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ELECTRONIC SUPPORTING INFORMATION

Quantitative kinetics for the atmospheric reactions of Criegee intermediates with acetonitrile

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Computational details for pressure-dependent rate constants of R1.

For the R1 reaction, we calculate the pressure-dependent rate constants using system-specific quantum Rice-Ramsperger-Kassel (SS-QRRK).[1,2,3] The F_E is computed based on the numerically integrated Whitten-Rabinovitch approximation.[4] The collision efficiency is computed based on the exponential gap model (also called the exponential down model), with the energy transfer parameter $<\triangle E>_{down}$ = 200 cm^{-1}.

The van der Waals parameters used to calculate the collision rates are as follows:

molecules	σ (in Å)	ε (in K)	Reference
N_2 bath gas	3.74	82	5
CH_2OO	3.79	520	6
CH_3CN	4.37	491.6	7
M1[a]	4.08	505.6	

[a]Where van der Waals parameters of M1 is obtained by fitting the following two formulas:

$$\sigma = \frac{\sigma_1 \sigma_2}{2} \qquad (1) \qquad\qquad \varepsilon = \sqrt{\varepsilon_1 \varepsilon_2} \qquad (2)$$

σ is the hard-core diameter, and ε is a measure of the strength of the spherically symmetric part of the perturbation.

TST for high-pressure-limit rate constants of R1, R2 and R3.

Title reactions can be expressed as:

$$SCI + CH_3CN \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C1\ (SCI\cdots CH_3CN) \xrightarrow{k_2} M$$

Where C1 is a pre-reactive complex and M is the products of these reactions. By the Steady-State Approximation, as well as introducing the assumption of $k_2 \ll k_{-1}$, we can get an expression for the rate constants:

$$\frac{d[SCI\cdots CH_3CN]}{dt} = k_1[SCI][CH_3CN] - k_{-1}[SCI\cdots CH_3CN] - k_2[SCI\cdots CH_3CN] = 0$$

$$[SCI\cdots CH_3CN] = \frac{k_1}{k_{-1} + k_2}[SCI][CH_3CN] \approx \frac{k_1}{k_{-1}}[SCI][CH_3CN]$$

$$\frac{d[M]}{dt} = k_2[SCI\cdots CH_3CN] = k_2\frac{k_1}{k_{-1}}[SCI][CH_3CN] = k_2 K_c [SCI][CH_3CN]$$

finally, the total rate constant is expressed as:

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \approx \frac{k_1}{k_{-1}} k_2 = K_c\, k_2$$

Then, we using conventional transition state theory to predict rate constants and equilibrium constants, they can express as:

$$K_c(T) = \sigma \frac{Q_{C1}(T)}{Q_{SCI}(T)\, Q_{NH_3}(T)} exp(-\frac{E_{C1}}{k_B T}) \quad (3)$$

$$k_2(T) = \kappa \frac{k_B T\, Q_{TS}(T)}{h \quad Q_{C1}(T)} exp(-\frac{E_a}{k_B T}) \quad (4)$$

$$k(T) = \sigma\kappa \frac{k_B T \qquad Q_{TS}(T)}{h \quad Q_{SCI}(T)\, Q_{NH_3}(T)} exp(-\frac{E_a + E_{C1}}{k_B T}) \quad (5)$$

where k_B is Boltzmann's constant, T is the temperature in K, h is Planck's constant, κ is the transmission coefficient, and σ is symmetry factor.

Table S1. Scale factors applied to vibrational frequencies

Methods	Scale Factor
CCSD(T)-F12a/cc-pVTZ-F12	0.984
CCSD(T)-F12a/cc-pVDZ-F12	0.983
DF-CCSD(T)-F12b/jun-cc-pVTZ	0.983
DF-CCSD(T)-F12b/jun-cc-pVDZ	0.981
M06CR/MG3S	0.980
MN15-L/MG3S	0.977
M11-L/MG3S	0.985

Table S2. Mean unsigned deviations of classical barrier heights and classical reaction energies (in kcal/mol)

Methods	(ΔV)			MUD
	C1	TS1	M1	
W2X//CCSD(T)-F12a/cc-pVTZ-F12	-8.29	-3.29	-56.59	0.00
W2X//CCSD(T)-F12a/cc-pVDZ-F12	-8.29	-3.29	-56.59	0.00
W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	-8.26	-3.28	-56.73	0.06

Table S3. Mean unsigned deviations of relative zero-point vibrational energies for R1 (in kcal/mol)

Methods	(ΔE_{ZPE})			MUD
	C1	TS1	M1	
CCSD(T)-F12a/cc-pVTZ-F12	1.24	2.35	5.10	0.00
DF-CCSD(T)-F12b/jun-cc-pVDZ	1.23	2.36	5.22	0.05
CCSD(T)-F12a/cc-pVDZ-F12	1.28	2.21	5.14	0.07

Table S4. The relative enthalpies at 0 K for the CH_2OO + CH_3CN reaction at different methods.

Methods	ΔH_0			MUD
	C1	TS1	M1	
W2X//CCSD(T)-F12a/cc-pVTZ-F12	-7.05	-0.94	-51.49	0.00
W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	-7.03	-0.92	-51.51	0.02
W2X//CCSD(T)-F12a/cc-pVDZ-F12	-7.01	-1.08	-51.45	0.07

Table S5. High-pressure-limit rate constant k_1 (cm^3 $molecule^{-1}$ s^{-1}) and transmission coefficients (unitless), and activation energies (in kcal/mol) for the R1 reaction.

T(K)	k_{HL}^{TST} [a]	Γ_{LL} [b]	k_{LL}^{SCT} [c]	$\Gamma_{LL}k_{LL}^{SCT}$	k_1 [c]	E_{a1} [d]
190	1.51×10^{-14}	0.95	1.35	1.29	1.94×10^{-14}	-0.71
200	1.42×10^{-14}	0.95	1.31	1.25	1.77×10^{-14}	-0.67
210	1.35×10^{-14}	0.95	1.28	1.21	1.63×10^{-14}	-0.64
220	1.29×10^{-14}	0.95	1.25	1.18	1.53×10^{-14}	-0.60
230	1.24×10^{-14}	0.95	1.22	1.16	1.44×10^{-14}	-0.56
240	1.21×10^{-14}	0.95	1.20	1.14	1.37×10^{-14}	-0.52
250	1.17×10^{-14}	0.95	1.18	1.12	1.32×10^{-14}	-0.48
260	1.15×10^{-14}	0.95	1.17	1.11	1.27×10^{-14}	-0.44
270	1.13×10^{-14}	0.94	1.16	1.09	1.23×10^{-14}	-0.40
280	1.11×10^{-14}	0.94	1.14	1.08	1.20×10^{-14}	-0.36
290	1.10×10^{-14}	0.94	1.13	1.07	1.18×10^{-14}	-0.31
298	1.10×10^{-14}	0.94	1.13	1.06	1.16×10^{-14}	-0.28
300	1.09×10^{-14}	0.94	1.12	1.06	1.16×10^{-14}	-0.27
310	1.09×10^{-14}	0.94	1.12	1.05	1.14×10^{-14}	-0.24
320	1.09×10^{-14}	0.94	1.11	1.04	1.13×10^{-14}	-0.20
330	1.09×10^{-14}	0.94	1.10	1.03	1.12×10^{-14}	-0.16
340	1.09×10^{-14}	0.94	1.09	1.02	1.11×10^{-14}	-0.12

350	1.09×10^{-14}	0.93	1.09	1.02	1.11×10^{-14}	-0.09

[a] k_{HL}^{TST} is the conventional transition state theory rate constant calculated with the high level.

[b] The Γ_{LL} is the LL recrossing transmission coefficient, which equals $k_{LL}^{CVT}/k_{LL}^{TST}$.

[c] The high-pressure limit rate constant k is calculated by the dual-level CVT/SCT method and k equals $k_{HL}^{TST}\,\Gamma_{LL}\,k_{LL}^{SCT}$.

[d] E_a is Arrhenius activation energies (kcal/mol) for the high-pressure limit , and which is calculated as $-R\frac{d\ln k}{d(1/T)}$ in the high-pressure limit from the dual-level CVT/SCT calculations.

[e] Where HL denote higher level with W3X-L//CCSD(T)-F12a/cc-pVTZ-F12 level, and LL denote lower level with M06CR/MG3S level.

Table S6. High-pressure-limit rate constants k_2 (cm^3 $molecule^{-1}$ s^{-1}) and transmission coefficients (unitless),and activation energies (in kcal/mol) for the R2 reaction.

T(K)	k_{HL}^{TST}	Γ_{LL}	k_{LL}^{SCT}	$\Gamma_{LL}k_{LL}^{SCT}$	k_2	E_{a2}
190	1.54×10^{-13}	0.96	1.64	1.58	2.43×10^{-13}	-2.04
200	1.25×10^{-13}	0.96	1.56	1.50	$1.88- \times 10^{-13}$	-1.95
210	1.04×10^{-13}	0.96	1.49	1.43	1.50×10^{-13}	-1.87
220	8.87×10^{-14}	0.96	1.44	1.38	1.22×10^{-13}	-1.81
230	7.67×10^{-14}	0.96	1.39	1.33	1.02×10^{-13}	-1.75
240	6.73×10^{-14}	0.96	1.35	1.30	8.71×10^{-14}	-1.70
250	5.98×10^{-14}	0.96	1.32	1.26	7.55×10^{-14}	-1.65
260	5.38×10^{-14}	0.96	1.29	1.23	6.64×10^{-14}	-1.61
270	4.89×10^{-14}	0.96	1.26	1.21	5.91×10^{-14}	-1.58
280	4.49×10^{-14}	0.96	1.24	1.19	5.33×10^{-14}	-1.55
290	4.15×10^{-14}	0.96	1.22	1.17	4.85×10^{-14}	-1.52
298	3.92×10^{-14}	0.95	1.21	1.16	4.53×10^{-14}	-1.50
300	3.87×10^{-14}	0.95	1.21	1.15	4.45×10^{-14}	-1.50
310	3.63×10^{-14}	0.95	1.19	1.14	4.12×10^{-14}	-1.48
320	3.42×10^{-14}	0.95	1.18	1.12	3.84×10^{-14}	-1.46
330	3.25×10^{-14}	0.95	1.17	1.11	3.61×10^{-14}	-1.45
340	3.10×10^{-14}	0.95	1.16	1.10	3.41×10^{-14}	-1.44

350	2.97×10^{-14}	0.95	1.15	1.09	3.23×10^{-14}	-1.43

[a] It is worth noting that where HL denote higher level with W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ level, and LL denote lower level with M11-L/MG3S level.

Table S7. High-pressure-limit rate constants k_3 (cm^3 $molecule^{-1}$ s^{-1}) and transmission coefficients (unitless), and activation energies (in kcal/mol) for the R3 reaction.

T(K)	k_{HL}^{TST}	Γ_{LL}	k_{LL}^{SCT}	$\Gamma_{LL}k_{LL}^{SCT}$	k_3	E_{a3}
190	5.76×10^{-20}	0.96	1.73	1.67	9.59×10^{-20}	3.60
200	9.87×10^{-20}	0.96	1.63	1.57	1.55×10^{-19}	3.66
210	1.61×10^{-19}	0.96	1.55	1.49	2.41×10^{-19}	3.72
220	2.53×10^{-19}	0.96	1.49	1.43	3.62×10^{-19}	3.77
230	3.83×10^{-19}	0.96	1.44	1.38	5.28×10^{-19}	3.83
240	5.62×10^{-19}	0.96	1.39	1.33	7.51×10^{-19}	3.88
250	8.03×10^{-19}	0.96	1.35	1.30	1.04×10^{-18}	3.93
260	1.12×10^{-18}	0.96	1.32	1.27	1.41×10^{-18}	3.99
270	1.52×10^{-18}	0.96	1.29	1.24	1.89×10^{-18}	4.04
280	2.04×10^{-18}	0.96	1.27	1.21	2.47×10^{-18}	4.09
290	2.68×10^{-18}	0.96	1.25	1.19	3.19×10^{-18}	4.14
298	3.29×10^{-18}	0.95	1.23	1.18	3.87×10^{-18}	4.18
300	3.46×10^{-18}	0.95	1.23	1.17	4.06×10^{-18}	4.19
310	4.41×10^{-18}	0.95	1.21	1.16	5.10×10^{-18}	4.24
320	5.55×10^{-18}	0.95	1.20	1.14	6.33×10^{-18}	4.29
330	6.90×10^{-18}	0.95	1.19	1.13	7.78×10^{-18}	4.34
340	8.49×10^{-18}	0.95	1.17	1.11	9.46×10^{-18}	4.39
350	1.03×10^{-17}	0.95	1.16	1.10	1.14×10^{-17}	4.44

[a] Where HL denote higher level with W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ level, and LL denote lower level with M11-L/MG3S level.

Table S8. Parameters used to fit high-pressure limit rate constants k_1, k_2 and k_3 (cm^3 $molecule^{-1}$ s^{-1})

	A	n	E	T_0
k_1	2.95×10^{-14}	-0.02	1.45	-152.07
k_2	9.88×10^{-14}	-1.82	1.69	-107.90
k_3	5.79×10^{-16}	2.22	3.04	-8.27

Table S9. Pressure-dependent rate constants k_1(T, p) of the R1 as a function of temperature and pressure by system-specific quantum Rice-Ramsperger-Kassel (SS-QRRK)theory.

***p* (bar)**	***T* = 350 K**	***T* = 330 K**	***T* = 310 K**	***T* = 298 K**
0.0316	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
0.1	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
0.178	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
0.316	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
0.562	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
1	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
1.78	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
3.16	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
5.62	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
10	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
31.6	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
100	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
1000	1.11×10^{-14}	1.12×10^{-14}	1.14×10^{-14}	1.16×10^{-14}
***p* (bar)**	***T* = 290 K**	***T* = 270 K**	***T* = 250 K**	***T* = 230 K**
0.0316	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
0.1	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
0.178	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
0.316	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
0.562	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
1	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
1.78	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}

3.16	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
5.62	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
10	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
31.6	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
100	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}
1000	1.18×10^{-14}	1.23×10^{-14}	1.32×10^{-14}	1.44×10^{-14}

[a] For this table, $k_1(T, p)$ is calculated by the SS-QRRK theory method. Here, the SS-QRRK calculations are carried out using the bimolecular association-reaction formula.

Table S10. The rate ratio between OH + CH_3CN and CH_2OO + CH_3CN for various concentrations in molecules/cm^3.

T/K	k_{OH}	k_1[b]	v_1[a]		
			$[CH_2OO]=10^5$		
			[OH] $=10^4$	[OH] $=10^5$	[OH] $=10^6$
250	1.08×10^{-14}	1.32×10^{-14}	12.22	1.22	0.12
260	1.27×10^{-14}	1.27×10^{-14}	9.98	1.00	0.10
270	1.48×10^{-14}	1.23×10^{-14}	8.31	0.83	0.08
280	1.71×10^{-14}	1.20×10^{-14}	7.02	0.70	0.07
290	1.95×10^{-14}	1.18×10^{-14}	6.02	0.60	0.06
298	2.16×10^{-14}	1.16×10^{-14}	5.37	0.54	0.05
300	2.21×10^{-14}	1.16×10^{-14}	5.22	0.52	0.05
310	2.49×10^{-14}	1.14×10^{-14}	4.59	0.46	0.05
320	2.77×10^{-14}	1.13×10^{-14}	4.07	0.41	0.04
330	3.07×10^{-14}	1.12×10^{-14}	3.64	0.36	0.04
340	3.38×10^{-14}	1.11×10^{-14}	3.29	0.33	0.03
350	3.70×10^{-14}	1.11×10^{-14}	2.99	0.30	0.03

[a] $v_1 = \frac{k_1[CH_2OO][CH_3CN]}{k_{OH}[OH][CH_3CN]} = \frac{k_1[CH_2OO]}{k_{OH}[OH]}$, where k_{OH} is the rate constant of OH + CH_3CN from the preferred values of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement IV. $k_{OH} = 8.1 \times 10^{-13} \exp(-1080/T)$ cm^3 $molecule^{-1}$ s^{-1}.(Journal of Physical and Chemical Reference Data 21, 1125 (1992)).

[b] The bimolecular rate constants of CH_2OO + CH_3CN (pressure-independent) are calculated in the present work by using the dual-level strategy.

Table S11. The rate ratio between OH + CH_3CN and *anti*-CH_3CHOO + CH_3CN for various concentrations in molecules/cm^3.

T/K	k_{OH}	k_2[b]	v_2[a]		
			[*anti*-CH_3CHOO]=10^5		
			[OH] =10^4	[OH] =10^5	[OH] =10^6
250	1.08×10^{-14}	7.55×10^{-14}	70.08	7.01	0.70
260	1.27×10^{-14}	6.64×10^{-14}	52.21	5.22	0.52
270	1.48×10^{-14}	5.92×10^{-14}	39.88	3.99	0.40
280	1.71×10^{-14}	5.33×10^{-14}	31.15	3.11	0.31
290	1.95×10^{-14}	4.85×10^{-14}	24.81	2.48	0.25
298	2.16×10^{-14}	4.53×10^{-14}	20.96	2.10	0.21
300	2.21×10^{-14}	4.45×10^{-14}	20.13	2.01	0.20
310	2.49×10^{-14}	4.12×10^{-14}	16.59	1.66	0.17
320	2.77×10^{-14}	3.84×10^{-14}	13.87	1.39	0.14
330	3.07×10^{-14}	3.61×10^{-14}	11.75	1.18	0.12
340	3.38×10^{-14}	3.41×10^{-14}	10.08	1.01	0.10
350	3.70×10^{-14}	3.23×10^{-14}	8.73	0.87	0.09

[a] $v_2 = \frac{k_2[anti-CH_3CHOO][CH_3CN]}{k_{OH}[OH][CH_3CN]} = \frac{k_2[anti-CH_3CHOO]}{k_{OH}[OH]}$, where k_{OH} is the rate constant of OH + CH_3CN from the preferred values of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement IV. $k_{OH} = 8.1 \times 10^{-13} \exp(-1080/T)$ cm^3 $molecule^{-1}$ s^{-1}.(Journal of Physical and Chemical Reference Data 21, 1125 (1992)).

[b] The bimolecular rate constants of *anti*-CH_3CHOO + CH_3CN are calculated in the present work by using the dual-level strategy.

Table S12. Frequencies and zero-point vibrational energies for R1 path.

(a) CH_2OO

Methods	ZPE(kcal/mol)	Frequencies (cm^{-1})		
CCSD(T)-F12a/cc-pVTZ-F12	19.27	535.36 951.74 1488.18	637.03 1239.56 3139.81	869.95 1314.85 3302.70
CCSD(T)-F12a/cc-pVDZ-F12	19.23	534.12 950.85 1486.38	628.58 1237.42 3140.72	860.08 1307.55 3304.76
DF-CCSD(T)-F12b/jun-cc-pVDZ	19.22	535.46 913.08 1477.68	632.71 1224.03 3169.35	837.62 1313.63 3340.94
M06CR/MG3S	19.37	549.95 1008.64 1562.70	705.40 1247.02 3121.80	949.47 1401.47 3282.74
M11-L/MG3S	19.00	538.79 1005.57 1546.21	680.05 1240.77 3020.85	890.58 1371.45 3197.17
MN15-L/MG3S	19.14	535.78 968.15 1550.10	683.96 1251.56 3103.81	936.49 1408.29 3265.72

(b) CH_3CN.

Methods	ZPE(kcal/mol)	Frequencies (cm^{-1})

CCSD(T)-F12a/cc-pVTZ-F12	28.36	361.26	361.66	924.09
		1061.99	1062.01	1415.65
		1486.26	1486.50	2306.28
		3066.02	3152.36	3152.36
CCSD(T)-F12a/cc-pVDZ-F12	28.39	361.68	361.94	922.38
		1064.05	1064.32	1418.82
		1490.44	1490.44	2304.59
		3069.46	3154.68	3154.91
DF-CCSD(T)-F12b/jun-cc-pVDZ	28.44	347.61	347.62	935.36
		1053.46	1053.47	1403.68
		1474.70	1474.77	2314.75
		3095.27	3195.64	3195.71
M06CR/MG3S	27.86	392.78	392.78	954.33
		1036.22	1036.22	1382.64
		1452.75	1452.75	2400.67
		3072.19	3156.70	3156.70
M11-L/MG3S	27.65	393.22	393.22	954.26
		1032.93	1032.93	1373.35
		1432.47	1432.47	2382.67
		2992.40	3106.36	3106.36
MN15-L/MG3S	27.72	391.85	391.85	942.74
		1051.24	1051.24	1401.00
		1472.64	1472.64	2361.84
		3042.77	3132.83	3132.83

(c) TS1.

Methods	ZPE(kcal/mol)	Frequencies (cm^{-1})		
CCSD(T)-F12a/cc-pVTZ-F12	50.02	142.08	156.59	214.48
		298.02	423.40	442.04
		474.79	560.18	817.72
		921.24	928.20	1040.18
		1066.01	1076.23	1221.78
		1356.97	1409.09	1475.72
		1482.41	1520.69	2149.92
		3063.16	3150.01	3150.81
		3159.20	3288.04	353.26i
CCSD(T)-F12a/cc-pVDZ-F12	49.87	106.57	141.54	217.82
		293.04	419.01	437.64
		471.44	556.64	807.26
		918.95	925.29	1037.00
		1063.39	1070.13	1218.17
		1352.34	1408.04	1475.00
		1482.55	1517.64	2147.12

		3064.46	3149.96	3151.63
		3161.02	3289.45	353.51i
DF-CCSD(T)-F12b/jun-cc-pVDZ	50.07	141.06	150.37	212.02
		294.31	413.35	440.73
		475.12	561.03	807.59
		899.76	937.09	1027.40
		1056.13	1065.22	1206.62
		1354.66	1396.42	1464.05
		1470.55	1512.24	2157.07
		3090.56	3174.58	3192.29
		3199.90	3321.81	357.96i
M06CR/MG3S	49.23	143.25	163.86	203.83
		279.42	442.46	459.66
		483.03	571.23	842.68
		953.00	990.32	1027.13
		1039.15	1086.29	1223.39
		1376.66	1383.94	1440.48
		1448.41	1540.54	2243.74
		3071.52	3133.64	3159.03
		3167.23	3269.04	328.47i
M11-L/MG3S	48.48	142.15	159.87	204.15
		280.16	431.26	451.25
		472.93	562.07	824.07
		945.11	972.05	1010.03
		1031.96	1044.08	1205.32
		1355.02	1363.45	1414.53
		1425.02	1526.27	2224.38
		2987.55	3012.87	3102.21
		3116.59	3164.82	398.76i
MN15-L/MG3S	48.83	142.26	178.62	203.91
		281.31	432.45	450.52
		475.20	562.78	835.81
		940.02	955.83	1036.77
		1052.52	1084.43	1224.27
		1384.35	1392.24	1457.15
		1466.11	1535.37	2196.44
		3037.46	3113.11	3129.98
		3144.00	3250.32	339.83i

(d) M1.

Methods	*ZPE*(kcal/mol)	Frequencies (cm^{-1})		
CCSD(T)-F12a/cc-pVTZ-F12	52.81	114.21	152.97	243.18
		342.27	593.81	653.42

		769.18	853.05	957.98
		959.05	995.45	1066.08
		1100.79	1122.61	1205.50
		1272.33	1371.17	1421.02
		1484.15	1486.68	1529.73
		1744.41	3020.57	3061.56
		3111.37	3135.24	3175.22
CCSD(T)-F12a/cc-pVDZ-F12	52.85	119.70	154.95	243.31
		342.56	593.12	652.36
		767.78	852.66	956.81
		957.96	994.40	1067.42
		1100.35	1122.18	1207.50
		1271.52	1373.78	1422.89
		1487.50	1489.88	1532.22
		1741.54	3021.72	3064.82
		3112.14	3137.04	3177.18
DF-CCSD(T)-F12b/jun-cc-pVDZ	52.98	116.21	184.64	242.19
		340.89	585.47	654.06
		769.60	830.64	952.99
		966.43	1000.35	1055.58
		1094.43	1122.12	1200.14
		1272.39	1362.44	1415.35
		1471.09	1475.91	1514.89
		1760.63	3045.02	3088.76
		3148.60	3175.86	3212.58
M06CR/MG3S	51.79	112.57	121.99	250.97
		354.43	615.30	671.66
		789.24	907.89	949.84
		996.10	1008.12	1046.21
		1095.42	1133.18	1192.97
		1268.67	1353.02	1399.43
		1454.22	1456.97	1509.67
		1786.70	2996.62	3074.59
		3076.82	3146.13	3194.80
M11-L/MG3S	51.61	122.67	167.42	252.10
		347.12	610.97	682.16
		810.31	923.46	968.28
		995.06	1025.70	1037.07
		1098.48	1144.79	1191.34
		1287.33	1351.37	1403.69
		1433.88	1441.44	1490.05
		1780.91	2859.95	2972.46
		3000.54	3099.90	3149.78
MN15-L/MG3S	51.50	123.51	154.65	247.93

		338.72	603.51	667.36
		786.06	904.43	969.83
		982.17	1008.57	1051.15
		1101.95	1129.09	1202.79
		1281.17	1367.62	1409.84
		1472.60	1475.85	1517.39
		1758.37	2936.72	3044.83
		3045.93	3121.21	3172.88

Table S13. Frequencies and zero-point vibrational energies for R2 path.
(a) *anti*-CH_3CHOO

Methods	*ZPE*(kcal/mol)	Frequencies (cm^{-1})		
DF-CCSD(T)-F12b/jun-cc-pVDZ	37.02	144.09	248.02	321.11
		557.37	829.85	879.37
		937.06	1040.73	1159.55
		1310.85	1408.94	1456.65
		1463.30	1527.31	3069.25
		3147.61	3192.44	3201.14
M11-L/MG3S	36.10	167.52	264.90	326.80
		575.62	851.54	905.05
		1026.14	1041.38	1145.35
		1315.96	1391.47	1416.83
		1423.64	1599.37	2967.37
		3047.28	3052.40	3121.55
MN15-L/MG3S	36.23	171.94	264.15	326.19
		565.33	863.02	906.31
		1011.66	1051.82	1160.22
		1340.05	1408.64	1456.70
		1458.50	1590.24	3011.83
		3072.60	3126.51	3150.73
M06CR/MG3S	36.55	167.52	264.90	326.80
		575.62	851.54	905.05
		1026.14	1041.38	1145.35
		1315.96	1391.47	1416.83
		1423.64	1599.37	2967.37

		3047.28	3052.40	3121.55

(b) TS2

Methods	*ZPE*(kcal/mol)	Frequencies (cm^{-1})		
DF-CCSD(T)-F12b/jun-cc-pVDZ	67.72	109.08	140.52	153.19
		182.66	248.86	314.19
		355.98	430.31	458.84
		479.21	586.85	885.96
		938.41	957.40	983.54
		1040.33	1055.62	1080.64
		1169.70	1315.82	1395.81
		1403.43	1449.21	1464.43
		1470.44	1471.27	1532.34
		2143.96	3077.38	3089.01
		3170.23	3190.40	3196.90
		3202.36	3223.29	
M11-L/MG3S	65.58	-430.98	111.65	140.99
		171.04	182.77	254.42
		315.44	335.98	446.63
		468.58	481.91	601.35
		894.75	941.15	954.00
		1008.33	1032.56	1043.71
		1065.66	1150.94	1302.54
		1363.39	1378.07	1412.57
		1419.75	1428.53	1431.38
		1548.94	2193.35	2987.38
		2988.30	3060.47	3096.03
		3103.67	3114.40	3134.78
MN15-L/MG3S	65.85	-357.16	111.98	143.34
		175.68	186.73	262.78
		314.29	338.33	449.51
		469.49	484.22	593.93
		896.65	944.56	960.47
		1029.80	1041.20	1052.58
		1087.70	1164.97	1327.63
		1391.70	1397.94	1443.81
		1459.53	1467.99	1471.57
		1540.46	2168.61	3029.38
		3037.08	3117.80	3129.43
		3140.08	3150.23	3164.72
M06CR/MG3S	66.38	-336.21	112.06	145.28
		163.53	183.18	261.38
		325.28	352.27	457.85

		477.59	493.93	603.12
		906.59	951.75	963.23
		1026.98	1039.70	1067.96
		1087.32	1165.67	1323.51
		1376.35	1388.33	1432.54
		1442.81	1450.33	1453.28
		1554.18	2219.09	3059.84
		3071.51	3142.09	3158.97
		3164.82	3172.55	3185.86

(c) M2

Methods	*ZPE*(kcal/mol)	Frequencies (cm^{-1})		
M11-L/MG3S	68.46	61.96	112.03	202.06
		233.52	319.33	386.93
		456.68	628.74	679.62
		771.59	861.26	909.12
		960.49	997.86	1032.42
		1034.76	1052.53	1120.53
		1168.43	1277.47	1322.57
		1347.12	1378.00	1398.15
		1434.45	1439.90	1445.77
		1449.35	1780.01	2910.65
		2980.16	3001.40	3100.85
		3102.08	3111.12	3150.32
MN15-L/MG3S	68.48	100.09	127.93	200.16
		244.69	323.89	383.87
		463.11	622.91	665.26
		766.68	862.38	902.71
		943.61	984.21	1018.93
		1045.24	1061.07	1128.47
		1152.15	1267.78	1321.04
		1360.08	1389.87	1404.79
		1472.63	1475.76	1479.65
		1483.02	1751.56	3020.69
		3022.88	3044.04	3117.69
		3120.22	3129.44	3171.96
M06CR/MG3S	68.86	49.78	118.27	201.61
		238.46	323.40	398.27
		463.75	632.69	671.59
		764.87	838.62	910.68
		951.16	997.93	1024.79
		1044.45	1054.11	1126.91

		1165.48	1266.52	1317.86
		1361.34	1383.81	1395.73
		1454.57	1457.40	1464.67
		1466.81	1784.64	3039.55
		3059.97	3074.44	3145.93
		3151.10	3154.74	3194.38

Table S14. Frequencies and zero-point vibrational energies for R3 path.
(a) *syn*-CH_3CHOO

Methods	*ZPE*(kcal/mol)	Frequencies (cm^{-1})		
DF-CCSD(T)-F12b/jun-cc-pVDZ	37.27	208.36	305.54	434.75
		672.61	711.11	883.94
		980.16	1019.76	1114.55
		1304.51	1385.54	1437.70
		1458.49	1523.40	3059.37
		3128.18	3203.79	3236.14
M11-L/MG3S	36.36	227.91	309.26	471.05
		691.95	734.05	979.10
		992.62	998.59	1098.15
		1310.97	1367.77	1384.06
		1421.21	1591.93	2963.63
		3038.49	3097.86	3139.64
MN15-L/MG3S	36.47	242.78	314.92	463.44
		677.56	744.30	950.85
		991.20	1025.09	1109.78
		1337.97	1390.24	1429.49
		1457.45	1573.83	3007.19
		3059.58	3158.73	3175.24
M06CR/MG3S	36.75	210.92	309.73	482.13
		691.91	762.20	976.69
		1002.86	1024.73	1106.41
		1336.55	1385.47	1413.36
		1442.45	1591.03	3034.41

		3082.42	3182.83	3197.59

(b) TS3

Methods	*ZPE*(kcal/mol)	Frequencies (cm^{-1})		
DF-CCSD(T)-F12b/jun-cc-pVDZ	67.74	111.40	143.39	181.17
		216.02	272.13	272.58
		352.43	426.81	489.33
		501.47	658.71	859.37
		913.46	931.26	954.45
		1039.24	1055.41	1068.47
		1160.77	1318.94	1384.49
		1396.02	1449.24	1464.70
		1470.62	1476.51	1528.08
		2139.07	3065.57	3088.84
		3169.58	3189.83	3196.53
		3202.17	3233.62	
M11-L/MG3S	65.62	-440.84	114.07	162.51
		184.66	207.85	264.24
		281.29	351.12	447.51
		495.99	505.10	659.95
		869.94	923.16	958.41
		975.62	1018.04	1034.75
		1049.14	1142.03	1316.48
		1350.00	1364.85	1409.16
		1418.88	1427.92	1433.93
		1543.19	2194.84	2980.71
		2987.49	3043.35	3100.77
		3102.53	3114.40	3164.83
MN15-L/MG3S	65.88	-387.52	112.72	169.08
		196.83	207.20	269.31
		287.00	357.62	448.29
		496.61	503.63	655.97
		873.36	929.24	954.18
		965.34	1037.55	1052.80
		1066.66	1157.50	1333.82
		1379.18	1392.23	1446.56
		1459.55	1467.59	1474.60
		1534.49	2169.49	3015.99
		3036.47	3123.92	3128.45
		3138.00	3140.28	3190.33
M06CR/MG3S	66.41	-371.06	114.25	156.08
		189.68	212.00	268.52
		281.78	352.22	457.75

		505.52	521.32	671.35
		883.31	938.74	963.50
		991.30	1031.23	1039.67
		1067.37	1151.93	1344.09
		1370.49	1376.81	1431.45
		1442.96	1450.11	1458.45
		1542.28	2217.33	3048.46
		3071.14	3149.28	3158.20
		3164.70	3165.12	3212.23

(c) M3

Methods	*ZPE*(kcal/mol)	Frequencies (cm^{-1})		
M11-L/MG3S	68.57	102.71	127.43	208.31
		228.70	292.24	389.75
		469.75	622.84	679.67
		756.21	865.33	908.66
		956.92	1005.83	1031.47
		1039.04	1097.23	1121.63
		1183.03	1269.70	1330.52
		1355.52	1392.32	1406.91
		1433.80	1440.85	1447.75
		1451.95	1782.30	2828.81
		2989.02	3000.69	3099.86
		3111.00	3117.18	3150.09
MN15-L/MG3S	68.40	95.50	126.36	206.84
		225.81	290.13	380.43
		460.18	613.89	666.20
		740.31	859.40	902.67
		938.66	988.97	1025.04
		1053.01	1093.20	1127.38
		1172.71	1270.34	1338.56
		1374.81	1400.64	1406.54
		1472.79	1475.93	1481.21
		1485.68	1756.80	2914.04
		3031.36	3044.18	3120.41
		3129.62	3134.00	3172.10
M06CR/MG3S	68.89	82.97	121.32	208.92
		234.27	300.40	399.51
		469.70	625.27	673.74
		746.60	846.49	908.75
		943.90	1006.31	1026.70
		1046.83	1075.23	1126.50
		1178.64	1262.59	1324.91

		1368.13	1393.06	1401.90
		1454.46	1456.94	1465.91
		1468.83	1786.21	2977.20
		3064.98	3074.01	3145.38
		3155.59	3159.03	3194.14

Table S15. Cartesian coordinates (Å) and absolute energies (hartrees) of optimized structures for R1 path.

(a) by M06CR/MG3S

Species	Absolute energy (hartrees)	Cartesian coordinates			
CH_2OO	-189.47	C	1.06051700	-0.21853800	0.00000000
		O	0.00000000	0.44258900	0.00000000
		O	-1.16683800	-0.16194300	0.00000000
		H	1.00256900	-1.30226200	0.00000000
		H	1.96903400	0.36832400	0.00000000
CH_3CN	-132.66	C	0.00000000	0.00000000	0.27875800
		N	0.00000000	0.00000000	1.42650700
		C	0.00000000	0.00000000	-1.17009100
		H	0.00000000	1.02150500	-1.54585100
		H	0.88464900	-0.51075300	-1.54585100
		H	-0.88464900	-0.51075300	-1.54585100
TS1	-322.13	C	-1.63939300	0.52554000	0.21999400
		O	-1.40046300	-0.56492400	-0.37720200
		O	-0.38935300	-1.26604100	0.18609900
		H	-1.43477600	0.60353000	1.28005500
		H	-2.35243200	1.17034700	-0.27984600
		C	0.97308500	0.51383300	-0.03190500
		N	0.22136600	1.40326800	-0.08846800
		C	2.18406800	-0.28364600	-0.00097100
		H	2.18975700	-0.89497700	0.89884900
		H	2.20065900	-0.95298000	-0.85773100
		H	3.05920400	0.36455700	-0.01594200

M1	-322.22	C	1.44664800	0.63619900	0.05541100
		O	1.35379100	-0.79797700	-0.09185300
		O	-0.03210000	-1.08200600	0.06810400
		H	2.09400700	1.00071700	-0.74528100
		H	1.88262700	0.88776800	1.03076000
		C	-0.63960400	0.12865000	-0.00442600
		N	0.11023500	1.14143400	-0.04629500
		C	-2.11734600	0.07065500	-0.00864700
		H	-2.46991800	-0.48263200	-0.87801500
		H	-2.47423100	-0.44812300	0.88031100
		H	-2.51584500	1.07907100	-0.02773300

(b) by CCSD(T)-F12a/cc-pVTZ-F12

Species	Absolute energy (hartrees)	Cartesian coordinates			
CH_2OO	-189.41	C	-1.0649415951	0.1992476468	0.0000000000
		O	0.0146891002	-0.4698160766	0.0000000000
		O	1.1726406690	0.2082457675	0.0000000000
		H	-1.0049041189	1.2797686039	0.0000000000
		H	-1.9662640554	-0.3944549416	0.0000000000
CH_3CN	-132.59	C	0.0000000000	-0.0000035710	0.2849766443
		N	0.0000000000	-0.0000027010	1.4428019700
		C	0.0000000000	-0.0000084755	1.1777587326
		H	0.0000000000	1.0238364403	-1.5464111275
		H	0.8866476636	-0.5119113464	-1.5463938771
		H	-0.8866476636	-0.5119113464	-1.5463938771
TS1	-322.00	C	-1.6519584877	0.5147929532	0.2340577647
		O	-1.4037705250	-0.5726791139	-0.3852341859
		O	-0.3457058464	-1.2456238653	0.1979338565
		H	-1.4255955131	0.5828673451	1.2877543704
		H	-2.3759662780	1.1543923373	-0.2529756149
		C	0.9419608128	0.4954380716	-0.0260415001
		N	0.2077883989	1.4135554912	-0.0817420642
		C	2.1772578492	-0.2927310651	-0.0057011603
		H	2.1935957037	-0.9046462957	0.8938607964
		H	2.1956000642	-0.9527924794	-0.8696604150
		H	3.0383648214	0.3741066212	-0.0216168476
M1	-322.08	C	-1.4599072789	-0.6257522563	0.0771521984
		O	-1.3754767824	0.8019885219	-0.1194243465
		O	0.0373899037	1.0954460672	0.1116280936
		H	-2.1343764429	-1.0044217266	-0.6899019095

		H	-1.8422980717	-0.8517224915	1.0781566591
		C	0.6352261634	-0.1244862598	-0.0017451588
		N	-0.1169552163	-1.1438962142	-0.0665963409
		C	2.1213421397	-0.0735754792	-0.0117432328
		H	2.4694351431	0.4770907271	-0.8849893946
		H	2.4806472206	0.4398402098	0.8798731685
		H	2.5074522217	-1.0882290985	-0.0338297368

(c) by CCSD(T)-F12a/cc-pVDZ-F12

Species	Absolute energy (hartrees)	Cartesian coordinates			
CH_2OO	-189.38	C	-1.0653788937	0.1993413752	0.0000000000
		O	0.0157326658	-0.4711795226	0.0000000000
		O	1.1734170344	0.2088162868	0.0000000000
		H	-1.0054411078	1.2798271995	0.0000000000
		H	-1.9671096988	-0.3938143388	0.0000000000
CH_3CN	-132.57	C	0.0000000000	-0.0000035596	0.2854845029
		N	0.0000000000	-0.0000027441	1.4438564815
		C	0.0000000000	-0.0000085799	-1.1782580792
		H	0.0000000000	1.0238226777	-1.5467655604
		H	0.8866355509	-0.5119043971	-1.5467481724
		H	-0.8866355509	-0.5119043971	-1.5467481724
TS1	-321.96	C	-1.6542534416	0.5154804872	0.2343623134
		O	-1.4052915276	-0.5727575035	-0.3864893396
		O	-0.3470091992	-1.2460229808	0.1968330691
		H	-1.4277271256	0.5832284950	1.2879983539
		H	-2.3783251212	1.1550661108	-0.2524457329
		C	0.9420353003	0.4942689322	-0.0253758759
		N	0.2098211338	1.4146535311	-0.0811120120
		C	2.1786933372	-0.2936259346	-0.0055901580
		H	2.1976308504	-0.9041936942	0.8947248329
		H	2.1976393358	-0.9543286762	-0.8689386793
		H	3.0383574578	0.3749112331	-0.0233317717
M1	-322.04	C	-1.4607449949	-0.6257655648	0.0768587660
		O	-1.3768538458	0.8026566875	-0.1200343841
		O	0.0373679980	1.0963847653	0.1139073555
		H	-2.1359175599	-1.0045006455	-0.6896375751
		H	-1.8424374766	-0.8523524359	1.0780573678
		C	0.6352009130	-0.1244647956	-0.0016193969

		N	-0.1168537034	-1.1448191459	-0.0681444176
		C	2.1223420082	-0.0735494195	-0.0117322512
		H	2.4703416667	0.4758553694	-0.8857763657
		H	2.4815823485	0.4410527896	0.8791854073
		H	2.5084516463	-1.0882156046	-0.0324845063

(d) by DF-CCSD(T)-F12b/jun-cc-pVDZ

Species	Absolute energy (hartrees)	Cartesian coordinates			
CH_2OO	-189.28	C	-1.0660225872	0.1999444614	0.0000000000
		O	0.0192321342	-0.4711285542	0.0000000000
		O	1.1781680485	0.2053782480	0.0000000000
		H	-1.0066205545	1.2906313984	0.0000000000
		H	-1.9735370410	-0.4018345535	0.0000000000
CH_3CN	-132.50	C	-0.0000000054	-0.0000000934	0.2881692508
		N	0.0000000060	0.0000000470	1.4574605957
		C	-0.0000000015	-0.0000002169	-1.1808352630
		H	0.0000000004	1.0328441612	-1.5513246088
		H	0.8944694949	-0.5164224490	-1.5513244834
		H	-0.8944694943	-0.5164224490	-1.5513244913
TS1	-321.79	C	-1.6624770330	0.5181043251	0.2349678509
		O	-1.4116763635	-0.5730237547	-0.3879359460
		O	-0.3547733605	-1.2477677204	0.1953193050
		H	-1.4368176463	0.5830643958	1.2993100953
		H	-2.3966104810	1.1595060081	-0.2567998020
		C	0.9463864911	0.4924314699	-0.0276182717
		N	0.2086854567	1.4226131938	-0.0823016521
		C	2.1894199938	-0.2960880788	-0.0064612805
		H	2.2066487789	-0.9096761624	0.9030593478
		H	2.2087143557	-0.9634651718	-0.8764844379
		H	3.0540708082	0.3809814955	-0.0244202088
M1	-321.87	C	-1.4633752820	-0.6243637353	0.0732302080
		O	-1.3773292419	0.7984995342	-0.1461206027
		O	0.0320294506	1.0941233591	0.1375290970
		H	-2.1614077995	-1.0088016430	-0.6827998623
		H	-1.8296307946	-0.8413647688	1.0930965943
		C	0.6366054184	-0.1265182126	-0.0047908451
		N	-0.1205190258	-1.1510163366	-0.0908567843
		C	2.1267797089	-0.0725280863	-0.0101319638

		H	2.4780338947	0.4830418126	-0.8905761296
		H	2.4832258357	0.4466718123	0.8904942384
		H	2.5180668357	-1.0954617355	-0.0304939501

Table S16. Cartesian coordinates (Å) and absolute energies (hartrees) of optimized structures for R2 path(*anti*-CH_3CHOO + CH_3CN).

(a) by DF-CCSD(T)-F12b/jun-cc-pVDZ

Species	Absolute energy (hartrees)	Cartesian coordinates			
anti-CH_3CHOO	-228.52	C	0.0029814656	0.5642599882	0.0000000193
		O	0.1462898413	-0.6984780840	-0.0000000701
		O	1.4178602368	-1.1916911975	-0.0000000331
		H	0.9253204744	1.1566353372	0.0000001053
		C	-1.3751037059	1.1192691991	-0.0000000030
		H	-1.5232386555	1.7522052448	0.8885323728
		H	-1.5232386956	1.7522051348	-0.8885324524
		H	-2.1121809611	0.3069343774	0.0000000612
CH_3CN	-132.50	C	-0.0000000061	-0.0000000918	0.2859697628
		N	0.0000000064	0.0000000440	1.4552599343
		C	-0.0000000014	-0.0000002160	-1.1830361690
		H	0.0000000004	1.0328442880	-1.5535242582
		H	0.8944696043	-0.5164225121	-1.5535241308
		H	-0.8944696036	-0.5164225121	-1.5535241391
TS2	--361.03	C	1.2711180094	0.0644704854	0.3654569313
		O	0.7527261874	1.0148419534	-0.3284676816
		O	-0.4917893916	1.3814588989	0.1687145950
		H	0.9723566752	0.0019609944	1.4144430374
		C	-1.2421188912	-0.6045751702	-0.0070109955
		N	-0.2899859718	-1.3184888371	0.0147261085
		C	-2.6574437276	-0.2020664097	-0.0789246877
		H	-2.8912402661	0.4377627936	0.7814874045
		H	-2.8217614332	0.3769506169	-0.9959289165
		H	-3.2961093614	-1.0956722908	-0.0722424878
		C	2.5399373106	-0.5300793345	-0.1370002466
		H	3.3950774123	-0.0494744511	0.3633811931
		H	2.5458785650	-1.6005904990	0.1061297094
		H	2.6219498831	-0.3953647502	-1.2224109637

(b) by M11-L/MG3S

Species	Absolute energy (hartrees)	Cartesian coordinates		
anti-CH_3CHOO	-228.92	C 0.00000000	0.55187700	0.00000000
		O 0.15958700	-0.67614500	0.00000000
		O 1.38905800	-1.15242700	0.00000000
		H 0.90857200	1.16903200	0.00000000
		C -1.35782000	1.07589000	0.00000000
		H -1.53042800	1.71430100	0.87710400
		H -1.53042800	1.71430100	-0.87710400
		H -2.08995300	0.26434100	0.00000000
CH_3CN	-132.77	C 0.00000000	0.00000000	0.27418500
		N 0.00000000	0.00000000	1.41703300
		C 0.00000000	0.00000000	-1.15680700
		H 0.00000000	-1.02495100	-1.54116600
		H -0.88763300	0.51247500	-1.54116600
		H 0.88763300	0.51247500	-1.54116600
TS2	-361.67	C 1.22806500	0.07581900	0.35718200
		O 0.72329100	1.00118400	-0.32873500
		O -0.48834800	1.35444100	0.15462900
		H 0.92908800	0.01878400	1.40975300
		C -1.21289000	-0.61501500	-0.01120000
		N -0.26269600	-1.28735500	0.00280800
		C -2.58962000	-0.21546200	-0.07191500
		H -2.82671000	0.41865200	0.78794200
		H -2.76487100	0.37875600	-0.97316800
		H -3.24760300	-1.09205500	-0.07298100
		C 2.48166700	-0.50678300	-0.12061300
		H 3.33701500	-0.04084400	0.38552300
		H 2.49868500	-1.57388800	0.11533900
		H 2.59038300	-0.37427400	-1.19993200
M2	-361.77	C -1.12202900	-0.11399500	-0.47856400
		O -0.71277100	1.21571300	-0.17903300
		O 0.61573900	1.08734400	0.27936100
		H -1.61373500	-0.05915300	-1.47013900
		C 0.95685300	-0.14600500	-0.06308800
		N 0.06512100	-0.88456800	-0.54068100
		C 2.36234300	-0.47538100	0.18966500
		H 3.02362900	0.17776400	-0.38921300
		H 2.60822300	-0.32858100	1.24662600
		H 2.54600000	-1.51470300	-0.08287600
		C -2.07808500	-0.63198400	0.55521000

		H	-2.96765100	0.00307800	0.61786400
		H	-2.39411000	-1.64901000	0.30074700
		H	-1.59644900	-0.65769200	1.53980400

Table S17. Cartesian coordinates (Å) and absolute energies (hartrees) of optimized structures for R3 path(*syn*-CH_3CHOO + CH_3CN).
(a) by DF-CCSD(T)-F12b/jun-cc-pVDZ

Species	Absolute energy (hartrees)	Cartesian coordinates			
syn-CH_3CHOO	-228.53	C	0.4813796268	0.7090224817	-0.0000058374
		O	-0.7900931981	0.5834770668	0.0000008922
		O	-1.2750723867	-0.6867758358	0.0000092784
		C	1.3594699134	-0.4759395463	-0.0000042608
		H	1.1159534447	-1.0973786637	0.8776557326
		H	1.1159452788	-1.0973871276	-0.8776559913
		H	2.4149410153	-0.1815141263	-0.0000106037
		H	0.8002293057	1.7539867513	-0.0000122101
CH_3CN	-132.50	C	-0.0000000061	-0.0000000918	0.2859697628
		N	0.0000000064	0.0000000440	1.4552599343
		C	-0.0000000014	-0.0000002160	-1.1830361690
		H	0.0000000004	1.0328442880	-1.5535242582
		H	0.8944696043	-0.5164225121	-1.5535241308
		H	-0.8944696036	-0.5164225121	-1.5535241391
TS3	-361.03	C	1.4251925616	-0.0809268408	-0.4590154327
		O	0.8463913880	1.0675585657	-0.5873680967
		O	-0.1187803858	1.2872148058	0.3811840881
		H	2.0267636942	-0.3109319716	-1.3453204890
		C	-1.1597313850	-0.4882814521	-0.1972875666
		N	-0.3502970023	-1.1843090571	-0.7246905498
		C	-2.4688602533	-0.0590746327	0.3259863863
		H	-2.3617770713	0.2148750418	1.3833234155
		H	-2.8060302911	0.8256415975	-0.2279022601
		H	-3.1948318425	-0.8762476685	0.2179646416
		C	1.7741730954	-0.6991037738	0.8531939090
		H	1.0225997268	-0.4628501435	1.6117605342
		H	1.8748754151	-1.7845072607	0.7296173766
		H	2.7496843502	-0.2830022100	1.1596040438

(b) M11-L/MG3S

Species	Absolute energy (hartrees)	Cartesian coordinates			
syn-CH_3CHOO	-228.92	C	0.45794900	0.69941000	-0.00000600
		O	-0.77869300	0.56788800	0.00000100
		O	-1.22442600	-0.67690400	0.00000900
		C	1.32708500	-0.45293000	-0.00000400
		H	1.07743400	-1.08729500	0.86396800
		H	1.07742600	-1.08730300	-0.86396800
		H	2.38225700	-0.17723700	-0.00001000
		H	0.77762900	1.74508400	-0.00001200
CH_3CN	-132.77	C	0.00000000	0.00000000	0.27418500
		N	0.00000000	0.00000000	1.41703300
		C	0.00000000	0.00000000	-1.15680700
		H	0.00000000	-1.02495100	-1.54116600
		H	-0.88763300	0.51247500	-1.54116600
		H	0.88763300	0.51247500	-1.54116600
TS3	-361.69	C	1.37907100	-0.07943500	-0.43565600
		O	0.83174000	1.05078900	-0.57197100
		O	-0.10543600	1.27086400	0.37483900
		H	2.00087200	-0.32207800	-1.30825000
		C	-1.13836900	-0.49324900	-0.21259100
		N	-0.32564200	-1.14565800	-0.73074800
		C	-2.40341400	-0.06041100	0.30737100
		H	-2.29694900	0.20935700	1.36258900
		H	-2.73782100	0.83446900	-0.22503300
		H	-3.15433300	-0.85275100	0.20693500
		C	1.70196000	-0.68739700	0.85871300
		H	0.94306500	-0.45112200	1.60389100
		H	1.81068100	-1.76864300	0.75312700
		H	2.66805200	-0.27989900	1.19201400
M3	-361.77	C	1.08007600	-0.11834500	-0.42089300
		O	0.69102200	1.15864900	0.04889200
		O	-0.71840200	1.12565100	0.02432900
		H	1.31009700	-0.06225900	-1.51225300
		C	-0.99821300	-0.17224200	-0.02226100
		N	-0.04666500	-0.95887200	-0.23067300
		C	-2.41617800	-0.49176500	0.15832000
		H	-2.76347300	-0.17038900	1.14581300
		H	-3.02564400	0.03418900	-0.58429400
		H	-2.56393900	-1.56633600	0.05011100
		C	2.29614900	-0.53049600	0.34068600
		H	2.06282700	-0.62725900	1.40624600

		H	2.65425000	-1.49507800	-0.03106100
		H	3.10057500	0.20192000	0.21927100

Table S18. The reaction classic energy barrier for R1, R2 and R3 reactions.

Method	*anti*-CH_3CHOO	*syn*-CH_3CHOO	CH_3CN	TS2	TS3
W2X [a]	-229.0629212	-229.0688175	-132.8277606	-361.8976062	-361.8941424
W3X-L	-229.0662375	-229.0719358	-132.8290367	-361.9011746	-361.897677

Both W2X and W3X-L are based on DF-CCSD(T)-F12b/jun-cc-pVDZ geometric optimizations.

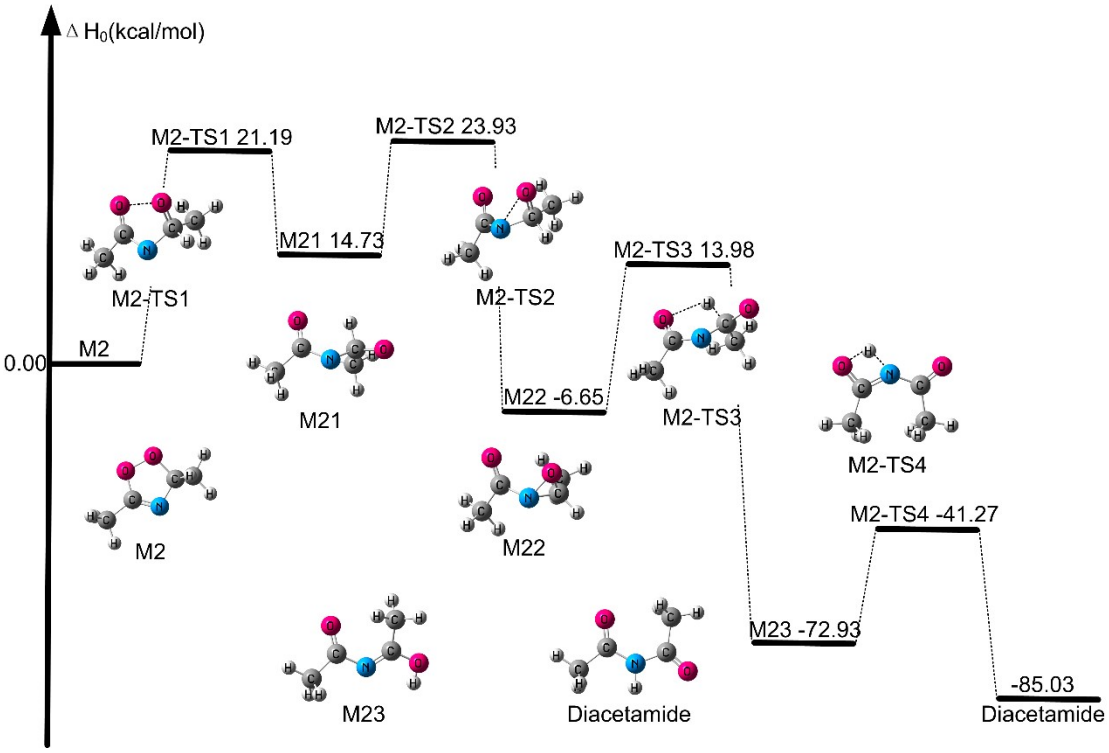

Figure S1. The enthalpies profile of the M2 isomerization channels for the *anti*-CH_3CHOO + CH_3CN reactions. Values are given for all species as calculated by M11-L/MG3S.

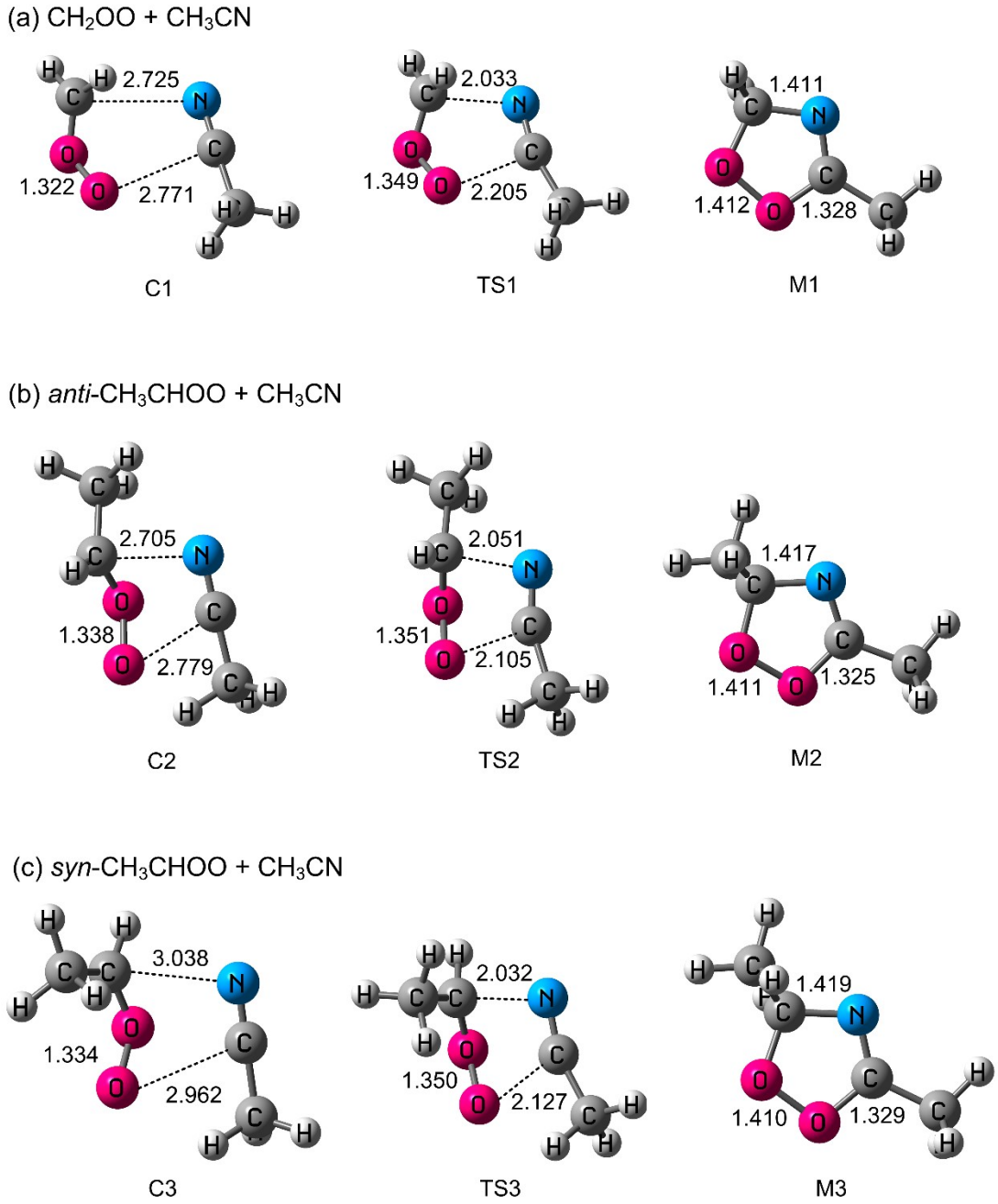

Figure S2. Optimized M11-L/MG3S geometries for the pre-reactive complex, transition

state, and product of the acetonitrile addition to the Criegee intermediates. Distances are given in angstroms (Å).

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