy in each case set to be $\text{R} + \text{HONO/HNO}_2$ and not $\text{RH} + \text{NO}_2$, then the barrier heights are consistent with the expectation that the most exothermic reaction, $\text{R} + \text{HNO}_2 \rightarrow \text{RH} + \text{NO}_2$, has the lowest barrier, and the least exothermic reaction, $\text{R} + \text{trans-HONO} \rightarrow \text{RH} + \text{NO}_2$, has the largest barrier. The role of any ring-like stabilization for cis-HONO is modest at best. The five-member ring-like structure involves a fairly acute H-R-O angle of approximately 42° . Additionally, torsional scans along the HC-ON axis revealed a rotational barrier of 0.3 kcal/mol, which is considerably smaller than the difference in barrier height between cis-HONO and the other two channels.

One remaining detail of the $\text{RH} + \text{NO}_2$ behavior requires explanation. Given that trans-HONO is more stable than cis-HONO by a mere ~ 0.5 kcal/mol, one would expect the barrier for $\text{R} + \text{trans-HONO} \rightarrow \text{RH} + \text{NO}_2$ to be close to the barrier for $\text{R} + \text{cis-HONO} \rightarrow \text{RH} + \text{NO}_2$. Instead, it is 6-9 kcal/mol higher. Additionally, the reference wavefunctions for the $\text{R} + \text{cis-HONO}$ and $\text{R} + \text{HNO}_2$ saddle points each have the radical orbital localized on the R, whereas the $\text{R} + \text{trans-HONO}$ saddle point has the

radical orbital localized on the oxygen atom. This behavior can be explained by the molecular orbitals of NO₂. The singularly occupied molecular orbital (SOMO) of NO₂ has two nodal planes, one centered on each oxygen atom, and one centered in the nitrogen atom. As the RH approached the nitrogen atom, it overlaps with only one lobe (*e.g.* positive). As the RH approaches either oxygen atom from the cis-HONO direction, it mostly overlaps with the positive (oxygen-centered) lobe, with minimal mixing of the negative lobe. When the RH approaches the oxygen atom from the trans-HONO direction, in contrast, it encounters the oxygen-centered nodal plane and thus experiences nearly equal amounts of positive and negative overlap. In order to avoid cancellation and ensure sufficient overlap, the RH must go to closer RH-NO₂ distances, which contributes to additional Coulombic repulsion and thereby increases the barrier.

Table 4: Rate coefficients for CH₄ + NO₂. The rate coefficients are of the form $k(T) = A (T/T_0)^n \exp[-E_a/RT]$, with A in cm³/mol-s, T₀ = 1 K, and E_a in kcal/mole.

product	A	n	E _a	k(1000K)
CH ₃ + cis-HONO	1.14x10 ⁻¹	4.28	26.3	1.12x10 ⁶
CH ₃ + trans-HONO	3.97x10 ⁻¹	4.18	31.2	2.02x10 ⁵
CH ₃ + HNO ₂	7.41x10 ¹	3.42	33.1	8.04x10 ⁴
CH ₃ + HONO (total), Slack [27]	1.2x10 ¹³	0.0	30.0	3.33x10 ⁶
CH ₃ + trans-HONO, Yamaguchi [32]	6.50x10 ¹⁴	0.0	45.8	6.35x10 ⁴
CH ₃ + HNO ₂ , Yamaguchi, [32]	6.00x10 ¹⁴	0.0	37.6	3.63x10 ⁶
CH ₃ + cis-HONO, Chan [24]	8.70x10 ¹³	0.0	35.2	1.76x10 ⁶
CH ₃ + trans-HONO, Chan [24]	2.10x10 ¹⁴	0.0	40.7	2.67x10 ⁵
CH ₃ + HNO ₂ , Chan [24]	9.50x10 ¹⁴	0.0	38.4	3.84x10 ⁶

3.3 Higher molecular weight fuels + NO₂

The results of the DFT benchmark tests are summarized in Table 5; columns 2-5 correspond to the DFT-only results, and columns 6-7 are for the CCSD(T)-F12a//DFT results. The DFT method with the

smallest Mean Absolute Deviation (MAD) for the stationary points in Table 1 and Table 3 (excluding the vdW complexes) was M062X/MG3S. The third column contains the product of the vibrational frequencies, which is a useful proxy for the high-temperature vibrational partition function; the imaginary frequencies and the low-frequency torsional mode in the CH₄+NO₂ transition state were not included in the product of frequencies. The DFT with the smallest MAD for the product of the vibrational frequencies was B2PLYPD3/cc-pVTZ. Since neither of these two tests was conclusive, the six rate constants of Table 2 in Table 4 were computed using all 13 methods. The DFT with the smallest MAD for the difference in log₁₀ of the rate constants was M11/jun-cc-pVTZ, with M11/cc-pVTZ being effectively equivalent. When the CCSD(T)-F12a/cc-pVTZ-f12 single-point calculations were included, the DFT methods all performed similarly well; the absolute lowest MAD for the rate coefficients was with CCSD(T)-F12a/cc-pVTZ-f12//B2PLYPD3/cc-pVTZ. Curiously, the CCSD(T)-F12a/cc-pVTZ-f12 T1 diagnostic for the saddle points was lower than those Table 1 and Table 3, with a maximum value of 0.029. The poor performance of CBS-QB3 is attributed to difficulties in the B3LYP/CBSB7 geometry optimization for several of the transition states, which showed unusually large distances; repeated attempts to obtain geometries that were more consistent with other methods failed, and this method is not recommended for RH + NO₂ reactions.

Table 5: Mean Absolute Deviation for different density functional and basis sets, relative to the coupled cluster benchmark values (lower is better).

method	$E_{0,DFT} - E_{0,CC}$	$\frac{\prod v_{DFT} - \prod v_{CC}}{\prod v_{CC}}$	$\log_{10}(k_{DFT}) - \log_{10}(k_{CC})$	$E_{0,F12} - E_{0,CC}$	$\log_{10}(k_{F12}) - \log_{10}(k_{CC})$
M062X/6-311++G(d,p)	1.77	0.06	0.39	0.15	0.16
M062X/ cc-pVTZ	1.18	0.08	0.29	0.12	0.17
M062X/ MG3S	1.01	0.10	0.24	0.12	0.18
M062X/jun-cc-pVTZ	1.38	0.07	0.31	0.10	0.15
M11/6-311++G(d,p)	1.55	0.03	0.24	0.13	0.16

M11/ cc-pVTZ	1.28	0.05	0.14	0.10	0.16
M11/ MG3S	1.19	0.05	0.16	0.13	0.16
M11/jun-cc-pVTZ	1.18	0.14	0.13	0.12	0.15
B2PLYPD3/6-311++G(d,p)	2.38	0.05	0.25	0.19	0.14
B2PLYPD3/cc-pVTZ	2.59	0.03	0.29	0.22	0.11
B2PLYPD3/MG3S	2.56	0.03	0.30	0.18	0.12
B2PLYPD3/jun-cc-pVTZ	2.22	0.05	0.22	0.20	0.12
CBS-QB3	1.77	0.06	0.29	1.77	0.29

The new compound method of choice, CCSD(T)-F12a/cc-pVTZ-f12//B2PLYPD3/cc-pVTZ, was used for RH + NO₂ for ethane, propane, n-butane, and iso-butane, and for propene, 1-butene, trans-2-butene, and iso-butene. For the alkenes, only abstraction of the allylic hydrogen was considered; barriers for abstraction of vinylic hydrogens on the double bond were assumed to be too large to be kinetically significant. Additionally, although addition of NO₂ to the double bond is possible, it is expected that the resulting nitro-alkyl radical would be weakly bound and immediately dissociate back. The Arrhenius coefficients for the four alkanes are summarized in Table 6; the four alkenes are summarized in Table 7.

Table 6: CCSD(T)-F12a/cc-pVTZ-f12//B2PLYPD3/cc-pVTZ rate coefficients for alkane + NO₂. The rate coefficients are of the form $k(T) = A (T/T_0)^n \exp[-E_a/RT]$, with A in cm³/mol-s, T₀ = 1 K, and E_a in kcal/mole.

Reactant	Product	A	n	E _a	k(1000K)
H ₂ + NO ₂	H + cis-HONO	1.21x10 ²	3.29	28.1	6.52x10 ⁵
	H + trans-HONO	4.37x10 ²	3.29	37.1	2.58x10 ⁴
	H + HNO ₂	2.41x10 ⁴	2.53	32.7	6.64x10 ⁴
CH ₄ + NO ₂	CH ₃ + cis-HONO	1.60x10 ⁰	3.95	27.8	9.58x10 ⁵
	CH ₃ + trans-HONO	1.51x10 ¹	3.75	34.7	7.08x10 ⁴
	CH ₃ + HNO ₂	6.87x10 ²	3.16	32.0	2.06x10 ⁵

C ₂ H ₆ + NO ₂	C ₂ H ₅ + cis-HONO	3.32x10 ⁰	3.84	23.9	6.45x10 ⁶
	C ₂ H ₅ + trans-HONO	8.49x10 ¹	3.45	32.0	1.92x10 ⁵
	C ₂ H ₅ + HNO ₂	3.20x10 ²	3.19	26.5	1.88x10 ⁶
C ₃ H ₈ + NO ₂	1-C ₃ H ₇ + cis-HONO	2.47x10 ⁰	3.83	24.1	4.03x10 ⁶
	1-C ₃ H ₇ + trans-HONO	4.90x10 ¹	3.5	32.6	1.18x10 ⁵
	1-C ₃ H ₇ + HNO ₂	8.43x10 ¹	3.28	26.5	9.45x10 ⁵
	2-C ₃ H ₇ + cis-HONO	1.65x10 ⁰	3.69	21.1	4.77x10 ⁶
	2-C ₃ H ₇ + trans-HONO	1.80x10 ¹	3.38	29.8	7.62x10 ⁴
	2-C ₃ H ₇ + HNO ₂	4.83x10 ¹	3.18	22.7	1.82x10 ⁶
n-C ₄ H ₁₀ + NO ₂	1-C ₄ H ₉ + cis-HONO	4.73x10 ⁰	3.83	24.0	8.23x10 ⁶
	1-C ₄ H ₉ + trans-HONO	9.03x10 ¹	3.51	32.5	2.38x10 ⁵
	1-C ₄ H ₉ + HNO ₂	1.13x10 ²	3.32	26.2	1.90x10 ⁶
	2-C ₄ H ₉ + cis-HONO	2.26x10 ⁰	3.72	21.3	7.11x10 ⁶
	2-C ₄ H ₉ + trans-HONO	1.47x10 ¹	3.49	29.8	1.31x10 ⁵
	2-C ₄ H ₉ + HNO ₂	5.50x10 ¹	3.23	22.3	3.65x10 ⁶
i-C ₄ H ₁₀ + NO ₂	i-C ₄ H ₉ + cis-HONO	2.24x10 ⁰	3.80	24.3	2.73x10 ⁶
	i-C ₄ H ₉ + trans-HONO	5.76x10 ¹	3.45	32.4	1.05x10 ⁵
	i-C ₄ H ₉ + HNO ₂	7.95x10 ¹	3.25	26.5	7.14x10 ⁵
	t-C ₄ H ₉ + cis-HONO	6.32x10 ⁰	3.40	18.7	8.01x10 ⁶
	t-C ₄ H ₉ + trans-HONO	2.88x10 ¹	3.20	27.2	1.28x10 ⁵
	t-C ₄ H ₉ + HNO ₂	7.17x10 ¹	3.02	19.1	5.42x10 ⁶

Table 7: CCSD(T)-F12a/cc-pVTZ-f12//B2PLYPD3/cc-pVTZ rate coefficients for alkene + NO₂. The rate coefficients are of the form $k(T) = A (T/T_0)^n \exp[-E_a/RT]$, with A in cm³/mol-s, T₀ = 1 K, and E_a in kcal/mole.

Reactant	Product	A	n	E _a	k(1000K)
C ₃ H ₆ + NO ₂	CH ₂ CHCH ₂ + cis-HONO	4.47x10 ⁻⁴	4.79	18.1	1.15x10 ⁷
	CH ₂ CHCH ₂ + trans-	2.63x10 ⁻⁶	5.32	25.2	7.39x10 ⁴

	HONO				
	$\text{CH}_2\text{CHCH}_2 + \text{HNO}_2$	2.54×10^{-2}	4.21	18.7	8.68×10^6
1- $\text{C}_4\text{H}_8 + \text{NO}_2$	$\text{CH}_2\text{CHCH}_2\text{CH}_3 + \text{cis-HONO}$	3.11×10^{-3}	4.4	15.7	1.83×10^7
	$\text{CH}_2\text{CHCH}_2\text{CH}_3 + \text{trans-HONO}$	1.35×10^{-3}	4.47	24.3	1.74×10^5
	$\text{CH}_2\text{CHCH}_2\text{CH}_3 + \text{HNO}_2$	7.83×10^{-2}	3.93	15.2	2.31×10^7
trans-2- $\text{C}_4\text{H}_8 + \text{NO}_2$	$\text{CH}_2\text{CHCH}_2\text{CH}_3 + \text{cis-HONO}$	1.31×10^{-3}	4.62	17.3	1.56×10^7
	$\text{CH}_2\text{CHCH}_2\text{CH}_3 + \text{trans-HONO}$	1.86×10^{-6}	5.29	22.5	1.67×10^5
	$\text{CH}_2\text{CHCH}_2\text{CH}_3 + \text{HNO}_2$	4.89×10^{-2}	4.06	17.6	1.08×10^7
iso- $\text{C}_4\text{H}_8 + \text{NO}_2$	$\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2 + \text{cis-HONO}$	1.67×10^{-3}	4.56	16.4	2.06×10^7
	$\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2 + \text{trans-HONO}$	8.91×10^{-6}	5.18	22.9	3.12×10^5
	$\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2 + \text{HNO}_2$	1.51×10^{-1}	3.95	17.7	1.41×10^7

Figure 3: Branching fraction versus carbon number, evaluated at 1000 K, (a) alkane + NO₂, and (b) alkene + NO₂.

For both alkanes and alkenes, the dominant product is *cis*-HONO. At 1000 K, for example, it accounts for roughly 80% of the total flux in alkanes + NO₂ (Figure 3a); for alkenes, it is closer to 60% (Figure 3b). This behavior is qualitatively similar at other temperatures. As depicted in Figure 3, the branching fraction to *cis*-HONO decreases as the size of the alkane increases. Although the barrier height (and activation energies) for $\text{RH} + \text{NO}_2 \rightarrow \text{R} + \text{cis-HONO}$ decrease with increasing molecular weight, the barrier heights for $\text{alkane} + \text{NO}_2 \rightarrow \text{R} + \text{HNO}_2$ decrease even more. Presumably the HNO₂ transition state experiences fewer repulsive interactions with neighboring moieties.

For the purposes of uncertainty quantification, the uncertainty in the saddle points in the benchmark data of Table 1 and Table 3 is assumed to be twice that of the minima, or ± 0.6 kcal/mol at two sigma. The standard deviation between the benchmark values and the CCSD(T)-F12a/cc-pVTZ-f12//B2PLYPD3/cc-pVTZ energies for all the stationary points in Table 1 and Table 3 was 0.2 kcal/mol. This result suggests that the uncertainty in the barrier heights for the compound methods is ± 1.0 kcal/mol at two sigma. However, the uncertainty in the activation energy is expected to be slightly larger, owing to the complex temperature dependence of anharmonicities in the transition state partition function. Accordingly, we assign an uncertainty of ± 1.5 kcal/mol for the activation energies.

Figure 4: BEP plots for (a) alkane + NO₂, and (b) alkene + NO₂.

The activation energies from Table 6 and Table 7 are plotted versus the heat of reaction (at zero Kelvin) in Figure 4 (*i.e.* a Brønsted/Bell-Evans-Polanyi (BEP) plots). The equations for the linear fits in Figure 4 are presented in Table 8. For the alkane + NO₂ reactions, the linear fit is very good, with an average $R^2 > 0.98$. For these reactions, the slopes in Figure 4 and Table 8 are nearly unity, indicating that the activation energy is approximately a constant value added to the heat of reaction in the endothermic direction. The N-H bond in HNO₂ is so weak, ~ 68.6 kcal/mol, that the reverse reaction $R + \text{HNO}_2$ is effectively barrierless, and the corresponding Arrhenius fits have a negative activation energy. For the alkene + NO₂ reactions, in contrast, the linear scaling relation is less successful. For these

reactions, the activation energy is only a weak function of the heat of reaction; the average deviation from the mean is less than 1 kcal/mol.

Table 8: BEP parameters for fuel + NO₂. E_a and ΔH in [kcal/mol]. The values in parentheses are one standard deviation.

Reaction class	BEP relation
alkane + NO ₂ → R + cis-HONO	E _a = 0.3 (± 0.8) + 1.1 (± 0.04) x ΔH(0K)
alkane + NO ₂ → R + trans-HONO	E _a = 12.6 (± 1.5) + 0.90 (± 0.08) x ΔH(0K)
alkane + NO ₂ → R + HNO ₂	E _a = -20.2 (± 2.3) + 1.5 (± 0.08) x ΔH(0K)
alkene + NO ₂ → R + cis-HONO	E _a = 13.7 (± 2.3) + 0.41 (± 0.3) x ΔH(0K)
alkene + NO ₂ → R + trans-HONO	E _a = 24.6 (± 3.6) - 0.13 (± 0.4) x ΔH(0K)
alkene + NO ₂ → R + HNO ₂	E _a = 4.7 (± 3.2) + 0.77 (± 0.2) x ΔH(0K)

4. Conclusions

Post-coupled cluster electronic structure theory and transition state theory calculations were used to predict the rate coefficients for the H-abstraction reactions H₂ + NO₂ and CH₄ + NO₂ going to H and CH₃, respectively, plus three different HNO₂ isomers: cis-HONO, trans-HONO, and HNO₂. The high-accuracy H₂NO₂ and CH₄NO₂ potential energy surfaces and rate constants were used as benchmarks to test different combinations of density functionals and basis sets. It was found that M062X/MG3S offered the best performance for the stationary points on the PES, B2PLYPD3/cc-pVTZ offered the best performance for vibrational frequencies, and M11/jun-cc-pVTZ offered the best overall performance in rate constants. If CCSD(T)-F12a single-point energies were included, the best performance was obtained by CCSD(T)-F12a/cc-pVTZ-f12//B2PLYPD3/cc-pVTZ. This compound method was used to calculate the rate constants for all C₂-C₄ alkanes and alkenes + NO₂. These results were generalized into BEP rules. Based upon these results, it is now possible to predict accurate rate coefficients for RH + NO₂ reactions for much larger hydrocarbons. The dominant product in RH + NO₂ is R + cis-HONO, followed

by $R + \text{HNO}_2$. Although trans-HONO is the most stable HNO_2 isomer, the rate constants leading to its formation are substantially smaller.

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