Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Atmospheric oxidation mechanism of OH-initiated reactions of diethyl ether – The fate of 1-ethoxy ethoxy radical.

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Table S1. CBS-QB3 Energies of the reactive species involved in the oxidation of diethyl ether by OH radical.

Reactive Species	CBS-QB3	
	H_{298}	G_{298}
$CH_3CH_2OCH_2CH_3$	-233.203536	-233.241957
$^{\bullet}OH$	-75.646415	-75.666647
$CH_3CH_2OCH_2\dot{C}H_2$	-232.543253	-232.582215
$CH_3CH_2O\dot{C}HCH_3$	-232.556056	-232.595230
H_2O	-76.333711	-76.355138
$CH_3CH_2OCH_2CH_2O\dot{O}$	-382.759440	-382.803813
O_2	-150.161303	-150.184576
$CH_3CH_2OCH(O\dot{O})CH_3$	-382.778821	-382.822742
$CH_3CH_2OCH_2CH_2\dot{O}$	-307.674643	-307.716156
NO	-129.745164	-129.768458
$CH_3CH_2OCH(\dot{O})CH_3$	-307.695526	-307.736829
NO_2	-204.848676	-204.876568
$CH_3CH_2OCH_2CH(=O)$	-307.151732	-307.191907
$CH_3CH_2OC(=O)CH_3$	-307.198981	-307.239867
HO_2	-150.737299	-150.763280
$CH_3\dot{C}HOCH(OOH)CH_3$	-382.765019	-382.809140
$CH_3CH_2OCH(=O)$	-267.962854	-267.998940
$CH_3CH_2\dot{O}$	-154.100558	-154.130914
$CH(=O)CH_3$	-153.577618	-153.607410
$^{\bullet}CH_3$	-39.740783	-39.764596
HNO	-130.319496	-130.344545
HONO	-205.470840	-205.499028

Table S1.1. Available literature data for the heat of formation [kJ/mol] for some of the reactive species involved in the oxidation of diethyl ether by OH radical.

Reactive Species	$\Delta_f H(298)$ [kJ/mol]
$CH_3CH_2OCH_2CH_3$	-252.7 ± 2.0[S1]
$^{\bullet}OH$	+37.3±0.3[S2]
$CH_3CH_2O^{\bullet}CHCH_3$	-81.2±4.2[S2]
H_2O	-241.8±0.04 [S1]
NO	+90.29 [S1]
NO_2	+33.10 [S1]
$CH_3CH_2OC(=O)CH_3$	-445.43 ± 0.84[S1]
HO_2	+12.3±0.25[S3]
$CH_3CH_2OCH(=O)$	-398.0[S1]
$CH_3CH_2O^{\bullet}$	-13.6±4.0[S1]
$CH(=O)CH_3$	-170.7 ± 1.5[S1]
$^{\bullet}CH_3$	+147. ± 1[S1]
HNO	+111.7± 3.4[S4]
HONO	-76.73[S1]

References

[S1] NIST Chemistry WebBook: *http://webbook.nist.gov/chemistry,* **2011.**

[S2] Y.-R. Luo, Comprehensive Handbook of Chemical Bond Energies, *CRC Press*, Boca Raton, **2007**.

[S3] *CRC Handbook of Chemistry and Physics*, 94th Edition, Ed. W. Haynes, **2013-2014**, CRC Press, Boca Raton.

[S4] T. L. Lee, C. E. Dateo, *J. Chem. Phys.*, *103*, **1995**, 9110-9111.

Table S1.2. Enthalpies of formation, ΔH_f^0 [kJ/mol] of the atoms.

Species	$\Delta H_f^0(0K)$ [S1,S2]	$H^{298} - H^0$ [S1,S2]
C(^{3}P)	+711.19±0.46	+1.051
H($^2S_{1/2}$)	+216.035±0.0006	+4.23
O($^3P_2$)	246.79±0.10	+4.34

References:

[S1] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, *J. Phys. Chem. Ref. Data*, 14, Suppl. No. 1, **1985.**
[S2] NIST-JANAF Thermochemical Tables, 4th ed., M. W. Chase, Jr., Ed.; J. Phys. Chem. Ref. Data Monogr. 9, American Institute of Physics and American Chemical Society: New York, **1998**.

Table S1.3. CBS-QB3 total energies of the atoms [in Hartrees].

Species	E_0
C(^{3}P)	-37.785377
H($^2S_{1/2}$)	-0.499818
O($^3P_2$)	-74.987630

Calculation of enthalpy of formation, $\Delta H_f^0(0K)$ and $\Delta H_f^0(298K)$ from atomization enthalpies:

For any molecule, $A_xB_yC_z$, the enthalpy of formation at 0K is given by,

$$\Delta H_f^0(A_xB_yC_z,0K) = x\Delta H_f^0(A,0K) + y\Delta H_f^0(B,0K) + z\Delta H_f^0(C,0K) - \sum D_0$$

Here,

$$\sum D_0 = \sum_{atoms} x\varepsilon_0(X) - \varepsilon_0(M) - \varepsilon_{ZPE}(M)$$

where, the first summation term represents the electronic energies of the individual atoms, $\varepsilon_0(M)$ is the total energy of the molecule and $\varepsilon_{ZPE}(M)$ is the molecules's zero point energy correction.

The theoretical enthalpy of formation, $\Delta H_f^0(298K)$, at 298 K is given by:

$$\Delta H_f^0(A_xB_yC_z,298K) = \Delta H_f^0(A_xB_yC_z,0K) + [H^0(A_xB_yC_z,298K) - H^0(A_xB_yC_z,0K)] - x[H^0(A,298K) - H^0(A,0K)]_{st} - y[H^0(B,298K) - H^0(B,0K)]_{st} - z[H^0(C,298K) - H^0(C,0K)]_{st}$$

where, $[H^0(A_xB_yC_z,298K) - H^0(A_xB_yC_z,0K)]$ is denoted as H_{corr}, in the following calculations.

Heat of formation of 1-ethoxy ethoxy radical:

Using the energy values given in Tables S1.2 and S1.3, we now calculate the heat of formation of 1-ethoxy ethoxy radical using CBS-QB3 method.

<u>CBS-QB3 Method</u>

$$\Delta H_f^0(C_4H_9O_2,0K) = 4\times(+711.19) + 9\times(+216.035) + 2\times(+246.79) - [(4\times-37.785377) + (9\times-0.499818) + (2\times-74.987630) + 307.695526)] = \text{kJ/mol.}$$

$$\Delta H_f^0(C_7H_8O_2,298K) = \Delta H_f^0(C_7H_8O_2,0K) + H_{corr} - 7\times(H_{298}^0, C - H_0^0, C) - 8\times(H_{298}^0, H - H_0^0, H) - 2\times(H_{298}^0, O - H_0^0, O)$$

$$\Delta H_f^0(C_7H_8O_2,298K) = -2.680214 + 24.191357 - 7.357 - 33.84 - 8.68 = -28.36 \text{ kJ/mol.}$$

Table S1. 4. Reaction enthalpies (**ΔH_{298}**, kJ/mol) and free energies (ΔG_{298}, kJ/mol) of the reactions involved in the oxidation of diethyl ether by OH radical using CBS-QB3 method.

Reactions	ΔH_{298}	ΔG_{298}	Exp. [ΔH_{298}]*
$CH_3CH_2OCH_2CH_3 + {}^{\bullet}OH \longrightarrow CH_3CH_2OCH_2\dot{C}H_2 + H_2O$	-70.9	-75.5	
$CH_3CH_2OCH_2CH_3 + {}^{\bullet}OH \longrightarrow CH_3CH_2O\dot{C}HCH_3 + H_2O$	-104.5	-109.6	-107.6±1.94
$CH_3CH_2OCH_2\dot{C}H_2 + {}^3O_2 \longrightarrow CH_3CH_2OCH_2CH_2O\dot{O}$	-144.0	-97.2	
$CH_3CH_2O\dot{C}HCH_3 + {}^3O_2 \longrightarrow CH_3CH_2OCH(O\dot{O})CH_3$	-161.4	-112.7	
$CH_3CH_2OCH_2CH_2O\dot{O} + NO \longrightarrow CH_3CH_2OCH_2CH_2\dot{O} + NO_2$	-49.2	-53.7	
$CH_3CH_2OCH(O\dot{O})CH_3 + NO \longrightarrow CH_3CH_2OCH(\dot{O})CH_3 + NO_2$	-53.0	-58.3	
$CH_3CH_2OCH_2CH_2\dot{O} + {}^3O_2 \longrightarrow CH_3CH_2OCH_2CH(=O) + HO_2$	-139.4	-142.9	
$CH_3CH_2OCH(\dot{O})CH_3 + {}^3O_2 \longrightarrow CH_3CH_2OC(=O)CH_3 + HO_2$	-208.6	-214.6	-225.3±1.09
$CH_3CH_2OCH(O\dot{O})CH_3 \longrightarrow CH_3\dot{C}HOCH(OOH)CH_3$	+36.2	+35.7	
$CH_3CH_2OCH(\dot{O})CH_3 \longrightarrow CH_3CH_2OCH(=O) + \dot{C}H_3$	-21.3	-70.2	-18.5±1
$CH_3CH_2OCH(\dot{O})CH_3 \longrightarrow CH_3CH_2OC(=O)CH_3 + \dot{H}$	-2.4	-35.5	+3.02 ±0.85
$CH_3CH_2OCH(\dot{O})CH_3 \longrightarrow CH_3CH_2\dot{O} + CH(=O)CH_3$	+45.5	-3.9	+48.2± 4
$CH_3CH_2OCH(\dot{O})CH_3 + NO \longrightarrow CH_3CH_2OC(=O)CH_3 + HNO$	-204.2	-207.7	-191.6± 4.24
$CH_3CH_2OCH(\dot{O})CH_3 + NO_2 \longrightarrow CH_3CH_2OC(=O)CH_3 + HONO$	-329.8	-329.5	-322.8± 0.84

*Obtained using a combination of values from Tables S1.1, S1.2 and S1.3 and also the heat of formation of 1-ethoxy ethoxy radical calculated using atomization enthalpies in the present study.

Scheme S1. OH initiated oxidation reactions of diethyl ether.

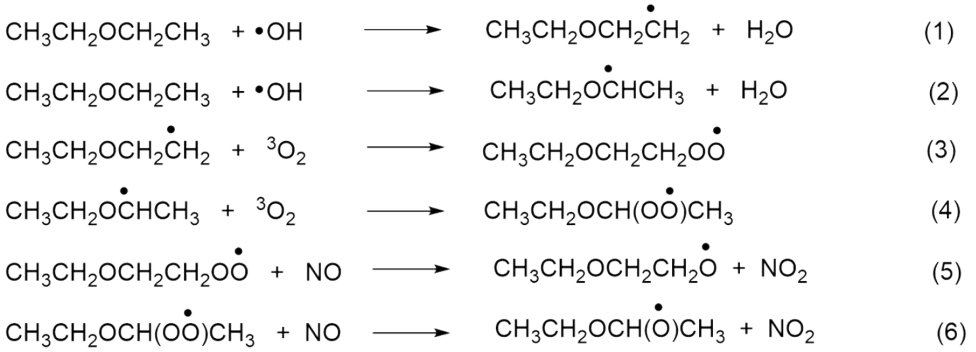


Table S2. Energetics of the stationary points in the PES of reactions in Scheme S1.

Stationary points	UM06-2X/6-311++G(d,p)			UM06-2X/aug-cc-pVTZ//UM06-2X/6-311++G(d,p)		
	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}
$CH_3CH_2OCH_2CH_3$						
a	-233.6095177	-233.464266	-233.502156	-233.6350119	-233.4897602	-233.5276502
b	-233.6077838	-233.462261	-233.499134			
c	-233.6075742	-233.462352	-233.500083			
$^{\bullet}OH$	-75.7265746	-75.714689	-75.734914	-75.7336844	-75.7217988	-75.7420238
$CH_3CH_2OCH_2CH_3 + {}^{\bullet}OH \longrightarrow CH_3CH_2O\dot{C}HCH_3 + H_2O$						
RC	-309.3502249	-309.190688	-309.236432	-309.3814548	-309.2219179	-309.2676619
TS	-309.3351635	-309.180949	-309.223687	-309.3676655	-309.213451	-309.256189
PC	-309.3713551	-309.212620	-309.262351	-309.4042255	-309.2454904	-309.2952214
$CH_3CH_2OCH_2CH_3 + {}^{\bullet}OH \longrightarrow CH_3CH_2O\dot{C}HCH_3 + H_2O$						
RC	-309.3520303	-309.192238	-309.238026	-309.3832806	-309.2234883	-309.2692763
TS	-309.339387	-309.183989	-309.228337	-309.3722205	-309.2168225	-309.2611705
PC	-309.383998	-309.224173	-309.270739	-309.4172221	-309.2573971	-309.3039631
$CH_3CH_2OCH_2\dot{C}H_2$	-232.9396975	-232.809055	-232.847814	-232.9649684	-232.8343259	-232.8730849
H_2O	-76.4208889	-76.395489	-76.416903	-76.4298691	-76.4044692	-76.4258832
$CH_3CH_2O\dot{C}HCH_3$	-232.9522782	-232.820850	-232.859775	-232.9779795	-232.8465513	-232.8854763
$CH_3CH_2OCH_2\dot{C}H_2 + {}^3O_2 \longrightarrow CH_3CH_2OCH_2CH_2O\dot{O}$						
$CH_3CH_2OCH_2\dot{C}H_2$	-232.9396975	-232.809055	-232.847814	-232.9649684	-232.8343259	-232.8730849
$^3O_2$	-150.3086142	-150.301268	-150.324513	-150.3238531	-150.3165069	-150.3397519
$CH_3CH_2OCH_2CH_2O\dot{O}$						
a	-383.3071033	-383.162750	-383.205498	-383.3483791	-383.2040258	-383.2467738
b	-383.3065981	-383.162373	-383.206655			
c	-383.3057363					
$CH_3CH_2O\dot{C}HCH_3 + {}^3O_2 \longrightarrow CH_3CH_2OCH(O\dot{O})CH_3$						
$CH_3CH_2OCH_2\dot{C}H_2$	-232.9396975	-232.809055	-232.847814	-232.9649684	-232.8343259	-232.8730849

$^3O_2$	-150.3086142	-150.301268	-150.324513	-150.3238531	-150.3165069	-150.3397519
$CH_3CH_2OCH(\dot{O}O)CH_3$	-383.324574	-383.181223	-383.224797	-383.3485699	-383.2052189	-383.2487929
$CH_3CH_2OCH_2CH_2\dot{O}O + NO \longrightarrow CH_3CH_2OCH_2CH_2\dot{O} + NO_2$						
$CH_3CH_2OCH_2CH_2\dot{O}O$	-383.3071033	-383.162750	-383.205498	-383.3483791	-383.2040258	-383.2467738
NO	-129.880285	-129.872217	-129.895494	-129.8933506	-129.8852826	-129.9085596
$CH_3CH_2OCH_2CH_2\dot{O}$	-308.1488335	-308.011618	-308.053301	-308.1801345	-308.042919	-308.084602
NO_2	-205.0507148	-205.037611	-205.065447	-205.0746185	-205.0615147	-205.0893507
$CH_3CH_2OCH(\dot{O}O)CH_3 + NO \longrightarrow CH_3CH_2OCH(\dot{O})CH_3 + NO_2$						
$CH_3CH_2OCH(\dot{O}O)CH_3$	-383.324574	-383.181223	-383.224797	-383.3485699	-383.2052189	-383.2487929
NO	-129.880285	-129.872217	-129.895494	-129.8933506	-129.8852826	-129.9085596
$CH_3CH_2OCH(\dot{O})CH_3$	-308.1688339	-308.031855	-308.072404	-308.200898	-308.0639111	-308.1044601
NO_2	-205.0507148	-205.037611	-205.065447	-205.0746185	-205.0615147	-205.0893507

Table S2.1. Energetics of the stationary points in the PES of reactions in Scheme S1.

Stationary points	UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)			UCCSD(T)/aug-cc-pVDZ//UM06-2X/6-311++G(d,p)		
	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}
$CH_3CH_2OCH_2CH_3$						
a	-233.1100218	-232.9647701	-233.0026601	-233.0633082	-232.9180565	-232.9559465
$^{\bullet}OH$	-75.5963733	-75.5844877	-75.6047127	-75.5840691	-75.5721835	-75.5924085
$CH_3CH_2OCH_2CH_3 + {}^{\bullet}OH \longrightarrow CH_3CH_2OCH^{\bullet}CH_2 + H_2O$						
RC	-308.7181045	-308.5585676	-308.6043116	-308.6599811	-308.5004442	-308.5461882
TS	-308.7013203	-308.5471058	-308.5898438	-308.6449525	-308.490738	-308.5339025
PC	-308.7363494	-308.5776143	-308.6273453	-308.6791475	-308.5204124	-308.5701434
$CH_3CH_2OCH_2CH_3 + {}^{\bullet}OH \longrightarrow CH_3CH_2O^{\bullet}CHCH_3 + H_2O$						
RC	-308.7204601	-308.5606678	-308.6064558	-308.661724	-308.5019317	-308.5477197
TS	-308.7069946	-308.5515966	-308.5959446	-308.6503496	-308.4949516	-308.5392996
PC	-308.7492618	-308.5894368	-308.6360028	-308.6791475	-308.5193225	-308.5658885
$CH_3CH_2OCH_2CH_2^{\bullet}$	-232.4410031	-232.3103606	-232.3491196	-232.3960649	-232.2654224	-232.3041814
H_2O	-76.2864621	-76.2610622	-76.2824762	-76.2738902	-76.2484903	-76.2699043
$CH_3CH_2O^{\bullet}CHCH_3$	-232.4539241	-232.3224959	-232.3614209	-232.407766	-232.2763378	-232.3152628
$CH_3CH_2OCH_2CH_2^{\bullet} + {}^3O_2 \longrightarrow CH_3CH_2OCH_2CH_2OO^{\bullet}$						
$CH_3CH_2OCH_2CH_2^{\bullet}$	-232.4410031	-232.3103606	-232.3491196	-232.3960649	-232.2654224	-232.3041814
$^3O_2$	-150.0448436	-150.0374974	-150.0607424	-150.0210321	-150.0136859	-150.0369309
$CH_3CH_2OCH_2CH_2OO^{\bullet}$						
a	-382.5561685	-382.4118152	-382.4545632	-382.4894161	-382.3450628	-382.3878108
$CH_3CH_2O^{\bullet}CHCH_3 + {}^3O_2 \longrightarrow CH_3CH_2OCH(OO^{\bullet})CH_3$						
$CH_3CH_2O^{\bullet}CHCH_3$	-232.4539241	-232.3224959	-232.3614209	-232.407766	-232.2763378	-232.3152628
$^3O_2$	-150.0448436	-150.0374974	-150.0607424	-150.0210321	-150.0136859	-150.0369309
$CH_3CH_2OCH(OO^{\bullet})CH_3$	-382.5561737	-382.4128227	-382.4563967	-382.4890342	-382.3456832	-382.3892572

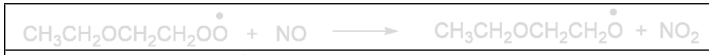
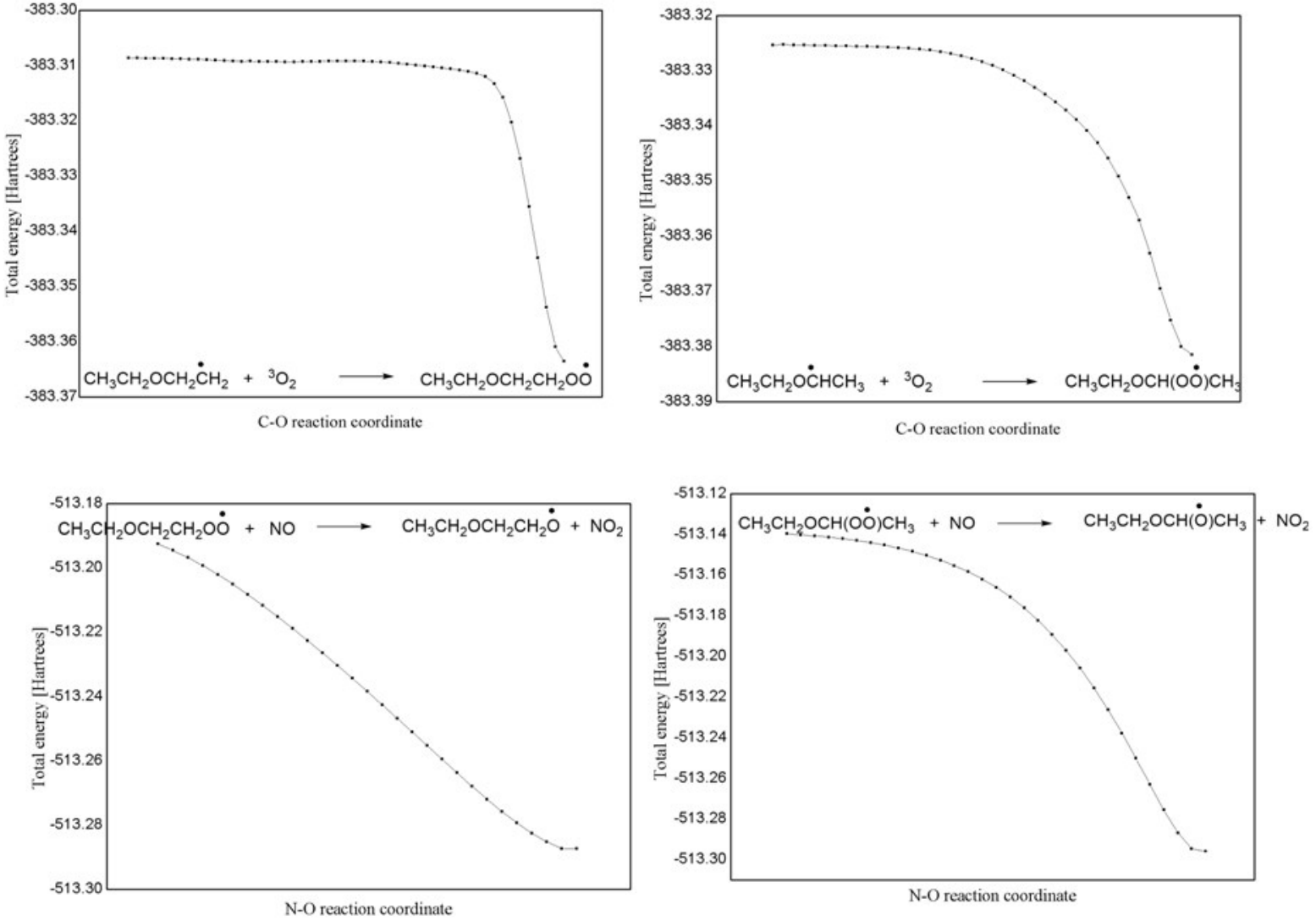
						
	-382.5561685	-382.4118152	-382.4545632	-382.4894161	-382.3450628	-382.3878108
NO	-129.645716	-129.637648	-129.660925	-129.6235547	-129.6154867	-129.6387637
	-307.5147753	-307.3775598	-307.4192428	-307.4581439	-307.3209284	-307.3626114
NO_2	-204.683194	-204.6700902	-204.6979262	-204.6502141	-204.6371103	-204.6649463
						
	-382.5561737	-382.4128227	-382.4563967	-382.4890342	-382.3456832	-382.3892572
NO	-129.645716	-129.637648	-129.660925	-129.6235547	-129.6154867	-129.6387637
	-307.5350326	-307.3978194	-307.4377424	-307.4778268	-307.3408479	-307.3813969
NO_2	-204.683194	-204.6700902	-204.6979262	-204.6502141	-204.6371103	-204.6649463

Table S2.2 Relative energy [kJ/mol] of the reactive species involved in Scheme S1.

Stationary points	UM06-2X/6-311++G(d,p)		UM06-2X/aug-cc-pVTZ//UM06-2X/6-311++G(d,p)		UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)		UCCSD(T)/aug-cc-pVDZ//UM06-2X/6-311++G(d,p)	
	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}
$CH_3CH_2OCH_2CH_3 + {}^{\bullet}OH \longrightarrow CH_3CH_2OCH_2\dot{C}H_2 + H_2O$								
RC	-30.8	+1.7	-27.2	+5.3	-24.4	+8.0	-26.8	+5.7
TS	-5.3	+35.1	-4.9	+35.4	+5.6	+46.0	-1.3	+37.9
PC	-88.4	-66.4	-79.2	-67.0	-74.4	-52.4	-79.2	-57.2
$CH_3CH_2OCH_2\dot{C}H_2 + H_2O$	-67.2	-72.6	-71.5	-76.9	-58.2	-63.6	-62.2	-67.5
$CH_3CH_2OCH_2CH_3 + {}^{\bullet}OH \longrightarrow CH_3CH_2O\dot{C}HCH_3 + H_2O$								
RC	-34.9	-2.5	-31.3	+1.0	-29.9	+2.4	-30.7	+1.7
TS	-13.2	+22.9	-13.8	+22.3	-6.2	+30.0	-12.4	+23.7
PC	-118.7	-88.4	-120.3	-90.0	-105.5	-75.2	-76.3	-46.0
$CH_3CH_2O\dot{C}HCH_3 + H_2O$	-98.2	-103.9	-103.6	-109.4	-90.0	-95.9	-90.8	-96.6
$CH_3CH_2OCH_2\dot{C}H_2 + {}^3O_2 \longrightarrow CH_3CH_2OCH_2CH_2O\dot{O}$	-137.6	-87.0	-139.6	-89.1	-167.9	-117.4	-173.2	-122.6
$CH_3CH_2O\dot{C}HCH_3 + {}^3O_2 \longrightarrow CH_3CH_2OCH(O\dot{O})CH_3$	-186.2	-137.7	-142.8	-94.4	-138.7	-89.8	-146.2	-97.3
$CH_3CH_2OCH_2CH_2O\dot{O} + NO \longrightarrow CH_3CH_2OCH_2CH_2\dot{O} + NO_2$	-37.4	-4.4	-39.7	-48.8				
$CH_3CH_2OCH(O\dot{O})CH_3 + NO \longrightarrow CH_3CH_2OCH(\dot{O})CH_3 + NO_2$	-45.8	-46.1	-44.0	-95.7	-45.8	-48.2	-44.0	-48.1

Figure S1. PES Scan of the reactions (3) –(6) performed at UM06-2X/6-311++G(d,p) level of theory.



Scheme S2. Reactions of alkoxy radical with molecular oxygen

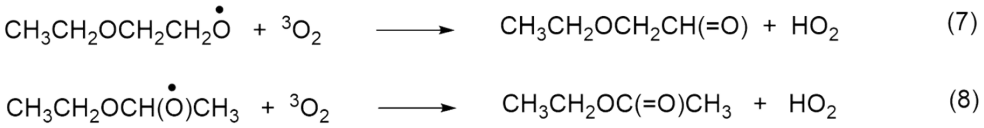


Table S3. Energetics of the stationary points in the PES of reactions in Scheme S2.

Stationary points	UM06-2X/6-311++G(d,p)			UM06-2X/aug-cc-pVTZ//UM06-2X/6-311++G(d,p)		
	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}
$CH_3CH_2OCH_2CH_2O + {}^3O_2 \rightarrow CH_3CH_2OCH_2CH(=O) + HO_2$						
$CH_3CH_2OCH_2CH_2O$	-308.1488335	-308.011618	-308.053301	-308.1801345	-308.042919	-308.084602
$^3O_2$	-150.3086142	-150.301268	-150.324513	-150.3238531	-150.3165069	-150.3397519
RC	-458.4615814	-458.315337	-458.366596	-458.4179203	-458.2716759	-458.3229349
TS	-458.4411967	-458.300187	-458.347715	-458.4902669	-458.3492572	-458.3967852
PC	-458.5220306	-458.374137	-458.423407	-458.5710181	-458.4231245	-458.4723945
$CH_3CH_2OCH_2CH(=O)$	-307.6136374	-307.486771	-307.526480	-307.6462089	-307.5193425	-307.5590515
HO_2	-150.8905895	-150.872151	-150.898087	-150.9075296	-150.8890911	-150.9150271
$CH_3CH_2OCH(O)CH_3 + {}^3O_2 \rightarrow CH_3CH_2OC(=O)CH_3 + HO_2$						
$CH_3CH_2OCH(O)CH_3$	-308.1688339	-308.031855	-308.072404	-308.20089	-308.0639111	-308.1044601
$^3O_2$	-150.3086142	-150.301268	-150.324513	-150.3238531	-150.3165069	-150.3397519
RC	-458.4818339	-458.336174	-458.386943	-458.5289573	-458.3832974	-458.4340664
TS	-458.4655783	-458.325593	-458.373353	-458.5137411	-458.3737558	-458.4215158
PC	-458.5704133	-458.423127	-458.471709	-458.6195818	-458.4722955	-458.5208775
$CH_3CH_2OC(=O)CH_3$	-307.6614547	-307.534029	-307.573923	-307.694402	-307.5669763	-307.6068703
HO_2	-150.8905895	-150.872151	-150.898087	-150.9075296	-150.8890911	-150.9150271

Table S3.1. Energetics of the stationary points in the PES of reactions in Scheme S2.

Stationary points	UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)			UCCSD(T)/aug-cc-pVDZ//UM06-2X/6-311++G(d,p)		
	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}
$CH_3CH_2OCH_2CH_2\dot{O} + {}^3O_2 \longrightarrow CH_3CH_2OCH_2CH(=O) + HO_2$						
$CH_3CH_2OCH_2CH_2\dot{O}$	-307.5147753	-307.3775598	-307.4192428	-307.4581439	-307.3209284	-307.3626114
${}^3O_2$	-150.0448436	-150.0374974	-150.0607424	-150.0210321	-150.0136859	-150.0369309
RC	-457.5608157	-457.4145713	-457.467334			
TS	-457.5473225	-457.4063128	-457.4538408	-457.4711107	-457.3248663	-457.377629
PC	-457.6197376	-457.471844	-457.521114	-457.5405732	-457.3926796	-457.4419496
$CH_3CH_2OCH_2CH(=O)$	-306.9821274	-306.855261	-306.89497	-306.9241228	-306.7972564	-306.8369654
HO_2	-150.6236014	-150.6051629	-150.6310989	-150.6007347	-150.5822962	-150.6082322
$CH_3CH_2OCH(\dot{O})CH_3 + {}^3O_2 \longrightarrow CH_3CH_2OC(=O)CH_3 + HO_2$						
$CH_3CH_2OCH(\dot{O})CH_3$	-307.5350326	-307.3978194	-307.4377424	-307.4778268	-307.3408479	-307.3813969
${}^3O_2$	-150.0448436	-150.0374974	-150.0607424	-150.0210321	-150.0136859	-150.0369309
RC	-457.5666251	-457.4209652	-457.4717342	-457.5017567	-457.3560968	-457.4068658
TS	-457.566108	-457.4261227	-457.4738827	-457.4882224	-457.3482371	-457.3959971
PC	-457.6677761	-457.5204898	-457.5690718	-457.5871102	-457.4398239	-457.4884059
$CH_3CH_2OC(=O)CH_3$	-307.0281755	-306.9007498	-306.9406438	-306.9694175	-306.8419918	-306.8818858
HO_2	-150.6236014	-150.6051629	-150.6310989	-150.6007347	-150.5822962	-150.6082322

Table S3.2. Relative energy [kJ/mol] of the reactive species involved in Scheme S2.

Stationary points	UM06-2X/6-311++G(d,p)		UM06-2X/aug-cc-pVTZ//UM06-2X/6-311++G(d,p)		UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)		UCCSD(T)/aug-cc-pVDZ//UM06-2X/6-311++G(d,p)	
	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}
$CH_3CH_2OCH_2CH_2\dot{O}$ + $^3O_2$ ⟶ $CH_3CH_2OCH_2CH(=O)$ + HO_2								
RC	-6.4	+29.4			+1.3	+33.2		
TS	+33.3	+79.0	+26.7	+74.7	+22.9	+68.6	+25.6	+57.5
PC	-160.8	-119.7	-167.3	-123.8	-149.0	-107.9	-152.4	-111.3
$CH_3CH_2OCH_2CH(=O)$ + HO_2	-119.1	-120.9	-128.7	-128.2	-119.1	-120.9	-117.9	-119.8
$CH_3CH_2OCH(\dot{O})CH_3$ + $^3O_2$ ⟶ $CH_3CH_2OC(=O)CH_3$ + HO_2								
RC	-8.0	+26.2	-7.5	+26.6	+37.7	+70.2	-4.1	+30.0
TS	+19.8	+61.9	+17.5	+59.6	+24.2	+64.6	+16.5	+58.6
PC	-236.3	-196.4	-241.2	-201.3	-223.6	-185.3	-223.9	-189.3
$CH_3CH_2OC(=O)CH_3$ + HO_2	-191.8	-197.2	-198.6	-203.9	-185.3	-192.3	-183.2	-188.5

Scheme S3. Isomerization reactions of peroxy radical and unimolecular dissociation of 1-ethoxy ethoxy radical.

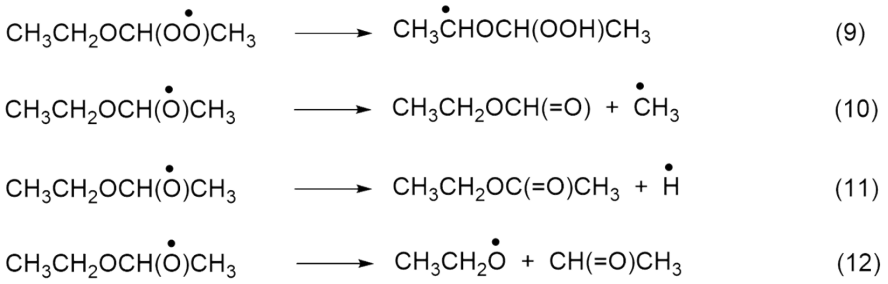


Table S4. Energetics of the stationary points in the PES of reactions in Scheme S3.

Stationary points	UM06-2X/6-311++G(d,p)			UM06-2X/aug-cc-pVTZ//UM06-2X/6-311++G(d,p)		
	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}
$CH_3CH_2OCH(OO)CH_3 \rightarrow CH_3CHOCH(OOH)CH_3$						
$CH_3CH_2OCH(OO)CH_3$	-383.324574	-383.181223	-383.224797	-383.3661007	-383.2227497	-383.2663237
TS	-383.2863832	-383.149304	-383.189910	-383.3293437	-383.1922645	-383.2328705
$CH_3CHOCH(OOH)CH_3$	-383.3085651	-383.166570	-383.210582	-383.3514742	-383.2094791	-383.2534911
$CH_3CH_2OCH(O)CH_3 \rightarrow CH_3CH_2OCH(=O) + CH_3$						
$CH_3CH_2OCH(O)CH_3$	-308.1665462	-308.029333	-308.069256	-308.1986046	-308.0613914	-308.1013144
TS	-308.1507627	-308.016796	-308.057710	-308.183756	-308.0497893	-308.0907033
PC	-308.1719432	-308.039017	-308.084271	-308.205141	-308.0722148	-308.1174688
$CH_3CH_2OCH(=O)$	-268.3466229	-268.248585	-268.284221	-268.3755461	-268.2775082	-268.3131442
CH_3	-39.8209088	-39.787179	-39.811048	-39.8253464	-39.7916166	-39.8154856
$CH_3CH_2OCH(O)CH_3 \rightarrow CH_3CH_2OC(=O)CH_3 + H$						

$CH_3CH_2OCH(\dot{O})CH_3$	-308.168834	-308.031854	-308.072402	-308.20089	-308.06391	-308.104458
TS	-308.143593	-308.013591	-308.053728	-308.1767128	-308.0467108	-308.0868478
PC	-308.1593781	-308.028922	-308.072895	-308.1928789	-308.0624228	-308.1063958
$CH_3CH_2OC(=O)CH_3$	-307.6614547	-307.534029	-307.573923	-307.694402	-307.5669763	-307.6068703
H	-0.4981948	-0.495834	-0.508849	-0.4982065	-0.4958457	-0.5088607
$CH_3CH_2OCH(\dot{O})CH_3 \longrightarrow CH_3CH_2\dot{O} + CH(=O)CH_3$						
$CH_3CH_2OCH(\dot{O})CH_3$	-308.1564478	-308.018383	-308.059065	-308.20089	-308.06391	-308.104458
TS	-308.1302148	-307.995333	-308.036612	-308.1621306	-308.0272488	-308.0685278
PC	-308.1516513	-308.016774	-308.062402	-308.1826057	-308.0477284	-308.0933564
$CH_3CH_2\dot{O}$	-154.3385759	-154.268199	-154.299442	-153.8207571	-153.7600235	-153.7898445
$CH(=O)CH_3$	-153.8045726	-153.743839	-153.773660	-154.3542633	-154.2838864	-154.3151294

Table S4.1 Energetics of the stationary points in the PES of reactions in Scheme S3.

Stationary points	UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)			UCCSD(T)/aug-cc-pVDZ//UM06-2X/6-311++G(d,p)		
	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}
$CH_3CH_2OCH(O\dot{O})CH_3 \longrightarrow CH_3\dot{C}HOCH(OOH)CH_3$						
$CH_3CH_2OCH(O\dot{O})CH_3$	-382.5561693	-382.4128183	-382.4563923	-382.4890305	-382.3456795	-382.3892535
TS	-382.5169414	-382.3798622	-382.4204682	-382.4524325	-382.3153533	-382.3559593
$CH_3\dot{C}HOCH(OOH)CH_3$	-382.538185	-382.3961899	-382.4402019	-382.4720126	-382.3300175	-382.3740295
$CH_3CH_2OCH(\dot{O})CH_3 \longrightarrow CH_3CH_2OCH(=O) + \dot{C}H_3$						
$CH_3CH_2OCH(\dot{O})CH_3$	-307.5350326	-307.3978194	-307.4377424	-307.4778268	-307.3408479	-307.3813969
TS	-307.5165399	-307.3825732	-307.4234872	-307.4601092	-307.3261425	-307.3670565
PC	-307.5399224	-307.4069962	-307.4522502	-307.4808161	-307.3478899	-307.3931439
$CH_3CH_2OCH(=O)$	-267.8045158	-267.7064779	-267.7421139	-267.7537313	-267.6556934	-267.6913294
$\dot{C}H_3$	-39.7336302	-39.6999004	-39.7237694	-39.7243036	-39.6905738	-39.7144428

$CH_3CH_2OCH(\dot{O})CH_3 \longrightarrow CH_3CH_2OC(=O)CH_3 + \dot{H}$						
$CH_3CH_2OCH(\dot{O})CH_3$	-307.5350326	-307.3980526	-307.4386006	-307.4778268	-307.3408468	-307.3813948
TS	-307.5088562	-307.3788542	-307.4189912	-307.4524996	-307.3224976	-307.3626346
PC	-307.527372	-307.3969159	-307.4408889	-307.4690603	-307.3386042	-307.3825772
$CH_3CH_2OC(=O)CH_3$	-307.0281755	-306.9007498	-306.9406438	-306.9694175	-306.8419918	-306.8818858
H	-0.4998179	-0.4974571	-0.5104721	-0.4993343	-0.4969735	-0.5099885
$CH_3CH_2OCH(\dot{O})CH_3 \longrightarrow CH_3CH_2\dot{O} + CH(=O)CH_3$						
$CH_3CH_2OCH(\dot{O})CH_3$	-307.5350326	-307.3980526	-307.4386006	-307.4778268	-307.3408468	-307.3813948
TS	-307.5088562	-307.3739744	-307.4152534	-307.4454224	-307.3105406	-307.3518196
PC	-307.5146087	-307.3797314	-307.4253594	-307.456291	-307.3214137	-307.3670417
$CH_3CH_2\dot{O}$	-154.0232264	-153.9528495	-153.9840925	-153.9939081	-153.9235312	-153.9547742
$CH(=O)CH_3$	-153.4918624	-153.4311288	-153.4609498	-153.461373	-153.4006394	-153.4304604

Table S4.2: Relative energy [kJ/mol] of the reactive species involved in Scheme S3.

Stationary points	UM06-2X/6-311++G(d,p)		UM06-2X/aug-cc-pVTZ//UM06-2X/6-311++G(d,p)		UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)		UCCSD(T)/aug-cc-pVDZ//UM06-2X/6-311++G(d,p)	
	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}
$CH_3CH_2OCH(\dot{O}O)CH_3 \longrightarrow CH_3\dot{C}HOCH(OOH)CH_3$								
TS	+83.8	+91.6	+80.0	+87.8	+86.5	+94.3	+79.6	+87.4
$CH_3\dot{C}HOCH(OOH)CH_3$	+38.5	+37.3	+34.8	+33.7	+43.6	+42.5	+41.2	+39.9
$CH_3CH_2OCH(\dot{O})CH_3 \longrightarrow CH_3CH_2OCH(=O) + \dot{C}H_3$								
TS	+32.9	+30.3	+30.5	+27.8	+40.0	+37.4	+38.6	+37.6
PC	-25.4	-39.4	-28.4	-39.4	-24.0	-38.0	-18.5	-30.8
$CH_3CH_2OCH(=O) + \dot{C}H_3$	-16.9	-68.3	-20.3	-71.7	-22.5	-73.9	-14.2	-63.9
$CH_3CH_2OCH(\dot{O})CH_3 \longrightarrow CH_3CH_2OC(=O)CH_3 + \dot{H}$								
TS	+47.9	+51.5	+45.2	+46.2	+50.4	+51.8	+48.2	+49.3
PC	+7.7	-1.3	+3.9	-5.0	+2.9	-6.0	+5.9	-3.1
$CH_3CH_2OC(=O)CH_3 + \dot{H}$	+5.2	-27.2	+2.8	-29.6	-0.5	-32.8	+4.9	-27.5
$CH_3CH_2OCH(\dot{O})CH_3 \longrightarrow CH_3CH_2\dot{O} + CH(=O)CH_3$								
TS	+60.5	+58.9	+96.3	+94.3	+63.2	+61.3	+79.6	+77.6
PC	+4.2	-8.7	-18.5	+37.7	+48.1	+34.8	+51.0	+37.7
$CH_3CH_2\dot{O} + CH(=O)CH_3$	+16.6	-36.8	-14.2	-1.4	+36.9	-16.9	+48.8	-10.1

Scheme S4. Reactions of alkoxy radical with NO and NO_2

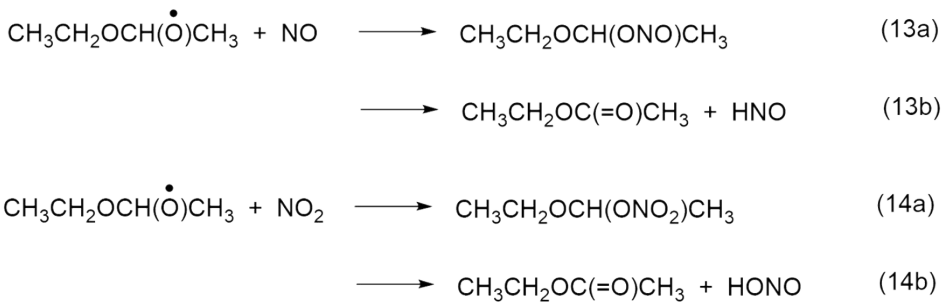


Table S5. Energetics of the stationary points in the PES of reactions in Scheme S4.

Stationary points	UM06-2X/6-311++G(d,p)			UM06-2X/aug-cc-pVTZ//UM06-2X/6-311++G(d,p)		
	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}
$CH_3CH_2OCH(\dot{O})CH_3 + NO \longrightarrow CH_3CH_2OC(=O)CH_3 + HNO$						
$CH_3CH_2OCH(\dot{O})CH_3$	-308.1688339	-308.031855	-308.072404	-308.20089	-308.0639111	-308.1044601
NO	-129.880285	-129.872217	-129.895494	-129.8933506	-129.8852826	-129.9085596
RC	-438.1052921	-437.955465	-437.999553	-438.1528936	-438.0030665	-438.0471545
TS	-438.046473	-437.902619	-437.946185	-438.0944188	-437.9505648	-437.9941308
PC	-438.1286342	-437.980450	-438.031137	-438.1738774	-438.0256932	-438.0763802
$CH_3CH_2OC(=O)CH_3$	-307.6614547	-307.534029	-307.573923	-307.694402	-307.5669763	-307.6068703
HNO	-130.4596368	-130.441347	-130.466371	-130.4736402	-130.4553504	-130.4803744
$CH_3CH_2OCH(\dot{O})CH_3 + NO_2 \longrightarrow CH_3CH_2OC(=O)CH_3 + HONO$						
$CH_3CH_2OCH(\dot{O})CH_3$	-308.1688339	-308.031855	-308.072404	-308.20089	-308.0639111	-308.1044601
NO_2	-205.0507148	-205.037611	-205.065447	-205.0746185	-205.0615147	-205.0893507
RC	-513.2821262	-513.125711	-513.171915	-513.340222	-513.1838068	-513.2300108
TS	-513.2093759	-513.060197	-513.106797	-513.2657827	-513.1166038	-513.1632038
PC	-513.3642642	-513.208874	-513.260947	-513.419615	-513.2642248	-513.3162978

$CH_3CH_2OC(=O)CH_3$	-307.6614547	-307.534029	-307.573923	-307.694402	-307.5669763	-307.6068703
HONO	-205.6854544	-205.660258	-205.688284	-205.7091629	-205.6839665	-205.7119925

Table S5.1. Energetics of the stationary points in the PES of reactions in Scheme S4.

Stationary points	UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)			UCCSD(T)/aug-cc-pVDZ//UM06-2X/6-311++G(d,p)		
	E_{Tot}	H_{298}	G_{298}	E_{Tot}	H_{298}	G_{298}
$CH_3CH_2OCH(\dot{O})CH_3 + NO \longrightarrow CH_3CH_2OC(=O)CH_3 + HNO$						
$CH_3CH_2OCH(\dot{O})CH_3$	-307.5350326	-307.3978194	-307.4377424	-307.4778268	-307.3408479	-307.3813969
NO	-129.645716	-129.637648	-129.660925	-129.6235547	-129.6154867	-129.6387637
RC	-437.232404	-437.0825769	-437.1266649	-437.1571621	-437.007335	-437.051423
TS	-437.1819466	-437.0380926	-437.0816586	-437.1092293	-436.9653753	-437.0089413
PC	-437.2577195	-437.1095353	-437.1602223	-437.1787275	-437.0305433	-437.0812303
$CH_3CH_2OC(=O)CH_3$	-307.0281755	-306.9007498	-306.9406438	-306.9694175	-306.8419918	-306.8818858
HNO	-130.2235338	-130.205244	-130.230268	-130.2021149	-130.1838251	-130.2088491
$CH_3CH_2OCH(\dot{O})CH_3 + NO_2 \longrightarrow CH_3CH_2OC(=O)CH_3 + HONO$						
$CH_3CH_2OCH(\dot{O})CH_3$	-307.5350326	-307.3978194	-307.4377424	-307.4778268	-307.3408479	-307.3813969
NO_2	-204.683194	-204.6700902	-204.6979262	-204.6502141	-204.6371103	-204.6649463
RC	-512.2712022	-512.114787	-512.160991	-512.187135	-512.0307198	-512.0769238
TS	-512.2116127	-512.0624338	-512.1090338	-512.1271326	-511.9779537	-512.0245537
PC	-512.3564705	-512.2010803	-512.2531533	-512.2673204	-512.1119302	-512.1640032
$CH_3CH_2OC(=O)CH_3$	-307.0281755	-306.9007498	-306.9406438	-306.9694175	-306.8419918	-306.8818858
HONO	-205.3139017	-205.2887053	-205.3167313	-205.2811186	-205.2559222	-205.2839482

Table S5.2. Relative energy [kJ/mol] of the reactive species involved in Scheme S4.

Stationary points	UM06-2X/6-311++G(d,p)		UM06-2X/aug-cc-pVTZ//UM06-2X/6-311++G(d,p)		UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)		UCCSD(T)/aug-cc-pVDZ//UM06-2X/6-311++G(d,p)	
	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}
$CH_3CH_2OCH(\dot{O})CH_3 + NO \longrightarrow CH_3CH_2OC(=O)CH_3 + HNO$								
RC	-134.9	-83.1	-141.4	-89.6	-123.7	-73.5	-133.9	-82.0
TS	+3.8	+57.0	-3.6	+49.6	-6.7	+44.6	-23.7	+29.5
PC	-200.5	-161.6	-200.8	-166.3	-194.5	-161.6	-194.8	-160.3
$CH_3CH_2OC(=O)CH_3 + HNO$	-187.2	-207.7	-192.0	-194.9	-185.2	-189.7	-182.4	-185.3
$CH_3CH_2OCH(\dot{O})CH_3 + NO_2 \longrightarrow CH_3CH_2OC(=O)CH_3 + HONO$								
RC	-147.7	-89.4	-153.3	-95.0	-123.0	-66.5	-138.5	-80.3
TS	+24.3	+81.5	+23.2	+80.4	+14.4	+69.9	0.01	+57.2
PC	-366.0	-323.2	-364.4	-321.6	-349.6	-308.5	-351.7	-308.9
$CH_3CH_2OC(=O)CH_3 + HONO$	-327.7	-326.5	-329.5	-328.3	-319.1	-319.5	-314.9	-313.7

Table S6. Calculated rate constants ($cm^3molecule^{-1}s^{-1}$) of reaction (8)

Temperature (K)	TST ($x10^{-20}$)	CVT ($x10^{-21}$)	TST/SCT ($x10^{-19}$)	CVT/SCT ($x10^{-20}$)
218	0.003	0.005	0.14	0.14
228	0.01	0.017	0.25	0.23
238	0.03	0.050	0.40	0.37
248	0.09	0.13	0.66	0.60
258	0.23	0.34	1.09	0.99
268	0.57	0.81	1.78	1.62
278	1.28	1.83	2.87	2.61
288	2.72	3.74	4.60	4.17
298	5.52	7.63	7.27	6.42
308	10.71	14.66	11.35	10.26
318	19.94	27.01	17.49	15.78
328	35.76	48.07	26.55	23.90
338	61.94	82.32	39.41	35.79
348	104.4	137.8	58.62	52.81

Table S6.1. Calculated rate constants (s^{-1}) of reaction (10)

T(K)	TST	CVT	TST/SCT	CVT/SCT
218.00	4.0870E+05	2.7269E+05	3.1833E+06	2.0190E+06
228.00	9.3888E+05	6.2558E+05	5.9595E+06	3.7816E+06
238.00	2.0169E+06	1.3421E+06	1.0743E+07	6.8200E+06
248.00	4.0841E+06	2.7145E+06	1.8701E+07	1.1876E+07
258.00	7.8483E+06	5.2106E+06	3.1514E+07	2.0020E+07
268.00	1.4396E+07	9.5473E+06	5.1537E+07	3.2751E+07
278.00	2.5328E+07	1.6781E+07	8.1977E+07	5.2112E+07
288.00	4.2926E+07	2.8415E+07	1.2709E+08	8.0817E+07
298.00	7.0339E+07	4.6521E+07	1.9242E+08	1.2239E+08
308.00	1.1180E+08	7.3881E+07	2.8499E+08	1.8132E+08
318.00	1.7284E+08	1.1413E+08	4.1358E+08	2.6321E+08

328.00	2.6055E+08	1.7193E+08	5.8897E+08	3.7492E+08
338.00	3.8383E+08	2.5310E+08	8.2417E+08	5.2476E+08
348.00	5.5362E+08	3.6483E+08	1.1346E+09	7.2261E+08

Table S6.2. Calculated rate constants (s^{-1}) of reaction (11)

T(K)	TST	CVT	TST/SCT	CVT/SCT
218.00	2.0462E+01	3.1475E+00	8.9924E+03	8.2610E+02
228.00	6.7950E+01	1.0285E+01	1.4843E+04	1.3598E+03
238.00	2.0446E+02	3.0484E+01	2.4474E+04	2.2366E+03
248.00	5.6413E+02	8.2919E+01	4.0261E+04	3.6715E+03
258.00	1.4416E+03	2.0907E+02	6.5960E+04	6.0034E+03
268.00	3.4413E+03	4.9277E+02	1.0740E+05	9.7580E+03
278.00	7.7301E+03	1.0937E+03	1.7344E+05	1.5734E+04
288.00	1.6442E+04	2.2998E+03	2.7729E+05	2.5120E+04
298.00	3.3299E+04	4.6073E+03	4.3826E+05	3.9650E+04
308.00	6.4513E+04	8.8340E+03	6.8396E+05	6.1804E+04
318.00	1.2006E+05	1.6279E+04	1.0532E+06	9.5060E+04
328.00	2.1542E+05	2.8933E+04	1.5993E+06	1.4420E+05
338.00	3.7383E+05	4.9759E+04	2.3945E+06	2.1569E+05
348.00	6.2925E+05	8.3035E+04	3.5350E+06	3.1813E+05

Calculation of rate constant using conventional transition state theory

The rate constant for the reactions studied can be modelled using conventional transition state theory, which is defined as,

$$k = \frac{k_B T}{h} \frac{Q_{TS}}{Q_R} \exp\left[-\Delta E^{\ddagger} / RT \right] \qquad (1)$$

where,

$k_B = 1.3806 \times 10^{-23} m^2 kgs^{-2} K^{-1}$

$h = 6.626 \times 10^{-34} m^2 kgs^{-1}$

Q_{TS} and Q_R are the partition functions corresponding to the reactant and the transition state and the partition functions are evaluated for the translational, electronic, rotational and vibrational energies.

$\Delta E^{\ddagger}$ is the zero-point corrected energy barrier between the reactant and the transition state.

$R = 1.987 kcal/(molK)$.

Using the zero-point corrected energy barriers from higher level methods employed in the present state, the rate constant for reactions (8), (10) and (11) will be calculated using equation (1).

Table S7.1. Energetics [in Hartrees] of the reactive species used in the calculation of rate constant using conventional transition state theory.

Stationary points	UM06-2X/6-311++G(d,p)		UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)	UCCSD(T)/aug-cc-pVDZ//UM06-2X/6-311++G(d,p)
	E_0	Q	$E_{Tot} + E_0$	$E_{Tot} + E_0$
				
	0.128635608	0.386699×10^{15}	-307.406396992	-307.349191192
TS	0.125355547	0.721694×10^{15}	-307.391184353	-307.334753653
				
	0.128635608	0.386699×10^{15}	-307.406396992	-307.349191192
TS	0.121645357	0.414973×10^{15}	-307.387210843	-307.330854243

Table S7.2. Rate constant, k [s^{-1}] of reactions (10) and (11) calculated using conventional transition state theory.

Reactions	UCCSD(T)/6-311++G(d,p)//UM06-2X/6-311++G(d,p)	UCCSD(T)/aug-cc-pVDZ//UM06-2X/6-311++G(d,p)	Experimental[a] k [s^{-1}]
	1.19 x 10^6	2.65 x 10^6	2 x 10^6
	0.99 x 10^4	2.45 x 10^4	2 x 10^4

[a] J. J. Orlando, *Phys. Chem. Chem Phys.*, 2007, **9**, 4189-4199.

Optimized Structure of the stationary points involved in the oxidation of diethyl ether by OH radical

Reaction (1)

$CH_3CH_2OCH_2CH_3$

1\1\GINC-T1\FOpt\RM062X\6-311++G(d,p)\C4H10O1\SANDHIYA\03-Nov-2015\0\\
#p m062x/6-311++g(d,p) opt freq\\rea conformer 2\\0,1\O,0.0876198143,-
1.1022557032,0.1119802038\H,-1.4614797782,0.2372918914,0.3391245721\H,
-1.8725855252,-1.4174727369,-0.1363625761\C,1.0652049888,-0.2772373319
,0.7095751084\H,0.7644932406,0.7772418354,0.6176775091\H,1.1608380334,
-0.5040794435,1.7792105601\C,-1.2351151755,-0.8234623476,0.5208060667\
C,2.3822467943,-0.5220916512,0.0028788224\H,2.2948455909,-0.2751308993
,-1.0561089812\H,3.173199686,0.0883553319,0.4430956268\H,2.6637404746,
-1.5728257116,0.0889627389\C,-1.5104389173,-1.1800252816,1.9759166453\
H,-2.5759517314,-1.0723345452,2.190250219\H,-1.2216380751,-2.215154974
9,2.1693769296\H,-0.9664701902,-0.5324267518,2.6658311349\\Version=ES6
4L-G09RevD.01\State=1-A\HF=-233.6095177\RMSD=7.959e-09\RMSF=1.030e-05\
Dipole=-0.1302686,0.3679883,0.3830823\Quadrupole=1.7286428,-0.5392651,
-1.1893777,0.5193821,0.1618549,-0.5311704\PG=C01 [X(C4H10O1)]\\@

•OH

1\1\GINC-S2\FOpt\UM062X\6-311++G(d,p)\H1O1(2)\SANDHIYA\17-Nov-2015\0\\
#P UM062X/6-311++G(d,p) Opt Freq\\int 5 single point\\0,2\O,0.,0.,0.10
37622166\H,0.,0.,-0.8682502166\\Version=ES64L-G09RevD.01\HF=-75.726574
6\S2=0.752708\S2-1=0.\S2A=0.750005\RMSD=7.594e-09\RMSF=2.012e-07\Dipol
e=0.,0.,-0.7297844\Quadrupole=0.1378819,-0.8613209,0.723439,0.,0.,0.\P
G=C*V [C*(H1O1)]\\@

RC1

1\1\GINC-T1\FOpt\UM062X\6-311++G(d,p)\C4H11O2(2)\SANDHIYA\03-Nov-2015\
0\\#p m062x/6-311++g(d,p) opt scf=qc\\rea conformer 2 ts\\0,2\O,-0.208
4125855,-0.6539947438,0.0442594651\H,0.9209023637,-1.243771976,1.66163
2958\H,1.5437691162,-1.6281525104,0.0491895297\C,-1.0827179872,0.19722

21291,0.7730355167\H,-1.116787059,-0.1369791612,1.8183517374\H,-0.7072
697855,1.2270603498,0.7546627969\C,1.0643182108,-0.8512479322,0.646749
7053\C,-2.4516187315,0.1224662033,0.1308147937\H,-2.8223396961,-0.9032
757564,0.1452252306\H,-3.1564616078,0.7593219821,0.6683350162\H,-2.402
5058145,0.4630127477,-0.9052598314\C,1.9227630994,0.4054652444,0.66748
14243\H,2.9274052247,0.1571792922,1.0156530513\H,2.0045695558,0.828683
3545,-0.3372637088\H,1.5185320897,1.1669481757,1.3362699241\O,0.359445
7105,0.6423804658,-2.3419933049\H,0.0421538964,0.0346141354,-1.6375553
042\\Version=ES64L-G09RevD.01\State=2-A\HF=-309.3502249\S2=0.752694\S2
-1=0.\S2A=0.750006\RMSD=0.000e+00\RMSF=4.860e-06\Dipole=-0.0980909,-0.
2323609,1.2680969\Quadrupole=3.155468,-0.0716224,-3.0838456,-1.2786771
,1.4652211,1.9306106\PG=C01 [X(C4H11O2)]\\@

TS1

1\1\GINC-T1\FTS\UM062X\6-311++G(d,p)\C4H11O2(2)\SANDHIYA\03-Nov-2015\0
\\#p um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc)\\rea conformer 2
ts\\0,2\O,-0.0703815195,-0.3786769343,-0.5537871948\H,1.1749327926,-0
.7913078648,1.040087318\H,1.6947505384,-1.3281244855,-0.5673476212\C,-
0.9004461873,0.5349946253,0.1454713393\H,-0.8984889048,0.2809287105,1.
2144157193\H,-0.5147659018,1.5561561427,0.0367833581\C,1.2350997773,-0
.503952623,-0.0199688339\C,-2.2953558908,0.4365554734,-0.4337629561\H,
-2.681227273,-0.5779399713,-0.3258198576\H,-2.9682541891,1.1265895107,
0.0783274213\H,-2.2819170045,0.6918894506,-1.4949467628\C,2.0649945011
,0.7541683262,-0.1806258798\H,3.1347669416,0.5708076116,-0.0826598373\
H,1.9032809513,1.1269446186,-1.312185267\H,1.7532608381,1.5906826628,0
.444018229\O,1.3038495399,1.2656948529,-2.4993130367\H,0.5733318905,0.
6451257335,-2.3250464078\\Version=ES64L-G09RevD.01\State=2-A\HF=-309.3
351635\S2=0.758946\S2-1=0.\S2A=0.75004\RMSD=8.822e-09\RMSF=3.753e-06\D
ipole=-0.207053,-0.2490573,1.1554585\Quadrupole=2.6295372,-0.9423796,-
1.6871576,-2.2851365,2.7184362,2.0112284\PG=C01 [X(C4H11O2)]\\@

PC1

1\1\GINC-T1\FOpt\UM062X\6-311++G(d,p)\C4H11O2(2)\SANDHIYA\03-Nov-2015\
 0\\#p um062x/6-311++g(d,p) opt scf=tight\\rea conformer 2 ts\\0,2\O,-0
 .1637141295,-0.7668376994,0.1719468668\H,0.8611087851,-1.1861367216,1.
 9064764652\H,1.5464199891,-1.8075524399,0.4000569202\C,-1.0802630843,0
 .0956718815,0.8340897388\H,-1.2522694498,-0.281103039,1.8509755227\H,-
 0.6603220396,1.1063155989,0.9069384342\C,1.0720086102,-0.9358639604,0.
 8533131503\C,-2.3635254041,0.1219495736,0.0317661018\H,-2.7747427687,-
 0.8844900845,-0.0586286578\H,-3.0999618599,0.7594613838,0.5244126617\H
 ,-2.1740340341,0.5201002585,-0.9664494801\C,1.9694184188,0.2514944375,
 0.760720843\H,3.0318462588,0.1191254695,0.6090381753\H,1.153879169,1.2
 778865397,-1.9057587314\H,1.6120102843,1.2371194593,1.0275821548\O,0.2
 427245976,1.0030086865,-2.028499653\H,0.139888657,0.2404946562,-1.4409
 845124\\Version=ES64L-G09RevD.01\State=2-A\HF=-309.3713551\S2=0.755144
 \S2-1=0.\S2A=0.750021\RMSD=2.939e-09\RMSF=2.686e-06\Dipole=0.5805171,-
 0.1671478,1.216371\Quadrupole=4.4735568,-0.3636996,-4.1098571,0.118974
 4,-1.590883,1.3426828\PG=C01 [X(C4H11O2)]\\@

1\1\GINC-S2\FOpt\UM062X\6-311++G(d,p)\C4H9O1(2)\SANDHIYA\16-Nov-2015\0
 \\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\
 O,-0.0270406044,-0.4401059922,-0.6311130777\H,1.3565083482,-1.95302547
 43,-0.3542200369\H,1.7878459868,-0.6394354043,-1.4541006733\C,-0.85783
 48819,-0.8566975985,0.4353132836\H,-0.8262560974,-1.9532306232,0.51644
 27854\H,-0.4902105077,-0.4444449051,1.384334402\C,1.3133681051,-0.8619
 562111,-0.4894375618\C,-2.2658885424,-0.3792270296,0.1511997518\H,-2.6
 238039876,-0.7953929308,-0.7916720683\H,-2.9419353677,-0.6891689439,0.
 9504869814\H,-2.2873861221,0.7092222526,0.0776000321\C,2.0293271367,-0
 .1718234352,0.6193641273\H,2.8790799239,-0.6342347238,1.1029595485\H,1
 .8359696104,0.8784300194,0.7966985059\\Version=ES64L-G09RevD.01\State=
 2-A\HF=-232.9396975\S2=0.755103\S2-1=0.\S2A=0.75002\RMSD=9.878e-09\RMS
 F=9.335e-06\Dipole=0.1860152,-0.2759536,0.3711452\Quadrupole=1.4568675
 ,-0.042937,-1.4139304,-0.1976795,-0.7500466,0.5440724\PG=C01 [X(C4H9O1
)]\\@

H_2O

```
1\1\GINC-S2\FOpt\RM062X\6-311++G(d,p)\H2O1\SANDHIYA\17-Nov-2015\0\\#P
 M062X/6-311++G(d,p) opt freq\\int 7 single point\\0,1\H,0.,0.761675424
 3,-0.474152254\H,0.,-0.7616754243,-0.474152254\O,0.,0.,0.108848508\\Ve
 rsion=ES64L-G09RevD.01\State=1-A1\HF=-76.4208889\RMSD=4.216e-09\RMSF=1
 .123e-05\Dipole=0.,0.,-0.8578395\Quadrupole=-1.131309,1.3407516,-0.209
 4427,0.,0.,0.\PG=C02V [C2(O1),SGV(H2)]\\@
```

Reaction (2)

RC2

```
1\1\GINC-T4\FOpt\UM062X\6-311++G(d,p)\C4H11O2(2)\SANDHIYA\05-Nov-2015\
 0\\#p m062x/6-311++g(d,p) opt scf=qc\\rea conformer 2 ts\\0,2\O,-0.108
 5620998,0.2021882247,-0.0137955917\H,0.8317716774,1.8464002579,0.79228
 76922\H,1.1627811337,0.3018768715,1.602204558\C,-1.3103899364,0.332741
 9092,0.7266807458\H,-1.1843284462,-0.1467504911,1.7062072757\H,-1.5154
 642037,1.3978245653,0.8964365619\C,1.0193576277,0.7779617391,0.6233870
 478\C,-2.4314384915,-0.3175804067,-0.0553728143\H,-2.2198336369,-1.375
 3369311,-0.2204699103\H,-3.3711883373,-0.231837936,0.492842972\H,-2.55
 00645386,0.1642116648,-1.0273251396\C,2.229924621,0.5731242466,-0.2619
 769259\H,3.1152402807,1.0076801106,0.2053625788\H,2.4091871474,-0.4908
 271209,-0.4255357451\H,2.079500508,1.0487360068,-1.2325653168\O,0.0259
 29007,-1.0768992324,-2.5094577225\H,-0.0215423127,-0.6296884782,-1.636
 602266\\Version=ES64L-G09RevD.01\State=2-A\HF=-309.3520303\S2=0.752827
 \S2-1=0.\S2A=0.750006\RMSD=0.000e+00\RMSF=3.888e-06\Dipole=-0.0733458,
 0.6958419,1.3577452\Quadrupole=3.4371983,0.2390993,-3.6762975,0.509573
 4,0.1967765,-2.6915723\PG=C01 [X(C4H11O2)]\\@
```

TS2

```
1\1\GINC-T1\FTS\UM062X\6-311++G(d,p)\C4H11O2(2)\SANDHIYA\04-Nov-2015\0
 \\#p um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc) scf=tight\\rea c
```

onformer 2 ts\\0,2\O,0.1685746181,0.2709813327,-0.2246235958\H,1.35034
10625,0.8360119753,1.371559833\H,1.605268275,-0.8309845077,0.782253817
8\C,-0.9348806764,-0.0230226587,0.6183369449\H,-0.769789695,-0.9952294
376,1.1004097025\H,-1.0012801341,0.7380744201,1.4071565978\C,1.3916439
443,0.2496813575,0.4421313256\C,-2.1890314749,-0.0368761121,-0.2277766
434\H,-2.1120356531,-0.7956489518,-1.0080370159\H,-3.0599051927,-0.261
6555212,0.390523297\H,-2.3386249084,0.9334682641,-0.7034752614\C,2.492
9052634,0.6991734745,-0.4859536606\H,3.4611242676,0.6254165373,0.01092
49481\H,2.5111138575,0.0727065569,-1.379238909\H,2.329172114,1.7343850
207,-0.7926318808\O,1.5305531674,-2.3476011101,0.5818990541\H,1.135434
8349,-2.27120138,-0.3025565739\\Version=ES64L-G09RevD.01\State=2-A\HF=
-309.339387\S2=0.75803\S2-1=0.\S2A=0.750034\RMSD=3.635e-09\RMSF=5.294e
-06\Dipole=-0.3413659,0.530807,-0.0844416\Quadrupole=1.6784965,-1.7950
873,0.1165908,2.7873942,-1.4600246,3.4433496\PG=C01 [X(C4H11O2)]\\@

PC2

1\1\GINC-T4\FOpt\UM062X\6-311++G(d,p)\C4H11O2(2)\SANDHIYA\04-Nov-2015\
0\\#p um062x/6-311++g(d,p) opt scf=tight\\rea conformer 2 ts\\0,2\O,-0
.1671766883,0.53829482,-0.2511147505\H,0.868442683,1.4237050477,1.3233
869114\H,0.9951454993,-2.1125607776,0.4205210295\C,-1.3108088904,0.394
4987922,0.59309442\H,-1.0696489209,-0.3164434367,1.3912483013\H,-1.535
4145957,1.3667208603,1.0461838455\C,0.9847983077,0.8707844242,0.394227
8902\C,-2.4609209599,-0.1065718268,-0.2503602665\H,-2.2256127754,-1.08
81143998,-0.6655537126\H,-3.3593694776,-0.19845257,0.362244091\H,-2.66
55627535,0.5858803847,-1.068178434\C,2.1522324858,1.0805204602,-0.4990
93383\H,3.0598381745,1.2163110835,0.0898158137\H,2.2919911891,0.219366
6378,-1.1584592556\H,2.0235806085,1.9647074653,-1.1377394116\O,0.42850
43986,-2.2825015812,-0.3364028824\H,0.2259227151,-1.4002793839,-0.6690
412063\\Version=ES64L-G09RevD.01\State=2-A\HF=-309.383998\S2=0.753995\
S2-1=0.\S2A=0.750013\RMSD=5.479e-09\RMSF=4.496e-06\Dipole=-0.065653,1.
0471307,0.6552585\Quadrupole=3.9792089,-4.9169395,0.9377306,0.3692682,
0.1252127,-1.2350014\PG=C01 [X(C4H11O2)]\\@

1\1\GINC-T4\FOpt\UM062X\6-311++G(d,p)\C4H9O1(2)\SANDHIYA\16-Nov-2015\0
\\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\
O,-0.0368120556,-0.4563018871,-0.2420508066\H,-1.1540138802,-1.4082176
815,1.2320942281\C,1.1503589258,-0.7175781224,0.4927057679\H,1.1658232
704,-0.0814964145,1.3849792018\H,1.1459206811,-1.7650221571,0.82007930
62\C,-1.1901035861,-0.655752304,0.4462227304\C,2.335496198,-0.43404299
75,-0.4034133814\H,2.3278289267,0.6090415271,-0.722382648\H,3.26715214
7,-0.6290129919,0.1308392508\H,2.3023124641,-1.0680329334,-1.290620714
3\C,-2.4263480995,-0.4223765032,-0.3423235852\H,-3.303079776,-0.467310
4066,0.3049952353\H,-2.3940274412,0.5615351143,-0.8167891893\H,-2.5532
157746,-1.1672962421,-1.1401013958\\Version=ES64L-G09RevD.01\State=2-A
\HF=-232.9522782\S2=0.754196\S2-1=0.\S2A=0.750014\RMSD=8.943e-09\RMSF=
5.202e-06\Dipole=0.239487,-0.268206,0.2771722\Quadrupole=1.8181842,-0.
6899732,-1.1282109,0.1774792,0.5383401,-0.5497484\PG=C01 [X(C4H9O1)]\\
@

Reaction (3):

1\1\GINC-T2\FOpt\UM062X\6-311++G(d,p)\O2(3)\SANDHIYA\17-Nov-2015\0\\#P
M062X/6-311++G(d,p) opt freq scf=tight\\o2 triplet SP\\0,3\O,0.,0.,0.
5943764538\O,0.,0.,-0.5943764538\\Version=ES64L-G09RevD.01\State=3-SGG
\HF=-150.3086142\S2=2.012026\S2-1=0.\S2A=2.000071\RMSD=4.374e-09\RMSF=
1.570e-06\Dipole=0.,0.,0.\Quadrupole=0.1841973,0.1841973,-0.3683947,0.
,0.,0.\PG=D*H [C*(O1.O1)]\\@

1\1\GINC-T3\FOpt\UM062X\6-311++G(d,p)\C4H9O3(2)\SANDHIYA\18-Nov-2015\0

\\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\
O,-0.8724916878,-0.9256031038,-0.3233139529\H,-0.0030858115,-2.5277033
359,0.6559337582\H,0.6491457848,-2.0709535053,-0.9341462835\C,-1.62096
59483,-0.4537109643,0.784537297\H,-1.8179298307,-1.2879123483,1.473841
8219\H,-1.0541508675,0.3149857333,1.3218111357\C,0.2591761725,-1.67801
44273,0.006656031\C,-2.9143796914,0.1263938484,0.2543184625\H,-3.48100
09225,-0.6347732952,-0.2837096073\H,-3.5248214845,0.5057832225,1.07587
41545\H,-2.6988444588,0.9484108321,-0.4295048802\C,1.3538478529,-0.883
603755,0.7058811218\H,2.2333091463,-1.5120147127,0.8558940147\H,1.0319
070572,-0.4568822232,1.6562376355\O,1.7944379588,0.1997130917,-0.13058
80942\O,1.0688570504,1.2651491428,0.0370145854\\Version=ES64L-G09RevD.
01\State=2-A\HF=-383.3071035\S2=0.755107\S2-1=0.\S2A=0.750016\RMSD=8.2
99e-09\RMSF=1.053e-05\Dipole=-0.069697,-1.0703448,0.9294437\Quadrupole
=0.8787457,-0.6776987,-0.2010471,-3.8620664,0.43713,0.2380773\PG=C01 [
X(C4H9O3)]\\@

Reaction (4):

1\1\GINC-HP1\FOpt\UM062X\6-311++G(d,p)\C4H9O3(2)\SANDHIYA\17-Nov-2015\
0\\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2
\O,0.4990335672,-0.6412576687,-0.1222043681\H,-0.8105733128,-0.0943557
095,1.3618481295\C,1.4510455649,0.3651417179,0.2238092387\H,1.21880722
77,1.2891666401,-0.3144891287\H,1.3778331154,0.57331594,1.2982433171\C
,-0.7837752502,-0.4124447552,0.3131410363\C,2.8218944976,-0.1533065536
,-0.1492080362\H,2.8640480804,-0.3714593959,-1.2171784783\H,3.58155805
05,0.5951302415,0.0828792839\H,3.0501233485,-1.0671333898,0.4010915181
\C,-1.6413466152,-1.6102207427,0.0042796381\H,-2.669501523,-1.42961026
25,0.3169009913\H,-1.61639735,-1.8040975752,-1.0685294603\H,-1.2468905
454,-2.4787454184,0.5308363879\O,-1.358955581,0.7113434985,-0.43038811
91\O,-1.1823672745,1.8445294334,0.1804970498\\Version=ES64L-G09RevD.01
\State=2-A\HF=-383.324574\S2=0.755138\S2-1=0.\S2A=0.750015\RMSD=3.145e

-09\RMSF=7.470e-06\Dipole=0.3678181,-0.6807172,0.4897245\Quadrupole=2.
0412392,-2.3578064,0.3165672,4.1943194,-0.6037393,-0.3659733\PG=C01 [X
(C4H9O3)]\\@

Reaction (5):

NO

1\1\GINC-HP3\FOpt\UM062X\6-311++G(d,p)\N1O1(2)\SANDHIYA\20-Nov-2015\0\
\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\N
,-2.0042157528,-0.1535570357,-0.2830270255\O,-2.6943532472,-0.78111196
43,0.3693640255\\Version=ES64L-G09RevD.01\HF=-129.880285\S2=0.753884\S
2-1=0.\S2A=0.75001\RMSD=9.462e-09\RMSF=3.477e-06\Dipole=-0.0199449,-0.
0181363,0.018854\Quadrupole=-0.2714288,0.2944546,-0.0230257,-0.3364842
,0.0912023,0.565643\PG=C*V [C*(N1O1)]\\@

1\1\GINC-T4\FOpt\UM062X\6-311++G(d,p)\C4H9O2(2)\SANDHIYA\16-Nov-2015\0
\\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\
O,1.4358027006,-0.8514122378,-0.3420373004\H,-0.2722257918,-0.28037141
45,-1.3730180539\H,0.0587137464,-2.0174813406,-1.2339939844\C,1.726507
1425,0.4764440855,0.0518206017\H,1.3871936455,1.171704009,-0.728747814
9\H,1.194800133,0.7304231049,0.9788545923\C,0.0927737557,-1.0668477463
,-0.6993089005\C,3.2217048201,0.588339437,0.2601281502\H,3.7493519753,
0.3484435877,-0.663881616\H,3.4891253527,1.6015980274,0.5654236238\H,3
.5474476423,-0.1077511849,1.0343704818\C,-0.8232813863,-1.15857639,0.5
248073895\H,-0.8837862199,-0.1803508162,1.0395836487\H,-0.4190007408,-
1.8578177667,1.2731725253\O,-2.1177317754,-1.4566213544,0.2089836568\\
Version=ES64L-G09RevD.01\State=2-A\HF=-308.1488335\S2=0.754216\S2-1=0.
\S2A=0.750013\RMSD=6.982e-09\RMSF=5.302e-06\Dipole=0.516632,0.6665489,
0.2129823\Quadrupole=-4.8027927,2.4647572,2.3380356,-0.5127455,0.26860

69,0.1773118\PG=C01 [X(C4H9O2)]\\@

NO_2

1\1\GINC-HP2\FOpt\UM062X\6-311++G(d,p)\N1O2(2)\SANDHIYA\20-Nov-2015\0\
\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\N
,-2.6638727804,0.3889317525,-0.3392436147\O,-2.9899130838,-0.265472227
,0.5886381573\O,-1.6433959258,0.5925555046,-0.8983946726\\Version=ES64
L-G09RevD.01\State=2-A'\HF=-205.0507148\S2=0.755026\S2-1=0.\S2A=0.7500
15\RMSD=4.865e-09\RMSF=2.216e-05\Dipole=-0.1217562,0.0790555,-0.064675
\Quadrupole=-0.2791524,0.520045,-0.2408926,-0.4026883,0.9105922,0.8248
017\PG=CS [SG(N1O2)]\\@

Reaction (6):

1\1\GINC-T4\FOpt\UM062X\6-311++G(d,p)\C4H9O2(2)\SANDHIYA\16-Nov-2015\0
\\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\
O,0.23146,-0.429907,-0.078376\H,-1.017363,0.322295,1.377324\C,1.341089
,0.394935,0.246823\H,1.249662,1.355587,-0.270084\H,1.342182,0.589714,1
.329042\C,-1.002161,0.118133,0.284239\C,2.602523,-0.329309,-0.170499\H
,2.591555,-0.515268,-1.245264\H,3.48166,0.270905,0.071356\H,2.680142,-
1.287514,0.345369\C,-2.088865,-0.903567,-0.060592\H,-3.060311,-0.54023
6,0.269558\H,-2.098169,-1.055876,-1.139687\H,-1.850992,-1.845803,0.430
569\O,-1.285695,1.308037,-0.292625\\Version=ES64L-G09RevD.01\State=2-A
\HF=-308.168834\S2=0.754297\S2-1=0.\S2A=0.750014\RMSD=6.872e-09\RMSF=1
.371e-05\Dipole=0.1072226,-0.2747879,0.5330073\Quadrupole=2.0691733,-2
.4687159,0.3995426,2.885418,-0.5140215,0.6248275\PG=C01 [X(C4H9O2)]\\@

Reaction (7):

RC3

1\1\GINC-P1\FOpt\UM062X\6-311++G(d,p)\C4H9O4(2)\SANDHIYA\19-Jan-2015\0
\\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\
O,1.3387623674,-0.3064479089,-1.1472880746\H,0.011031381,1.2065368348,
-0.6547657695\H,-0.1068332528,0.5340537424,-2.2878415293\C,1.924593895
4,-0.2032990388,0.1387704259\H,1.9881585018,0.8557171863,0.4246686511\
H,1.303428327,-0.710280035,0.8888546126\C,0.0616047689,0.2788096112,-1
.2400673815\C,3.3010574044,-0.8292903118,0.081064495\H,3.9178543374,-0
.3147125468,-0.6570438575\H,3.7897419803,-0.7627090368,1.0549484342\H,
3.2282180939,-1.8803833136,-0.2021499008\C,-1.0326263639,-0.681527364,
-0.7737722982\H,-0.8202188257,-1.1087368195,0.2195520613\H,-1.07480984
05,-1.5573825855,-1.4464946038\O,-2.2867048258,-0.1347232033,-0.789821
9863\O,-0.8476562416,0.8412640854,1.9598805838\O,-1.8453917071,1.25887
87038,1.4655891376\\Version=AM64L-G09RevC.01\State=2-A\HF=-458.4615814
\S2=1.745676\S2-1=0.\S2A=0.799889\RMSD=6.394e-09\RMSF=1.027e-05\Dipole
=0.5484605,-0.103859,0.4498242\Quadrupole=-3.4661999,2.3043583,1.16184
16,1.1380085,1.0739862,0.1153151\PG=C01 [X(C4H9O4)]\\@

TS3

1\1\GINC-Q1\FTS\UM062X\6-311++G(d,p)\C4H9O4(2)\ROOT\05-Nov-2015\0\\#p
um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc) scf=qc\\rea conformer
2 ts\\0,2\O,0.4911976053,0.0089891902,-0.7825007887\H,-0.641561445,1.
7456343777,-0.6514599271\H,-0.939393357,0.6670138895,-2.0315384108\C,1
.0561090872,0.153897493,0.5079399314\H,1.0368458139,1.2133834809,0.799
7249217\H,0.4685044265,-0.4074086911,1.2486822943\C,-0.7172428838,0.69
48311102,-0.962474713\C,2.4750831338,-0.3708746957,0.464567986\H,3.064
0801961,0.1981018292,-0.255836497\H,2.9421483829,-0.2869592273,1.44739
44636\H,2.4795955132,-1.419413349,0.1636807649\C,-1.8931036381,0.03341
77972,-0.2273089371\H,-1.6039622274,0.227194022,0.9885382891\H,-1.8667
183696,-1.0743316387,-0.2217121901\O,-3.0307149967,0.6052224112,-0.264
4605828\O,-1.903175064,0.8876968314,2.2158802529\O,-2.9554355973,1.437
1303094,2.0141354229\\Version=ES64L-G09RevD.01\State=2-A\HF=-458.44119
67\S2=1.280088\S2-1=0.\S2A=0.769812\RMSD=0.000e+00\RMSF=5.278e-06\Dipo

le=0.9051891,-0.1289116,0.4589404\Quadrupole=-3.4158129,2.1169818,1.29
88312,1.9559372,0.8596607,-0.8781918\PG=C01 [X(C4H9O4)]\\@

PC3

1\1\GINC-T2\FOpt\UM062X\6-311++G(d,p)\C4H9O4(2)\SANDHIYA\06-Nov-2015\0
\\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\
O,1.3779079844,-0.1522944244,-1.256452568\H,-0.1104916408,1.1435096465
,-0.5898268081\H,-0.2339870908,0.5331295054,-2.2582411061\C,1.93269912
81,-0.2709585149,0.0501972579\H,1.885046692,0.7033833265,0.5518070195\
H,1.332947255,-0.970800194,0.6485935909\C,0.0459453223,0.2685368693,-1
.2320160244\C,3.3580674612,-0.7539516458,-0.0888720181\H,3.939285588,-
0.0471500669,-0.6827372925\H,3.8212562577,-0.84831516,0.8948016387\H,3
.3853248675,-1.7263766619,-0.582832784\C,-0.8793175192,-0.84966622,-0.
803936632\H,-2.1658661851,0.5571950681,0.996093295\H,-0.5188388326,-1.
8693340435,-1.0375722755\O,-1.9548316265,-0.6816894715,-0.2836855012\O
,-1.836291075,1.1003207806,1.7504933774\O,-0.5817855863,0.7670492065,1
.8843418304\\Version=ES64L-G09RevD.01\State=2-A\HF=-458.5220306\S2=0.7
55096\S2-1=0.\S2A=0.750014\RMSD=6.659e-09\RMSF=3.208e-05\Dipole=0.3509
718,-0.3339914,-0.7357846\Quadrupole=0.2919706,1.5687791,-1.8607497,-0
.3812817,3.9767371,-2.1977049\PG=C01 [X(C4H9O4)]\\@

$CH_3CH_2OCH_2CH(=O)$

1\1\GINC-T4\FOpt\UM062X\6-311++G(d,p)\C4H8O2\SANDHIYA\16-Nov-2015\0\\#
p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,1\O,1
.488355099,-0.7277193699,-0.5119561672\H,-0.3689087616,-0.2260927633,-
1.3153529287\H,0.148006922,-1.9187183523,-1.4405040051\C,1.6399988916,
0.5501301979,0.0844760273\H,1.24846812,1.3172046324,-0.5974528799\H,1.
0551817551,0.6050584401,1.0142660701\C,0.1511665014,-1.0381409305,-0.7
907038735\C,3.1097789257,0.7712666665,0.3644014388\H,3.6805446158,0.71
93730239,-0.5637307809\H,3.2661900267,1.7512481928,0.818546579\H,3.485
1080966,0.0058620878,1.0450961097\C,-0.6224513298,-1.3984139654,0.4656
451438\H,0.0111948135,-1.6972189679,1.3270366182\O,-1.8191016761,-1.39
78428921,0.5322436484\\Version=ES64L-G09RevD.01\State=1-A\HF=-307.6136
374\S2=0.\S2-1=0.\S2A=0.\RMSD=7.740e-09\RMSF=8.630e-06\Dipole=0.768451

1,0.4687254,-0.0783701\Quadrupole=-5.7535184,3.2454163,2.5081021,-0.23
45656,2.5285208,0.4684708\PG=C01 [X(C4H8O2)]\\@

HO_2

1\1\GINC-T3\FOpt\UM062X\6-311++G(d,p)\H1O2(2)\SANDHIYA\18-Nov-2015\0\\
#P UM062X/6-311++G(d,p) opt freq scf=tight\\int opt\\0,2\H,-0.88741093
25,-0.8670414963,0.\O,0.0484104703,-0.5995588656,0.\O,0.0565774622,0.7
071993619,0.\\Version=ES64L-G09RevD.01\State=2-A"\HF=-150.8905895\S2=0
.754728\S2-1=0.\S2A=0.750013\RMSD=6.463e-09\RMSF=1.209e-04\Dipole=-0.7
413396,-0.5788685,0.\Quadrupole=0.5750827,-0.3547186,-0.2203641,1.3161
311,0.,0.\PG=CS [SG(H1O2)]\\@

Reaction (8):

RC4

1\1\GINC-R2\FOpt\UM062X\6-311++G(d,p)\C4H9O4(2)\SANDHIYA\10-Nov-2015\0
\\#p um062x/6-311++g(d,p) guess=read opt freq scf=tight\\rea conformer
2 ts\\0,2\O,0.1019770682,-0.549698845,-1.0790262958\H,0.2103683402,0.
6419431686,2.0345055764\C,-1.0392697306,-0.782688765,-0.2239311412\H,-
0.7089898707,-1.3625463957,0.6417457727\H,-1.4113368881,0.1803783367,0
.1297971352\C,1.1292728226,0.1001645353,-0.5504088461\C,-2.0668468287,
-1.5281744022,-1.0419782517\H,-1.6697542628,-2.4833467399,-1.388033801
8\H,-2.9493220822,-1.7189402178,-0.4293290701\H,-2.36805873,-0.9387458
245,-1.9088650915\C,2.2368173378,0.3108516043,-1.539872911\H,3.0837857
913,0.7751239571,-1.0424767295\H,2.5242614513,-0.6448423369,-1.9788077
358\H,1.8767935712,0.9522364475,-2.3458881368\O,1.1631929317,0.4812856
345,0.5993605189\O,-0.424863329,0.7794910794,2.7775610484\O,-1.4782725
922,1.3344617633,2.2396339599\\Version=ES64L-G09RevD.01\State=2-A\HF=-
458.5709845\S2=0.755098\S2-1=0.\S2A=0.750014\RMSD=1.776e-09\RMSF=8.121
e-06\Dipole=0.5841464,-0.7643614,-1.5129108\Quadrupole=3.2157476,0.604
0706,-3.8198183,2.4677188,0.3335815,-3.4426353\PG=C01 [X(C4H9O4)]\\@

TS4

1\1\GINC-R2\FTS\UM062X\6-311++G(d,p)\C4H9O4(2)\SANDHIYA\09-Nov-2015\0\
\#p um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc) scf=tight\\rea co
nformer 2 ts\\0,2\O,-0.1541577662,-0.2946555621,-0.7291320824\H,0.7003
390308,0.8546027302,0.7273724322\C,-0.9819010168,-1.260657567,-0.08083
46178\H,-0.5044493006,-2.2420418487,-0.1430374382\H,-1.0669548402,-1.0
077948381,0.9825414464\C,1.0495795252,-0.0310643263,-0.0991011354\C,-2
.3290868744,-1.2386821011,-0.767227421\H,-2.220563065,-1.4756151793,-1
.8266173136\H,-2.993084627,-1.9759497,-0.3123718553\H,-2.7854200491,-0
.2517432523,-0.677085635\C,1.9502299325,0.7690517362,-1.0383303502\H,2
.8182285329,1.1256723535,-0.4874144907\H,2.2751662996,0.1015674712,-1.
8384407052\H,1.401884123,1.6035770144,-1.4733079866\O,1.5423764731,-0.
864253059,0.718951429\O,-0.3159009118,1.8830990906,1.2281666877\O,-1.3
598401459,1.8151912577,0.633731536\\Version=ES64L-G09RevD.01\State=2-A
\HF=-458.4655783\S2=1.479035\S2-1=0.\S2A=0.787412\RMSD=7.398e-09\RMSF=
1.071e-05\Dipole=-0.3178352,0.3226689,-0.3211321\Quadrupole=0.2175237,
0.6700512,-0.8875749,4.0100612,-2.8970974,1.0901208\PG=C01 [X(C4H9O4)]
\\@

PC4

1\1\GINC-T5\FOpt\UM062X\6-311++G(d,p)\C4H9O4(2)\SANDHIYA\09-Nov-2015\0
\\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\
O,-0.0007912474,-0.5620306989,-1.0462963962\H,0.491680989,0.6646030874
,2.0248295407\C,-1.0137120807,-1.0373763452,-0.1339724266\H,-0.5525555
488,-1.7537938954,0.5489800449\H,-1.3778643727,-0.1857316686,0.4432108
777\C,1.1123786853,-0.0775883281,-0.5145778244\C,-2.1056114242,-1.6654
313643,-0.9680943569\H,-1.7154167516,-2.5003844375,-1.5516353854\H,-2.
8966908689,-2.0371272624,-0.3148662579\H,-2.5367455728,-0.9323018602,-
1.6506917305\C,2.0686345256,0.4250050285,-1.5544499733\H,3.0542706727,
0.544539886,-1.1123561685\H,2.0988878378,-0.2531828691,-2.4059372611\H
,1.7102261835,1.3948825981,-1.9066284067\O,1.3240489915,-0.0425656738,

0.6787735756\O,-0.1201286421,1.2526697575,2.5283916077\O,-0.8407373761
,1.8468690459,1.616111541\\Version=ES64L-G09RevD.01\State=2-A\HF=-458.
5704133\S2=0.755147\S2-1=0.\S2A=0.750015\RMSD=6.027e-09\RMSF=1.246e-05
\Dipole=0.2871814,-0.9183405,-1.1570036\Quadrupole=2.9369732,-0.854731
9,-2.0822413,3.5229589,-1.1922343,-3.6393178\PG=C01 [X(C4H9O4)]\\@

1\1\GINC-T5\FOpt\UM062X\6-311++G(d,p)\C4H8O2\SANDHIYA\16-Nov-2015\0\\#
p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,1\O,1
.2552579719,-0.2142734543,0.1615430473\C,0.9639403301,1.1014140582,-0.
3358065376\H,0.8855779977,1.0560739759,-1.4241571537\H,-0.0055673416,1
.4178392013,0.0552217788\C,0.3689425054,-1.1724103081,-0.1565996973\C,
2.0839283128,2.0106119812,0.1166361092\H,3.0406282319,1.6672622938,-0.
2796090793\H,1.9046615658,3.0263943296,-0.240134232\H,2.1463771248,2.0
308634224,1.2055755506\C,0.7701086323,-2.4985946241,0.4269238659\H,0.0
81255462,-3.266326046,0.0848184407\H,1.791060952,-2.7406374571,0.13069
13936\H,0.7473982743,-2.4345070177,1.515993542\O,-0.6123700196,-0.9671
853552,-0.817962028\\Version=ES64L-G09RevD.01\State=1-A\HF=-307.661454
6\S2=0.\S2-1=0.\S2A=0.\RMSD=6.382e-09\RMSF=1.650e-05\Dipole=0.6750936,
0.1613633,0.3905647\Quadrupole=-3.6742143,4.2658125,-0.5915982,-0.8292
846,-2.4289784,-1.4548371\PG=C01 [X(C4H8O2)]\\@

Reaction (9):

TS5

1\1\GINC-R2\FTS\UM062X\6-311++G(d,p)\C4H9O3(2)\SANDHIYA\06-Nov-2015\0\
\#p um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc) scf=tight\\rea co
nformer 2 ts\\0,2\O,-0.5269286141,0.849747236,0.1894287331\H,0.9671158
659,0.0093509814,1.3336318114\C,-1.4399061595,-0.1508875172,0.46327797
3\H,-0.7947224951,-1.2104373251,-0.0108882656\H,-1.4662023467,-0.41558

0453,1.5279424622\C,0.8169101446,0.4278578661,0.330596905\C,-2.7618542
3,0.0950923399,-0.1981440101\H,-2.6323299762,0.1970965128,-1.276266770
2\H,-3.4474958991,-0.7281390659,0.0044507621\H,-3.2085293606,1.0194606
908,0.1822431107\C,1.7280444791,1.5773168137,0.0010214765\H,2.76710645
72,1.2603001819,0.0827545446\H,1.5287098262,1.9157681559,-1.0158478363
\H,1.5434583333,2.3968875911,0.69485339\O,1.0273965942,-0.5925071505,-
0.6153072784\O,0.3139862807,-1.7112925577,-0.208850408\\Version=ES64L-
G09RevD.01\State=2-A\HF=-383.2863832\S2=0.759401\S2-1=0.\S2A=0.750044\
RMSD=5.576e-09\RMSF=7.135e-06\Dipole=-0.4608611,0.7169658,0.6887762\Qu
adrupole=3.5272792,-3.4056978,-0.1215814,3.6799261,0.9327147,-0.993270
1\PG=C01 [X(C4H9O3)]\\@

1\1\GINC-T2\FOpt\UM062X\6-311++G(d,p)\C4H9O3(2)\SANDHIYA\09-Nov-2015\0
\\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\
O,-0.4350912578,0.6616295574,-0.0956443345\H,0.8779942489,0.0288889249
,1.3510962446\C,-1.434500397,-0.1572520607,0.3482835435\H,0.0457268762
,-2.0291515473,-0.515987608\H,-1.2618526856,-0.6293017423,1.3134019445
\C,0.8794822129,0.3378556607,0.2993540066\C,-2.7934298924,0.2654923528
,-0.0749523114\H,-2.8375940695,0.3865384875,-1.1598080024\H,-3.5313590
902,-0.4792290752,0.225089647\H,-3.0774760102,1.2268496049,0.374236881
6\C,1.7573533585,1.5334598625,0.024147438\H,2.7808668868,1.3215881253,
0.3301012046\H,1.7367497604,1.7577198435,-1.0428325598\H,1.3794434858,
2.3937491221,0.5752625838\O,1.3952661995,-0.7181007858,-0.4713171757\O
,0.8588893737,-1.9425273304,0.0033664976\\Version=ES64L-G09RevD.01\Sta
te=2-A\HF=-383.3085651\S2=0.75432\S2-1=0.\S2A=0.750015\RMSD=2.794e-09\
RMSF=9.216e-06\Dipole=-0.5819608,0.4151999,0.3717344\Quadrupole=0.8030
48,-1.0773271,0.2742791,4.252334,0.8027662,1.0111705\PG=C01 [X(C4H9O3)
]\\@

Reaction (10):

TS6

1\1\GINC-T3\FTS\UM062X\6-311++G(d,p)\C4H9O2(2)\SANDHIYA\06-Nov-2015\0\
 \#p um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc) scf=tight\\rea co
 nformer 2 ts\\0,2\O,-0.3961238858,0.3641157018,0.7944698712\H,1.351428
 8365,0.4908599358,1.7790219932\C,-1.2625665304,-0.4915433534,0.0473372
 753\H,-0.7972797292,-0.7229774033,-0.9168954482\H,-1.3848106817,-1.435
 2632364,0.5844801383\C,0.8607345387,-0.1276726792,1.0125851694\C,-2.57
 69722788,0.2351601115,-0.1294612593\H,-2.4288145477,1.1735786655,-0.66
 60880213\H,-3.2729506088,-0.3846784087,-0.6976273096\H,-3.0232413382,0
 .4583231908,0.840708597\C,1.8846562922,0.757517352,-0.426906544\H,2.90
 5562994,0.4572212864,-0.2256443716\H,1.4318772768,0.3080945189,-1.3028
 590854\H,1.6385165164,1.7979128002,-0.2472997203\O,1.156300286,-1.3094
 93202,0.8274485855\\Version=ES64L-G09RevD.01\State=2-A\HF=-308.1507627
 \S2=0.767418\S2-1=0.\S2A=0.750099\RMSD=7.465e-09\RMSF=6.741e-06\Dipole
 =-0.1758649,0.7053341,-0.4156788\Quadrupole=2.0843667,-2.8188432,0.734
 4765,4.1076146,0.2045074,0.6926989\PG=C01 [X(C4H9O2)]\\@

PC5

1\1\GINC-T4\FTS\UM062X\6-311++G(d,p)\C4H9O2(2)\SANDHIYA\06-Nov-2015\0\
 \#p um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc) scf=tight\\rea co
 nformer 2 ts\\0,2\O,-0.3744545196,0.163298267,0.8881340428\H,1.2278598
 901,0.0633940528,2.0645070824\C,-1.121464522,-0.4359138239,-0.18600985
 07\H,-0.4408470587,-0.6079249228,-1.0226264027\H,-1.4969086768,-1.4049
 237936,0.1504410493\C,0.7236537366,-0.4904421539,1.2619925018\C,-2.236
 605065,0.5184712738,-0.5444965741\H,-1.8288110508,1.4789331433,-0.8638
 323562\H,-2.8302013023,0.1049492038,-1.3616733747\H,-2.8923470339,0.68
 70525708,0.3107765831\C,1.7602716342,1.124102644,-1.3874603838\H,2.569
 0780241,1.15886875,-0.6738086288\H,1.7848812197,0.3941323833,-2.181840
 93\H,1.0029071944,1.8930428583,-1.3789111638\O,1.1074835298,-1.5261754
 527,0.8017104055\\Version=ES64L-G09RevD.01\State=2-A\HF=-308.1719432\S
 2=0.754626\S2-1=0.\S2A=0.750015\RMSD=7.593e-09\RMSF=3.593e-06\Dipole=-
 0.560325,0.5630525,-0.1532033\Quadrupole=1.0391013,-3.0830031,2.043901
 7,2.7764225,1.4609645,0.9757845\PG=C01 [X(C4H9O2)]\\@

```
1\1\GINC-T4\FOpt\UM062X\6-311++G(d,p)\C3H6O2\SANDHIYA\16-Nov-2015\0\\#
 p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,1\O,-
 0.2099138515,-0.4835320364,0.6900151957\H,1.5151336338,-1.1761786222,1
 .4036344004\C,-1.0235252086,-0.231388126,-0.4712010732\H,-0.4751046714
 ,0.4343355229,-1.1409097198\H,-1.1823144313,-1.1762630062,-0.995099461
 2\C,0.982711923,-1.0283442126,0.4554516726\C,-2.3185396337,0.380652997
 1,0.0093264459\H,-2.1303919211,1.3170637065,0.5361548658\H,-2.96732588
 05,0.5869713787,-0.843612817\H,-2.8393404554,-0.2998042903,0.684291123
 2\O,1.4144554968,-1.3155213117,-0.6226056324\\Version=ES64L-G09RevD.01
 \State=1-A\HF=-268.3466229\S2=0.\S2-1=0.\S2A=0.\RMSD=8.836e-09\RMSF=1.
 140e-05\Dipole=-0.6912445,0.3330764,0.3265974\Quadrupole=-0.307211,0.4
 295202,-0.1223091,0.9077297,3.7505482,-1.7470031\PG=C01 [X(C3H6O2)]\\@
```



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1\1\GINC-T4\FOpt\UM062X\6-311++G(d,p)\C1H3(2)\SANDHIYA\16-Nov-2015\0\\
 #p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\C,
 1.4081985736,2.2295428373,-0.0115533397\H,2.2815266992,1.838820962,0.4
 875310163\H,1.4021161431,2.3296806738,-1.0858297132\H,0.5419005841,2.5
 176695269,0.5634260366\\Version=ES64L-G09RevD.01\State=2-A\HF=-39.8209
 088\S2=0.754639\S2-1=0.\S2A=0.750015\RMSD=2.948e-09\RMSF=1.007e-04\Dip
 ole=0.0000073,-0.0006415,0.0000942\Quadrupole=0.2976144,-0.7827718,0.4
 851575,-0.5040182,-0.0483374,-0.1163201\PG=C01 [X(C1H3)]\\@
```

Reaction (11):

TS7

```
1\1\GINC-T1\FTS\UM062X\6-311++G(d,p)\C4H9O2(2)\SANDHIYA\06-Nov-2015\0\
 \#p um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc) scf=tight\\rea co
 nformer 2 ts\\0,2\O,-0.2267662697,0.4323175606,-0.2206228081\H,1.05247
```

83757,0.0582245933,1.5792286385\C,-1.3363141435,-0.4598102409,-0.07143
44916\H,-1.2383064973,-1.2758000583,-0.7905875707\H,-1.3000477848,-0.8
955912418,0.9326579099\C,0.9956039113,-0.1155284678,-0.0012534013\C,-2
.5970106203,0.3460030925,-0.2903164205\H,-2.6034162742,0.7817890902,-1
.2904455477\H,-3.4727429753,-0.2969208364,-0.186060672\H,-2.6683988701
,1.1530462168,0.440183386\C,2.0944737456,0.8830418318,-0.3068131353\H,
3.0283081512,0.5387081354,0.1316012115\H,2.2013008011,0.9254243032,-1.
3934912979\H,1.8342483046,1.8739890533,0.0596063966\O,1.1728223857,-1.
3307345617,0.0433183325\\Version=ES64L-G09RevD.01\State=2-A\HF=-308.14
3593\S2=0.765171\S2-1=0.\S2A=0.750029\RMSD=6.072e-09\RMSF=8.856e-06\Di
pole=-0.3362493,0.6358875,-0.0294917\Quadrupole=2.7311668,-3.1991223,0
.4679555,3.8020974,-0.4272008,0.4322565\PG=C01 [X(C4H9O2)]\\@

PC6

1\1\GINC-S2\FOpt\UM062X\6-311++G(d,p)\C4H9O2(2)\SANDHIYA\09-Nov-2015\0
\\#p um062x/6-311++g(d,p) geom=(checkpoint,newdefinition) opt freq scf
=qc\\rea conformer 2 ts\\0,2\O,-0.1745437798,0.3961035679,-0.237603536
5\H,0.1322099119,0.6596700364,2.4540773491\C,-1.2921367661,-0.47027149
07,0.0111121974\H,-1.2767155175,-1.2813177473,-0.7204542269\H,-1.17732
31873,-0.9141532297,1.0033216124\C,1.0414618898,-0.1454181646,-0.05396
18324\C,-2.5431965957,0.3715285667,-0.092303186\H,-2.6250375991,0.8202
66302,-1.083277494\H,-3.424248299,-0.2484098339,0.0826184086\H,-2.5271
524914,1.1707231245,0.6508043546\C,2.1265242974,0.8714167727,-0.271094
0623\H,3.0932666452,0.3748980262,-0.2705069124\H,1.964112443,1.4026962
601,-1.208745224\H,2.0869544314,1.6040970893,0.5380718366\O,1.20959761
71,-1.2915112795,0.263785716\\Version=ES64L-G09RevD.01\State=2-A\HF=-3
08.1593781\S2=0.750833\S2-1=0.\S2A=0.75\RMSD=0.000e+00\RMSF=7.714e-06\
Dipole=-0.3953939,0.6605467,-0.1867008\Quadrupole=2.7474847,-2.9277901
,0.1803054,3.8767991,-0.9358147,0.8807874\PG=C01 [X(C4H9O2)]\\@

H

Reaction (12):

TS8

1\1\GINC-R2\FTS\UM062X\6-311++G(d,p)\C4H9O2(2)\SANDHIYA\06-Nov-2015\0\
 \#p um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc) scf=qc\\rea confo
 rmer 2 ts\\0,2\O,-0.3093235716,0.2857945657,-0.3098145509\H,0.92937924
 68,-0.137220721,1.4981442779\C,-1.4218642541,-0.4858800016,0.057817396
 3\H,-1.5029575683,-1.3663845717,-0.5834981735\H,-1.3415731985,-0.80549
 07133,1.1028311684\C,1.2558382748,-0.2495200267,0.4502632702\C,-2.6339
 155085,0.426428248,-0.134810009\H,-2.7085159775,0.7464239476,-1.174229
 6464\H,-3.5382974395,-0.124145387,0.1306814736\H,-2.5580613819,1.30786
 94321,0.5024440958\C,2.1747426012,0.8246067074,-0.061784403\H,3.161344
 5667,0.6725301417,0.3839558325\H,2.2562911136,0.7468788549,-1.14512554
 47\H,1.8080334031,1.8111715222,0.2226253149\O,1.2247372938,-1.38506804
 82,-0.0678022921\\Version=ES64L-G09RevD.01\State=2-A\HF=-308.1302148\S
 2=0.775943\S2-1=0.\S2A=0.750138\RMSD=0.000e+00\RMSF=6.802e-05\Dipole=-
 0.5515904,0.6634218,0.5479736\Quadrupole=3.4236112,-3.2724372,-0.15117
 41,2.9951495,0.9620496,-0.1569611\PG=C01 [X(C4H9O2)]\\@

PC7

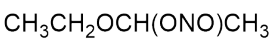
1\1\GINC-T1\FOpt\UM062X\6-311++G(d,p)\C4H9O2(2)\SANDHIYA\10-Nov-2015\0
 \\#p um062x/6-311++g(d,p) geom=(checkpoint,newdefinition) opt freq\\re
 a conformer 2 ts\\0,2\O,-0.7683491001,1.1722510506,-0.8359580448\H,0.7
 446536569,1.209247538,1.5680185316\C,-1.5136536505,0.0200210601,-0.888
 1284768\H,-2.0963508846,-0.0370999549,-1.8150158672\H,-0.8711961992,-0
 .8620111132,-0.7662684756\C,1.0878989496,0.3082466521,1.0238833554\C,-
 2.4711071322,0.0782620072,0.3223741683\H,-3.0951394652,0.9701670359,0.
 2694739229\H,-3.1072149663,-0.807319043,0.2961407321\H,-1.897024517,0.
 0763172857,1.2478673067\C,2.1901519737,0.5329982071,0.0316799757\H,3.0
 848071179,0.8725251968,0.5620077319\H,2.4088076371,-0.3865699042,-0.50
 95361787\H,1.8921893851,1.3255288057,-0.6581212838\O,0.5924101948,-0.7
 641638241,1.2566296023\\Version=ES64L-G09RevD.01\State=2-A\HF=-308.151
 6513\S2=0.754197\S2-1=0.\S2A=0.750013\RMSD=9.864e-09\RMSF=8.837e-06\Di

pole=-0.0100651,0.2566638,-0.2350349\Quadrupole=4.6419028,-3.2893409,-
1.3525619,2.4652856,0.3690491,3.4948453\PG=C01 [X(C4H9O2)]\\@

1\1\GINC-T4\FOpt\UM062X\6-311++G(d,p)\C2H5O1(2)\SANDHIYA\16-Nov-2015\0
\\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,2\
O,0.7188194769,-1.2681015172,0.2637446051\C,1.5248089574,-0.4648265044
,-0.4996564704\H,2.2480747321,-1.128868725,-1.004927449\H,0.9027587145
,-0.0757130383,-1.3245682768\C,2.2193182022,0.6519652339,0.2633243541\
H,2.8501152423,0.2354224351,1.0501135906\H,2.8444010296,1.2489950478,-
0.4044037024\H,1.480811645,1.3079470681,0.7267203488\\Version=ES64L-G0
9RevD.01\State=2-A\HF=-154.3385759\S2=0.754137\S2-1=0.\S2A=0.750013\RM
SD=5.409e-09\RMSF=2.642e-05\Dipole=0.5089556,0.5019923,-0.4901488\Quad
rupole=-0.0549992,-0.5688913,0.6238904,-1.5706775,0.5114474,0.4715499\
PG=C01 [X(C2H5O1)]\\@

1\1\GINC-T5\FOpt\UM062X\6-311++G(d,p)\C2H4O1\SANDHIYA\16-Nov-2015\0\\#
p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,1\H,-
1.2576208169,0.5106144563,1.4788586358\C,-1.4275430297,0.474470467,0.3
835427073\C,-2.2947748808,-0.6519750952,-0.1018309151\H,-3.2735406964,
-0.5904968698,0.3817655744\H,-2.4059279838,-0.6081610787,-1.183759448\
H,-1.849965064,-1.6058864817,0.194466358\O,-0.9307375284,1.3026456022,
-0.3293999124\\Version=ES64L-G09RevD.01\State=1-A\HF=-153.8045726\S2=0
.\S2-1=0.\S2A=0.\RMSD=1.850e-09\RMSF=7.797e-06\Dipole=-0.5523534,-0.87
22441,0.5298081\Quadrupole=0.1176547,-0.8386982,0.7210434,-1.0849059,0
.5263296,0.7565743\PG=C01 [X(C2H4O1)]\\@

Reaction (13):



1\1\GINC-V2\FOpt\UM062X\6-311++G(d,p)\C4H9N1O3\SANDHIYA\20-Nov-2015\0\
 \#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,1\O
 ,-0.4365402406,1.1460588812,0.6202303969\H,1.4847547688,0.7637982762,0
 .9549390043\C,-1.6647226593,0.5817346983,0.1668511136\H,-1.7269872517,
 -0.4660529859,0.4774226463\H,-2.4193540194,1.1380675154,0.7231619357\C
 ,0.7717601591,0.6346126382,0.136657953\C,-1.9215990417,0.6958195598,-1
 .3274131862\H,-1.2738936457,0.0283996706,-1.8974111867\H,-2.9558037883
 ,0.4108625744,-1.533429954\H,-1.7736040551,1.7222441636,-1.6692560363\
 C,1.2761298157,1.3133591074,-1.1211937666\H,2.2829066584,0.9599431825,
 -1.3483806462\H,0.630953537,1.1095217954,-1.9736632697\H,1.305201074,2
 .3892816793,-0.9476008395\O,0.6727679558,-0.7626400636,-0.1431222551\N
 ,0.8550529375,-1.5117259199,1.0181072174\O,0.6628817953,-2.6413697728,
 0.818452873\\Version=ES64L-G09RevD.01\State=1-A\HF=-438.1052921\S2=0.\
 S2-1=0.\S2A=0.\RMSD=4.425e-09\RMSF=1.459e-05\Dipole=-0.0667119,0.58181
 3,-0.4462597\Quadrupole=4.4038554,-3.5556591,-0.8481963,1.4629751,0.08
 37613,-0.9757078\PG=C01 [X(C4H9N1O3)]\\@

TS9

1\1\GINC-V1\FTS\UM062X\6-311++G(d,p)\C4H9N1O3\SANDHIYA\19-Nov-2015\0\\
 #p um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc) scf=tight\\rea con
 former 2 ts\\0,1\O,-0.3196639644,0.45842555,1.2586998067\H,1.528505602
 6,-0.3668517368,1.6696102945\C,-1.6018659324,-0.1163981043,0.987571451
 2\H,-1.5798424451,-1.1931938771,1.1676412125\H,-2.264054585,0.34691767
 11,1.7191386783\C,0.7795340547,-0.1337482868,0.6334338677\C,-2.0528671
 168,0.1778843596,-0.4317111414\H,-1.3947781365,-0.3156716409,-1.149292
 3567\H,-3.0685671746,-0.1931996055,-0.5866706168\H,-2.0438221203,1.253
 8434729,-0.6175004613\C,1.5999311215,0.8813117668,-0.1407313437\H,2.55
 5997413,0.4416787798,-0.4209947302\H,1.0426469772,1.135616341,-1.04673
 34913\H,1.7514100704,1.7848863025,0.4482933429\O,0.6323794823,-1.32579
 68262,0.1585625282\N,1.2413852846,-1.8038686067,1.9270111147\O,0.39598
 58688,-1.9727135094,2.6492621145\\Version=ES64L-G09RevD.01\State=1-A\H
 F=-438.046473\S2=0.\S2-1=0.\S2A=0.\RMSD=7.225e-09\RMSF=1.057e-05\Dipol
 e=0.0374898,0.2460022,0.325406\Quadrupole=2.7207569,-1.7638334,-0.9569

235,0.7706048,1.3271218,-3.2654715\PG=C01 [X(C4H9N1O3)]\\@

PC8

1\1\GINC-Q1\FOpt\UM062X\6-311++G(d,p)\C4H9N1O3\ROOT\21-Nov-2015\0\\#p
um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,1\O,-0.
6628791865,0.9850081674,-0.5652199574\H,-2.344593872,0.9725852581,0.65
27870596\H,-2.5701806051,0.5006118343,-1.032093219\C,0.1940421872,1.29
51596531,0.5326751309\H,-0.3545909835,1.9269600546,1.244393012\H,0.491
7177422,0.3745426357,1.0471059799\C,-1.8785720185,0.427971463,-0.18442
11369\C,1.397913602,2.0320320106,-0.0113566421\H,1.0918107454,2.971061
9565,-0.4745318001\H,2.1020562933,2.2468062566,0.7943990157\H,1.913018
5387,1.4319796554,-0.7633080995\C,-1.7957935898,-1.034802299,0.1950397
281\H,-2.7547800164,-1.4900862163,0.5152315651\H,1.0269069097,-0.97761
68976,-0.840037254\O,-0.7886214171,-1.6851398899,0.1471552257\N,2.0495
195021,-1.2042537386,-0.7243720425\O,2.2869999383,-1.2477039139,0.4459
740845\\Version=ES64L-G09RevD.01\State=1-A\HF=-438.0838545\S2=0.\S2-1=
0.\S2A=0.\RMSD=9.197e-09\RMSF=4.849e-06\Dipole=-1.667773,0.8661544,0.3
217274\Quadrupole=2.5397518,-2.0059495,-0.5338023,3.4931115,-0.2178142
,1.8524639\PG=C01 [X(C4H9N1O3)]\\@

HNO

1\1\GINC-S1\FOpt\UM062X\6-311++G(d,p)\H1N1O1\SANDHIYA\24-Nov-2015\0\\#
p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,1\H,-
0.9205971609,0.9770329167,-0.831807956\N,-1.9459072302,1.2019573709,-0
.7008624536\O,-2.1784546089,1.2480357124,0.4654774096\\Version=ES64L-G
09RevD.01\State=1-A'\HF=-130.4596368\S2=0.\S2-1=0.\S2A=0.\RMSD=2.198e-
09\RMSF=1.598e-05\Dipole=0.6598668,-0.1440122,-0.2556302\Quadrupole=0.
5193743,0.5274187,-1.0467931,0.0060769,-0.880196,0.2004245\PG=CS [SG(H
1N1O1)]\\@

Reaction (14):

$CH_3CH_2OCH(ONO_2)CH_3$

1\1\GINC-S1\FOpt\UM062X\6-311++G(d,p)\C4H9N1O4\SANDHIYA\23-Nov-2015\0\
\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,1\O
,0.8940259924,0.0052577485,-1.2538939632\H,-0.7159417098,1.1653436066,
-1.2730234734\C,1.617505032,-0.9818472893,-0.5199469544\H,0.9169576707
,-1.6621587713,-0.023532466\H,2.1262122048,-1.5487365547,-1.2994254476
\C,0.0853869443,0.9118903422,-0.5795743513\C,2.6248181547,-0.446245346
1,0.4843870556\H,2.1352151182,-0.0208869986,1.3610168884\H,3.255496657
3,-1.270491914,0.824766378\H,3.2665410214,0.3082782998,0.0247216852\C,
0.7853263353,2.1649157799,-0.0888987237\H,0.0455031645,2.8755729042,0.
2809571242\H,1.4990329953,1.9525215195,0.7039853768\H,1.3129935,2.6067
095874,-0.9345473517\O,-0.4987573251,0.3270318006,0.6027842118\N,-1.49
89566495,-0.6193570212,0.3701327355\O,-1.7827820898,-1.2369023494,1.34
85261674\O,-1.9505710168,-0.6977193441,-0.7342328918\\Version=ES64L-G0
9RevD.01\State=1-A\HF=-513.2821262\S2=0.\S2-1=0.\S2A=0.\RMSD=3.633e-09
\RMSF=1.779e-05\Dipole=1.0051712,0.7307468,-0.0097099\Quadrupole=0.045
6878,3.3799745,-3.4256623,-3.475646,1.1999824,0.1447161\PG=C01 [X(C4H9
N1O4)]\\@

TS10

1\1\GINC-T3\FTS\UM062X\6-311++G(d,p)\C4H9N1O4\SANDHIYA\23-Nov-2015\0\\
#p um062x/6-311++g(d,p) opt=(ts,noeigentest,calcfc) scf=tight\\rea con
former 2 ts\\0,1\O,0.7445339014,0.1102848215,-1.0798167496\H,-1.259882
7757,0.6640390843,-0.8347396734\C,1.3729423588,-1.0550320242,-0.546691
473\H,0.6209202977,-1.73634453,-0.1407822899\H,1.8404779369,-1.5311438
726,-1.4084009071\C,-0.1444204515,0.7768482687,-0.2343288529\C,2.40549
50256,-0.7011261648,0.5105171534\H,1.9329555067,-0.2390772311,1.379369
2848\H,2.9190653582,-1.6042778274,0.8473405684\H,3.1467847312,-0.01367
33015,0.0990349959\C,0.0947089926,2.286512506,-0.237589399\H,-0.723815
344,2.7899042666,0.2747187204\H,1.0317529116,2.4852690955,0.2866988829

\H,0.178431718,2.6474535805,-1.2609297719\O,-0.5042254821,0.2171528921
,0.852828577\N,-2.2552263972,-0.5165262855,0.347422674\O,-2.9341988962
,-1.2325342561,0.9955255862\O,-2.475983132,-0.029266012,-0.7370726261\
\Version=ES64L-G09RevD.01\State=1-A\HF=-513.2093759\S2=0.\S2-1=0.\S2A=
0.\RMSD=5.289e-09\RMSF=3.072e-05\Dipole=0.6701829,0.4403144,-0.238718\
Quadrupole=-0.7015258,3.6622339,-2.960708,-2.9342528,1.5213254,0.98618
86\PG=C01 [X(C4H9N1O4)]\\@

PC9

1\1\GINC-S2\FOpt\UM062X\6-311++G(d,p)\C4H9N1O4\SANDHIYA\23-Nov-2015\0\
\#p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,1\O
,1.7883748622,0.6667429332,-0.9879689172\H,-1.1591320885,0.0461328032,
0.8034878718\C,1.5571629216,-0.7312420782,-0.7062620098\H,0.5280809152
,-0.9801020606,-0.9661894557\H,2.2344857404,-1.2520529109,-1.380686245
\C,0.8367796866,1.5281065804,-0.6490490278\C,1.8584211552,-1.054846946
8,0.7430157179\H,1.1930005251,-0.5116558255,1.4155035623\H,1.710386806
9,-2.1228661689,0.9136964551\H,2.8918672001,-0.8024666094,0.9858449341
\C,1.2109616944,2.9400107385,-0.9912377558\H,0.392339159,3.6055524551,
-0.7324353873\H,2.1118055844,3.2165692324,-0.4414541676\H,1.438892633,
3.0080643714,-2.0555190912\O,-0.2098803581,1.2073026306,-0.1312189551\
N,-1.2930997169,-1.8096704015,0.7726447931\O,-1.7581472306,-2.72084182
5,1.3452683563\O,-1.6044244901,-0.6259169179,1.3598543217\\Version=ES6
4L-G09RevD.01\State=1-A\HF=-513.3642642\S2=0.\S2-1=0.\S2A=0.\RMSD=7.63
4e-09\RMSF=5.966e-06\Dipole=1.4254849,0.97417,-0.8830387\Quadrupole=-2
.3303617,2.5550578,-0.2246961,-2.345177,3.2243502,0.774534\PG=C01 [X(C
4H9N1O4)]\\@

HONO

1\1\GINC-S2\FOpt\UM062X\6-311++G(d,p)\H1N1O2\SANDHIYA\24-Nov-2015\0\\#
p um062x/6-311++g(d,p) opt freq scf=tight\\rea conformer 2 ts\\0,1\H,0
.980997737,1.269950032,-0.224067264\N,2.4233581341,0.2277639525,0.3605
358105\O,3.5709435587,0.1113709968,0.2191942383\O,1.9277425701,1.26685

90187,-0.4160107848\\Version=ES64L-G09RevD.01\State=1-A\HF=-205.685454
4\S2=0.\S2-1=0.\S2A=0.\RMSD=3.501e-09\RMSF=6.684e-05\Dipole=-0.9080596
,0.1018433,0.1011891\Quadrupole=1.7699705,-0.9128216,-0.8571489,-0.782
453,0.2975406,0.9167133\PG=C01 [X(H1N1O2)]\\@