Supplementary Information

Kinetic and mechanism study on gas phase reactions of ozone with a series of *cis*-3-hexenyl esters

Qilei Zhang, ‡[ab] Xiaoxiao Lin, ‡[a] Yanbo Gai,*[a] Qiao Ma,[ab] Weixiong Zhao,[a] Bo Fang,[a] Bo Long [c] and Weijun Zhang*[ad]

[a] *Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, 230031, Anhui, China*

[b] *University of Science and Technology of China, Hefei 230026, China*

[c] *School of Materials Science and Engineering, Guizhou Minzu University, Guiyang 550025, China*

[d] *School of Environmental Science and Optoelectronic Technology, University of Science and Technology of China, Hefei, 230026, Anhui, China*

* Corresponding author：

Dr. Yanbo Gai: gaiyanbo@aiofm.ac.cn

Prof. Weijun Zhang: wjzhang@aiofm.ac.cn

SUMMARY:

11 pages, including 12 figures and 1 tables.

Figure Captions:

Fig. S1 Schematic of the experimental setup and instrumentation

Fig.S2 One example of comparative experiments in the reaction of O_3 with cis-3-hexenyl acetate with and without cyclohexane as OH scavenger.

Fig. S3 Pseudo-first-order plots for O_3 reactions with different concentrations of Isoprene (in molecule cm^{-3}).

Fig. S4 Pseudo-first-order plots for O_3 reactions with different concentrations of cis-3-Hexenyl Formate (in molecule cm^{-3}).

Fig. S5 Pseudo-first-order plots for O_3 reactions with different concentrations ofcis-3-Hexenyl propionate (in molecule cm^{-3}).

Fig. S6 Pseudo-first-order plots for O_3 reactions with different concentrations ofcis-3-Hexenyl Butyrate (in molecule cm^{-3}).

Fig. S7 The structures for the reactants, transition states and products along the *cis*-3-hexenyl acetate + O_3 reaction profile.

Fig. S8 The structures for the reactants, transition states and products along the *cis*-3-hexenyl propionate + O_3 reaction profile.

Fig. S9 The structures for the reactants, transition states and products along the *cis*-3-hexenyl butyrate + O_3 reaction profile.

Fig. S10 BHandHLYP/6-311+G(d,p) energy profile (in kJ mol^{-1}) for the *cis*-3-hexenyl acetate ozonolysis.

Fig. S11 BHandHLYP/6-311+G(d,p) energy profile (in kJ mol^{-1}) for the *cis*-3-hexenyl propionate ozonolysis.

Fig. S12 BHandHLYP/6-311+G(d,p) energy profile (in kJ mol^{-1}) for the *cis*-3-hexenyl butyrate ozonolysis.

Fig.S1

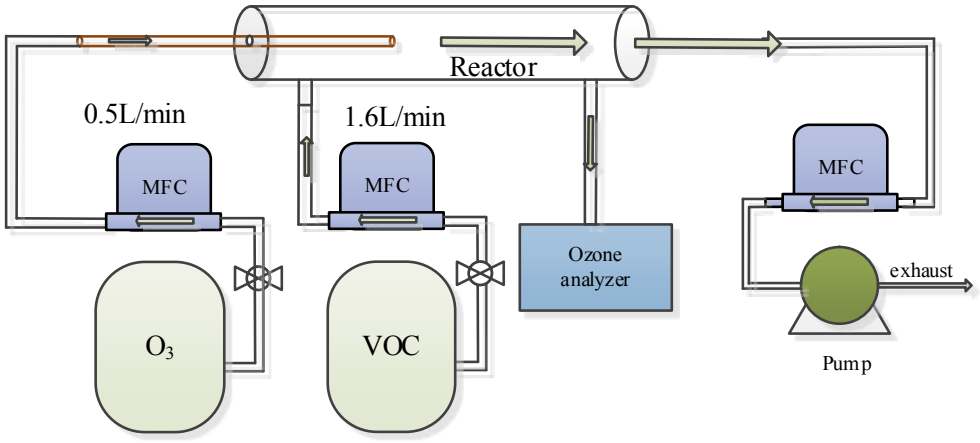
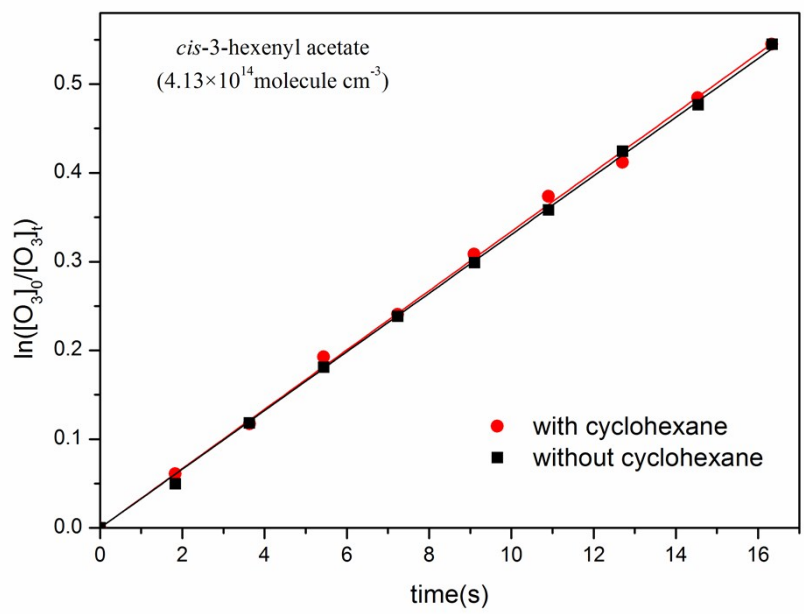


Fig. S2



Comparative experiments with and without cyclohexane as OH scavenger were conducted, and no significant difference was found in the rate constants. Fig.S2 gives one example of comparative experiments in the reaction of O_3 with 4.13×10^{14} molecule cm^{-3} *cis*-3-hexenyl acetate. As can be seen, regardless of the addition of excess cyclohexane (6.36×10^{15} molecule cm^{-3}) or not, the slope values of the lines (k') could be considered to be the same within the error.

Fig. S3

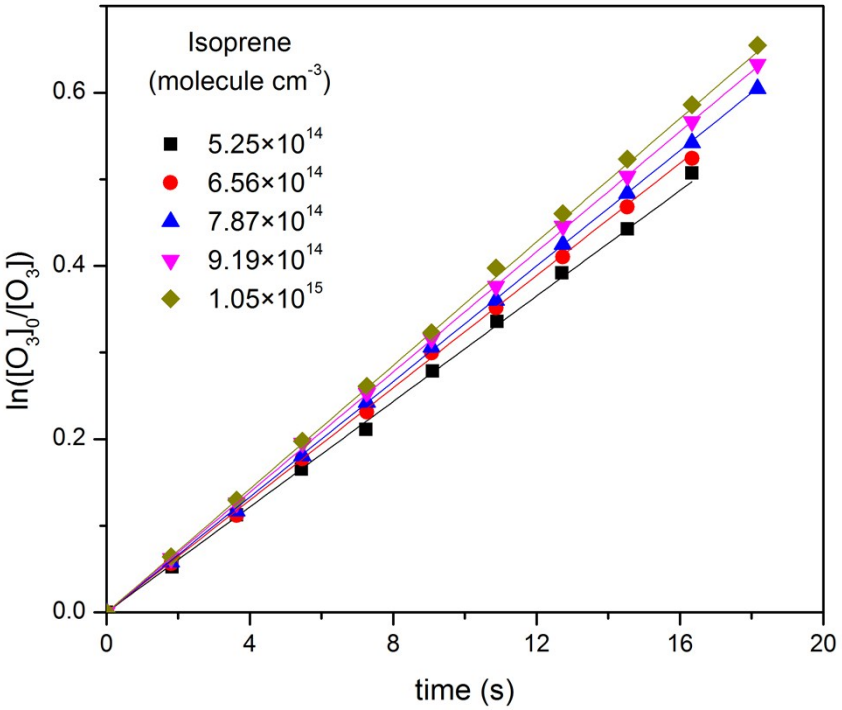

Isoprene
(molecule cm-3)
5.25×10^14
6.56×10^14
7.87×10^14
9.19×10^14
1.05×10^15
ln([O3]0/[O3])
time (s)
0.0
0.2
0.4
0.6
0
4
8
12
16
20

Fig. S4

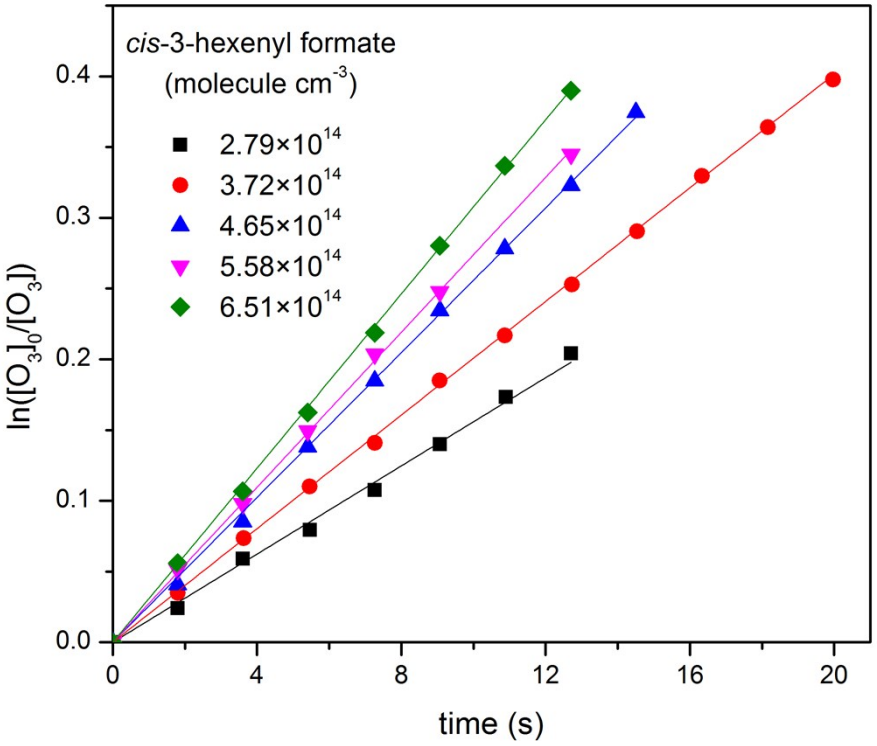

cis-3-hexenyl formate
(molecule cm-3)
2.79×10^14
3.72×10^14
4.65×10^14
5.58×10^14
6.51×10^14
ln([O3]0/[O3])
time (s)
0.0
0.1
0.2
0.3
0.4
0
4
8
12
16
20

Fig. S5

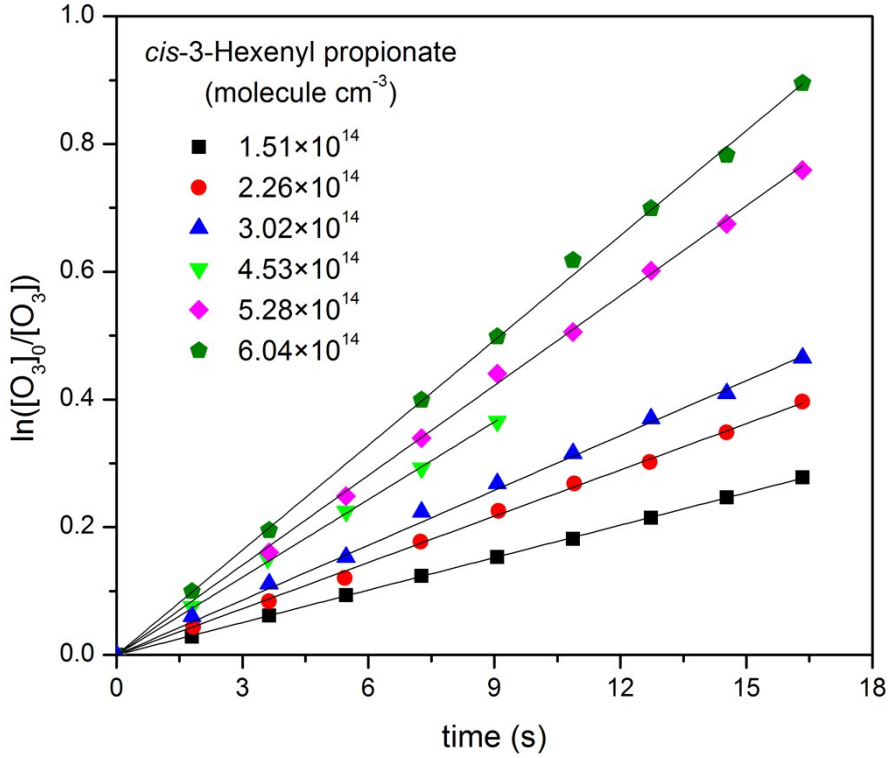

cis-3-Hexenyl propionate
(molecule cm-3)
1.51×10^14
2.26×10^14
3.02×10^14
4.53×10^14
5.28×10^14
6.04×10^14
ln([O3]0/[O3])
time (s)
0.0
0.2
0.4
0.6
0.8
1.0
0
3
6
9
12
15
18

Fig.S6

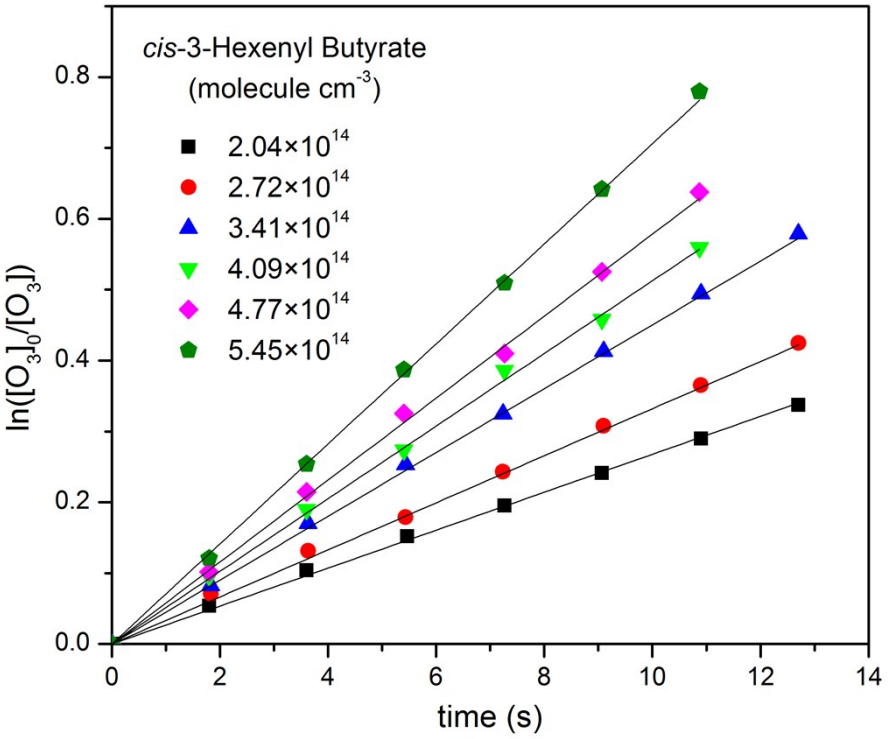

cis-3-Hexenyl Butyrate
(molecule cm-3)
2.04×10^14
2.72×10^14
3.41×10^14
4.09×10^14
4.77×10^14
5.45×10^14
ln([O3]0/[O3])
time (s)
0.0
0.2
0.4
0.6
0.8
0
2
4
6
8
10
12
14

Fig. S7

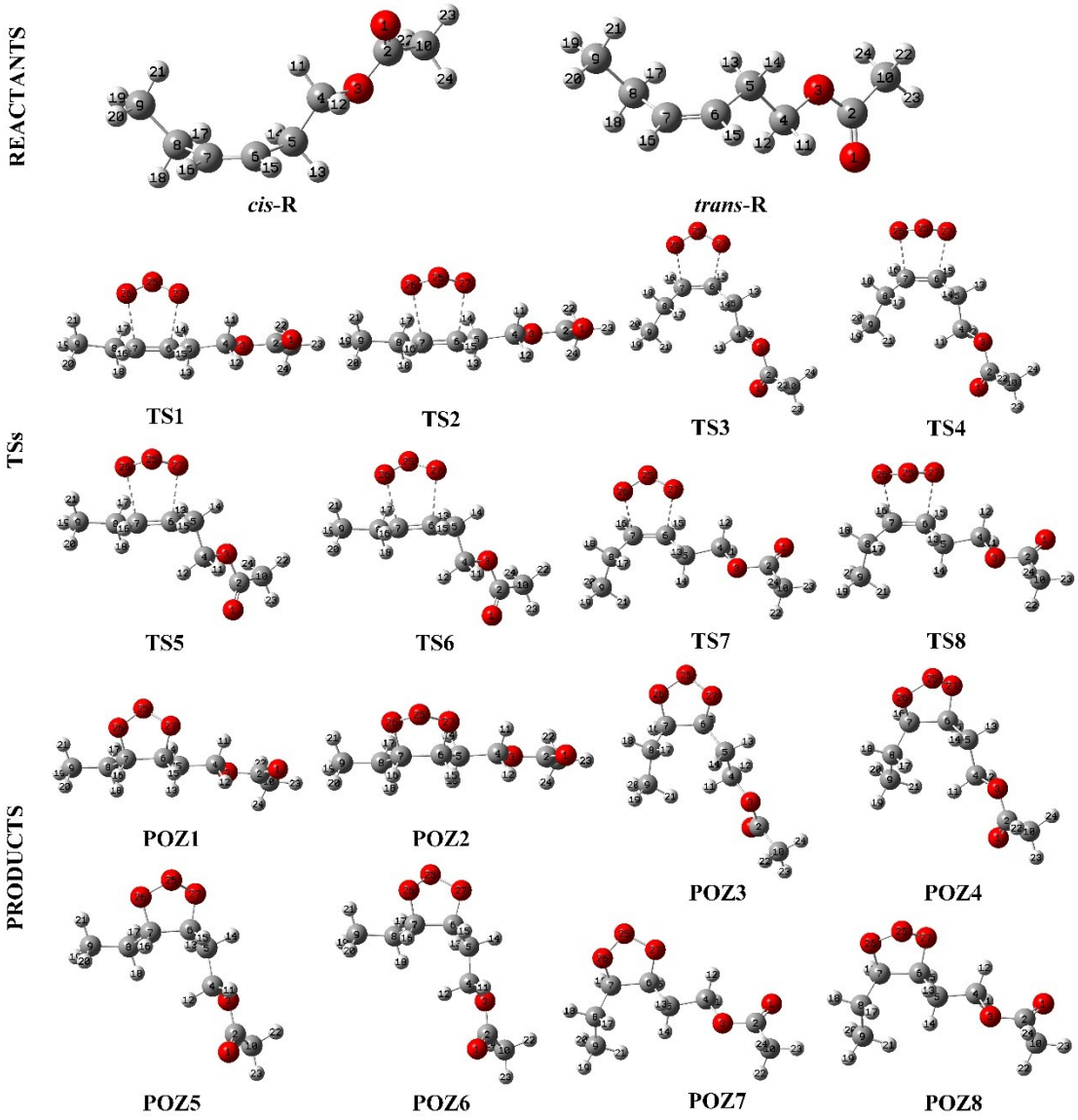

REACTANTS
cis-R
trans-R
TSs
TS1
TS2
TS3
TS4
TS5
TS6
TS7
TS8
PRODUCTS
POZ1
POZ2
POZ3
POZ4
POZ5
POZ6
POZ7
POZ8

Fig.S8

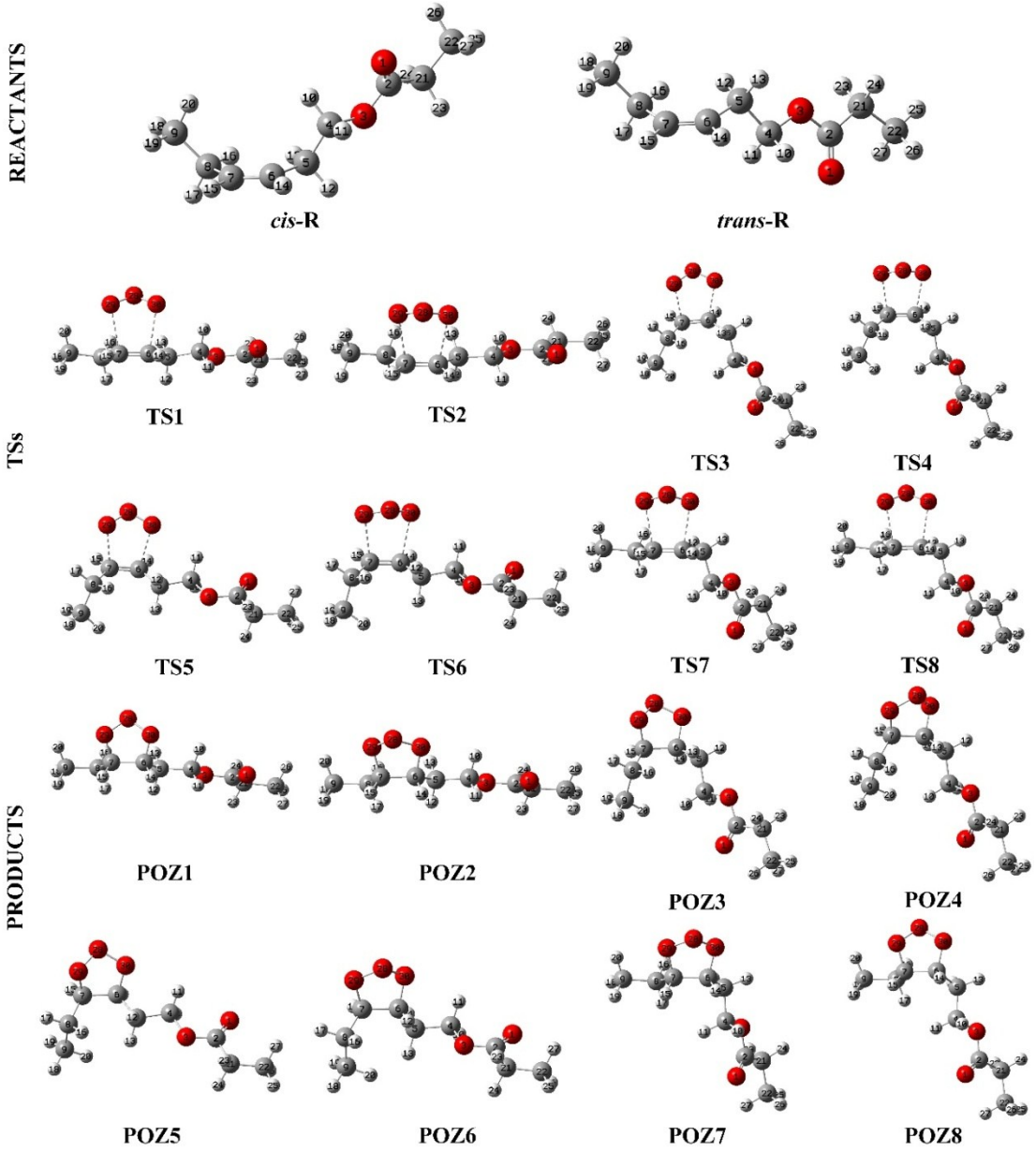

REACTANTS
cis-R
trans-R
TSs
TS1
TS2
TS3
TS4
TS5
TS6
TS7
TS8
PRODUCTS
POZ1
POZ2
POZ3
POZ4
POZ5
POZ6
POZ7
POZ8

Fig.S9

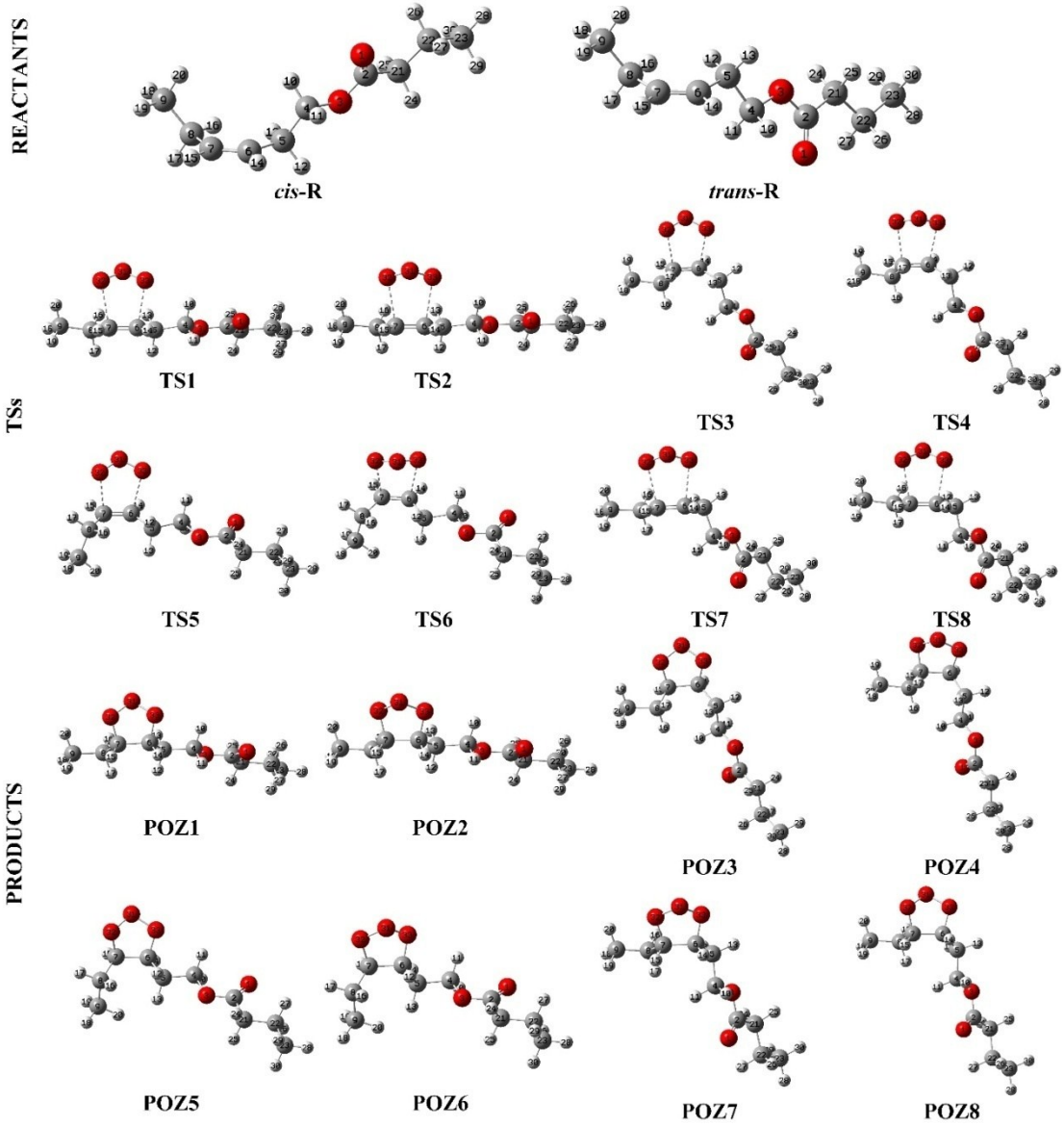

REACTANTS
cis-R
trans-R
TSs
TS1
TS2
TS3
TS4
TS5
TS6
TS7
TS8
PRODUCTS
POZ1
POZ2
POZ3
POZ4
POZ5
POZ6
POZ7
POZ8

Fig.S10

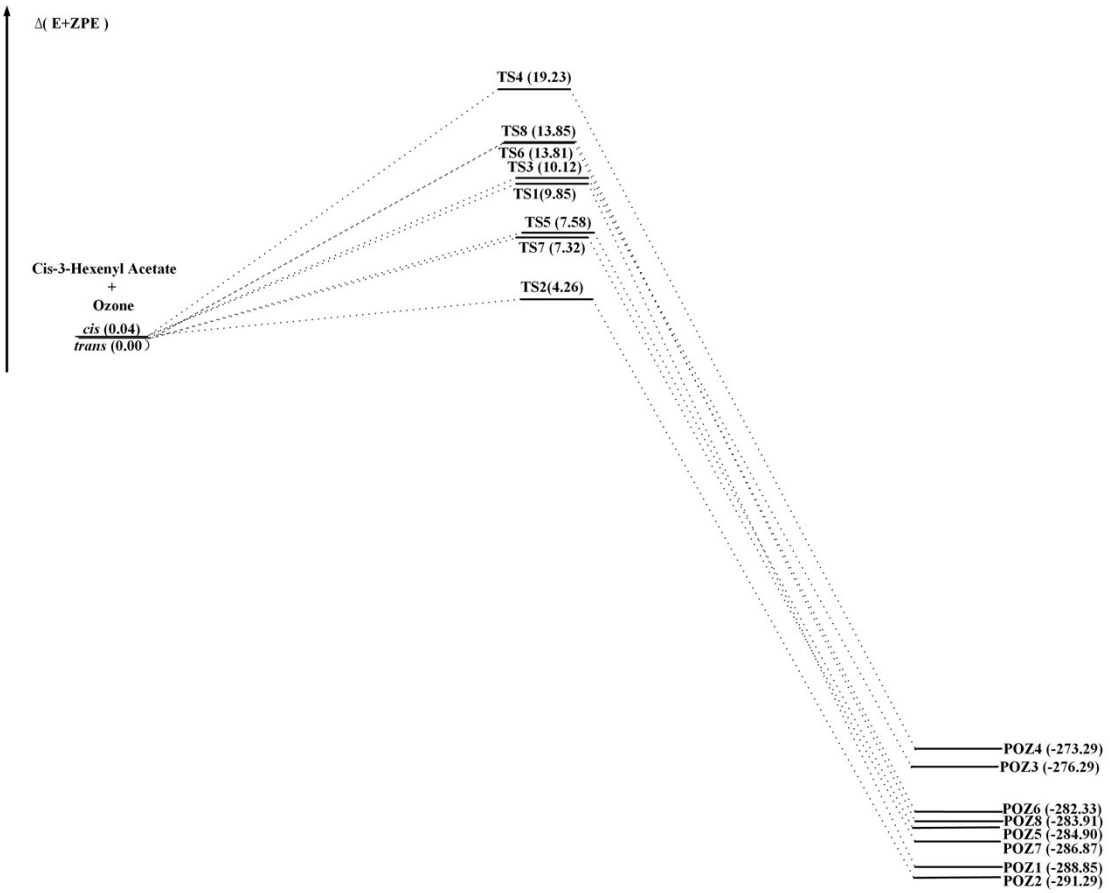

Δ(E+ZPE)
TS4 (19.23)
TS8 (13.85)
TS6 (13.81)
TS3 (10.12)
TS1(9.85)
TS5 (7.58)
TS7 (7.32)
TS2(4.26)
Cis-3-Hexenyl Acetate
+
Ozone
cis (0.04)
trans (0.00)
POZ4 (-273.29)
POZ3 (-276.29)
POZ6 (-282.33)
POZ8 (-283.91)
POZ5 (-284.90)
POZ7 (-286.87)
POZ1 (-288.85)
POZ2 (-291.29)

Fig.S11

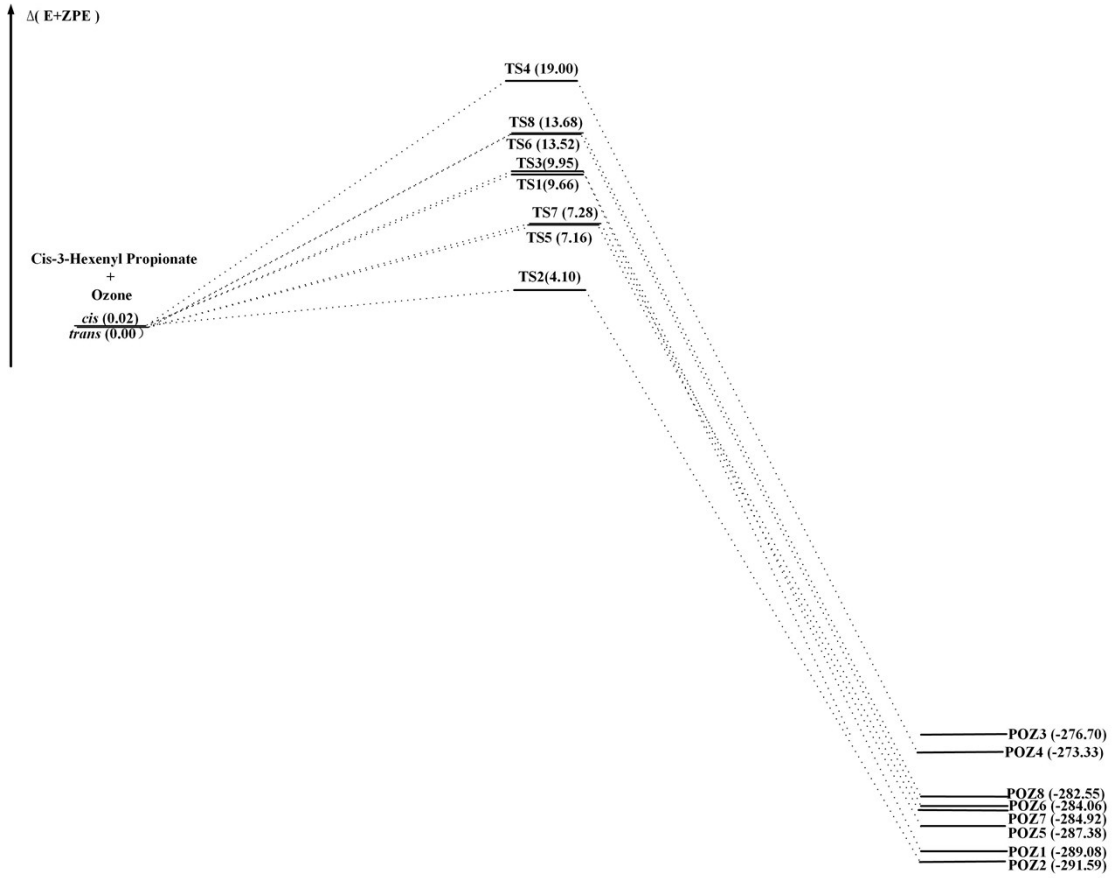

Δ(E+ZPE)
Cis-3-Hexenyl Propionate
+
Ozone
cis (0.02)
trans (0.00)
TS4 (19.00)
TS8 (13.68)
TS6 (13.52)
TS3(9.95)
TS1(9.66)
TS7 (7.28)
TS5 (7.16)
TS2(4.10)
POZ3 (-276.70)
POZ4 (-273.33)
POZ8 (-282.55)
POZ6 (-284.06)
POZ7 (-284.92)
POZ5 (-287.38)
POZ1 (-289.08)
POZ2 (-291.59)

Fig.S12

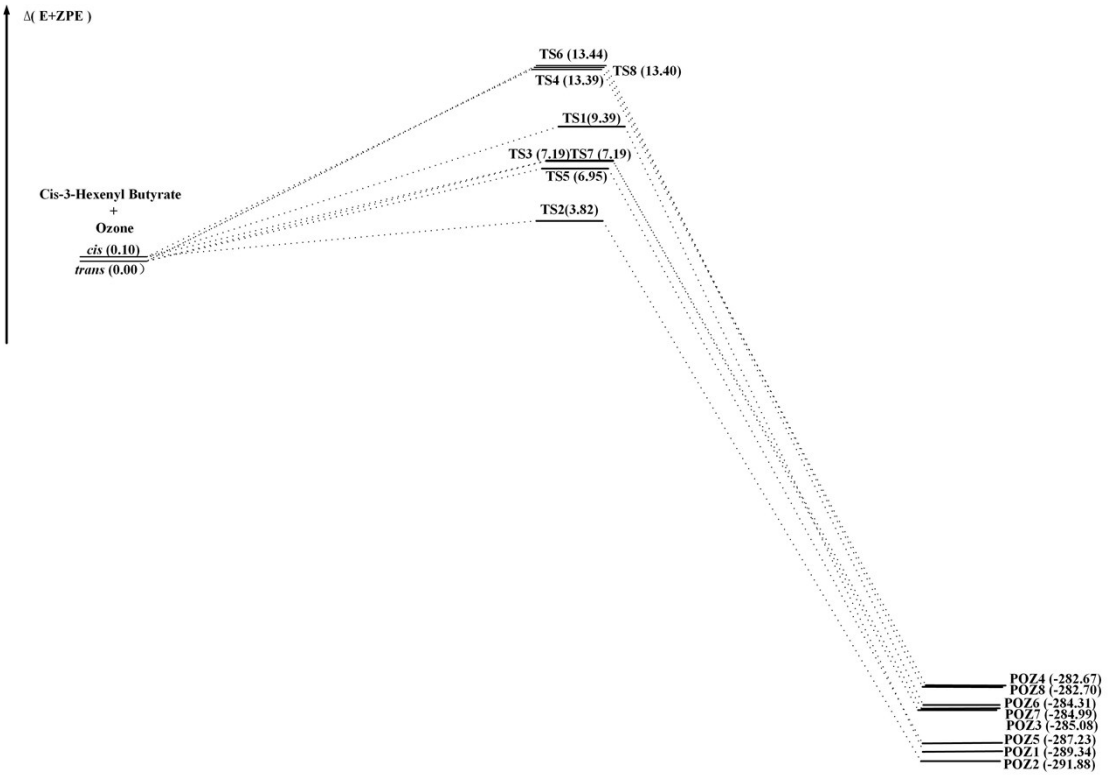


Table S1 The HOMO energies of the unsaturated esters and the parent hexene calculated at HF/6-31G** level of theory.

Compounds	HOMO energies
cis-3-hexenyl formate	-0.35465 Hartree (-9.65052 ev)
cis-3-hexenyl acetate	-0.35205 Hartree (-9.57977 ev)
cis-3-hexenyl propionate	-0.35174 Hartree (-9.57133 ev)
cis-3-hexenyl butyrate	-0.35159 Hartree (-9.56725 ev)
cis-3-hexene	-0.34030 Hartree (-9.26003 ev)