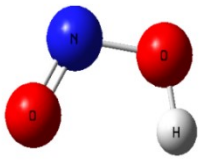
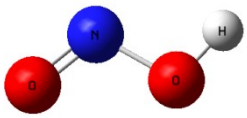
Supplementary Information

1. Ball-and-stick models of cis-HNO_2 and trans-HNO_2



cis-HNO_2



trans-HNO_2

Fig. S1. cis-HNO_2 and trans-HNO_2

2. RRKM theory and the Arrhenius equation

According to the RRKM theory and TS theory, the reaction mechanism can be represented by the following process:

$$\begin{cases} ①: A + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + M \\ ②: A^* \xrightarrow{k_3} A^{\neq} \xrightarrow{k^{\neq}} P \end{cases}$$

The relationship between the microcanonical rate constant and energy for the unimolecular dissociation reaction, as described by the RRKM theory, is expressed as follows:

$$k(E) = \frac{\sigma}{h} \frac{W^{\neq}(E - E^{\neq})}{\rho(E)} \quad \text{（S1）}$$

in the formula, σ is the degeneracy of the reaction, h is Planck's constant, E and $E^{\neq}$ represent the total energy given to the system and the activation energy, respectively, $\rho(E)$ is the density of states of the reactant, and $W^{\neq}(E - E^{\neq})$ is the total number of states of the activated complex.

The expression for the rate constant under the canonical ensemble, based on the three-parameter (*A, n, E*) Arrhenius equation, is given by:

$$k = AT^n e^{-\frac{E}{RT}} \quad \text{（S2）}$$

where, *A* is the pre-exponential factor, *n* is the exponent of temperature, and *E* represents the activation energy for the reaction. *R* is the molar gas constant (8.314 $J / mol \cdot K^{-1}$).

3. Effects of the Morse oscillator parameter x_i, density of states, and total number of states on the rate constants

Table S1: Transition state vibrational frequencies (cm^{-1}), anharmonicity parameters (x_i), and the ratio of harmonic to anharmonic rate constants (R) for bimolecular reactions at 4000 K.

Reactions	Frequencies	x_i	R	Reactions	Frequencies	x_i	R
$PODE_1+H\rightarrow CH_2OCH_2OCH_3+H_2$	0-200 cm-1	2.19	3.05×10^{2}	$PODE_1+HO_2\rightarrow CH_2OCH_2OCH_3+H_2O_2$	0-200 cm-1	1.04	5.60×10^{3}
	200-1100 cm^{-1}	0.16			200-1100 cm^{-1}	0.18	
	1100-1500 cm^{-1}	0.27			1100-1500 cm^{-1}	0.10	
$PODE_1+H\rightarrow CH_3OCHOCH_3+H_2$	0-200 cm-1	0.53	4.25×10^{3}	$PODE_1+HO_2\rightarrow CH_3OCHOCH_3+H_2O_2$	0-200 cm-1	0.93	1.26×10^{6}
	200-1100 cm^{-1}	0.54			200-1100 cm^{-1}	0.09	
	1100-1500 cm^{-1}	0.35			1100-1500 cm^{-1}	0.09	
$PODE_1+NH_2\rightarrow CH_2OCH_2OCH_3+NH_3$	0-200 cm-1	0.59	8.05×10^{3}	$PODE_1+OH\rightarrow H_2O+CH_2OCH_2OCH_3$	0-200 cm-1	0.70	3.73×10^{4}
	200-1100 cm^{-1}	0.16			200-1100 cm^{-1}	0.39	
	1100-1500 cm^{-1}	0.09			1100-1500 cm^{-1}	0.10	
$PODE_1+NH_2\rightarrow CH_3OCHOCH_3+NH_3$	0-200 cm-1	0.80	4.65×10^{5}	$PODE_1+CH_3\rightarrow CH_4+CH_2OCH_2OCH_3$	0-200 cm-1	1.35	3.50×10^{3}
	200-1100 cm^{-1}	0.43			200-1100 cm^{-1}	0.07	
	1100-1500 cm^{-1}	0.27			1100-1500 cm^{-1}	0.07	
$PODE_1+NO_2\rightarrow CH_2OCH_2OCH_3+cis-HNO_2$	0-200 cm-1	0.58	4.88×10^{5}	$PODE_1+CH_3\rightarrow CH_4+CH_3OCHOCH_3$	0-200 cm-1	0.71	1.37×10^{4}
	200-1100 cm^{-1}	0.17			200-1100 cm^{-1}	0.13	
	1100-1500 cm^{-1}	0.10			1100-1500 cm^{-1}	0.19	
$PODE_1+NO_2\rightarrow CH_2OCH_2OCH_3+trans-HNO_2$	0-200 cm-1	1.66	2.23×10^{10}	$PODE_1+CH_3O_2\rightarrow CH_3O_2H+CH_2OCH_2OCH_3$	0-200 cm-1	1.22	5.25×10^{7}
	200-1100 cm^{-1}	0.18			200-1100 cm^{-1}	0.14	
	1100-1500 cm^{-1}	0.14			1100-1500 cm^{-1}	0.10	
$PODE_1+NO_2\rightarrow CH_3OCHOCH_3+cis-HNO_2$	0-200 cm-1	0.73	9.98×10^{5}	$PODE_1+CH_3O_2\rightarrow CH_3O_2H+CH_3OCHOCH_3$	0-200 cm-1	1.47	2.65×10^{7}
	200-1100 cm^{-1}	0.08			200-1100 cm^{-1}	0.11	
	1100-1500 cm^{-1}	0.09			1100-1500 cm^{-1}	0.11	
$PODE_1+NO_2\rightarrow CH_3OCHOCH_3+trans-HNO_2$	0-200 cm-1	1.96	2.59×10^{8}				
	200-1100 cm^{-1}	0.16					
	1100-1500 cm^{-1}	0.14					

Table S2: Values of $W(E)$ and $\rho(E)$ for Reaction R12 Across Energy Levels, along with the harmonic-to-anharmonic rate constant ratio (R) at 4000 K.

	$W(E)$		$\rho(E)$		R
E(kcal/mol)	Anharmonic	harmonic	Anharmonic	harmonic	
32.55	1.31×10^{5}	1.74×10^{5}	1.02×10^{8}	2.39×10^{8}	4.17
41.87	5.75×10^{7}	2.01×10^{8}	2.25×10^{9}	7.38×10^{9}	4.54
51.66	5.55×10^{9}	3.78×10^{10}	3.81×10^{10}	1.69×10^{11}	4.86
61.84	2.48×10^{11}	2.86×10^{12}	5.17×10^{11}	3.03×10^{12}	5.15

72.3	6.61×10^{12}	1.18×10^{14}	5.74×10^{12}	4.31×10^{13}	5.41
82.98	1.21×10^{14}	3.15×10^{15}	5.35×10^{13}	5.04×10^{14}	5.66
93.85	1.66×10^{15}	6.03×10^{16}	4.28×10^{14}	4.95×10^{15}	5.90
104.85	1.80×10^{16}	8.75×10^{17}	2.99×10^{15}	4.17×10^{16}	6.14
115.98	1.60×10^{17}	1.02×10^{19}	1.85×10^{16}	3.07×10^{17}	6.37
127.2	1.21×10^{18}	9.83×10^{19}	1.03×10^{17}	2.01×10^{18}	6.60
138.51	7.99×10^{18}	8.07×10^{20}	5.26×10^{17}	1.18×10^{19}	6.83
149.88	4.65×10^{19}	5.76×10^{21}	2.45×10^{18}	6.26×10^{19}	7.05
161.31	2.44×10^{20}	3.64×10^{22}	1.06×10^{19}	3.06×10^{20}	7.28
172.78	1.16×10^{21}	2.06×10^{23}	4.27×10^{19}	1.38×10^{21}	7.50
184.3	5.10×10^{21}	1.06×10^{24}	1.62×10^{20}	5.78×10^{21}	7.72

Table S3: Values of $W(E)$ and $\rho(E)$ for Reaction R13 Across Energy Levels, along with the anharmonic-to-harmonic rate constant ratio (R) at 4000 K.

	$W(E)$		$\rho(E)$		R
E(kcal/mol)	Anharmonic	harmonic	Anharmonic	harmonic	
32.52	3.13×10^{2}	3.13×10^{2}	3.01×10^{4}	3.01×10^{4}	5.80
41.83	1.73×10^{6}	1.77×10^{6}	1.11×10^{6}	1.42×10^{7}	6.68
51.63	4.11×10^{8}	6.96×10^{8}	3.16×10^{7}	6.02×10^{8}	7.66
61.8	3.48×10^{10}	8.44×10^{10}	6.87×10^{8}	1.85×10^{10}	8.75
72.26	1.58×10^{12}	5.03×10^{12}	1.17×10^{10}	4.26×10^{11}	9.95
82.95	4.65×10^{13}	1.82×10^{14}	1.58×10^{11}	7.59×10^{12}	11.27
93.81	9.71×10^{14}	4.46×10^{15}	1.75×10^{12}	1.08×10^{14}	12.70
104.83	1.54×10^{16}	8.09×10^{16}	1.63×10^{13}	1.27×10^{15}	14.22
115.95	1.94×10^{17}	1.14×10^{18}	1.30×10^{14}	1.24×10^{16}	15.80
127.18	2.02×10^{18}	1.29×10^{19}	9.08×10^{14}	1.05×10^{17}	17.44
138.48	1.76×10^{19}	1.23×10^{20}	5.60×10^{15}	7.72×10^{17}	19.11
149.86	1.33×10^{20}	9.97×10^{20}	3.11×10^{16}	5.05×10^{18}	20.79
161.29	8.82×10^{20}	7.06×10^{21}	1.57×10^{17}	2.96×10^{19}	22.48
172.77	5.22×10^{21}	4.44×10^{22}	7.31×10^{17}	1.58×10^{20}	24.15
184.29	2.79×10^{22}	2.51×10^{23}	3.14×10^{18}	7.69×10^{20}	25.80

4. Results of Kinetic and Thermodynamic Parameters Fitting

The fitting results of kinetic parameters are detailed in parts (a) and (b) of Table S4. The fitting results of thermodynamic parameters are detailed in Table S5 to S8. The comparison of ignition delay times is shown in Figure S2.

Table S4 The fitting results of kinetic parameters (A, n, E) over the temperature range from 300 K to 4000 K. ((a) Reactions involving R1- R8; (b) Reactions involving R9 - R17)

Transition state	Harmonic				Anharmonic				
	A	n	E(J/mol)	E(kcal/mol)	A	n	E(J/mol)	E(kcal/mol)	Barrier(kcal/mol)
TS1	2.29×10^{3}	3.53	3.41×10^{4}	8.15	4.23×10^{13}	-0.01	4.30×10^{4}	10.27	10.15
TS2	3.15×10^{3}	3.47	2.23×10^{4}	5.32	2.75×10^{18}	-1.69	3.40×10^{4}	8.12	7.24
TS3	8.96×10^{-5}	6.67	2.29×10^{4}	5.47	2.78×10^{10}	1.59	3.56×10^{4}	8.51	8.56
TS4	2.02×10^{-4}	6.56	1.17×10^{4}	2.80	5.32×10^{11}	0.68	1.75×10^{4}	4.17	5.64
TS5	9.67×10^{-5}	7.18	8.52×10^{4}	20.36	5.25×10^{14}	0.42	1.01×10^{5}	24.13	22.78
TS6	2.92×10^{-4}	7.06	1.18×10^{5}	28.20	2.73×10^{22}	-2.82	1.38×10^{5}	32.98	30.41
TS7	3.69×10^{-4}	7.06	6.94×10^{4}	16.58	7.17×10^{11}	1.18	7.99×10^{4}	19.10	18.39
TS8	6.69×10^{-4}	7.06	1.06×10^{5}	25.43	2.37×10^{25}	-3.14	1.31×10^{5}	31.40	27.29
TS9	4.99×10^{-5}	6.88	5.03×10^{4}	12.03	6.91×10^{11}	1.40	6.46×10^{4}	15.45	14.49
TS10	3.00×10^{-4}	6.97	4.37×10^{4}	10.44	2.00×10^{9}	1.73	5.04×10^{4}	12.05	12.69
TS11	1.02×10^{0}	0.32	1.11×10^{5}	-0.29	1.84×10^{11}	0.99	6.98×10^{3}	1.67	1.33
TS12	1.21×10^{13}	0.33	1.11×10^{5}	26.57	2.03×10^{13}	0.01	1.08×10^{5}	25.81	25.63
TS13	3.28×10^{12}	0.40	6.44×10^{4}	15.39	1.10×10^{9}	1.74	6.19×10^{4}	14.80	14.51
TS14	1.52×10^{-4}	6.84	6.59×10^{3}	1.58	1.45×10^{-2}	5.24	2.86×10^{3}	0.68	4.70
TS15	2.09×10^{-4}	6.76	3.37×10^{3}	0.81	1.23×10^{5}	3.19	8.72×10^{3}	2.08	3.72
TS16	4.50×10^{-4}	7.17	6.18×10^{4}	14.76	6.28×10^{12}	0.57	7.45×10^{4}	17.82	17.32
TS17	3.50×10^{-4}	7.05	4.32×10^{4}	10.32	2.96×10^{16}	-0.50	5.86×10^{4}	13.99	12.63

Table S5 The fitting results of thermodynamic parameters ($a_1 - a_7$) by calculating harmonic data over the temperature range from 300 K to 1000 K.

Reactant	a_1	a_2	a_3	a_4	a_5	a_6	a_7
H	2.50	-3.58×10^{-17}	5.54×10^{-20}	-3.31×10^{-23}	5.62×10^{-27}	-1.81	-0.49
OH	3.41	7.48×10^{-4}	-2.25×10^{-6}	2.70×10^{-9}	-9.26×10^{-13}	2.74×10^{3}	1.83
$PODE_1$	5.18	8.40×10^{-3}	6.14×10^{-5}	-7.77×10^{-8}	2.89×10^{-11}	3.62×10^{4}	5.42
NH_2	4.10	-1.51×10^{-3}	5.59×10^{-6}	-4.51×10^{-9}	1.37×10^{-12}	6.05×10^{3}	0.29
NO_2	3.73	2.51×10^{-4}	9.72×10^{-6}	-1.18×10^{-8}	4.25×10^{-12}	2.95×10^{3}	7.11
HO_2	3.97	-2.21×10^{-3}	1.30×10^{-5}	-1.44×10^{-8}	5.23×10^{-12}	4.64×10^{3}	5.06
CH_3	3.89	2.65×10^{-3}	2.13×10^{-6}	-2.45×10^{-9}	8.01×10^{-13}	9.38×10^{3}	1.20

CH_3O_2	3.54	4.85×10^{-3}	2.11×10^{-5}	-2.84×10^{-8}	1.09×10^{-11}	1.39×10^{4}	9.92

Table S6 The fitting results of thermodynamic parameters ($a_1 - a_7$) by calculating harmonic data over the temperature range from 1000 K to 4000 K

Reactant	a_1	a_2	a_3	a_4	a_5	a_6	a_7
H	2.50	-2.60×10^{-17}	1.55×10^{-20}	3.89×10^{-24}	3.52×10^{-28}	-6.89	-0.50
OH	2.77	1.02×10^{-3}	-8.68×10^{-8}	-3.51×10^{-11}	5.81×10^{-15}	2.75×10^{3}	5.43
$PODE_1$	5.29	3.25×10^{-2}	-1.42×10^{-5}	2.93×10^{-9}	-2.31×10^{-13}	3.49×10^{4}	-1.19
NH_2	2.53	3.52×10^{-3}	-1.20×10^{-6}	1.96×10^{-10}	-1.25×10^{-14}	6.46×10^{3}	8.27
NO_2	4.09	3.41×10^{-3}	-1.63×10^{-6}	3.58×10^{-10}	-2.95×10^{-14}	2.63×10^{3}	4.19
HO_2	3.47	3.17×10^{-3}	-1.26×10^{-6}	2.41×10^{-10}	-1.80×10^{-14}	4.59×10^{3}	6.66
CH_3	2.60	6.46×10^{-3}	-2.46×10^{-6}	4.51×10^{-10}	-3.22×10^{-14}	9.73×10^{3}	7.82
CH_3O_2	4.10	1.21×10^{-2}	-5.25×10^{-6}	1.07×10^{-9}	-8.44×10^{-14}	1.33×10^{4}	4.85

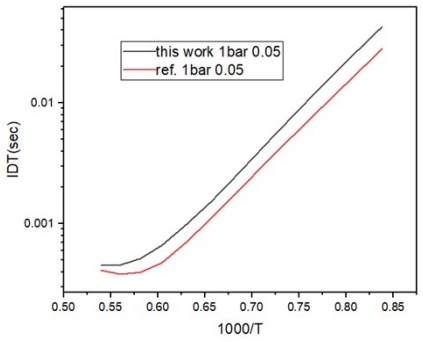
Table S7 The fitting results of thermodynamic parameters ($a_1 - a_7$) by calculating anharmonic data over the temperature range from 300 K to 1000 K.

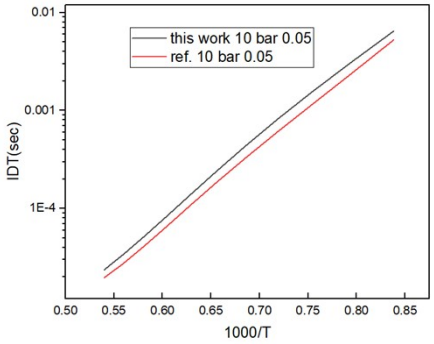
Reactant	a_1	a_2	a_3	a_4	a_5	a_6	a_7
$PODE_1$	4.26	1.48×10^{-2}	4.97×10^{-5}	-6.84×10^{-8}	2.62×10^{-11}	3.60×10^{4}	12.73
NH_2	4.11	-1.59×10^{-3}	5.77×10^{-6}	-4.76×10^{-9}	1.49×10^{-12}	6.14×10^{3}	0.24
NO_2	3.70	4.30×10^{-4}	9.64×10^{-6}	-1.19×10^{-8}	4.34×10^{-12}	2.94×10^{3}	7.26
HO_2	3.83	-1.25×10^{-3}	1.12×10^{-5}	-1.27×10^{-8}	4.66×10^{-12}	4.53×10^{3}	5.65
CH_3	3.22	5.78×10^{-3}	-4.05×10^{-6}	3.32×10^{-9}	-1.34×10^{-12}	5.72×10^{3}	4.09
CH_3O_2	3.08	7.66×10^{-3}	1.59×10^{-5}	-2.41×10^{-8}	9.49×10^{-12}	1.38×10^{4}	11.56

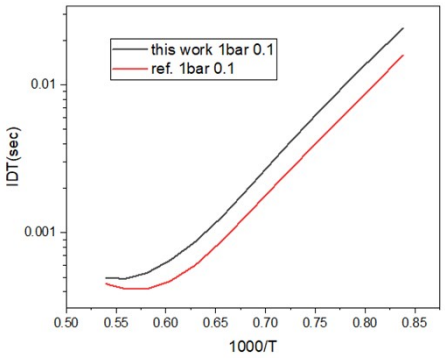
Table S8 The fitting results of thermodynamic parameters ($a_1 - a_7$) by calculating anharmonic data over the temperature range from 1000 K to 4000 K.

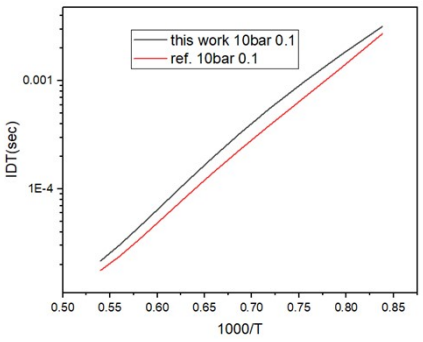
Reactant	a_1	a_2	a_3	a_4	a_5	a_6	a_7
$PODE_1$	5.91	3.21×10^{-2}	-1.41×10^{-5}	2.91×10^{-9}	-2.30×10^{-13}	3.45×10^{4}	-1.14

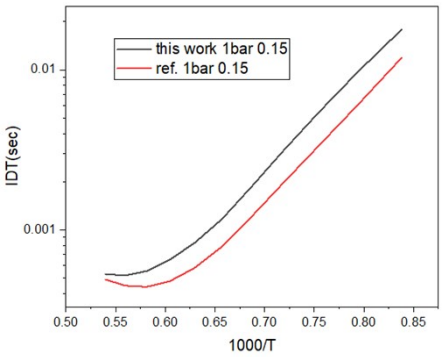
NH_2	2.57	3.38×10^{-3}	-1.11×10^{-6}	1.74×10^{-10}	-1.06×10^{-14}	6.55×10^{3}	8.05
NO_2	4.15	3.35×10^{-3}	-1.61×10^{-6}	3.53×10^{-10}	-2.92×10^{-14}	2.59×10^{3}	3.85
HO_2	3.45	3.40×10^{-3}	-1.41×10^{-6}	2.80×10^{-10}	-2.14×10^{-14}	4.46×10^{3}	6.76
CH_3	3.00	6.06×10^{-3}	-2.62×10^{-6}	5.32×10^{-10}	-4.15×10^{-14}	5.75×10^{3}	5.19
CH_3O_2	4.25	1.21×10^{-2}	-5.30×10^{-6}	1.09×10^{-9}	-8.62×10^{-14}	1.31×10^{4}	3.65

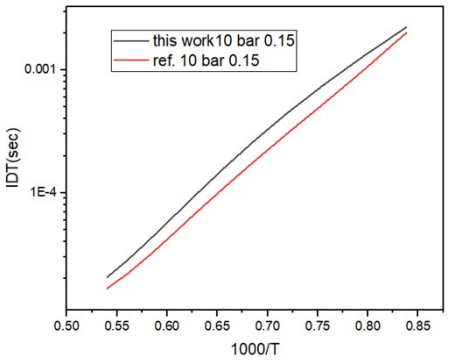












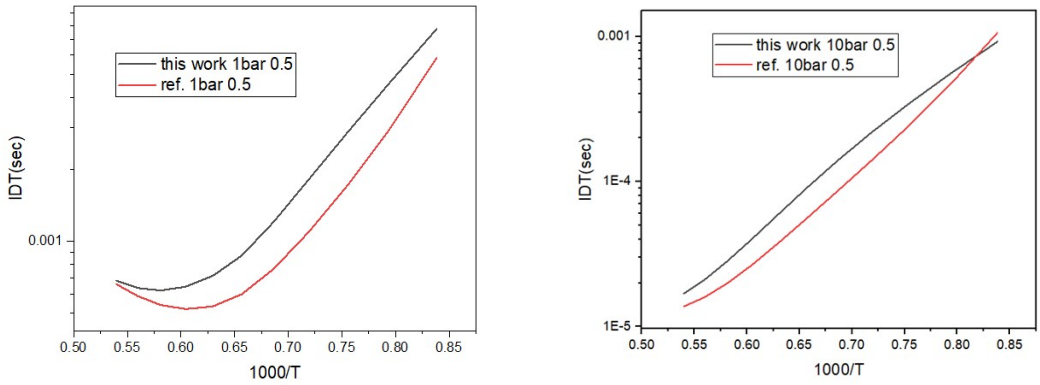


Fig. S2 Comparison of Kinetic and Thermodynamic Parameters with Ignition Delays from the Dai [1] $PODE_1/NH_3$ Mechanism

Reference

[1] Dai, L., Yuan, Y., Lin, Q., Li, W., Zou, C., Liu, J., & Luo, J. (2023). Shock tube and modeling study on the ignition delay times of ammonia/dimethoxymethane at high temperature. *Combustion and Flame*, *256*, 112967.