Supporting Information

for

An approach to the Atmospheric Chemistry of Methyl Nitrate and Methylperoxy Nitrite. Chemical Mechanisms of Their Formation and Decomposition Reactions in the Gas Phase

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Table S1a. Geometrical parameters for CH_3ONO_2.

Coordinate [a]	CAS-SCF [b]	B3-LYP[c]	CASPT2[d]	CASPT2[e]
R_{21}	1.415	1.442	1.432	1.433
R_{31}	1.078	1.095	1.084	1.089
R_{36}	1.079	1.096	1.086	1.086
R_{37}	1.079	1.096	1.086	1.086
R_{62}	1.421	1.416	1.413	1.413
R_{76}	1.207	1.213	1.210	1.210
R_{86}	1.199	1.204	1.201	1.201
A_{312}	103.9	103.1	103.2	103.2
A_{412}	111.1	110.8	111.0	111.0
A_{512}	111.1	110.8	111.0	111.0
A_{621}	114.0	113.4	112.4	112.4
A_{762}	117.4	117.4	117.2	117.2
A_{862}	112.7	112.8	112.7	112.7
Dh_{4123}	118.5	118.6	118.5	118.5
Dh_{5123}	-118.5	-118.6	-118.5	-118.5
Dh_{6213}	180.0	180.0	180.0	180.0
Dh_{7621}	0.0	0.0	0.0	0.0
Dh_{8627}	180.000	180.0	180.0	180.0
	Fig. 1a	Fig. 1a	Fig. 1a	Fig. 1a

[a] Atom labeling: C(1), O(2), H(3), H(4), H(5), N(6), O(7), O(8).

[b] CAS(16e, 12o)/ANO-L [C,N,O: 4*s*3*p*2*d*1*f*; H: 3*s*2*p*1*d*].

[c] B3LYP/aug-cc-pVDZ.

[d] Reference wave function: CAS(14e, 11o)/ANO-L [C,N,O: 4*s*3*p*2*d*1*f*; H: 3*s*2*p*1*d*].

[e] Reference wave function: CAS(16e, 13o)/ANO-L [C,N,O: 4*s*3*p*2*d*1*f*; H: 3*s*2*p*1*d*].

Table S1b. CASPT2(14,11) and CAS-SCF(14,11)/ANO-L geometrical parameters of Sd1 and Sd2.

Coordinate[a]	CAS-SCF Sd1	CASPT2 Sd1	CAS-SCF Sd2	CASPT2 Sd2
R_{21}	1.415	1.434	1.419	1.435
R_{31}	1.078	1.084	1.074	1.083
R_{41}	1.082	1.089	1.080	1.086
R_{51}	1.082	1.089	1.080	1.086
R_{62}	1.447	1.441	1.428	1.423
R_{76}	1.202	1.205	1.206	1.208
R_{87}	1.202	1.205	1.198	1.201
A_{312}	105.2	104.7	111.6	110.7
A_{412}	110.8	110.5	107.5	107.5
A_{512}	110.8	110.5	107.5	107.5
A_{621}	110.1	107.9	116.8	115.3
A_{762}	115.0	114.9	118.6	118.5
A_{876}	115.0	114.9	111.8	111.6
Dh_{4123}	118.4	118.4	-120.7	-120.4
Dh_{5123}	-118.4	-118.4	120.7	120.4
Dh_{6213}	180.0	180.0	0.0	0.0
Dh_{7621}	90.8	90.7	0.0	0.0
Dh_{8762}	178.5	178.5	180.0	180.0
	Fig. 1b	Fig. 1b	Fig 1c	Fig 1c

[a] Atom labeling: C(1), O(2), H(3), H(4), H(5), O(6), N(7), O(8).

Table S1c. CAS-SCF(14,11)/ANO-L geometrical parameters of cis- and trans-CH_3OONO.

Coordinate[a]	Cis	Trans
R_{21}	1.405	1.404
R_{31}	1.082	1.082
R_{41}	1.081	1.080
R_{51}	1.081	1.081
R_{62}	1.459	1.456
R_{76}	1.471	1.477
R_{87}	1.165	1.168
A_{312}	111.3	111.2
A_{412}	104.8	104.9
A_{512}	110.9	111. 0
A_{621}	106.9	107.0
A_{762}	110.7	104.4
A_{876}	115.4	109.3
Dh_{4123}	118.5	118.5
Dh_{5123}	-123.0	-123. 0
Dh_{6213}	64.1	64.5
Dh_{7621}	-107.9	-106.2
Dh_{8762}	2.3	-177.4
	Fig. 1d	Fig 1e

[a] Atom labeling: C(1), O(2), H(3), H(4), H(5), O(6), N(7), O(8).

Table S1d. Geometrical parameters for Ci1(S_1/S_0) and Ci2(S_1/S_0) conical intersections(CAS-SCF(14,11)/cc-pVDZ.

Coordinate [a]	Ci1	Ci2
R_{21}	1.382	1.386
R_{31}	1.094	1.094
R_{41}	1.093	1.092
R_{51}	1.093	1.092
R_{62}	2.744	2.321
R_{76}	1.260	1.568
R_{87}	1.281	1.167
A_{312}	106.0	105.5
A_{412}	111.7	111.6
A_{512}	111.7	112.0
A_{621}	97.4	101.1
A_{762}	107.2	89.1
A_{876}	107.3	110.6
Dh_{4123}	-117.9	-117.7
Dh_{5123}	180.0	118.1
Dh_{6213}	180.0	180.0
Dh_{7621}	180.0	140.3
Dh_{8762}	180.0	95.0
	Fig. 1f	Fig. 1g

[a] Atom labeling: C(1), O(2), H(3), H(4), H(5), O(6), N(7), O(8).

Table S1e. Geometrical parameters of the transition state (Ts1) for CH_2O elimination from CH_3ONO_2, $CH_3ONO_2 \rightarrow CH_2O + HONO$.

Coordinate [a]	CAS-SCF [b]	B3-LYP[c]	CASPT2[b]
R_{21}	1.278	1.289	1.291
R_{31}	1.312	1.322	1.334
R_{36}	1.938	1.910	1.876
R_{37}	1.353	1.311	1.266
R_{41}	1.085	1.106	1.094
R_{51}	1.085	1.106	1.094
R_{62}	2.161	2.024	2.014
R_{76}	1.266	1.246	1.256
R_{87}	1.194	1.194	1.193
A_{312}	97.6	96.6	94.9
A_{412}	117.2	117.8	118.0
A_{512}	117.2	117.8	118.0
A_{621}	97.8	99.8	100.1
A_{762}	100.5	102.3	101.7
A_{862}	135.0	131.8	132.6
Dh_{4123}	-107.4	-105.0	-104.4
Dh_{5123}	107.4	105.0	104.4
Dh_{6213}	0.0	0.0	0.0
Dh_{7621}	0.0	0.0	0.0
Dh_{8627}	180.0	180.0	180.0
	Fig. 1h	Fig. 1h	Fig. 1h

[a] Atom labeling: C(1), O(2), H(3), H(4), H(5), N(6), O(7), O(8).

[b] CAS-SCF reference wave function including 16 electrons in 13 orbitals.

[c] B3-LYP/aug-cc-pVDZ.

Table S2. B3-LYP/aug-cc-pVDZ geometrical parameters of *cis*- and *trans*-CH_3OONO and fictitious transition states for dissociation (Ts2 and Ts3).

Coordinate [a]	Cis	Trans	Ts2 [b]	Ts3 [b]	Ts Cis-Trans [c]
R_{21}	1.433	1.430	1.395	1.388	1.430
R_{31}	1.098	1.099	1.103	1.109	1.099
R_{41}	1.097	1.097	1.103	1.102	1.098
R_{51}	1.098	1.099	1.108	1.102	1.098
R_{62}	1.428	1.426	1.867	1.843	1.433
R_{76}	1.461	1.466	1.225	1.257	1.605
R_{87}	1.168	1.170	1.192	1.207	1.152
A_{312}	111.2	111.0	113.0	112.9	111.8
A_{412}	103.9	104.0	113.0	112.9	104.0
A_{512}	111.0	110.7	103.8	102.9	110.3
A_{621}	107.7	107.6	102.1	102.8	108.5
A_{762}	112.3	106.4	114.3	104.1	101.4
A_{876}	115.1	109.3	128.9	121.4	110.6
Dh_{4123}	118.3	118.3	-126.8	-127.9	118.5
Dh_{5123}	-123.6	-123.4	116.6	116.1	-123.2
Dh_{6213}	65.2	65.7	63.4	63.9	67.8
Dh_{7621}	-103.4	-100.7	180.0	180.0	-104.0
Dh_{8762}	2.9	-175.8	0.0	180.0	86.5
	Fig. 1d	Fig. 1e			

[a] Atom labeling: C(1), O(2), H(3), H(4), H(5), O(6), N(7), O(8).

[b] UB3LYP (guess=mix); $S^2 = 0.4$ for both transition states.

[c] Transition state for cis-trans isomerization.

Table S3. Energetic and kinetic parameters for the isomerization and elimination reactions of CH_3ONO_2 and CH_3OONO at the B3-LYP/aug-cc-pVDZ level.

Reaction	$\Delta U^{\#}(0)$ [a]	$\Delta H^{\#}$ [b]	$\Delta G^{\#}$ [c]	ΔE_a [d]	log$A$ [e]	k [f]	k [g]
$CH_3ONO_2 \rightarrow$ c-CH_3OONO	65.5	66.3	63.9	66.9	15.00	$8.77\ 10^{-35}$	$6.66\ 10^{-15}$
	(274.1)[h]	(277.6)	(267.4)	(280.0)			
c-$CH_3OONO \rightarrow CH_3ONO_2$	35.9	36.3	35.0	36.8	14.19	$1.49\ 10^{-13}$	$1.30\ 10^{-02}$
	(150.3)	(151.7)	(146.2)	(154.2)			
$CH_3ONO_2 \rightarrow H_2CO + HONO$	38.9	38.9	39.1	39.5	13.07	$1.40\ 10^{-16}$	$7.46\ 10^{-05}$
	(162.9)	(162.9)	(163.5)	(165.1)			
$CH_3ONO_2 \rightarrow H_2CO + HONO$	36.6	36.8	36.4	37.4	13.49	$1.24\ 10^{-14}$	$1.69\ 10^{-03}$
(**CASPT2**)	(153.2)	(153.9)	(152.4)	(156.4)			
c-$CH_3OONO \rightarrow H_2CO + HONO$	39.0	38.5	39.6	39.1	12.37	$5.23\ 10^{-17}$	$2.02\ 10^{-05}$
	(163.0)	(161.2)	(165.6)	(163.5)			
t-$CH_3OONO \rightarrow H_2CO + HNO_2$	22.3	21.9	22.6	22.5	12.69	$1.61\ 10^{-04}$	$7.41\ 10^{+02}$
	(93.1)	(91.6)	(94.7)	(94.1)			
$2CH_3ONO_2 \rightarrow$	72.8	73.5	73.7	74.6	13.32	$3.76\ 10^{-42}$	$1.71\ 10^{-19}$
$CH_3ONO+H_2C(OH)ONO_2$	(304.7)	(307.5)	(308.2)	(312.5)			
c-$CH_3OONO \rightarrow CH_3O + NO_2$	9.0	9.1	8.3	9.7	13.83	$5.00\ 10^{+05}$	$3.93\ 10^{+09}$
	(37.8)	(38.2)	(34.8)	(40.7)			
t-$CH_3OONO \rightarrow CH_3O + NO_2$	22.3	22.5	21.7	23.1	13.80	$7.00\ 10^{-04}$	$5.38\ 10^{+03}$
	(93.4)	(94.2)	(90.9)	(96.6)			
c-$CH_3OONO \rightarrow$ t-CH_3OONO	14.0	13.8	14.2	14.4	12.90	$2.27\ 10^{+02}$	$4.25\ 10^{+06}$
	(58.7)	(57.7)	(59.6)	(60.2)			
t-$CH_3OONO \rightarrow$ c-CH_3OONO	12.8	12.5	13.0	13.1	12.89	$1.85\ 10^{+03}$	$1.47\ 10^{+07}$
	(53.5)	(52.5)	(54.4)	(54.9)			

[a] Energy difference in kcal mol^{-1} including zero-point corrections. [b] Activation enthalpy at T=298.15 K. [c] Gibbs activation energy at T=298.15 K. [d] Arrhenius activation energy at 298.15 K. [e] Pre-exponential factor at 298.15 K in s^{-1} for unimolecular reactions and L s^{-1} mol^{-1} for bimolecular reactions. [f] Rate constant at 298.15 K. [g] Rate constant at 500.00 K. [h] In parentheses values in kJ mol^{-1}.

Table S4. B3-LYP/aug-cc-pVDZ geometrical parameters of the transition state (Ts4) for $CH_3ONO_2 \rightarrow$ *cis*-CH_3OONO rearrangement.

Coordinate [a]	Ts4
R_{21}	1.357
R_{31}	1.106
R_{41}	1.121
R_{51}	1.115
R_{62}	2.541
R_{76}	1.184
R_{87}	1.181
A_{312}	114.9
A_{412}	107.2
A_{512}	112.8
A_{621}	94.4
A_{762}	73.06
A_{876}	137.0
Dh_{4123}	120.6
Dh_{5123}	-127.3
Dh_{6213}	83.6
Dh_{7621}	151.8
Dh_{8762}	72.3

[a] Atom labeling: C(1), O(2), H(3), H(4), H(5), O(6), N(7), O(8).

Table S5. B3-LYP/aug-cc-pVDZ geometrical parameters of the transition states Ts5 and Ts6 .

Coordinate [a]	Ts5	Ts6
R_{21}	1.315	1.356
R_{31}	1.211	1.103
R_{41}	1.103	1.103
R_{51}	1.109	1.138
R_{62}	1.853	1.776
R_{76}	1.266	1.245
R_{87}	1.274	1.214
A_{312}	102.9	112.1
A_{412}	116.5	112.1
A_{512}	112.9	106.8
A_{621}	112.0	110.0
A_{762}	113.2	107.0
A_{876}	112.9	121.7
Dh_{4123}	115.9	130.4
Dh_{5123}	-102.9	-114.8
Dh_{6213}	-22.0	114.8
Dh_{7621}	-1.3	0.0
Dh_{8762}	47.9	180.0

[a] Atom labeling: C(1), O(2), H(3), H(4), H(5), O(6), N(7), O(8).

Table S6. Cartesian Coordinates in Å for Ts7 (B3-LYP/aug-cc-pVDZ).

Atomic Number	X	Y	Z
6	-0.732033	-0.411279	-0.030748
8	-0.100636	0.322994	1.044166
8	-0.100636	0.322994	1.044166
1	0.088747	-0.823609	-0.626311
1	-1.364597	-1.204113	0.376561
1	-1.330863	0.285696	-0.628270
7	-0.755407	0.168760	2.260960
8	-2.533390	-0.031592	2.165519
8	-0.234761	0.738271	3.149198
1	-3.453277	0.596883	2.353197
6	-4.674732	0.225563	1.998573
1	-4.795987	-0.854606	2.022063
1	-5.217662	0.778724	2.775006
8	-4.978403	0.825034	0.781902
7	-4.778110	-0.024175	-0.382910
8	-4.884699	0.598545	-1.403934
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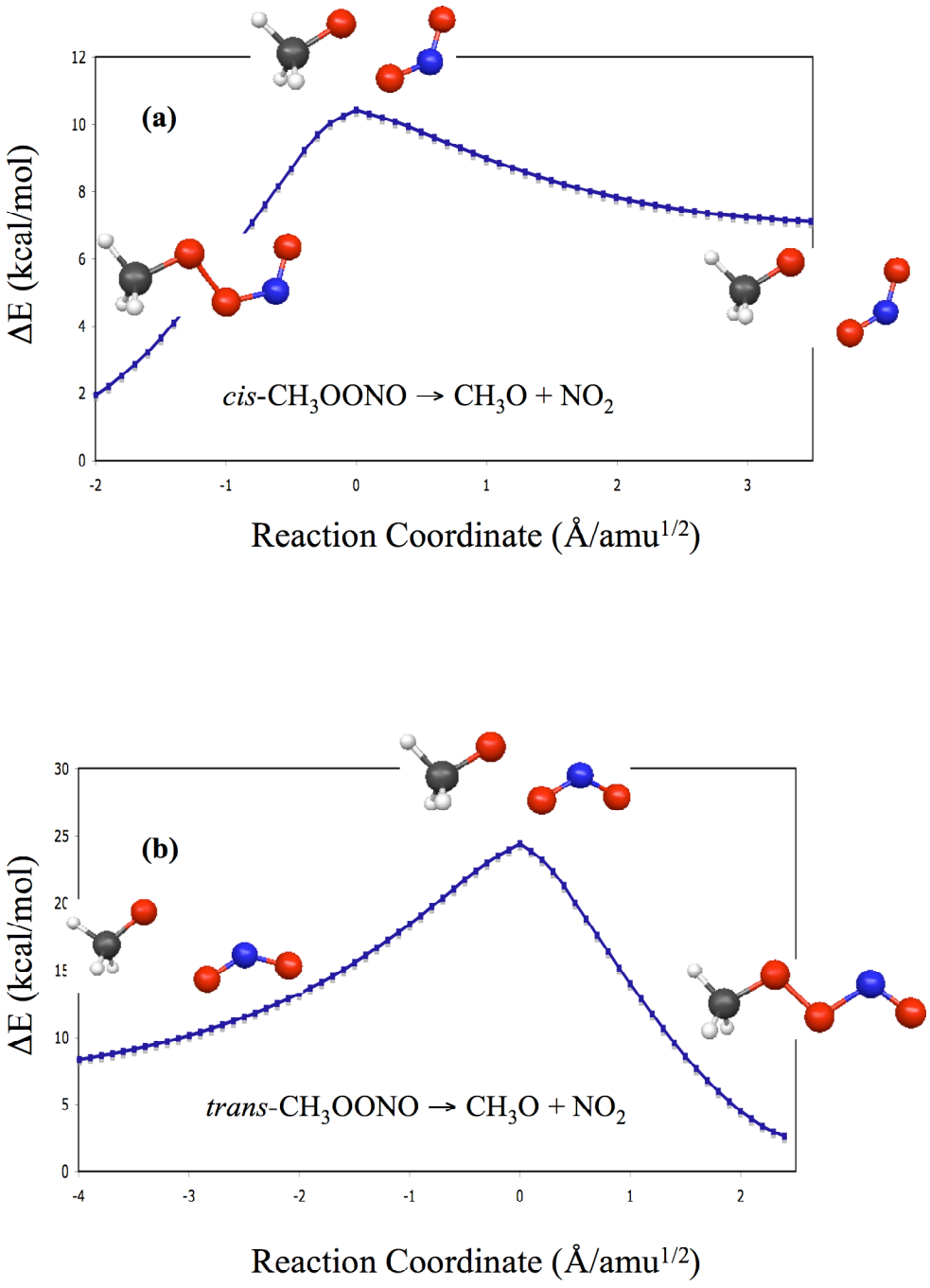

Figure S1. (a) B3-LYP/aug-cc-pVDZ IRC starting at the transition state Ts2. (b) B3-LYP/aug-cc-pVDZ IRC starting at Ts3.

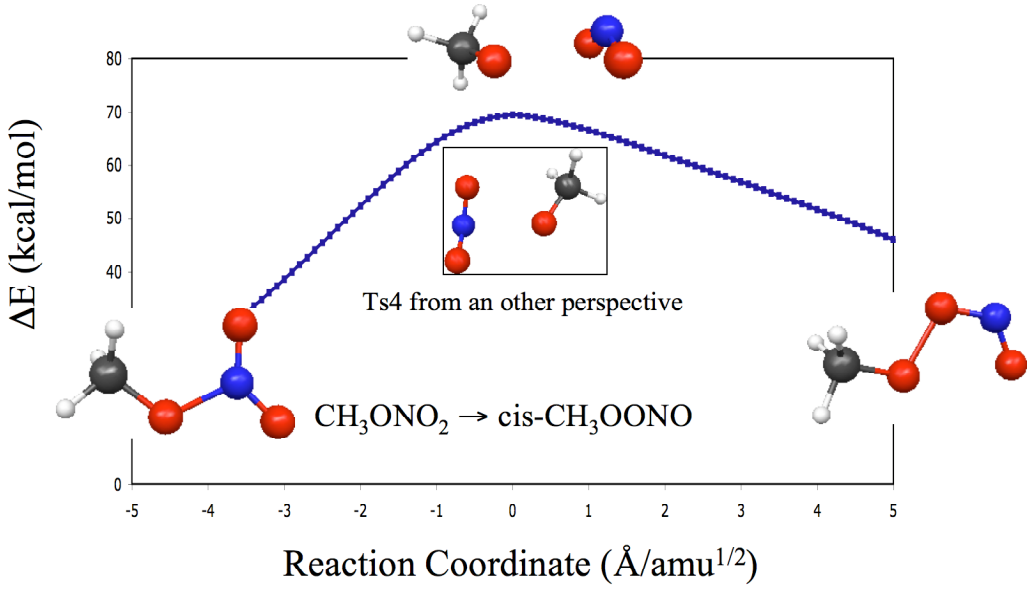

Figure S2. B3-LYP/aug-cc-pVDZ IRC starting at Ts4.

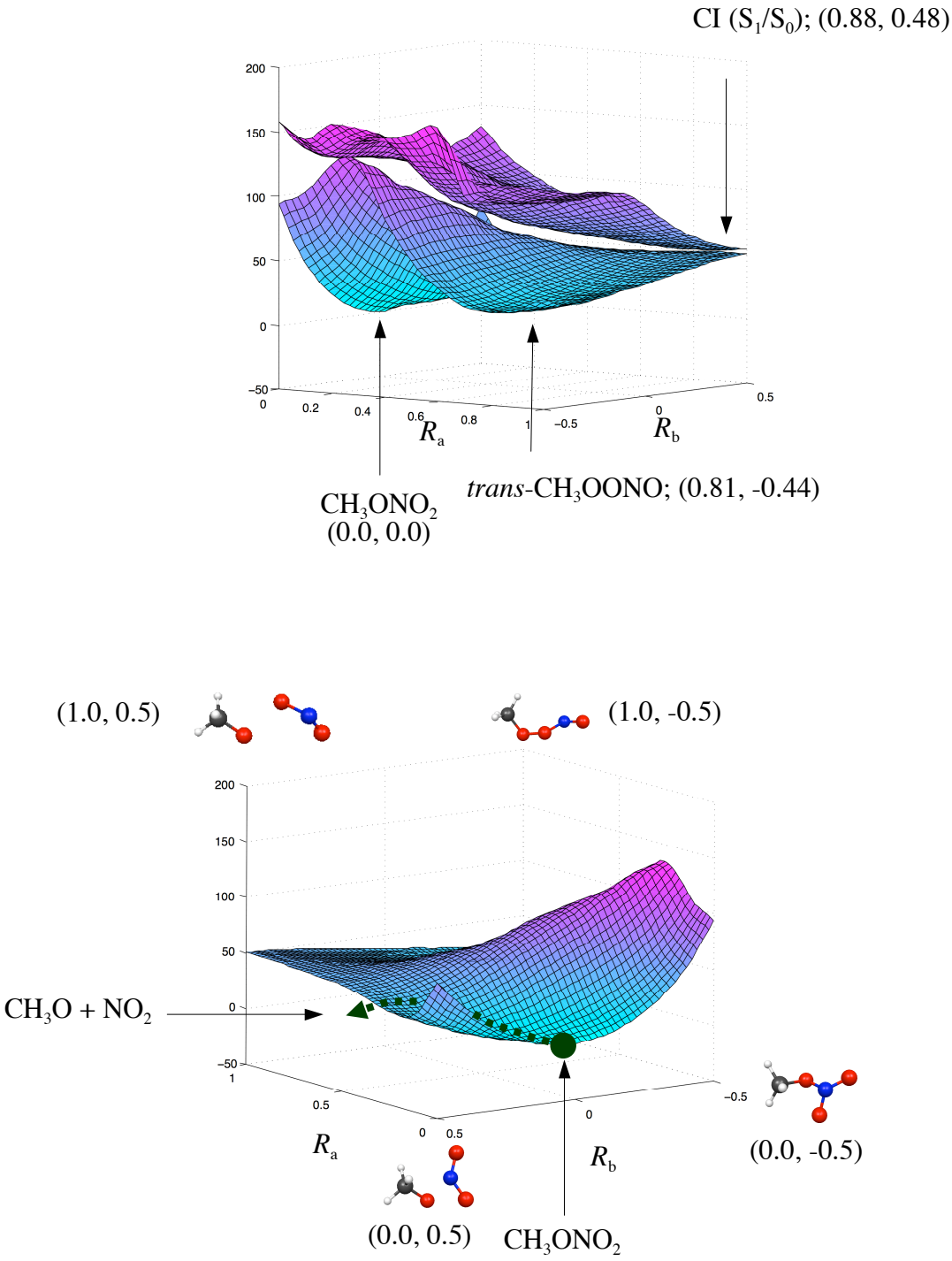

Figure S3. Potential energy surfaces for CH_3ONO_2 → *trans*-CH_3OONO reaction (a) S_0 and S_1 surfaces at the CAS(14, 11) level, (b) S_0 surface showing molecular arrangements of the four corners of the surfaces, labels denote coordinates.

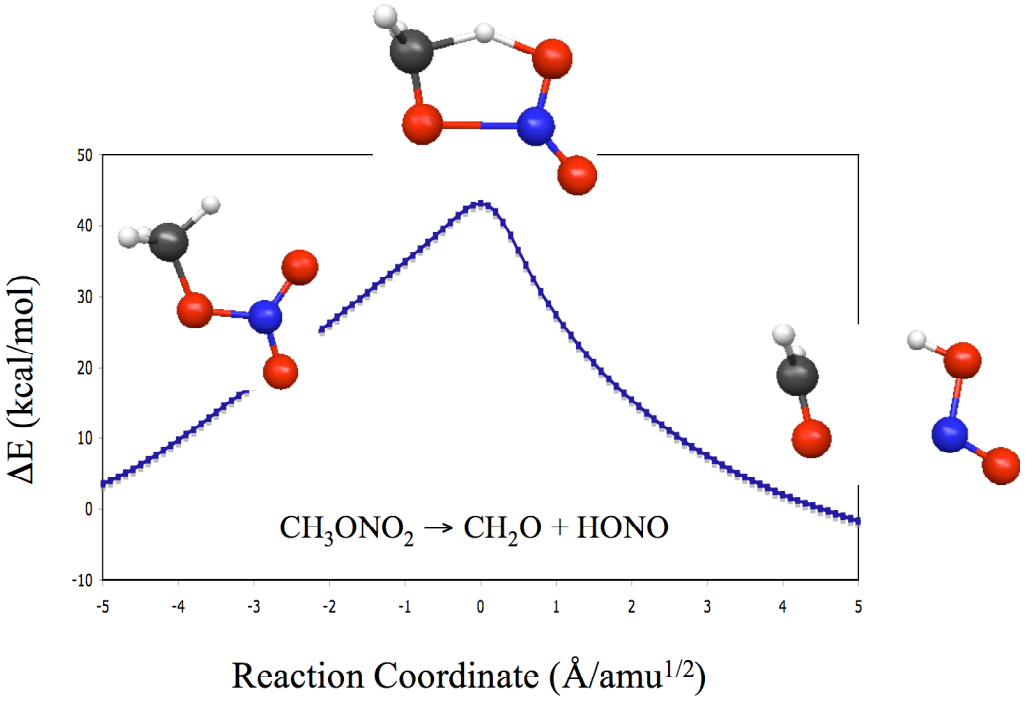

Figure S4. B3-LYP/aug-cc-pVDZ IRC starting at Ts1.

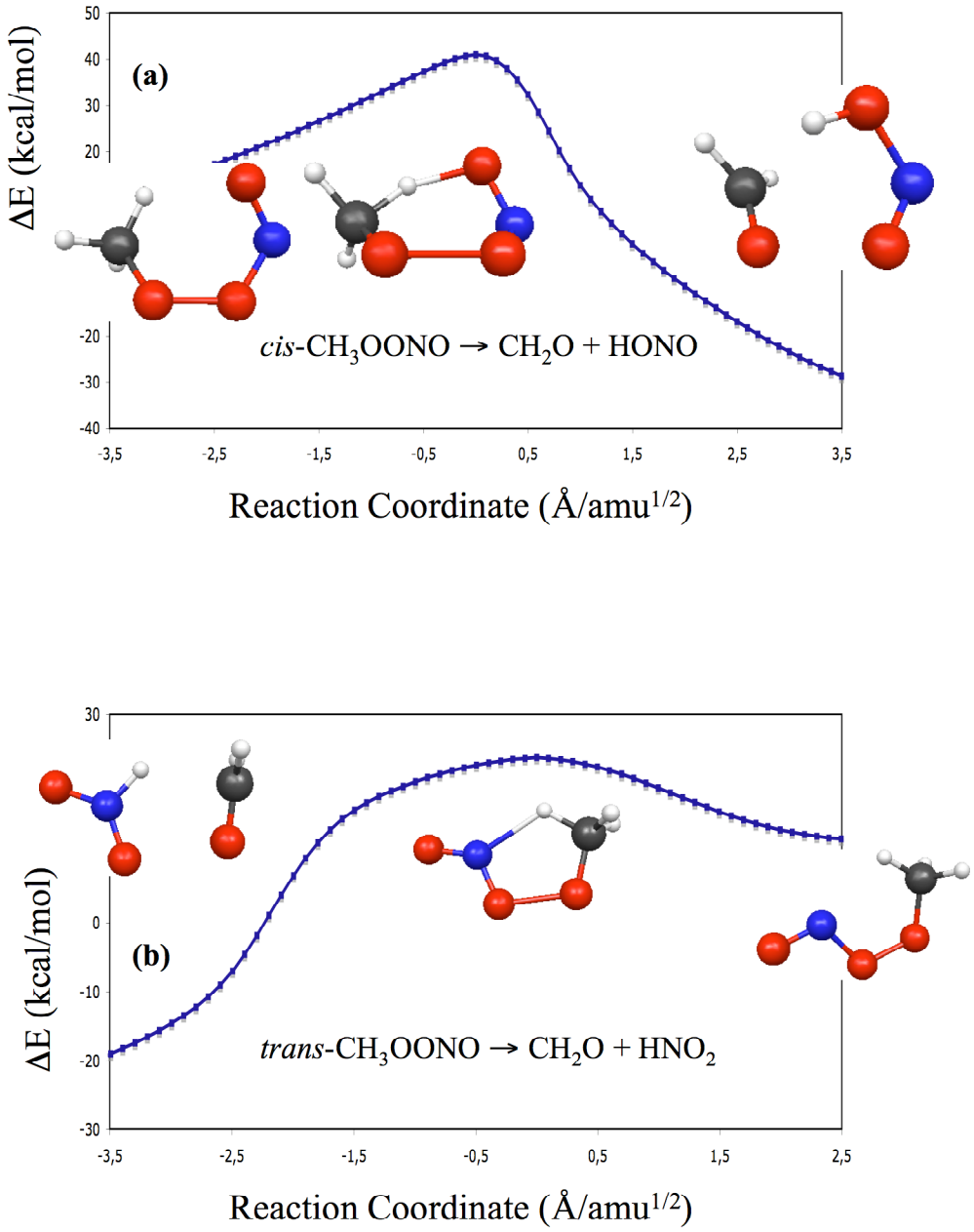

Figure S5. B3-LYP/aug-cc-pVDZ IRC starting at (a) Ts5 and (b) Ts6.