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Supplement of

Atmospheric chemistry, sources and sinks of carbon suboxide, C_3O_2

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1. Theoretical studies of additional reactions in the O_3-initiated oxidation of C_3O_2

As discussed in the main text, the primary ozonide (POZ) formed after O_3 addition on carbon suboxide was found to decompose either to an OOCCO Criegee intermediate + CO_2, or to a cyclic CO_2 dimer **INT1** + CO. The transition state for this later channel is intriguing, as its geometry resembles that expected for the formation of the OOCO Criegee intermediate (**INT2**, Figure S1) with coproduct moiety O=C=C=O readily falling apart to 2 CO. Minimum energy pathway (IRC) calculations, however, indicate that during the dissociation process, only one CO is formed, while the remaining OC(OO)CO moiety rearranges to **INT1**. Figure S2 shows an animation of this process. It is currently not clear if this reaction path is affected by the methodology used; conceivably, the post-TS pathway bifurcates towards the formation of the **OOCO** (**INT2**) carbonyl oxide. We have additionally characterized a Criegee intermediate **INT3**, where the cyclization process forms a ring structure with the C-O moiety rather than the C-O-O moiety of the original POZ cyclic trioxilane decomposition.

Though we were unable to find formation pathways for these Criegee intermediates (CI), we would like to briefly summarize some additional information on these carbon oxides. **INT3**, an isomer of the **POZ**, was found to be only 7.8 kcal mol^{-1} more stable than the POZ; compared to the exoergicity of as high as 72 kcal mol^{-1} for the main pathways leading to **INT1** + CO or **OOCCO** + CO_2 from this **POZ**, this suggest a high, non-competitive barrier for formation of **INT3**. The CI **INT2** was found not to be a stable minimum at the chosen level of theory, and cyclises without barrier to the O_2CO dioxirane. This dioxirane can open the three-membered ring forming the singlet bisoxy $OC(O^{\bullet})O^{\bullet}$. We have also characterized a triplet bisoxy $OC(O^{\bullet})O^{\bullet}$, 8.7 kcal mol^{-1} less stable than the singlet bisoxy, which is accessible through an intersystem crossing (ISC) in the dioxirane, analogous to channels characterized in β-pinene and β-caryophellene ozonolysis [Nguyen et al., 2009; Nguyen et al., 2009]. CO_3 carbon trioxides are expected to ultimately fall apart to CO + O_2 or CO_2 + O, subject to spin conservation rules; Table SI-1 lists the relative energies obtained at the M05-2X level of theory. Carbon trioxide has been experimentally observed, and is proposed to play a role in quenching of excited oxygen, as well as affecting isotope ratios in CO and CO_2. For more information on these aspects, we refer to existing theoretical and experimental work, including Kaiser and Mebel [2008], Jamieson et al. [2006], Kowalczyk and Krylov [2007], Liu et al. [2009], and references therein.

Table S1: Relative energies of [CO_3] isomers and fragments at the M05-2X/aug-cc-pVTZ level of theory

Compound	Relative energy (kcal mol^{-1})
OOCO Criegee intermediate	(unstable)
O_2CO dioxirane	0.0
$OC(O^{\bullet})O^{\bullet}$ singlet bisoxy	7.6
$OC(O^{\bullet})O^{\bullet}$ triplet bisoxy	16.3
$CO + {}^1O_2$	44.8
$CO + {}^3O_2$	4.8
$CO_2 + {}^1O$	58.9
$CO_2 + {}^3O$	-4.1

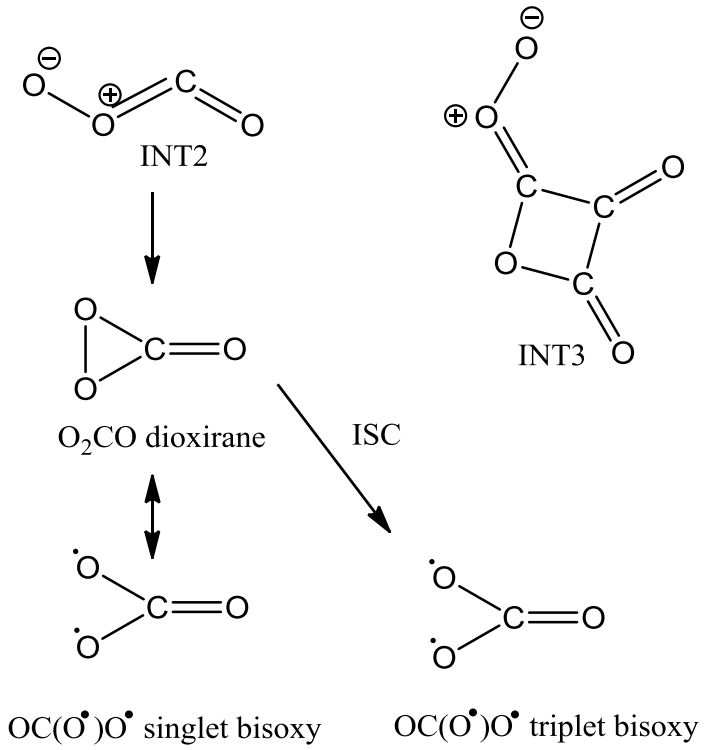


Figure S1: Exotic carbon oxides of potential interest in the ozonolysis of carbon suboxide

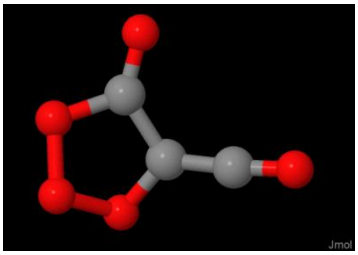
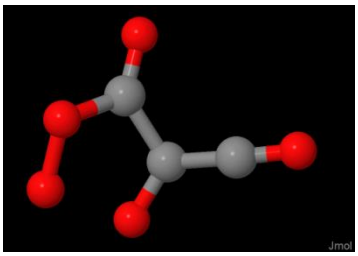
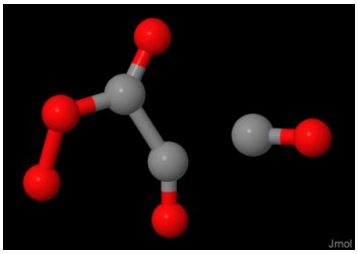
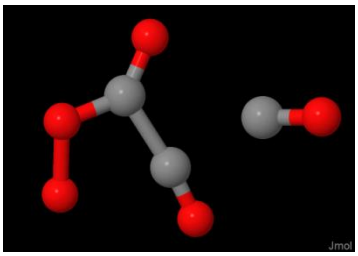
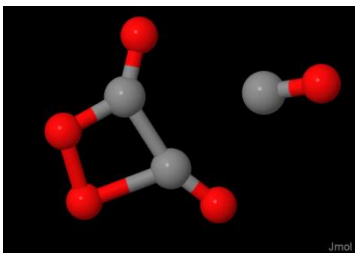
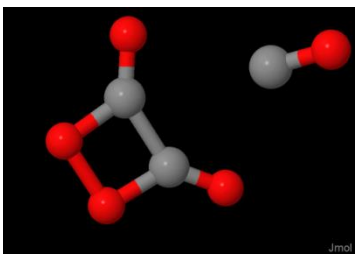
	Early in the reaction, here at -7.865 Å·amu$^{1/2}$ before the TS, the intermediate has a structure similar to most primary ozonides.
	At -1.973 Å·amu$^{1/2}$ before the TS, the O–O bond is breaking, and both the C–C bonds are elongating, where the exocyclic C–C bond elongates more.
	After the TS (here at +3.495 Å·amu$^{1/2}$) the exocyclic C–C bond is breaking, while the endocyclic C–C bond elongates slightly more, but not to the point of breaking.
	Subsequently, at +5.895 Å·amu$^{1/2}$ past the TS, the oxygen atom in the ozone carbonyl group migrates to the other side of the carbon, while the oxide attacks the central carbon.
	At +7.895 Å·amu$^{1/2}$ past the TS, the structure starts to form a new cyclic peroxide bond. The endocyclic C–C bond is strongly elongated (1.62 Å), but does not break along the minimum energy path.
	Finally, a cyclic peroxide diketone is formed, with a CO co-product.

Figure S2: Animation of the formation of INT1 + CO from the decomposition of POZ

2. Theoretical studies on additional reactions in the OH-initiated oxidation of C_3O_2

As discussed in the main text, **INT2** has a mobile hydrogen that can migrate to the radical peroxy site, forming a transient hydroperoxide acyloxy intermediate **INT5**. At the M05-2X level of theory, **INT5** is not a potential energy minimum; **INT5** thus isomerizes back to **INT2** without a barrier. **INT5** can cyclise to **INT6** (see Figure S3), with a barrier of 21.8 kcal mol^{-1}. **INT6** is isoenergetic with **INT5**, and can readily eliminate the OH radical [Vereecken et al., 2004] with a barrier of only 3.3 kcal mol^{-1} at the M05-2X level of theory, forming the cyclic carbon oxide, **INT7**, 22.7 kcal mol^{-1} more stable than **INT6**. **INT7** readily dissociates into CO_2 + 2 CO, exoergic by 38.1 kcal mol^{-1}.

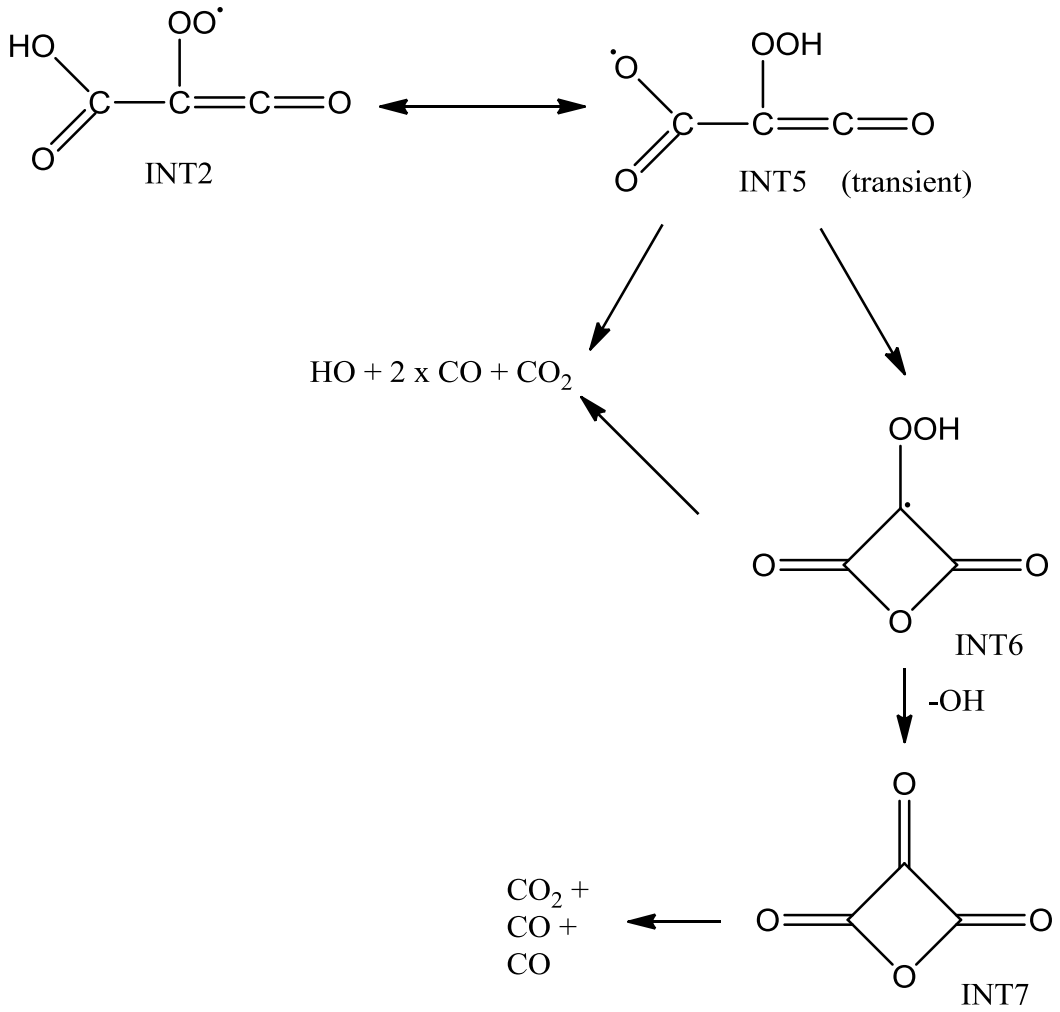


Figure S3: Formation of hydroperoxide and carbon oxide intermediates from INT5

INT4, a carboxylic acid acylperoxy radical, can undergo a 1,6-H-migration with a barrier of 33.1 kcal mol^{-1}, leading directly to HO_2 elimination and cyclisation to **INT7** (see Figure S4).

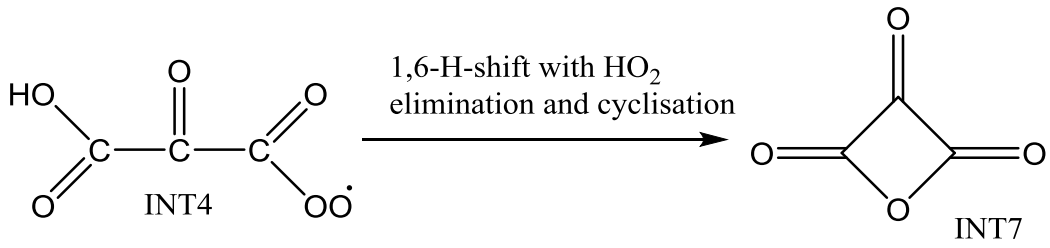


Figure S4: H-migration in INT4

Finally, CO elimination in the HOOC-C•=O acyl radical formed from **INT4** was calculated to have a 10.3 kcal mol^{-1} barrier (M05-2X), forming HOCO + CO.

3. IR spectrum of C_3O_2

Figure S5 shows the IR spectrum between 700 cm^{-1} and 2500 cm^{-1}. A known pressure of C_3O_2 (+ CO_2 impurity) was introduced into the cell and the CO_2 impurity was subsequently determined from its (calibrated) absorption features close to 2350 cm^{-1} (see inset). The absolute absorption cross-section $\sigma(\upsilon)$ at the maximum of the $\upsilon 3$ asymmetric stretch (feature at ~2262 cm^{-1}) was obtained using the Beer-Lambert law for absorbance (A) by varying the pressure of the mixture, combining the change of concentrations $[C_3O_2]$ obtained from the ideal gas law and the concomitant measured change in intensity I, for the known path length l :

$$A = \log\left(\frac{I_0}{I}\right) = \sigma(\upsilon)\cdot[C_3O_2]\cdot l$$

The cross section at 2262.4 cm^{-1} was $(3.7 \pm 0.5) \times 10^{-18}$ cm^2 $molecule^{-1}$. The errors combine the 2 σ standard deviation of the Beer-Lambert plot with uncertainty in the optical path-length (2900 ± 200 cm).

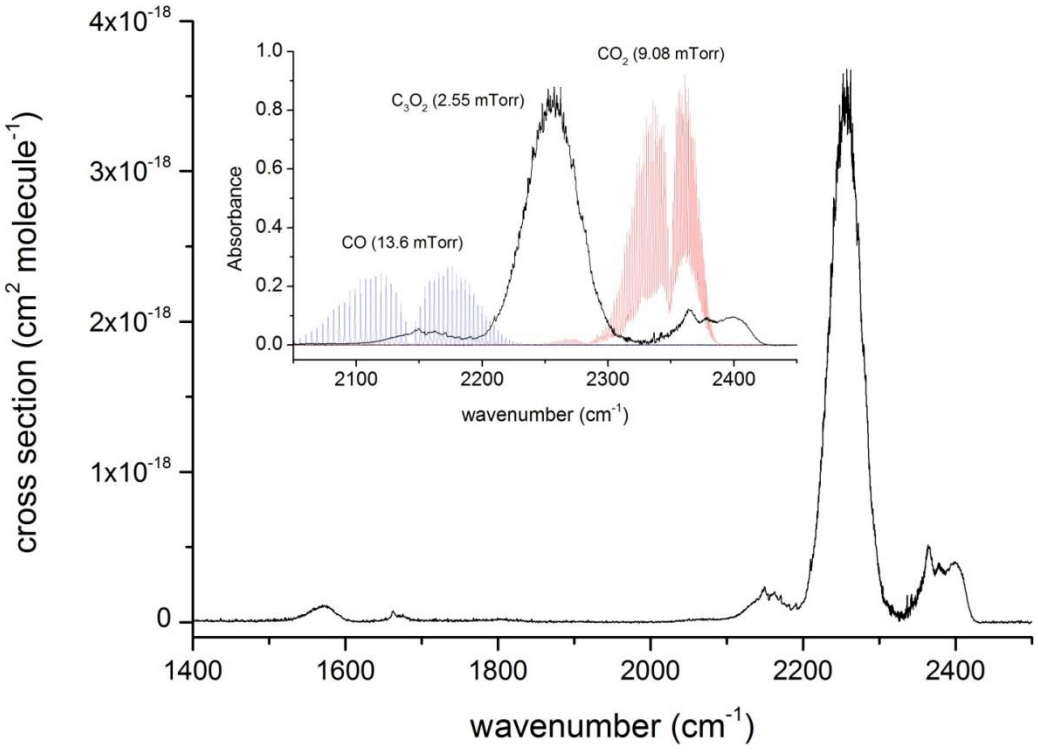


Figure S5: Infra-red absorption spectrum (0.5 cm^{-1} resolution of C_3O_2, between 1400 and 2400 cm^{-1}. The insert displays spectra of CO and CO_2 measured by the same instrument at the same resolution.

4. UV spectrum of C_3O_2

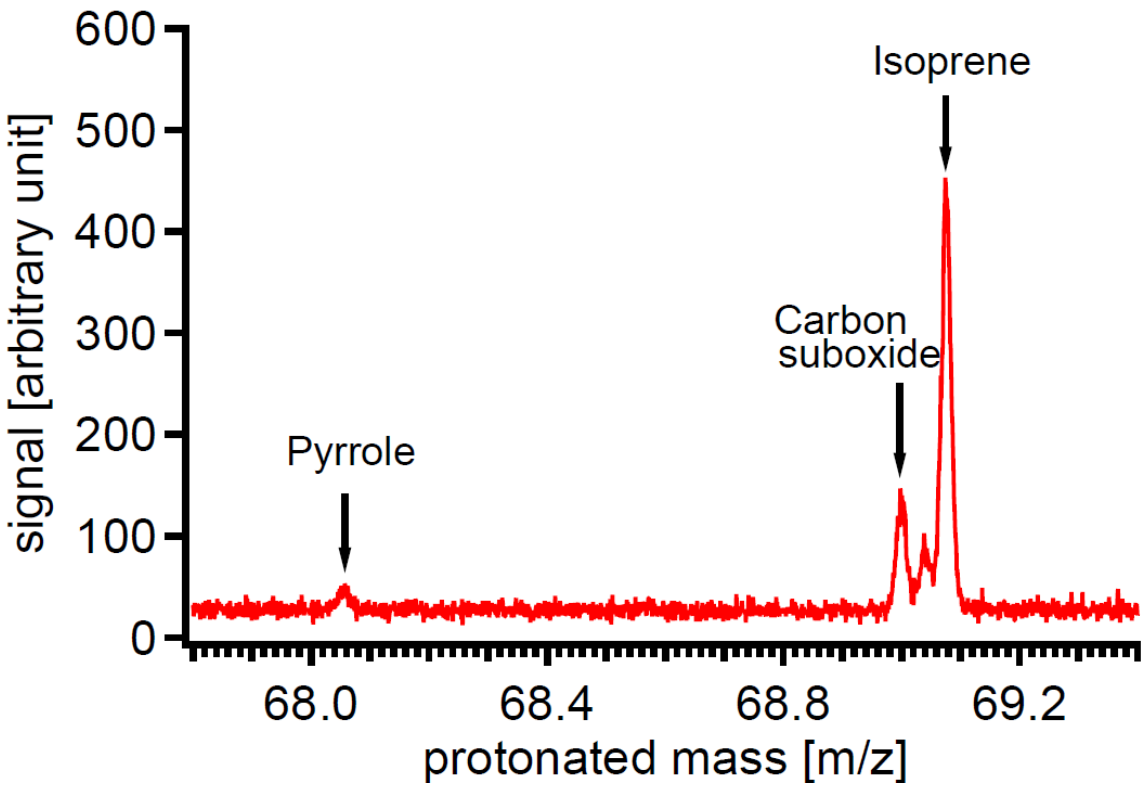
Table S2: Wavelength-dependent UV absorption cross sections $\sigma(\upsilon)$, prior to scaling by 1.17 (see main text).

Wavelength υ (nm)	Cross section $\sigma(\upsilon)$ (cm^2)
230	7.10E-020
231	7.05E-020
232	7.20E-020
233	7.34E-020
234	7.49E-020
235	7.82E-020
236	8.02E-020
237	8.50E-020
238	9.03E-020
239	9.56E-020
240	1.01E-019
241	1.09E-019
242	1.16E-019
243	1.25E-019
244	1.34E-019
245	1.43E-019
246	1.53E-019
247	1.64E-019
248	1.75E-019
249	1.85E-019
250	1.97E-019
251	2.08E-019
252	2.19E-019
253	2.29E-019
254	2.40E-019
255	2.49E-019
256	2.59E-019
257	2.68E-019
258	2.76E-019
259	2.83E-019
260	2.90E-019
261	2.93E-019
262	2.97E-019
263	2.99E-019
264	3.02E-019
265	3.00E-019
266	3.00E-019
267	3.02E-019

268	2.96E-019
269	2.89E-019
270	2.84E-019
271	2.79E-019
272	2.70E-019
273	2.62E-019
274	2.55E-019
275	2.45E-019
276	2.34E-019
277	2.24E-019
278	2.11E-019
279	1.99E-019
280	1.88E-019
281	1.75E-019
282	1.64E-019
283	1.51E-019
284	1.39E-019
285	1.28E-019
286	1.17E-019
287	1.06E-019
288	9.56E-020
289	8.50E-020
290	7.49E-020
291	6.67E-020
292	5.94E-020
293	5.12E-020
294	4.47E-020
295	3.85E-020
296	3.27E-020
297	2.80E-020
298	2.41E-020
299	2.06E-020
300	1.74E-020
301	1.47E-020
302	1.24E-020
303	1.05E-020
304	8.84E-021
305	7.49E-021
306	6.28E-021
307	5.31E-021
308	4.49E-021
309	3.77E-021

5. Extended Mass Spectrum

Shown below is an extended mass spectrum taken from data collected in summer 2014 on the island of Cyprus. In this data section isoprene was 35 ppt. Protonated ^{15}N pyrrole would appear at a m/z of 69.0465, where it would be expected to interfere with identification and signal allocation of the furan peak, however, is sufficiently removed from the C_3O_2 peak to allow spectral resolution. The appearance of an organic molecule with a ^{13}C isotopic contribution significant enough to observe on m/z 69 would be accompanied by a large signal on m/z 68 , which was not observed during the period over which the measurements of C_3O_2 were made in either Mainz or Cyprus. A third campaign dataset was examined from data taken on-board a ship off the coast of Peru but no C_3O_2 peak was found.



6. Additional references

C. S. Jamieson, A. M. Mebel, and R. I. Kaiser, *ChemPhysChem*, 2006, **7**, 2508–2513.

R. I. Kaiser and A. M. Mebel, *Chem. Phys. Lett.*, 2008, **465**, 1–9.

T. Kowalczyk and A. I. Krylov, *J. Phys. Chem. A*, 2007, **111**, 8271–8276.

Y. Liu, I. B. Bersuker, W. Zou, and J. E. Boggs, *J. Chem. Theory Comput.*, 2009, **5**, 2679–2686.

T. L. Nguyen, J. Peeters, and L. Vereecken, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5643–5656.

T. L. Nguyen, R. Winterhalter, G. Moortgat, B. Kanawati, J. Peeters, and L. Vereecken, *Phys. Chem. Chem. Phys.*, 2009, **11**, 4173–4183.

L. Vereecken, T.L. Nguyen, I. Hermans, and J. Peeters, *Chem. Phys. Lett.*, 2004, **393**, 432–436.

7. Quantum chemical data of key intermediates

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Reactants and products
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C3O2
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E(CBS-QB3) excl. ZPE (Hartree): -264.38987700
E(CBS-QB3) inc. ZPE scaled by 0.99 (Hartree): -264.36798900
E(CCSD(T)/6-31+(d')) (Hartree): -264.06549681
E(CCSD/6-31+(d')) (Hartree): -264.02769191
E(MP2/6-31+(d')) (Hartree): -264.03668222
E(MP2/CBSB3) (Hartree): -264.26608000
E(MP2/CBSB4) (Hartree): -264.03668222
E(MP3/6-31+(d')) (Hartree): -264.01395709
E(MP3/CBSB4) (Hartree): -264.01395709
E(RHF/6-31+(d')) (Hartree): -263.28791251
E(RHF/CBSB3) (Hartree): -263.37184480
E(RHF/CBSB4) (Hartree): -263.28791251
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -264.78960726
E(RHF-RCCSD(T)/AUG-CC-PVTZ) (Hartree): -264.32533799
E(RHF-RCCSD-T/AUG-CC-PVTZ) (Hartree): -264.32404520
E(RHF-RCCSD/AUG-CC-PVTZ) (Hartree): -264.27234246
     T1 diagnostic:  0.019782
     D1 diagnostic:  0.054354
E(RHF-RCCSD[T]/AUG-CC-PVTZ) (Hartree): -264.32902507
E(RHF-RMP2/AUG-CC-PVTZ) (Hartree): -264.29154155
     T1 diagnostic:  0.000002
E(RHF/AUG-CC-PVTZ) (Hartree): -263.37981258
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -264.78960726
Electronic state : 1-A
Cartesian coordinates (Angs):
     O       2.372636     -0.163764      -0.000356
     C       1.242104      0.046405       0.000806
     C       0.000012      0.343902      -0.000694
     C      -1.242094      0.046383       0.000870
     O      -2.372653     -0.163753      -0.000381
Rotational constants (GHz):  217.0150500    2.3277300    2.3030300
Vibrational harmonic frequencies (cm-1):
       64.6851                  600.9569                  602.8097
      611.3618                  613.6522                  858.2136
     1665.6088                 2314.9103                 2372.6011
Zero-point correction (Hartree): 0.022109

E(CBS-QB3) excl. ZPE (Hartree): -264.39061500
E(CBS-QB3) inc. ZPE scaled by 0.99 (Hartree): -264.36914300
E(CCSD(T)/6-31+(d')) (Hartree): -264.06711993
E(CCSD/6-31+(d')) (Hartree): -264.02854532
E(MP2/6-31+(d')) (Hartree): -264.03927171
E(MP2/CBSB3) (Hartree): -264.26825648
E(MP2/CBSB4) (Hartree): -264.03927171
E(MP3/6-31+(d')) (Hartree): -264.01396886
E(MP3/CBSB4) (Hartree): -264.01396886
E(RB+HF-LYP/CBSB7) (Hartree): -264.79974722
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E(RHF/6-31+(d')) (Hartree): -263.28636466
E(RHF/CBSB3) (Hartree): -263.36907337
E(RHF/CBSB4) (Hartree): -263.28636466
Electronic state : 1-A
Cartesian coordinates (Angs):
     O       0.000006     -0.004947      -2.433162
     C       0.000003     -0.002282      -1.272503
     C       0.000000      0.000276       0.000000
     C      -0.000003      0.002642       1.272503
     O      -0.000006      0.004470       2.433163

C3O2 triplet
------------
E(RHF-RMP2/AUG-CC-PVTZ) (Hartree): -264.15962242
     T1 diagnostic:  0.000731
E(RHF-UCCSD(T)/AUG-CC-PVTZ) (Hartree): -264.20379269
E(RHF-UCCSD-T/AUG-CC-PVTZ) (Hartree): -264.20258689
E(RHF-UCCSD/AUG-CC-PVTZ) (Hartree): -264.15517788
     T1 diagnostic:  0.027369
     D1 diagnostic:  0.092447
E(RHF-UCCSD[T]/AUG-CC-PVTZ) (Hartree): -264.20775759
E(ROHF/AUG-CC-PVTZ) (Hartree): -263.27458829
E(UM052X/Aug-CC-pVTZ) (Hartree): -264.66619064
Electronic state : 3-A
Cartesian coordinates (Angs):
     O      -2.338178     -0.185715      -0.080844
     C      -1.202766      0.021278       0.041668
     C       0.024409      0.323067       0.243509
     C       1.348037      0.402629      -0.213613
     O       2.210918     -0.374516       0.027171
Rotational constants (GHz):   68.3436200    2.4509100    2.3974000
Vibrational harmonic frequencies (cm-1):
       88.0459                  164.0693                  463.1294
      510.3575                  588.2619                  845.8857
     1514.8005                 1814.5276                 2195.1010
Zero-point correction (Hartree): 0.018645

C2O singlet
-----------
E(RHF-RCCSD(T)/AUG-CC-PVTZ) (Hartree): -150.99526585
E(RHF-RCCSD-T/AUG-CC-PVTZ) (Hartree): -150.99454562
E(RHF-RCCSD/AUG-CC-PVTZ) (Hartree): -150.96813741
     T1 diagnostic:  0.020967
     D1 diagnostic:  0.057794
E(RHF-RCCSD[T]/AUG-CC-PVTZ) (Hartree): -150.99719675
E(RHF-RMP2/AUG-CC-PVTZ) (Hartree): -150.95258576
     T1 diagnostic:  0.000003
E(RHF/AUG-CC-PVTZ) (Hartree): -150.46069044
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -151.25434943
Point group : C*V
Cartesian coordinates (Angs):
     C       0.000000      0.000000      -1.409976
     C       0.000000      0.000000      -0.057411
     O       0.000000      0.000000       1.100540
Rotational constants (GHz):    0.0000000   11.6799902   11.6799902
Vibrational harmonic frequencies (cm-1):
      363.8908 (  PI)           503.1104 (  PI)          1145.5168 (  SG)
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     2103.9533 (  SG)
Zero-point correction (Hartree): 0.009378

C2O triplet
-----------
E(RHF-RMP2/AUG-CC-PVTZ) (Hartree): -150.99056601
     T1 diagnostic:  0.000770
E(RHF-UCCSD(T)/AUG-CC-PVTZ) (Hartree): -151.02626196
E(RHF-UCCSD-T/AUG-CC-PVTZ) (Hartree): -151.02565120
E(RHF-UCCSD/AUG-CC-PVTZ) (Hartree): -151.00102683
     T1 diagnostic:  0.026743
     D1 diagnostic:  0.059946
E(RHF-UCCSD[T]/AUG-CC-PVTZ) (Hartree): -151.02831803
E(ROHF/AUG-CC-PVTZ) (Hartree): -150.51079078
E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -151.29719327
Point group : C*V
Electronic state : 3-SG
Cartesian coordinates (Angs):
     C       0.000000      0.000000      -1.405483
     C       0.000000      0.000000      -0.057214
     O       0.000000      0.000000       1.097023
Rotational constants (GHz):    0.0000000   11.7548852   11.7548852
Vibrational harmonic frequencies (cm-1):
      441.8766 (  PI)           441.8766 (  PI)          1159.3407 (  SG)
     2108.8195 (  SG)
Zero-point correction (Hartree): 0.009459

CO
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E(RHF-RCCSD(T)/AUG-CC-PVTZ) (Hartree): -113.16162782
E(RHF-RCCSD-T/AUG-CC-PVTZ) (Hartree): -113.16111424
E(RHF-RCCSD/AUG-CC-PVTZ) (Hartree): -113.14434062
     T1 diagnostic:  0.017784
     D1 diagnostic:  0.036961
E(RHF-RCCSD[T]/AUG-CC-PVTZ) (Hartree): -113.16299731
E(RHF-RMP2/AUG-CC-PVTZ) (Hartree): -113.14163315
     T1 diagnostic:  0.000001
E(RHF/AUG-CC-PVTZ) (Hartree): -112.78228285
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -113.34670612
Point group : C*V
Electronic state : 1-SG
Cartesian coordinates (Angs):
     C       0.000000      0.000000      -0.639983
     O       0.000000      0.000000       0.479987
Rotational constants (GHz):    0.0000000   58.7652698   58.7652698
Vibrational harmonic frequencies (cm-1):
     2272.9043 (  SG)
Zero-point correction (Hartree): 0.005178

CO2
---
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -188.63868109
Point group : D*H
Electronic state : 1-SGG
Cartesian coordinates (Angs):
     O       0.000000      0.000000       1.154715
     C       0.000000      0.000000       0.000000
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     O       0.000000      0.000000      -1.154715
Rotational constants (GHz):    0.0000000   11.8482842   11.8482842
Vibrational harmonic frequencies (cm-1):
      700.8860 ( PIU)           700.8860 ( PIU)          1407.2905 ( SGG)
     2433.2299 ( SGU)
Zero-point correction (Hartree): 0.011943

O3
--
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -225.45418490
Point group : C2V
Electronic state : 1-A1
Cartesian coordinates (Angs):
     O       0.000000      0.000000       0.420535
     O       0.000000      1.055249      -0.210267
     O       0.000000     -1.055249      -0.210267
Rotational constants (GHz):  119.1076900   14.1871500   12.6771500
Vibrational harmonic frequencies (cm-1):
      796.3874                1350.1808                1360.6626
Zero-point correction (Hartree): 0.007990

OH
--
E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree):  -75.75358072
Point group : C*V
Cartesian coordinates (Angs):
     O       0.000000      0.000000       0.107778
     H       0.000000      0.000000      -0.862222
Rotational constants (GHz):    0.0000000  566.5334585  566.5334585
Vibrational harmonic frequencies (cm-1):
     3779.9214 (  SG)
Zero-point correction (Hartree): 0.008611

O(3P)
-----
E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree):  -75.08477690
Point group : OH
Cartesian coordinates (Angs):
     O       0.000000      0.000000       0.000000
Zero-point correction (Hartree): 0.000000

O(1D)
-----
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree):  -74.98431530
Point group : OH
Cartesian coordinates (Angs):
     O       0.000000      0.000000       0.000000
Zero-point correction (Hartree): 0.000000

O2(3P)
------
E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -150.35976990
Point group : D*H
Electronic state : 3-SGG
Cartesian coordinates (Angs):
     O       0.000000      0.000000       0.593533
     O       0.000000      0.000000      -0.593533
```

Rotational constants (GHz):   0.0000000   44.8451832   44.8451832
Vibrational harmonic frequencies (cm-1):
     1753.7529 (SGG)
Zero-point correction (Hartree): 0.003995

O2(1D)

E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -150.29591782
Point group : D*H
Cartesian coordinates (Angs):
     O   0.000000   0.000000   0.593003
     O   0.000000   0.000000   -0.593003
Rotational constants (GHz):   0.0000000   44.9253902   44.9253902
Vibrational harmonic frequencies (cm-1):
     1741.1259 (SGG)
Zero-point correction (Hartree): 0.003967

HOCO

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -189.14863174
Point group : CS
Electronic state : 2-A'
Cartesian coordinates (Angs):
     O   1.148345   0.185221   0.000000
     C   0.000000   0.442142   0.000000
     O   -1.053748   -0.356563   0.000000
     H   -0.756778   -1.282110   0.000000
Rotational constants (GHz): 142.3028500   11.9151000   10.9945200
Vibrational harmonic frequencies (cm-1):
      591.1393 (A")   614.0118 (A')   1105.4733 (A')
     1301.4845 (A')   1910.6729 (A')   3674.9029 (A')
Zero-point correction (Hartree): 0.020954

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -189.15113553
Point group : CS
Electronic state : 2-A'
Cartesian coordinates (Angs):
     O   1.162028   0.259576   0.000000
     C   0.000000   0.405418   0.000000
     O   -0.936345   -0.546889   0.000000
     H   -1.805465   -0.134005   0.000000
Rotational constants (GHz): 170.9772600   11.5564600   10.8248000
Vibrational harmonic frequencies (cm-1):
      536.4657 (A")   634.6142 (A')   1108.3358 (A')
     1246.2075 (A')   1952.5643 (A')   3849.1180 (A')
Zero-point correction (Hartree): 0.021249

C3O2

E(RM062X/Aug-CC-pVTZ) (Hartree): -264.72392545
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -264.32521386
E(CCSD/Aug-CC-pVTZ) (Hartree): -264.27194567
     T1 diagnostic: 0.019926
E(MP2/Aug-CC-pVTZ) (Hartree): -264.29189277
E(MP3/Aug-CC-pVTZ) (Hartree): -264.26474687
E(RHF/Aug-CC-pVTZ) (Hartree): -263.37902445

```
Electronic state : 1-A
Cartesian coordinates (Angs):
     O       2.408714     -0.091822      -0.000039
     C       1.263275      0.026113       0.000103
     C       0.000000      0.192624       0.000031
     C      -1.263277      0.026131      -0.000177
     O      -2.408712     -0.091829       0.000071
Rotational constants (GHz):  691.0120700    2.2571400    2.2497900
Vibrational harmonic frequencies (cm-1):
       28.4329                590.6477                591.5180
      609.0874                610.3282                814.7058
     1683.2358               2320.3691               2387.5091
Zero-point correction (Hartree): 0.021952

OH
--
E(UM062X/Aug-CC-pVTZ) (Hartree):  -75.73381016
E(CCSD(T)/Aug-CC-pVTZ) (Hartree):  -75.64558436
E(CCSD/Aug-CC-pVTZ) (Hartree):  -75.63969620
     T1 diagnostic:  0.010031
E(MP2/Aug-CC-pVTZ) (Hartree):  -75.62633190
E(MP3/Aug-CC-pVTZ) (Hartree):  -75.63789728
E(PMP2/Aug-CC-pVTZ) (Hartree):  -75.62832220
E(PMP3/Aug-CC-pVTZ) (Hartree):  -75.63904001
E(PUHF/Aug-CC-pVTZ) (Hartree):  -75.42491597
E(UHF/Aug-CC-pVTZ) (Hartree):  -75.42156344
Point group : C*V
Cartesian coordinates (Angs):
     O       0.000000      0.000000       0.107984
     H       0.000000      0.000000      -0.863871
Rotational constants (GHz):    0.0000000  564.3727582  564.3727582
Vibrational harmonic frequencies (cm-1):
     3770.5842 (  SG)
Zero-point correction (Hartree): 0.008590

C3O2+OH inner addition
----------------------
E(UM062X/Aug-CC-pVTZ) (Hartree): -340.45861069
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -339.97355438
E(CCSD/Aug-CC-pVTZ) (Hartree): -339.91067611
     T1 diagnostic:  0.024647
E(MP2/Aug-CC-pVTZ) (Hartree): -339.91672514
E(MP3/Aug-CC-pVTZ) (Hartree): -339.89817582
E(PMP2/Aug-CC-pVTZ) (Hartree): -339.92109668
E(PMP3/Aug-CC-pVTZ) (Hartree): -339.90109557
E(PUHF/Aug-CC-pVTZ) (Hartree): -338.78298621
E(UHF/Aug-CC-pVTZ) (Hartree): -338.77703592
Electronic state : 2-A
Cartesian coordinates (Angs):
     O      -2.292337      0.814145       0.037618
     C      -1.202055      0.463551      -0.020145
     C       0.000024     -0.010744      -0.105198
     C       1.202142      0.463446      -0.020136
     O       2.292455      0.813951       0.037620
     O      -0.000185     -2.035201       0.135303
     H      -0.000124     -2.240685      -0.811454
Rotational constants (GHz):    5.1179600    2.4786600    1.6821600
```

```
Vibrational harmonic frequencies (cm-1):
     i301.4243                65.5767                101.3707
      109.2868               222.8245                573.9777
      579.2965               604.6385                606.1286
      735.6858               892.8511               1596.9408
     2295.2695              2308.5347               3800.7438
Zero-point correction (Hartree): 0.033018

C3O2+OH outer addition
----------------------
E(UM062X/Aug-CC-pVTZ) (Hartree): -340.45319282
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -339.96806786
E(CCSD/Aug-CC-pVTZ) (Hartree): -339.90436511
     T1 diagnostic:  0.029736
E(MP2/Aug-CC-pVTZ) (Hartree): -339.90632801
E(MP3/Aug-CC-pVTZ) (Hartree): -339.88942537
E(PMP2/Aug-CC-pVTZ) (Hartree): -339.91358111
E(PMP3/Aug-CC-pVTZ) (Hartree): -339.89444907
E(PUHF/Aug-CC-pVTZ) (Hartree): -338.77539878
E(UHF/Aug-CC-pVTZ) (Hartree): -338.76644124
Electronic state : 2-A
Cartesian coordinates (Angs):
     O      -2.073527     -0.872407      -0.165759
     C      -1.025831     -0.462269       0.055948
     C       0.221652     -0.286628       0.429847
     C       1.450184     -0.214047       0.060868
     O       2.571421     -0.142725      -0.189134
     O      -0.873135      1.505519      -0.149449
     H      -0.874107      1.854564       0.754759
Rotational constants (GHz):    8.3536600    2.1958300    1.7904700
Vibrational harmonic frequencies (cm-1):
     i437.8280                60.5555                 89.7801
      249.5496               350.7218                485.2900
      558.3783               596.2606                612.8247
      780.4953               848.6045               1603.3796
     2259.4923              2307.8823               3799.2978
Zero-point correction (Hartree): 0.033267

============================
Ozonolysis of carbon suboxide
============================
TS C3O2 + O3
------------
E(CBS-QB3) excl. ZPE (Hartree): -489.56836100
E(CBS-QB3) inc. ZPE scaled by 0.99 (Hartree): -489.53841600
E(CCSD(T)/6-31+(d')) (Hartree): -488.95336475
E(CCSD/6-31+(d')) (Hartree): -488.87595149
E(MP2/6-31+(d')) (Hartree): -488.90019375
E(MP2/CBSB3) (Hartree): -489.33841783
E(MP2/CBSB4) (Hartree): -488.90019375
E(MP3/6-31+(d')) (Hartree): -488.84038661
E(MP3/CBSB4) (Hartree): -488.84038662
E(RB+HF-LYP/CBSB7) (Hartree): -490.25135552
E(RHF/6-31+(d')) (Hartree): -487.49986657
E(RHF/CBSB3) (Hartree): -487.66219539
E(RHF/CBSB4) (Hartree): -487.49986657
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -490.22552155
```

```
Electronic state : 1-A
Cartesian coordinates (Angs):
     C       0.262934      1.212964       0.046060
     C      -0.552714      0.182662       0.110067
     C      -1.819563     -0.033168      -0.023057
     O       0.773354      2.240151       0.015747
     O      -2.934841     -0.274813      -0.128935
     O       1.984634     -0.206741      -0.021085
     O       0.391586     -1.500713       0.400525
     O       1.367274     -1.279728      -0.366055
Rotational constants (GHz):    3.0152300    1.7302900    1.1246600
Vibrational harmonic frequencies (cm-1):
     i460.6427                  67.5271                 106.3408
      128.4062                 181.1509                 283.6523
      504.6426                 528.6055                 606.7707
      625.3112                 632.0299                 793.6638
      896.2467                1162.5428                1225.9733
     1572.0273                2236.4663                2300.9583
Zero-point correction (Hartree): 0.031558

POZ
---
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -490.32826634
Electronic state : 1-A
Cartesian coordinates (Angs):
     C       0.560599      0.861639       0.054323
     C      -0.404646     -0.223355       0.180371
     C      -1.703643     -0.148099      -0.042704
     O       0.463911      2.040622       0.051853
     O      -2.837347     -0.056646      -0.164546
     O       1.779820      0.200869      -0.044912
     O       0.285025     -1.406969       0.383051
     O       1.469359     -1.145514      -0.369438
Rotational constants (GHz):    3.7377300    1.9088100    1.2991800
Vibrational harmonic frequencies (cm-1):
       93.6376                  140.6849                 232.2678
      378.5922                  455.1855                 513.5354
      570.0155                  676.5965                 733.9484
      745.3293                  792.0044                 902.2546
     1007.3939                 1055.4549                1242.2264
     1469.4376                 1920.2707                2291.8641
Zero-point correction (Hartree): 0.034675

TS POZ -> INT1 + CO
--------------------
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -490.29210402
Electronic state : 1-A
Cartesian coordinates (Angs):
     C      -0.504731      0.803132      -0.183980
     C       0.322973     -0.425351      -0.363746
     C       1.663497     -0.190850       0.218439
     O      -0.182247      1.935279      -0.365515
     O       2.773735     -0.074349       0.337633
     O      -1.587667      0.395590       0.521472
     O      -0.085796     -1.559828      -0.478377
     O      -2.029329     -0.836890       0.231752
Rotational constants (GHz):    3.6526200    1.7870100    1.2946000
```

Vibrational harmonic frequencies (cm-1):

i203.0082	87.6106	108.8308
203.6738	235.7746	379.1266
406.4341	470.8758	548.9478
658.6516	725.7992	770.5173
902.1470	1054.1258	1174.9348
1631.7556	1847.1429	2241.1643

Zero-point correction (Hartree): 0.030636

TS POZ -> CO2 + C2O3 Criegee

E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -490.28178480
Electronic state : 1-A
Cartesian coordinates (Angs):

C	-0.550010	0.985657	0.020390
C	0.266182	-0.345707	0.129305
C	1.601208	-0.338845	-0.010126
O	0.112061	1.999412	0.083064
O	2.733874	-0.280202	-0.017725
O	-1.748577	0.718563	-0.206233
O	-0.461813	-1.414742	-0.230603
O	-1.623580	-1.248860	0.266819

Rotational constants (GHz): 3.4175200 2.0017800 1.2815200
Vibrational harmonic frequencies (cm-1):

i462.5172	113.7804	133.9902
201.9473	388.0244	454.8180
510.2776	538.6805	619.9609
688.5780	756.3057	791.5803
1062.2084	1218.3957	1254.4700
1404.1700	1764.1676	2278.6263

Zero-point correction (Hartree): 0.032304

C2O3 Criegee anti

E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -301.69309075
Electronic state : 1-A
Cartesian coordinates (Angs):

O	2.352890	-0.071506	-0.000104
C	1.215892	-0.002280	0.000021
C	-0.053162	0.476241	0.000157
O	-1.008538	-0.364334	0.000137
O	-2.216399	0.080369	-0.000167

Rotational constants (GHz): 100.4733600 2.5122400 2.4509500
Vibrational harmonic frequencies (cm-1):

175.4358	188.1630	544.7128
586.1599	606.8666	972.4534
1203.9130	1499.6944	2208.5223

Zero-point correction (Hartree): 0.018193

C2O3 Criegee syn

E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -301.69399552
Electronic state : 1-A
Cartesian coordinates (Angs):

O	2.032932	-0.316913	-0.000128
C	0.966310	0.051055	-0.000034
C	-0.118950	0.962620	0.000126

```
     O      -1.256883      0.435265       0.000109
     O      -1.411569     -0.878609      -0.000049
Rotational constants (GHz):   17.9626300    3.7541900    3.1052000
Vibrational harmonic frequencies (cm-1):
      106.3506                249.7530                 408.0748
      609.4911                727.0657                 778.2728
     1031.9855               1476.7931                2228.1944
Zero-point correction (Hartree): 0.017350

C2O3 dioxirane
--------------
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -301.72917768
Electronic state : 1-A
Cartesian coordinates (Angs):
     O       1.354569      0.738365      -0.070383
     O       1.354607     -0.738321      -0.070401
     C       0.277496     -0.000051       0.316564
     C      -1.009918     -0.000037      -0.097290
     O      -2.159860      0.000022      -0.023672
Rotational constants (GHz):   26.7073100    3.4156100    3.0831400
Vibrational harmonic frequencies (cm-1):
      211.6211                213.1884                 381.9928
      653.7230                705.4475                 951.1451
      989.2463               1552.3554                2187.6799
Zero-point correction (Hartree): 0.017875

TS C2O3 Criegee syn decomposition
---------------------------------
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -301.69391877
Electronic state : 1-A
Cartesian coordinates (Angs):
     O       1.997501     -0.298083      -0.000129
     C       0.931783      0.059391      -0.000036
     C      -0.167805      1.014254       0.000134
     O      -1.262979      0.414596       0.000110
     O      -1.307506     -0.921747      -0.000055
Rotational constants (GHz):   16.7638300    3.9657900    3.2070900
Vibrational harmonic frequencies (cm-1):
     i151.3725                233.7820                 317.4630
      591.3454                651.3379                 785.7729
      982.6529               1487.4264                2246.9876
Zero-point correction (Hartree): 0.016623

INT1
----
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -377.08969402
Electronic state : 1-A
Cartesian coordinates (Angs):
     C       0.773429     -0.242043       0.000000
     C      -0.773422     -0.242051       0.000013
     O       1.693168     -0.959145       0.000000
     O       0.727362      1.140690      -0.000005
     O      -1.693154     -0.959162      -0.000007
     O      -0.727381      1.140687       0.000001
Rotational constants (GHz):    6.9745800    4.1091200    2.5857200
Vibrational harmonic frequencies (cm-1):
      244.2391                316.8797                 411.5502
```

```
      622.7715                 766.8385                 801.2436
      815.1720                 955.1159                 986.0669
     1206.4693                2011.7824                2043.1189
Zero-point correction (Hartree): 0.025473

INT3
----
E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -490.33959261
Electronic state : 1-A
Cartesian coordinates (Angs):
     C       0.517245     -0.457424       0.000194
     C      -0.287816      0.828720       0.000021
     C      -1.507130     -0.163631       0.000128
     O      -0.555580     -1.266252       0.000084
     O      -2.663037     -0.234675      -0.000025
     O       1.681043     -0.828377      -0.000494
     O      -0.130056      1.985546      -0.000152
     O       2.625906      0.188009       0.000329
Rotational constants (GHz):    4.5042700    1.6537700    1.2096400
Vibrational harmonic frequencies (cm-1):
      106.4653                 164.3562                 243.3031
      295.9645                 320.8414                 426.9257
      495.3373                 601.5163                 705.1669
      747.4804                 789.0467                 829.0635
      888.1603                1024.2069                1301.1837
     1740.2332                1991.2484                2066.2717
Zero-point correction (Hartree): 0.033573

O2CO dioxirane
--------------
E(RM052X+HF-M/Aug-CC-pVTZ) (Hartree): -263.71931503
Electronic state : 1-A
Cartesian coordinates (Angs):
     C       0.265684     -0.000096       0.000167
     O      -0.814191      0.766608      -0.000032
     O      -0.815453     -0.766139      -0.000032
     O       1.430381     -0.000396      -0.000060
Rotational constants (GHz):   26.8982500    9.2202800    6.8665400
Vibrational harmonic frequencies (cm-1):
      583.1732                 683.2619                 812.8197
      931.4061                1183.5043                2124.1875
Zero-point correction (Hartree): 0.014394

OC(O.)O. singlet bisoxy
-----------------------
E(UM052X+HF-M/Aug-CC-pVTZ) (Hartree): -263.70554257
Electronic state : 1-A
Cartesian coordinates (Angs):
     C      -0.077713     -0.000053       0.000001
     O      -1.270911     -0.001629       0.000000
     O       0.663129      1.084554       0.000000
     O       0.666066     -1.082885       0.000000
Rotational constants (GHz):   13.4515000   12.6227000    6.5119600
Vibrational harmonic frequencies (cm-1):
      314.7254                 459.9757                 763.5496
      968.7920                1322.0336                1746.1368
Zero-point correction (Hartree): 0.012701
```

OC(O.)O. triplet bisoxy

E(UM052X+HF-M/Aug-CC-pVTZ) (Hartree): -263.69156881
Electronic state : 3-A
Cartesian coordinates (Angs):

C	0.095984	-0.005534	0.000028
O	1.272654	-0.208314	-0.000008
O	-0.479981	1.167777	-0.000006
O	-0.864661	-0.955312	-0.000006

Rotational constants (GHz): 13.6205800 12.1310300 6.4163600
Vibrational harmonic frequencies (cm-1):

330.4231	572.5132	780.3873
945.0257	1163.8953	1718.5527

Zero-point correction (Hartree): 0.012555

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OH-initiated oxidation of carbon suboxide
==========
C3O2-OH adduct on inner carbon trans

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -340.57627170
Electronic state : 2-A
Cartesian coordinates (Angs):

O	-1.666687	-1.312172	0.006618
C	-0.993315	-0.384432	0.008490
C	-0.045855	0.553497	0.000082
C	1.270091	0.019751	-0.018546
O	1.815224	-1.020996	0.010102
O	-0.302481	1.901424	-0.102780
H	-0.153980	2.321064	0.748328

Rotational constants (GHz): 4.4491500 3.8708600 2.0820100
Vibrational harmonic frequencies (cm-1):

128.0469	224.9819	248.9167
271.2004	341.9336	457.5646
605.1586	673.4647	767.3279
1144.2702	1255.2140	1419.2371
1907.2933	2240.5131	3840.8477

Zero-point correction (Hartree): 0.035371

C3O2-OH adduct on inner carbon cis

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -340.57479937
Electronic state : 2-A
Cartesian coordinates (Angs):

O	2.314621	-0.607490	0.010066
C	1.243263	-0.214264	0.015045
C	-0.013091	0.256064	-0.008144
C	-1.001706	-0.764707	-0.008533
O	-2.183781	-0.709340	0.002542
O	-0.215632	1.619353	-0.096782
H	-0.692465	1.917263	0.683184

Rotational constants (GHz): 7.3759500 2.5997900 1.9309800
Vibrational harmonic frequencies (cm-1):

134.9588	182.6562	203.3319
290.8923	477.5831	568.4409
575.9712	636.3798	829.3410

```
     1218.2538                 1244.0934                 1409.8757
     1903.2885                 2272.0930                 3834.7087
Zero-point correction (Hartree): 0.035954

Conformers of INT1
------------------
E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -340.59898361
Electronic state : 2-A
Cartesian coordinates (Angs):
     O      -1.496886      1.190001      -0.084584
     C      -0.996983      0.105621       0.052119
     C       0.376631     -0.072463       0.406414
     C       1.601875     -0.037844       0.047058
     O       2.740038     -0.030878      -0.177835
     O      -1.657786     -1.051635      -0.078811
     H      -2.572063     -0.831797      -0.303712
Rotational constants (GHz):   11.4633000    1.9914900    1.7298100
Vibrational harmonic frequencies (cm-1):
       76.0507                   86.3916                  441.1820
      498.3328                  541.4851                  566.8810
      589.1141                  761.4280                  789.9110
     1168.4781                 1330.7422                 1583.3336
     1801.8459                 2190.2514                 3782.0540
Zero-point correction (Hartree): 0.036923

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -340.59258397
Electronic state : 2-A
Cartesian coordinates (Angs):
     O       1.400683      1.245375      -0.068599
     C       1.008194      0.121503       0.044386
     C      -0.346700     -0.158709       0.443560
     C      -1.565788     -0.057734       0.054194
     O      -2.697145     -0.016568      -0.189890
     O       1.806379     -0.937875      -0.154861
     H       1.346435     -1.757805       0.053955
Rotational constants (GHz):   11.0082000    2.0355100    1.7592200
Vibrational harmonic frequencies (cm-1):
       78.8897                   94.5109                  421.9140
      467.7555                  502.4922                  559.0272
      599.5282                  744.1067                  812.5627
     1156.9681                 1291.0501                 1541.7559
     1822.8336                 2181.3857                 3829.0952
Zero-point correction (Hartree): 0.036687

TS INT1 1,3-H-shift
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E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -340.52588102
Electronic state : 2-A
Cartesian coordinates (Angs):
     O      -1.654355     -1.148394      -0.076662
     C      -1.042769     -0.146614       0.064374
     C       0.269263      0.247097       0.638049
     C       1.446798     -0.012419       0.085126
     O       2.514061     -0.207628      -0.270515
     O      -1.331721      1.113083      -0.297914
     H      -0.263630      1.415129       0.435437
Rotational constants (GHz):    9.6295000    2.2947700    1.9668800
```

Vibrational harmonic frequencies (cm-1):

i2036.1962	127.4699	136.0705
498.6678	526.3069	603.2015
655.6197	745.4866	826.4422
900.9485	1071.2540	1337.1276
1873.7793	2092.0237	2236.2815

Zero-point correction (Hartree): 0.031053

TS INT1 reconformisation

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -340.59175383
Electronic state : 2-A
Cartesian coordinates (Angs):

O	1.475447	1.235671	-0.000242
C	1.046090	0.118472	0.000187
C	-0.360640	-0.123072	0.001192
C	-1.624866	-0.047360	0.000129
O	-2.788572	-0.020261	-0.000501
O	1.850256	-0.955039	-0.000369
H	1.339443	-1.771199	-0.000153

Rotational constants (GHz): 11.8927800 1.9278700 1.6589500
Vibrational harmonic frequencies (cm-1):

i88.0822	80.4842	423.3621
445.3483	480.4448	544.5316
597.4456	726.0843	791.9733
1158.2555	1292.4038	1602.6985
1816.4518	2198.4770	3833.1173

Zero-point correction (Hartree): 0.036430

Conformers of INT2

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -491.00075760
Electronic state : 2-A
Cartesian coordinates (Angs):

O	-0.687361	-1.954445	0.250691
C	-0.849334	-0.789296	-0.006192
C	0.252668	0.142030	-0.181111
O	-2.039012	-0.204177	-0.166959
H	-2.711268	-0.884673	-0.032390
C	1.496191	-0.316720	-0.052850
O	2.566225	-0.696481	0.039321
O	0.086697	1.492812	-0.496113
O	-0.262284	2.195864	0.557224

Rotational constants (GHz): 2.4941300 2.1484500 1.2141500
Vibrational harmonic frequencies (cm-1):

65.2900	94.6858	130.3841
168.4400	261.5269	449.2784
494.8542	540.0789	561.4418
617.1033	701.9716	771.5293
817.5325	1145.0104	1157.4569
1211.3421	1350.1410	1466.2246
1811.4955	2287.2383	3797.0543

Zero-point correction (Hartree): 0.045336

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -491.00263818
Point group : CS
Electronic state : 2-A"

```
Cartesian coordinates (Angs):
     O      -0.096706     -2.159665       0.000000
     C      -0.682640     -1.108215       0.000000
     C       0.000000      0.173239       0.000000
     O      -2.011883     -0.976426       0.000000
     H      -2.386245     -1.867245       0.000000
     C       1.338991      0.187332       0.000000
     O       2.475652      0.161960       0.000000
     O      -0.686241      1.374319       0.000000
     O       0.125196      2.393951       0.000000
Rotational constants (GHz):    3.0094900    1.8947400    1.1627100
Vibrational harmonic frequencies (cm-1):
       86.6593 (  A")           100.0837 (  A")           141.6633 (  A')
      182.3989 (  A')           261.9561 (  A")           391.4492 (  A')
      460.8756 (  A')           519.6547 (  A')           542.8783 (  A")
      573.9305 (  A")           710.2528 (  A')           783.7074 (  A")
      791.2026 (  A')          1159.8860 (  A')          1206.2241 (  A')
     1253.6936 (  A')          1346.9030 (  A')          1486.3948 (  A')
     1813.5201 (  A')          2283.2643 (  A')          3790.9331 (  A')
Zero-point correction (Hartree): 0.045307

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -491.00136388
Electronic state : 2-A
Cartesian coordinates (Angs):
     O       2.077490     -0.248118      -0.157686
     C       0.955427     -0.645380      -0.049555
     C      -0.231301      0.185765      -0.189307
     O       0.618770     -1.923776       0.217289
     H       1.437038     -2.429159       0.301278
     C      -1.458439     -0.302879      -0.052291
     O      -2.514980     -0.722082       0.049281
     O      -0.096893      1.541216      -0.489667
     O       0.286717      2.228277       0.561487
Rotational constants (GHz):    2.4254800    2.2140700    1.2168300
Vibrational harmonic frequencies (cm-1):
       68.5131                   93.8700                  134.3634
      170.4288                  268.5408                  433.4361
      522.1091                  531.4608                  545.8344
      608.8765                  692.9178                  765.7662
      818.2184                 1133.4365                 1149.7067
     1222.1864                 1362.3839                 1428.6062
     1860.7627                 2279.1616                 3802.9416
Zero-point correction (Hartree): 0.045321

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -491.00310029
Point group : CS
Electronic state : 2-A"
Cartesian coordinates (Angs):
     O      -2.206528     -0.596335       0.000000
     C      -1.031117     -0.815780       0.000000
     C       0.000000      0.208991       0.000000
     O      -0.481745     -2.046853       0.000000
     H      -1.204028     -2.687659       0.000000
     C       1.302591     -0.084510       0.000000
     O       2.402915     -0.378436       0.000000
     O      -0.394592      1.534224       0.000000
     O       0.626848      2.341832       0.000000
```

Rotational constants (GHz): 2.9966200 1.9084500 1.1659200
Vibrational harmonic frequencies (cm-1):

85.0138	(A")	98.5480	(A")	146.4386	(A')
183.4702	(A')	263.8532	(A")	403.7694	(A')
441.9978	(A')	509.6552	(A")	547.3613	(A')
556.9597	(A")	704.5488	(A')	777.7713	(A")
794.8329	(A')	1124.8658	(A')	1223.6503	(A')
1262.6324	(A')	1363.6315	(A')	1447.2103	(A')
1859.5807	(A')	2276.3451	(A')	3803.7369	(A')

Zero-point correction (Hartree): 0.045281

Conformers of INT3

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -415.87517254
Electronic state : 2-A
Cartesian coordinates (Angs):

O	0.747752	-1.546778	-0.000120
C	0.931641	-0.355243	-0.000018
C	-0.213399	0.594370	0.000082
C	-1.430220	-0.108366	-0.000130
O	-2.465309	-0.573964	0.000134
O	2.113654	0.242238	0.000087
H	2.792362	-0.445715	0.000300
O	-0.211159	1.836148	-0.000089

Rotational constants (GHz): 4.8370200 2.2802700 1.5497100
Vibrational harmonic frequencies (cm-1):

88.3022	137.1573	258.3230	
290.2416	445.9457	472.5753	
496.9468	592.7971	693.9014	
781.3515	782.4887	1121.0108	
1201.7553	1423.0166	1544.3129	
1808.6616	2233.0517	3792.2105	

Zero-point correction (Hartree): 0.041381

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -415.87828361
Electronic state : 2-A
Cartesian coordinates (Angs):

O	0.672837	-1.638273	-0.000197
C	0.911276	-0.463991	0.000034
C	-0.178215	0.561148	0.000035
C	-1.451433	-0.013102	-0.000015
O	-2.509608	-0.422451	0.000125
O	2.121364	0.073009	0.000189
H	2.024554	1.039555	0.000043
O	0.001117	1.794730	-0.000163

Rotational constants (GHz): 4.8226100 2.3001600 1.5573700
Vibrational harmonic frequencies (cm-1):

104.1429	135.2319	264.3303	
303.9526	445.3278	466.5577	
514.6957	664.8991	707.3505	
775.3355	810.0949	1147.6099	
1237.1555	1410.5029	1545.9598	
1862.4385	2252.2647	3700.7340	

Zero-point correction (Hartree): 0.041801

TS INT3 1,4-Hshift

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -415.84319852
Electronic state : 2-A
Cartesian coordinates (Angs):

O	0.651667	-1.719202	-0.000028
C	1.000690	-0.560386	0.000007
C	-0.194626	0.519761	0.000055
C	-1.486451	0.101474	-0.000009
O	-2.511823	-0.384871	-0.000058
O	2.041823	0.100961	-0.000013
O	0.180429	1.754651	0.000055
H	1.185561	1.622589	0.000031

Rotational constants (GHz): 4.6459000 2.3469300 1.5592600
Vibrational harmonic frequencies (cm-1):

i16.8008	110.6008	173.4836
279.9930	304.8771	447.4372
517.2724	688.1016	765.7740
775.7349	959.3907	1020.0088
1231.0242	1381.2171	1568.4205
1887.1622	2290.9831	3005.1681

Zero-point correction (Hartree): 0.039655

TS INT3 HOCO elimination

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -415.79798425
Electronic state : 2-A
Cartesian coordinates (Angs):

O	1.380797	-1.305932	-0.000650
C	1.057370	-0.179731	-0.000120
C	-1.023038	0.751114	-0.000130
C	-1.296821	-0.523726	0.000230
O	-1.383694	-1.684785	0.000180
O	1.752412	0.934247	0.000460
H	2.702532	0.726195	0.000350
O	-1.140465	1.929954	-0.000020

Rotational constants (GHz): 3.2179100 2.7372500 1.4790900
Vibrational harmonic frequencies (cm-1):

i369.4303	51.3572	138.0826
181.2770	294.3052	311.2040
401.4531	420.8295	436.0860
601.5334	622.7339	968.2704
1125.4927	1286.2280	1825.5852
1934.2715	2347.8291	3679.2781

Zero-point correction (Hartree): 0.037876

TS INT3 CO elimination

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -415.84791720
Electronic state : 2-A
Cartesian coordinates (Angs):

O	0.650858	-1.484161	-0.410472
C	0.948660	-0.379407	-0.061794
C	-0.033453	0.758870	0.054462
C	-1.720983	-0.164615	-0.266270
O	-2.579655	-0.468140	0.399807
O	2.138547	-0.002525	0.407846
H	2.712760	-0.780584	0.417343
O	0.055487	1.891263	-0.244146

Rotational constants (GHz): 4.3773200 2.0205600 1.4621400
Vibrational harmonic frequencies (cm-1):

i311.3638	54.4443	73.7322
196.0017	258.4268	334.8621
347.0007	494.4528	550.2022
602.6265	768.7674	818.6399
1155.1162	1357.9831	1836.7443
1932.5764	2153.6518	3778.2430

Zero-point correction (Hartree): 0.038076

Conformers of INT4

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -566.26626543
Electronic state : 2-A
Cartesian coordinates (Angs):

O	-1.038704	-1.031793	1.148630
C	-1.297138	-0.209645	0.318259
C	-0.194014	0.689176	-0.231710
O	-2.482466	0.044165	-0.205839
H	-3.128824	-0.555509	0.191714
C	1.197719	0.325788	0.317497
O	1.801561	0.925099	1.125405
O	-0.362032	1.639600	-0.922254
O	1.754556	-0.817663	-0.283706
O	0.938263	-1.293958	-1.189237

Rotational constants (GHz): 2.5059900 1.3903700 1.2639500
Vibrational harmonic frequencies (cm-1):

45.1791	82.4870	144.5715
165.5041	185.2087	306.1272
349.3122	410.1570	501.8340
545.9194	631.5797	660.2594
723.0852	743.0319	854.0540
998.8906	1173.2441	1221.1172
1247.0923	1442.4199	1863.6386
1901.0170	1969.8424	3780.5435

Zero-point correction (Hartree): 0.049997

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -566.26182703
Electronic state : 2-A
Cartesian coordinates (Angs):

O	1.498481	-1.327940	-0.756130
C	1.621748	-0.292272	-0.174221
C	0.412146	0.610078	0.064081
O	2.749752	0.240086	0.268855
H	3.477689	-0.356961	0.046799
C	-0.890256	-0.160242	0.278470
O	-1.017728	-1.058950	1.026435
O	0.456898	1.797714	0.082350
O	-1.908408	0.423047	-0.478237
O	-3.071435	-0.147509	-0.275371

Rotational constants (GHz): 3.5749300 1.0648500 0.9205300
Vibrational harmonic frequencies (cm-1):

23.7320	60.0194	116.7736
160.8557	205.2643	309.6228
330.3774	377.9238	472.0946
510.5494	636.0616	682.4565
744.9072	829.1323	869.5949

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      957.2686                1174.5119                1188.2531
     1256.2410                1434.7823                1868.7770
     1892.7063                1937.0376                3779.4524
Zero-point correction (Hartree): 0.049706

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -566.26391811
Electronic state : 2-A
Cartesian coordinates (Angs):
     O       2.503483      0.070955     -0.217499
     C       1.405128     -0.122879      0.186218
     C       0.194248      0.747455     -0.175241
     O       1.021728     -1.102561      1.012871
     H       1.787979     -1.649447      1.232877
     C      -1.175504      0.282608      0.346547
     O      -1.782314      0.760874      1.229854
     O       0.302515      1.774039     -0.760035
     O      -1.707576     -0.806464     -0.370788
     O      -0.879238     -1.171051     -1.316656
Rotational constants (GHz):    2.4507100    1.4181600    1.2816700
Vibrational harmonic frequencies (cm-1):
       43.9606                  79.2504                 146.1357
      162.7193                 186.0480                 315.7159
      354.7793                 408.7115                 479.5101
      532.9457                 633.9205                 648.9098
      722.4823                 748.9434                 848.5033
      991.1857                1173.6261                1189.2968
     1239.6601                1367.5805                1900.5772
     1913.6252                1965.2954                3785.9737
Zero-point correction (Hartree): 0.049754

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -566.26751871
Electronic state : 2-A
Cartesian coordinates (Angs):
     O       1.006662     -1.189025      1.092772
     C       1.302828     -0.314907      0.338824
     C       0.230515      0.631184     -0.201379
     O       2.518962     -0.046466     -0.101560
     H       2.481497      0.725046     -0.687992
     C      -1.182532      0.366569      0.333184
     O      -1.725315      0.984834      1.169477
     O       0.489663      1.563061     -0.899473
     O      -1.821904     -0.707423     -0.301306
     O      -1.041363     -1.207745     -1.226881
Rotational constants (GHz):    2.5277800    1.3777200    1.2627000
Vibrational harmonic frequencies (cm-1):
       65.0476                  84.2019                 144.2538
      166.8852                 189.7607                 320.6696
      345.4923                 430.2009                 503.6404
      567.0625                 634.8380                 649.8544
      745.3239                 759.2529                 853.2569
     1013.7068                1184.6696                1226.7565
     1267.2451                1416.9879                1878.8985
     1902.5997                1969.8742                3727.9002
Zero-point correction (Hartree): 0.050230

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -566.26236388
Electronic state : 2-A
```

Cartesian coordinates (Angs):

O	1.098654	-1.628604	0.322628
C	1.488578	-0.538110	0.043642
C	0.505967	0.631671	-0.039030
O	2.738559	-0.203868	-0.225080
H	2.780592	0.744331	-0.423431
C	-0.933291	0.287746	0.336829
O	-1.409305	0.438143	1.399437
O	0.851423	1.734794	-0.336660
O	-1.585747	-0.199367	-0.797916
O	-2.837100	-0.520119	-0.565560

Rotational constants (GHz): 3.1284000 1.1182200 0.9938300

Vibrational harmonic frequencies (cm-1):

27.0443	78.4653	100.3218
173.8641	186.8173	323.9869
341.3577	390.3975	485.2134
510.1973	636.5851	724.0793
751.1499	816.0853	872.2710
986.4974	1167.0271	1184.8213
1258.2350	1411.9550	1877.4985
1902.9360	1953.1883	3731.2379

Zero-point correction (Hartree): 0.049872

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -566.25747165

Electronic state : 2-A

Cartesian coordinates (Angs):

O	2.777684	-0.554352	-0.000474
C	1.792973	0.106015	-0.000127
C	0.412617	-0.615104	0.000262
O	1.781913	1.433039	-0.000029
H	0.876571	1.784964	0.000302
C	-0.873314	0.230616	0.000028
O	-0.923192	1.416469	0.000446
O	0.343416	-1.799423	0.000694
O	-1.981788	-0.594943	-0.000768
O	-3.106810	0.084944	-0.000030

Rotational constants (GHz): 3.7183500 1.1047200 0.8516900

Vibrational harmonic frequencies (cm-1):

15.5293	64.6284	117.7964
191.1896	290.6754	358.4210
367.2108	403.8739	432.5138
595.9123	598.9069	719.1502
738.6556	856.3756	874.6311
949.6803	1162.0557	1206.4448
1288.9177	1391.8135	1880.2961
1893.5496	1919.8740	3638.0605

Zero-point correction (Hartree): 0.050020

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -566.24868161

Electronic state : 2-A

Cartesian coordinates (Angs):

O	2.711269	-0.115698	0.321985
C	1.591781	-0.424296	0.086303
C	0.552560	0.698869	-0.182648
O	1.168982	-1.687308	0.049395
H	0.239329	-1.769003	-0.196273
C	-0.947511	0.536473	0.138011

```
     O      -1.637248      1.333391       0.644308
     O       0.906371      1.752642      -0.598795
     O      -1.396782     -0.736023      -0.305317
     O      -2.680131     -0.934163      -0.118293
Rotational constants (GHz):    2.8537300    1.2540600    0.9239100
Vibrational harmonic frequencies (cm-1):
       32.4881                  37.2674                 113.4743
      185.0833                 258.0278                 306.1577
      355.3290                 376.2226                 431.4777
      527.5781                 617.0191                 635.8458
      739.5211                 815.5103                 850.0185
      968.5071                1143.9743                1170.0525
     1220.8757                1352.9037                1885.6008
     1909.2356                1966.4945                3772.8427
Zero-point correction (Hartree): 0.049371

TS INT4 1,6-Hshift
------------------
E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -566.21009934
Electronic state : 2-A
Cartesian coordinates (Angs):
     O      -2.319180     -0.982321       0.056620
     C      -1.235318     -0.537141       0.266096
     C      -0.751337      0.841002      -0.235338
     O      -0.213472     -0.987019       0.938975
     C       0.687508      0.844251       0.395981
     O       1.462122      1.355159       1.047587
     O      -1.180262      1.714110      -0.884595
     O       1.573507     -0.267582      -0.921785
     O       1.555990     -1.504059      -0.578808
     H       0.765243     -1.514983       0.175617
Rotational constants (GHz):    2.1588400    1.5816800    1.2020800
Vibrational harmonic frequencies (cm-1):
     i227.3356                 69.4838                 119.6310
      152.7497                207.1026                 274.2501
      304.7026                364.6681                 395.9697
      443.5889                552.5381                 618.7393
      692.1791                790.3361                 840.1964
      980.2179               1144.2871                1200.5777
     1343.9525               1498.0866                1857.7484
     1964.5192               1982.0120                2177.8954
Zero-point correction (Hartree): 0.045507

INT6
----
E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -491.00433238
Electronic state : 2-A
Cartesian coordinates (Angs):
     O       2.161279     -1.272913      -0.023063
     C       1.301732     -0.470006      -0.008937
     C      -0.154515     -0.358116       0.034151
     O       1.415805      0.942372      -0.029054
     C       0.002524      1.094063       0.016330
     O      -0.618458      2.092582       0.034746
     O      -1.113830     -1.248198       0.105452
     O      -2.345297     -0.598212      -0.186749
     H      -2.894435     -0.920688       0.540085
```

Rotational constants (GHz): 3.1350300 2.0144700 1.2328500
Vibrational harmonic frequencies (cm-1):

69.0590	159.1932	163.3295
184.1557	236.8289	333.5141
434.6919	643.9624	682.5636
697.0334	725.5112	763.7785
790.9263	1020.5519	1148.5683
1193.1083	1429.5836	1602.2471
1898.8781	2039.4957	3796.0226

Zero-point correction (Hartree): 0.045593

TS INT6 -> INT5

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -490.96561714
Electronic state : 2-A
Cartesian coordinates (Angs):

O	-2.020303	-1.290342	-0.000239
C	-1.517353	-0.198644	0.000007
C	0.111084	-0.196451	-0.000089
O	-1.834581	0.990816	0.000353
C	0.612483	1.078172	-0.000001
O	1.005400	2.140620	-0.000226
O	0.868435	-1.254785	-0.000001
O	2.243507	-0.879721	0.000138
H	2.663053	-1.751174	0.000295

Rotational constants (GHz): 2.9569300 1.8896200 1.1528800
Vibrational harmonic frequencies (cm-1):

i211.8233	39.4690	109.6664
117.4722	159.1869	169.8762
290.5276	353.5546	449.8528
505.3385	699.7914	762.5795
766.9325	959.0901	1054.2284
1293.5252	1392.2616	1546.6156
1908.3115	2285.7681	3791.2622

Zero-point correction (Hartree): 0.042500

TS INT6 -> CO2 + CO + CO + OH

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -490.95905358
Electronic state : 2-A
Cartesian coordinates (Angs):

O	-2.399476	-1.098689	0.006161
C	-1.312581	-0.775128	-0.001032
C	0.000675	-0.384996	-0.009796
O	-1.153650	1.609494	0.020834
C	0.034544	1.305151	-0.001946
O	1.121040	1.801605	-0.028284
O	0.870845	-1.367182	-0.040097
O	2.183751	-0.847011	0.064592
H	2.684100	-1.655895	-0.108997

Rotational constants (GHz): 2.7168507 2.0198207 1.1591910

TS INT6 -> INT7 + OH

E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -490.99629745
Electronic state : 2-A
Cartesian coordinates (Angs):

```
     O       1.994591     -1.466835      -0.122521
     C       1.233338     -0.581648      -0.025313
     C      -0.206082     -0.303553       0.291157
     O       1.464779      0.800348      -0.198591
     C       0.121098      1.138640       0.063211
     O      -0.378105      2.199718       0.067497
     O      -1.216096     -0.979458       0.569346
     O      -2.344444     -0.690745      -0.566676
     H      -3.055926     -0.424864       0.033225
Rotational constants (GHz):    2.8351900    2.0019600    1.2447200
Vibrational harmonic frequencies (cm-1):
     i855.3515                105.9337                 126.2719
      164.7688                205.5305                 307.6161
      348.9349                422.9114                 630.7341
      693.4087                727.0329                 764.0201
      785.2350                819.7479                1063.1710
     1155.1104               1197.3670                1496.5855
     1924.5676               2047.2512                3795.5960
Zero-point correction (Hartree): 0.042788

INT7
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E(RM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -415.28025092
Electronic state : 1-A
Cartesian coordinates (Angs):
     O      -2.193769     -0.488358       0.000378
     C      -1.039957     -0.300791      -0.000003
     C       0.000126      0.856303       0.000141
     O      -0.000194     -1.240973      -0.000592
     C       1.039758     -0.301104      -0.000096
     O       2.193541     -0.488905       0.000411
     O       0.000476      2.027430      -0.000228
Rotational constants (GHz):    4.6369400    2.8093700    1.7494400
Vibrational harmonic frequencies (cm-1):
      148.1622                276.4751                 298.3506
      348.6537                568.4690                 694.0789
      706.6311                768.8860                 794.8629
      861.1071               1025.2028                1196.8664
     1939.3421               1997.2802                2076.1680
Zero-point correction (Hartree): 0.031212

HOCOCO
------
E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -302.51003386
Electronic state : 2-A
Cartesian coordinates (Angs):
     O       0.977979      1.195098      -0.052276
     C       0.472946      0.118466       0.038227
     O       1.090638     -1.059739      -0.040213
     H       2.030198     -0.893535      -0.200861
     C      -0.976612     -0.064818       0.420544
     O      -1.944643     -0.063903      -0.226482
Rotational constants (GHz):   11.2537200    4.3509200    3.2620400
Vibrational harmonic frequencies (cm-1):
      126.8398                256.7483                 438.0833
      512.0920                563.0598                 767.8834
      790.0587               1161.0084                1355.6845
```

```
     1847.7385                2030.1840                3771.9380
Zero-point correction (Hartree): 0.031032

HOCOCO -> HOCO + CO
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E(UM052X+HF-M052X/Aug-CC-pVTZ) (Hartree): -302.49009896
Electronic state : 2-A
Cartesian coordinates (Angs):
     O       1.081737      1.224958       0.035553
     C       0.664679      0.126749      -0.037127
     O       1.303884     -1.027830      -0.077666
     H       2.261078     -0.864116      -0.058507
     C      -1.350875     -0.333045       0.438939
     O      -2.153609      0.065609      -0.251933
Rotational constants (GHz):   10.8306800    3.2421600    2.5835800
Vibrational harmonic frequencies (cm-1):
     i234.3157                  31.9399                 159.4320
      169.7255                 352.1418                 594.2964
      615.9313                1114.8334                1296.4819
     1911.7274                2141.0805                3691.1647
Zero-point correction (Hartree): 0.027517
```