Electronic Supplementary Material (ESI) for Green Chemistry

Automated identification of energetically feasible mechanisms for oxygenates conversion on heterogeneous catalysts: Application to glycerol conversion on transition metals

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Supporting Information

S1. Reaction rules input into RING

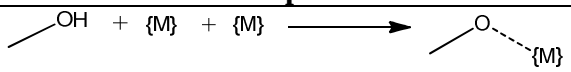
An input file into RING "glycerol_decomposition_GA_final.txt" (See S8) is provided in the supporting files. Interested readers can read about the language grammar and syntax from Rangarajan et al [1] and the online documentation [1a].

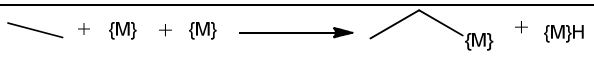
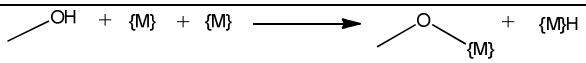
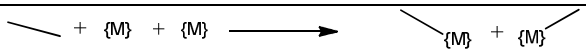
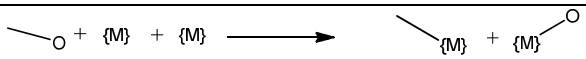
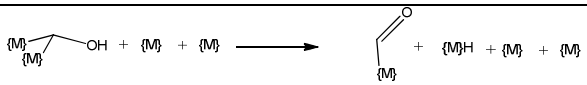
The following bonding rules taken from Salcccicioli et al. [2] are used as global constraints:

1. All atoms and species will gas-phase bond order rules.
2. Hydroxyl groups will interact with the surface if the neighboring carbon is free. However, if there are three consecutive free C-OH groups in a molecule, only two consecutive ones among them will bond to the surface.
3. Carbonyl groups will prefer forming M-C-O-M rings unless a carbon alpha to it is bonded to the surface or there are two consecutive C, one of which is bonded to the carbonyl C, that are both bonded to the surface.

Table S1 contains the rules input into ring. Only the forward steps are given here. In the actual input file, reverse rules are also explicitly specified. The rules are represented in a manner described in the input into RING. M corresponds to a metal atom. Different versions of the same rule

Table S1. Reaction rule description

Rule name	Pictorial representation	Description
Physisorption		This rule involves forming a weak (partial) O – M bond with the metal for a gaseous reactant having a hydroxyl group. This bond is represented with a "_". Depending upon the number of oxygen atoms in the gaseous

		reactant, we have multiple rules describing the bond formation step.
C-H scission		This involves breaking a C – H bond. This scission steps can affect the weak OH interactions. Therefore, depending on the nature of the Carbon (free or bound) and the presence or absence of a hydroxyl group, different versions of this rule is used.
O-H scission		This involves breaking an O – H bond. Different versions exist depending upon whether or not OH is interacting with the surface.
C-C scission		This involves breaking a C – C bond. Again, on the basis of the neighboring OH groups (weakly bound or not), C=O groups, or just double bonded oxygen atoms different versions of it are written.
C-O scission		This involves breaking a C – O bond. This again has multiple versions depending on the nature of OH groups (already weakly bound or not)
C=O formation		A form of OH scission wherein the C is bonded to the surface to account for two of its valence electrons (i.e. two C-M bonds). Here, upon OH scission the C-O bond forms a carbonyl group.

S2. Alternative method for thermochemistry calculation

We describe herein a detailed procedure for using the energy calculation method proposed by Liu and Greeley [3-5] within RING.

The binding energy of a species as defined by these authors is

$$BE(CxH_yO_z^*) = E(C_xH_yO_z) - E_{slab} - E(C_xH_{2x+2}O_z(g)) + \tfrac{1}{2}(2x-y+2)E(H_2(g))$$

That is, the binding energy is the total energy of a surface species minus the energies of the slab, gas phase fully hydrogenated molecule corresponding to the species, and an appropriate amount of gas phase hydrogen molecule (needed to fully hydrogenate this species).

This binding energy is further written as

$BE(CxH_yO_z^*)$ = Sum of group contributions + $BE(C_xH_{2x+2}O_z^*)$

That is, the binding energy of a surface species is written as a correction to the binding energy of the fully hydrogenated stable gas phase molecule. Therefore, if (a) the binding energy of the fully hydrogenated gas phase stable molecules such as glycerol, propane diols, ethylene glycol, ethanol, methanol, etc., (b) the corresponding gas phase energy of these molecules, (c) energy of hydrogen, and (d) the energy of a clean slab are known, the energy of a surface species can be calculated based on group contributions feature in RING. The individual group contributions can be specified for each group (e.g. primary carbon, oxygen pertaining to the primary carbon, secondary/primary carbon without neighboring oxygen, etc.). The group additivity value will be the product $p_{xi}\nu_{xi}$ (for more details on what these terms mean, interested readers can find the definitions in Liu and Greeley [3-5]).

The contribution of an integer multiple of half the energy of hydrogen gas can be specified for each group depending on how many more hydrogen atoms are required to saturate it. For example, CH_2OH^* needs one more hydrogen atom and $\frac{1}{2}E(H_2)$ value could be added to group the primary C (connected O) in the group additivity feature. The energy and binding energy of the fully hydrogenated molecule can be specified as group corrections. To make these corrections applicable for the appropriate species, constraints can be specified. For example, to use methanol for C_1 surface oxygenate species, a constraint can be specified (as characteristic declarations) that stipulates that the correction is applicable only for those molecules having exactly one C and O bond and is surface bonded.

In GroupCorrections1.txt, it will be noted that some corrections are specified by the following syntax:

```
surfaceSpecies fragment {
….
} enthalpy….entropy….cp(….)
```

The word “surfaceSpecies” refers to a characteristic declaration that acts as a constraint. This characteristic is for specifying that the fragment correction is applicable only for a species that is bonded to a surface. A similar characteristic could be defined for a C_1 oxygenate. The syntax for that would look like

```
define characteristic C1Oxygenate on mol{
  fragment f{
    C labeled c1
    O labeled o1 any bond to c1
}
Mol is surfaceSpecies && contains 1 of f
}
```

The energy of the slab can be specified as a molecular correction.

S3. Alternative method for calculating activation barriers

RING can calculate thermochemistry using the TSS method based on the final state energies relative to the initial state gas phase values. The initial state surface energetics is available from group additivity scheme of Salciccioli et al. [2] or Liu and Greeley [3-5](discussed above). To calculate its gas phase values, the binding energy (defined as the energy of a surface species minus the energy of the corresponding gas phase species and the slab) of the reactants are required. This can be provided to RING by making use of the linear scaling correlations by Norskov and coworkers [6]. The implementation of this method is similar to how linear scaling relationships were used (as discussed in the paper). To use the TSS method then only requires replacing "BEP" to "LFER" in the kinetics file provided in the supporting files (glycerolKineticsGreenChem.txt).

S4. Atomic binding energies used

All values, except when explicitly stated, were taken from Sutton and Vlachos [7]. Note that these are atom-metal bond dissociation energies (or the reverse of binding energies).

Table S4. Bond dissociation values for atomic C, H, and O bonds with different metal

Metal	C-M dissociation energy	O-M dissociation energy	H-M dissociation energy
Pt	680.22	379.19	264.4
Pd	644.52	369.54	279.8 [8]
Rh	701.45	455.41	277.9
Ru	663.82	486.29	278.8

S5. Surface ring corrections used and their contributions

The surface ring groups (and their supplementary angles) included in RING are given here. The contribution of these ring fragments are based on values given by Salciccioli et al. [9].

Table S5. Supplementary angles for each surface ring included in this analysis

Groups	Sum of supplementary angles
C(M3)C(M3)	0
C(M3)C(M2)	54.75
C(M3)C(M)	70.5
C(M3)O(M)	70.5
C(M3)C(=O)(M)	60
C(M2)C(M)	125.25
C(M2)O(M)	125.25
C(M2)C(=O)(M)	114.75
C(M2)C(M2)	109.5
C(M)C(M)	141
C(M)O(M)	141
C(M)C(=O)(M)	130.5
O(M)O(M)	141
O(M)C(=O)M	130.5
C(=O)(M)C(=O)(M)	120
C(M)(M)C(=O)C(M)(M)	169.5
C(M)(M)C(=O)C(=O)(M)	174.75
C(M)(M)(M)CC(M)(M)(M)	70.5
C(M)(M)(M)OC(M)(M)(M)	70.5
C(M)(M)(M)C(=O)C(M)(M)(M)	60
C(M)(M)(M)CC(M)(M)	125.25
C(M)(M)(M)C(=O)C(M)(M)	114.75
C(M)(M)(M)CC(M)	141
C(M)(M)(M)OC(M)	141
C(M)(M)(M)C(=O)C(M)	130.5
C(M)(M)(M)CO(M)	141
C(M)(M)(M)OO(M)	141
C(M)(M)(M)C(=O)O(M)	130.5
C(M)(M)(M)OC(=O)(M)	130.5
C(M)(M)(M)C(=O)C(=O)(M)	120
C(M)(M)(M)CCC(M)(M)(M)	141
C(M)(M)(M)COC(M)(M)(M)	141
C(M)(M)(M)CC(=O)C(M)(M)(M)	130.5
C(M)(M)(M)OOC(M)(M)(M)	141
C(M)(M)(M)OC(=O)C(M)(M)(M)	130.5
C(M)(M)(M)C(=O)C(=O)C(M)(M)(M)	120
C(M)(M)(M)C(=O)C(=O)C(M)(M)	174.75

S6. Thermochemistry comparison

The table below shows the thermochemistry predicted by RING and the corresponding DFT values taken from Vlachos and coworkers [2,7,9]. The absolute deviation is about 8 kJ/mol (or 2 kcal/mol) for enthalpy of formation and standard deviation is about 11 kJ/mol.

SMILES	Molecule formula	Heat of formation	
		RING calculated	DFT
C([{M}])O	CH2OH*	-205.907	-222.794
C(CO_[{M}])([{M}])([{M}])O	OHCH2COH*	-433.382	-429.704
O([{M}])C	CH3O*	-145.046	-145.882
C(=O)(C([{M}])O)[{M}]	HOCHCO*	-391	-391.666
C(=O)C[{M}]	CH2CHO*	-158.297	-157.168
C(CO[{M}])([{M}])[{M}]	CHCH2O*	-121.3	-120.802
C(=O)(C[{M}])[{M}]	CH2CO*	-200.4	-198.55
C(=O)C(O[{M}])[{M}]	OCHCHO*	-280.011	-275.462
O=CC([{M}])O	HOCHCHO*	-355.425	-354.046
C(=O)(CO_[{M}])[{M}]	HOCH2CO*	-401.656	-405.46
C(O[{M}])([{M}])C	CH3CHO*	-199.726	-205.656
C([{M}])([{M}])(O)C	CH3COH*	-258.839	-270.446
C(C[{M}])([{M}])[{M}]	CHCH2*	12.1028	-16.72
C(C([{M}])[{M}])([{M}])[{M}]	CHCH*	71.51	32.604
C([{M}])CCC[{M}]	CH2CH2CH2CH2	-119.012	-116.204
C([{M}])C([{M}])C	CH2CHCH3	-83.1045	-86.944

S7. Results

The excel file included has all the pathways identified by RING for different metals. Note that a pictorial representation of these pathways can be obtained using molecule editors such as ChemDraw. However, note that "_" (partial bonds) that are in several of these pathways cannot be read by most software. Probably the best way to get a pictorial representation is to convert "_" into "~" ("~" in ChemDraw is a wildcard bond query. Therefore, these will have "any" over their bonds).

S8. Main input file into RING (glycerol_decomposition_GA_final.txt)

```
input reactant "C(O)C(O)CO"
input reactant "{M}"
input reactant "[H][H]"
input temperature 550 K

define composite atom M (heterogeneous site)

import "GroupAdditivity1.txt" //This has group additivity information
```

```
import "GroupCorrections1.txt" //This has group corrections information
import "glycerolKineticsGreenChem.txt" //This has kinetics information

//defining a characteristic called ManyCarbons that basically has more than one C
define characteristic ManyCarbons on mol{
        fragment f{
                C labeled c1}
        mol contains >1 of f
}

//defining a characteristic to describe a surface bound molecule
define characteristic adsorbedMol on mol{
  fragment f{
    heavy atom labeled x1
        M labeled m1 partial bond to x1
  }

  fragment f2 {
    heavy atom labeled x1
        M labeled m1 single bond to x1
  }

  mol contains >=1 of f || mol contains >=1 of f2

}

define characteristic gasphaseMol on mol {
 ! mol is adsorbedMol
}

global constraints on mol //Specifying all global constraints
{
   //mol.size between 0 and 9
        fragment b
        {
                C labeled c1
                C labeled c2 double bond to c1
                X labeled x1 double bond to c2
        }
        ! (mol contains >= 1 of b && mol.size >3)//no consecutive double bonds!
        fragment c
        {
                M labeled m1
        }
        fragment d
        {
                C labeled c1
        }
        fragment e
        {
                O labeled o1
        }
        //! (mol contains >4 of c)
        ! (mol contains >3 of d)
        ! (mol contains >3 of e)

        fragment f
        {
          C labeled c1
          C labeled c2 single bond to c1
          O labeled o1 single bond to c2
          M labeled m1 single bond to c1
```

```
   M labeled m2 single bond to c2
   M labeled m3 single bond to o1
}
! (mol contains >=1 of f) // C-O comes off the surface if neighboring C is bound to the surface

fragment g
{
   O labeled o1
   M labeled m1 partial bond to o1
}

fragment g2
{
  O labeled o1 {connected to >=2 M with partial bond}
}

! (mol contains >2 of g) //this system will never have more than 3 C in a molecule -- so preventing three consecutive weakly bonded O
! (mol contains >=1 of g2) // never have one oxygen connected to several oxygen atoms weakly


fragment h {
  O labeled o1
  M labeled m1 partial bond to o1
  C labeled c1 any bond to o1
  M labeled m2 single bond to c1
  }
  ! mol contains >=1 of h //preventing weak oxygen bonding when the adjacent C is bound to the surface

fragment i {
  O labeled o1
  M labeled m1 partial bond to o1
  M labeled m2 single bond to o1
 }

 ! mol contains >=1 of i //preventing weak oxygen bond when O is already bound

 fragment j{
   C labeled c1 {connected to >=2 M with single bond}
   O labeled o1 single bond to c1 {connected to 1 M with single bond}
}
! mol contains >=1 of j

fragment k{
  C labeled c1
  O labeled o1 double bond to c1
}

fragment k2 {
  C labeled c1 {connected to >=1 M with single bond}
  C labeled c2 single bond to c1
  O labeled o1 double bond to c2
}

fragment k3 {
  C labeled c1 {connected to >=1 M with single bond}
  O labeled o1 double bond to c1
  }

  (! mol contains >=1 of k) || (mol contains >=1 of k2 || mol contains >=1 of k3)

fragment l{
```

```
    O labeled o1 {! connected to M with any bond}
          C labeled c1 single bond to o1 {connected to 2 C with any bond, ! connected to >=1 M with any bond}
        }
        ! (mol contains 2 of g && mol contains >=1 of l) // this basically prevents the case that the central C-OH bond is not weakly bonded in glycerol

        fragment m{
          O labeled o1 {connected to 1 H with single bond, ! connected to >=1 M with any bond}
          C labeled c1 single bond to o1 {!connected to >=1 M with any bond}
        }
        //! (mol contains 1 of g && mol contains >=1 of m )

        ! (mol contains <=1 of g && mol contains >=1 of m && mol contains >=1 of c) // non surface C-OH cannot exist if the molecule is adsorbed and has less than 2 weakly bonded O-- basically saying the only case where an OH in not bonded to a surface is in the case of glycerol

        fragment mn{
          C labeled c1 {connected to >=1 C with double bond, connected to >=1 M with single bond}
         }
         ! mol contains >=1 of mn
}

//rules begin here. Note the various forms of the same parent rule.
rule OHadsorption{
gasphaseMol reactant r1{
  O labeled o1
  H labeled h1 single bond to o1
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
constraints {
  fragment f{
    O labeled o1 {connected to 1 H with single bond}
  }

  ! r1 contains >1 of f
}
form partial bond (o1,m1)
}

rule OHadsorption2{
gasphaseMol reactant r1{
  O labeled o1
  H labeled h1 single bond to o1
  C labeled c1 single bond to o1
  C labeled c2 any bond to c1
  O labeled o2 single bond to c2
  H labeled h2 single bond to o2
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)

form partial bond (o1,m1)
form partial bond (o2,m2)
}

rule OHdesorption{
adsorbedMol reactant r1{
  O labeled o1
```

```
  M labeled m1 partial bond to o1
}
constraints {
  fragment f{
    M labeled m1
  }
  ! r1 contains >1 of f
}
break partial bond (o1,m1)
}

rule OHdesorption2{
adsorbedMol reactant r1 {
  O labeled o1
  M labeled m1 partial bond to o1
  C labeled c1 single bond to o1
  C labeled c2 any bond to c1
  O labeled o2 single bond to c2
  M labeled m2 partial bond to o2
}
constraints {
  fragment f{
    M labeled m1
  }
  ! r1 contains >2 of f
}
break partial bond (o1,m1)
break partial bond (o2,m2)
}

rule OHdesorption3{
adsorbedMol reactant r1 {
  O labeled o1
  M labeled m1 partial bond to o1
  C labeled c1 single bond to o1
  C labeled c2 any bond to c1
  C labeled c3 any bond to c2
  O labeled o2 single bond to c3
  M labeled m2 partial bond to o2
}
constraints {
  fragment f{
    M labeled m1
  }
  ! r1 contains >2 of f
}
break partial bond (o1,m1)
break partial bond (o2,m2)
}


rule CHscission{
adsorbedMol reactant r1{
        C labeled c1
        H labeled h1 single bond to c1
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond }
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
        fragment a{
```

```
                M labeled m1}
        ! r1 contains >3 of a
}*/
form bond (c1,m1)
form bond (h1,m2)
break bond (c1,h1)
}

//the only difference between this and the prev is that here C is bonded to a weakly bound O
rule CHscission2{
adsorbedMol reactant r1{
        C labeled c1
        H labeled h1 single bond to c1
        O labeled o1 any bond to c1
        M labeled mp partial bond to o1
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond }
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}*/
form bond (c1,m1)
form bond (h1,m2)
break bond (c1,h1)
break partial bond (o1,mp)
}

//CH scission where the C-O surface ring is adjacent to the central C
rule CHscission3{
adsorbedMol reactant r1{
        C labeled c1
        H labeled h1 single bond to c1
        C labeled c2 single bond to c1
        M labeled p1 single bond to c2
        O labeled o1 single bond to c2
        M labeled p2 single bond to o1
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond }
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}*/
form bond (c1,m1)
form bond (h1,m2)
break bond (c1,h1)
break bond (c2,p1)
break bond (o1,p2)
increase bond order (o1,c2)
}

//CH scission where the carbon of C-O surface ring is central
rule CHscission4{
adsorbedMol reactant r1{
        C labeled c1
```

```
		H labeled h1 single bond to c1
		M labeled p1 single bond to c1
		O labeled o1 single bond to c1
		M labeled p2 single bond to o1
}
reactant r2{
		M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond }
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
		fragment a{
			M labeled m1}
		! r1 contains >3 of a
}*/
form bond (c1,m1)
form bond (h1,m2)
break bond (c1,h1)
break bond (c1,p1)
break bond (o1,p2)
increase bond order (o1,c1)
}

//CH scission where there the central C is connected to an oxygen that is weakly bonded, and also connected to to C-O surface ring
rule CHscission5{
adsorbedMol reactant r1{
		C labeled c1
		H labeled h1 single bond to c1
		C labeled c2 single bond to c1
		M labeled p1 single bond to c2
		O labeled o1 single bond to c2
		M labeled p2 single bond to o1
		O labeled o2 single bond to c1
		M labeled mp1 partial bond to o2
}
reactant r2{
		M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond }
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
		fragment a{
			M labeled m1}
		! r1 contains >3 of a
}*/
form bond (c1,m1)
form bond (h1,m2)
break bond (c1,h1)
break bond (c2,p1)
break bond (o1,p2)
increase bond order (o1,c2)
break partial bond (mp1,o2)
}

//CH scission where central C is both a part of C-O surface ring and is bonded to an O which is weakly bonded
rule CHscission6{
adsorbedMol reactant r1{
		C labeled c1
		H labeled h1 single bond to c1
		M labeled p1 single bond to c1
		O labeled o1 single bond to c1
		M labeled p2 single bond to o1
		O labeled o2 single bond to c1
```

```
		M labeled mp1 partial bond to o2
}
reactant r2{
		M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond }
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
		fragment a{
			M labeled m1}
		! r1 contains >3 of a
}*/
form bond (c1,m1)
form bond (h1,m2)
break bond (c1,h1)
break bond (c1,p1)
break bond (o1,p2)
increase bond order (o1,c1)
break partial bond (mp1,o2)
}

rule CHscission7{
adsorbedMol reactant r1{
		C labeled c1
		H labeled h1 single bond to c1
		O labeled o1 any bond to c1
		M labeled mp partial bond to o1
		C labeled c2 single bond to c1
		O labeled o2 single bond to c2 {! connected to >=1 M with any bond}
}
reactant r2{
		M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond }
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
		fragment a{
			M labeled m1}
		! r1 contains >3 of a
}*/
form bond (c1,m1)
form bond (h1,m2)
break bond (c1,h1)
break partial bond (o1,mp)
form partial bond (o2,mp)
}

rule CCscission{
adsorbedMol reactant r1{
		C labeled c1
		C labeled c2 single bond to c1
}
reactant r2{
		M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
		fragment a{
			M labeled m1}
		! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
```

```
/*product constraints on Mol{
  fragment f{
    C labeled c1 {connected to 1 O with double bond, connected to 2 M with single bond}
  }
  ! Mol contains >=1 of f
 }*/

}

//CC scission where one of hte carbon is bonded to an oxygen that is weakly bound to the surface
rule CCscission2{
adsorbedMol reactant r1{
        C labeled c1
        C labeled c2 single bond to c1
        O labeled o1 any bond to c1
        M labeled mp partial bond to o1
}
reactant r2{
        M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break partial bond (o1,mp)
}

//CC scission where both carbon atoms are bonded to oxygen atoms that are weakly bonded to the surface
rule CCscission3{
adsorbedMol reactant r1{
        C labeled c1
        C labeled c2 single bond to c1
        O labeled o1 any bond to c1
        O labeled o2 any bond to c2
        M labeled mp1 partial bond to o1
        M labeled mp2 partial bond to o2
}
reactant r2{
        M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break partial bond (o1,mp1)
break partial bond (o2,mp2)

}

//CC scission where one the central Cs is bonded to a surface C-O ring
```

```
rule CCscission4{
adsorbedMol reactant r1{
        C labeled c1
        C labeled c2 single bond to c1
        C labeled c3 single bond to c1
        O labeled o1 single bond to c3
        M labeled p1 single bond to c3
        M labeled p2 single bond to o1
}
reactant r2{
        M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break bond (c3,p1)
break bond (o1,p2)
increase bond order (c3,o1)

}

//NOTE: No need for the case of two surface bound C-O groups, one on each of the central carbons (c1,c2) because
# C <=3 always!

//CC scission where one C is adjacent to surface C-O ring and other C is a part of another (combination of the above
two)
rule CCscission5{
adsorbedMol reactant r1{
        C labeled c1
        C labeled c2 single bond to c1
        C labeled c3 single bond to c1
        O labeled o1 single bond to c3
        M labeled p1 single bond to c3
        M labeled p2 single bond to o1
        M labeled p3 single bond to c1
        O labeled o2 single bond to c1
        M labeled p4 single bond to o2
}
reactant r2{
        M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break bond (c3,p1)
break bond (o1,p2)
increase bond order (c3,o1)
break bond (c1,p3)
break bond (o2,p4)
increase bond order (c1,o2)
```

```
}

//both CC carbons are part of C-O rings
rule CCscission6{
adsorbedMol reactant r1{
        C labeled c1
        C labeled c2 single bond to c1
        O labeled o1 single bond to c1
        M labeled p1 single bond to c1
        M labeled p2 single bond to o1
        O labeled o2 single bond to c2
        M labeled p3 single bond to c2
        M labeled p4 single bond to o2
}
reactant r2{
        M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break bond (c1,p1)
break bond (o1,p2)
increase bond order (c1,o1)
break bond (c2,p3)
break bond (o2,p4)
increase bond order (c2,o2)
}


//CC-O scission
rule CCscission7{
adsorbedMol reactant r1{
        C labeled c1
        C labeled c2 single bond to c1
        O labeled o1 single bond to c2
        M labeled p1 single bond to c2
        M labeled p2 single bond to o1
}
reactant r2{
        M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break bond (c2,p1)
break bond (o1,p2)
increase bond order (c2,o1)
}

//(O_)CCC-O scission
```

```
rule CCscission8{
adsorbedMol reactant r1{
        C labeled c1
        C labeled c2 single bond to c1
        C labeled c3 single bond to c1
        O labeled o1 single bond to c3
        M labeled p1 single bond to c3
        M labeled p2 single bond to o1
        O labeled o2 single bond to c2
        M labeled mp1 partial bond to o2
}
reactant r2{
        M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break bond (c3,p1)
break bond (o1,p2)
increase bond order (c3,o1)
break partial bond (o2,mp1)
}

//CC(O_)C-O scission
rule CCscission9{
adsorbedMol reactant r1{
        C labeled c1
        C labeled c2 single bond to c1
        C labeled c3 single bond to c1
        O labeled o1 single bond to c3
        M labeled p1 single bond to c3
        M labeled p2 single bond to o1
        O labeled o2 single bond to c1
        M labeled mp1 partial bond to o2
}
reactant r2{
        M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break bond (c3,p1)
break bond (o1,p2)
increase bond order (c3,o1)
break partial bond (o2,mp1)
}

//(O_)CC(O_)C-O
rule CCscission10{
adsorbedMol reactant r1{
```

```
		C labeled c1
		C labeled c2 single bond to c1
		C labeled c3 single bond to c1
		O labeled o1 single bond to c3
		M labeled p1 single bond to c3
		M labeled p2 single bond to o1
		O labeled o2 single bond to c1
		M labeled mp1 partial bond to o2
		O labeled o3 single bond to c2
		M labeled mp2 partial bond to o3
}
reactant r2{
		M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
		fragment a{
			M labeled m1}
		! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break bond (c3,p1)
break bond (o1,p2)
increase bond order (c3,o1)
break partial bond (o2,mp1)
break partial bond (o3,mp2)

}

//(O_)CC-O
rule CCscission11{
adsorbedMol reactant r1{
		C labeled c1
		C labeled c2 single bond to c1
		O labeled o1 single bond to c2
		M labeled p1 single bond to c2
		M labeled p2 single bond to o1
		O labeled o2 single bond to c1
		M labeled mp1 partial bond to o2
}
reactant r2{
		M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
		fragment a{
			M labeled m1}
		! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break bond (c2,p1)
break bond (o1,p2)
increase bond order (c2,o1)
break partial bond (mp1,o2)

}

//(O-C)C(O_)C-O
```

```
rule CCscission12{
adsorbedMol reactant r1{
        C labeled c1
        C labeled c2 single bond to c1
        O labeled o1 single bond to c2
        M labeled p1 single bond to c2
        M labeled p2 single bond to o1
        O labeled o2 single bond to c1
        M labeled mp1 partial bond to o2
        C labeled c3 single bond to c1
        O labeled o3 single bond to c3
        M labeled p3 single bond to c3
        M labeled p4 single bond to o3
}
reactant r2{
        M labeled m1 {! connected to >=1 H,! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}
form bond (c1,m1)
form bond (c2,m2)
break bond (c1,c2)
break bond (c2,p1)
break bond (o1,p2)
increase bond order (c2,o1)
break partial bond (mp1,o2)
break bond (c3,p3)
break bond (o3,p4)
increase bond order (c3,o3)
}


rule CCScissionToFormCOgas{
reactant r1{
        C labeled c1
        C labeled c2 single bond to c1 {connected to 1 O with double bond}
        M labeled m1 single bond to c2
}
/*
constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}
*/
break bond (c2,m1)
form bond (c1,m1)
break bond (c1,c2)
modify atomtype (c2,C:)
}

rule CCScissionToFormCOgas2{
reactant r1{
        C labeled c1
        C labeled c2 single bond to c1 {connected to 1 O with double bond}
        M labeled m1 single bond to c2
        O labeled o1 single bond to c1
        M labeled mp1 partial bond to o1
```

```
}

/*
constraints {
	fragment a{
		M labeled m1}
	! r1 contains >3 of a
}
*/
break bond (c2,m1)
form bond (c1,m1)
break bond (c1,c2)
modify atomtype (c2,C:)
break partial bond (mp1,o1)
}

rule CCScissionToFormCOgas3{
reactant r1{
	C labeled c1
	C labeled c2 single bond to c1 {connected to 1 O with double bond}
	M labeled m1 single bond to c2
	C labeled c3 single bond to c1
	O labeled o1 single bond to c3
	M labeled p1 single bond to c3
	M labeled p2 single bond to o1
}
/*

constraints {
	fragment a{
		M labeled m1}
	! r1 contains >3 of a
}

*/
break bond (c2,m1)
form bond (c1,m1)
break bond (c1,c2)
modify atomtype (c2,C:)
break bond (p1,c3)
break bond (p2,o1)
increase bond order (c3,o1)
}

rule CCScissionToFormCOgas4{
reactant r1{
	C labeled c1
	C labeled c2 single bond to c1 {connected to 1 O with double bond}
	M labeled m1 single bond to c2
	O labeled o1 single bond to c1
	M labeled mp1 partial bond to o1
	C labeled c3 single bond to c1
	O labeled o2 single bond to c3
	M labeled p1 single bond to c3
	M labeled p2 single bond to o2
}

/*
constraints {
	fragment a{
		M labeled m1}
	! r1 contains >3 of a
```

```
}
*/
break bond (c2,m1)
form bond (c1,m1)
break bond (c1,c2)
modify atomtype (c2,C:)
break partial bond (mp1,o1)
break bond (c3,p1)
break bond (o2,p2)
increase bond order (c3,o2)
}



rule OHscission{
adsorbedMol reactant r1{
        O labeled o1
        H labeled h1 single bond to o1
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}*/
form bond (o1,m1)
form bond (h1,m2)
break bond (o1,h1)
}

rule OHscission2{
adsorbedMol reactant r1{
        O labeled o1
        H labeled h1 single bond to o1
        M labeled mp1 partial bond to o1
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
        fragment a{
                M labeled m1}
        ! r1 contains >3 of a
}*/
form bond (o1,m1)
form bond (h1,m2)
break bond (o1,h1)
break partial bond (o1,mp1)
}

rule OHscission3{
adsorbedMol reactant r1{
        O labeled o1
        H labeled h1 single bond to o1
        M labeled mp1 partial bond to o1
        C labeled c1 single bond to o1
        O labeled o2 single bond to c1 {! connected to >=1 M with partial bond}
```

```
}
reactant r2{
	M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
	fragment a{
		M labeled m1}
	! r1 contains >3 of a
}*/
form bond (o1,m1)
form bond (h1,m2)
break bond (o1,h1)
break partial bond (o1,mp1)
form partial bond (o2,mp1)
}


rule OHscission4{
adsorbedMol reactant r1{
	O labeled o1
	H labeled h1 single bond to o1
	M labeled mp1 partial bond to o1
	C labeled c1 any bond to o1
	C labeled c2 any bond to c1
	O labeled o2 single bond to c2 {! connected to >=1 M with partial bond}

}
reactant r2{
	M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
/*constraints {
	fragment a{
		M labeled m1}
	! r1 contains >3 of a
}*/
form bond (o1,m1)
form bond (h1,m2)
break bond (o1,h1)
break partial bond (o1,mp1)
form partial bond (o2,mp1)
}

rule HHscission{
reactant r1{
	H labeled h1
	H labeled h2 single bond to h1
}
reactant r2{
	M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)

break bond (h1,h2)
form bond (h1,m1)
form bond (h2,m2)

}

rule CHformation{
reactant r1{
```

```
        C labeled c1
        M labeled m1 single bond to c1
}
reactant r2{
        M labeled m2
        H labeled h1 single bond to m2}

form bond (c1,h1)
break bond (c1,m1)
break bond (h1,m2)
}

rule CHformation2{
reactant r1{
        C labeled c1
        M labeled m1 single bond to c1
        O labeled o1 single bond to c1 {! connected to >=1 M with partial bond}
}
reactant r2{
        M labeled m2
        H labeled h1 single bond to m2}

form bond (c1,h1)
break bond (c1,m1)
break bond (h1,m2)
form partial bond (o1,m1)
}

rule CHformation3{
reactant r1{
  C labeled c1
  M labeled m1 single bond to c1
  O labeled o1 single bond to c1 {! connected to >=1 M with partial bond}
  C labeled c2 any bond to c1
  O labeled o2 single bond to c2
  M labeled mp1 partial bond to o2
}
reactant r2{
        M labeled m2
        H labeled h1 single bond to m2}
form bond (c1,h1)
break bond (c1,m1)
break bond (h1,m2)
form partial bond (o1,m1)
break partial bond (o2,mp1)
}

rule HHformation{
reactant r1{

        M labeled m1
        H labeled h1 single bond to m1
}
reactant r2{
        M labeled m2
        H labeled h2 single bond to m2}

form bond (h1,h2)
break bond (h1,m1)
break bond (h2,m2)
}
```

```
rule OHformation{
reactant r1{
  O labeled o1
  M labeled m1 single bond to o1
}
reactant r2{
  M labeled m2
  H labeled h1 single bond to m2}

form bond (o1,h1)
break bond (o1,m1)
break bond (h1,m2)
}

rule OHformation2{
reactant r1{
  O labeled o1
  M labeled m1 single bond to o1
}
reactant r2{
  M labeled m2
  H labeled h1 single bond to m2}

form bond (o1,h1)
modify bond (o1,m1, partial)
break bond (h1,m2)
}

rule OHformation3{
reactant r1{
  O labeled o1
  M labeled m1 single bond to o1
  C labeled c1 single bond to o1
  O labeled o2 single bond to c1
  M labeled mp1 partial bond to o2
}
reactant r2{
  M labeled m2
  H labeled h1 single bond to m2}

form bond (o1,h1)
modify bond (o1,m1, partial)
break bond (h1,m2)
break partial bond (o2,mp1)
}


rule CdoubleCFormation{
reactant r1{
  C labeled c1
  C labeled c2 single bond to c1
  M labeled m1 single bond to c1
  M labeled m2 single bond to c2
}

break bond (c1,m1)
break bond (c2,m2)
increase bond order (c1,c2)
}

rule CdoubleOFormation
{
```

```
reactant r1{
  C labeled c1
  O labeled o1 single bond to c1
  H labeled h1 single bond to c1
  M labeled m1 single bond to o1

}

break bond (o1,m1)
break bond (c1,h1)
form bond (h1,m1)

increase bond order (c1,o1)
}

rule CdoubleOFromCOH{
reactant r1{
  C labeled c1
  M labeled m1 single bond to c1
  O labeled o1 single bond to c1
  H labeled h1 single bond to o1
}
break bond (c1,m1)
form bond (h1,m1)
break bond (o1,h1)
increase bond order (c1,o1)
}

rule CarbonMonoxideFormation
{
reactant r1{
C labeled c1
O labeled o1 double bond to c1
M labeled m1 single bond to c1
M labeled m2 single bond to c1
}

break bond (c1,m1)
break bond (c1,m2)
modify atomtype (c1,C:)
}

rule COScission{
reactant r1{
  C labeled c1
  O labeled o1 single bond to c1
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
break bond (c1,o1)
form bond (c1,m1)
form bond (o1,m2)
}

rule COScission2{
reactant r1{
  C labeled c1
  O labeled o1 single bond to c1
  M labeled mp1 partial bond to o1
}
```

```
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
break bond (c1,o1)
form bond (c1,m1)
form bond (o1,m2)
break partial bond (o1,mp1)
}

rule COScission3{
reactant r1{
  C labeled c1
  O labeled o1 single bond to c1
  O labeled o2 single bond to c1
  M labeled mp1 partial bond to o2
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
break bond (c1,o1)
form bond (c1,m1)
form bond (o1,m2)
break partial bond (o2,mp1)
}

rule COScission4{
reactant r1{
  C labeled c1
  O labeled o1 single bond to c1
  O labeled o2 single bond to c1
  M labeled mp1 partial bond to o2
  M labeled mp2 partial bond to o1
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
break bond (c1,o1)
form bond (c1,m1)
form bond (o1,m2)
break partial bond (o2,mp1)
break partial bond (o1,mp2)
}

rule COScission5{
reactant r1{
  C labeled c1
  O labeled o1 single bond to c1
  C labeled c2 single bond to c1
  O labeled o2 single bond to c2
  M labeled bm1 single bond to c2
  M labeled bm2 single bond to o2
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
break bond (c1,o1)
form bond (c1,m1)
form bond (o1,m2)
```

```
break bond (bm1,c2)
break bond (bm2,o2)
increase bond order (c2,o2)
}

rule COScission6{
reactant r1{
  C labeled c1
  O labeled o1 single bond to c1
  C labeled c2 single bond to c1
  O labeled o2 single bond to c2
  M labeled bm1 single bond to c2
  M labeled bm2 single bond to o2
  M labeled mp1 partial bond to o1
}
reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
break bond (c1,o1)
form bond (c1,m1)
form bond (o1,m2)
break bond (bm1,c2)
break bond (bm2,o2)
increase bond order (c2,o2)
break partial bond (mp1,o1)
}

rule COScission7{
reactant r1{
  C labeled c1
  O labeled o1 single bond to c1
  M labeled bm1 single bond to c1
  O labeled o2 single bond to c1
  M labeled bm2 single bond to o2
}

reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
reactant r3 duplicates r2(m1=>m2)
break bond (c1,o1)
form bond (c1,m1)
form bond (o1,m2)
break bond (bm1,c1)
break bond (bm2,o2)
increase bond order (c1,o2)
}

rule COScission8{
reactant r1{
  C labeled c1
  O labeled o1 single bond to c1
  M labeled bm1 single bond to c1
  O labeled o2 single bond to c1
  M labeled bm2 single bond to o2
  M labeled mp1 partial bond to o1
}

reactant r2{
        M labeled m1 {! connected to >=1 H, ! connected to >=1 $ with any bond}
}
```

```
reactant r3 duplicates r2(m1=>m2)
break bond (c1,o1)
form bond (c1,m1)
form bond (o1,m2)
break bond (bm1,c1)
break bond (bm2,o2)
increase bond order (c1,o2)
break partial bond (mp1,o1)
}

//reaction query
find all reactions {
  reaction rule is COScission || reaction rule is COScission2 || reaction rule is COScission3 || reaction rule is COScission4 || reaction rule is COScission5 || reaction rule is COScission6 || reaction rule is COScission7 || reaction rule is COScission8
  reaction with >=1 reactant m1{
     fragment f{ C labeled c1}
              fragment f2{ O labeled o1}
              m1 contains >=3 of f && m1 contains >=3 of f2
              }
} store in "ThreeCarbonCOScissionRxns.txt"

/* -- Pathway query to 1,2 propane diol
find pathways to mol{
mol is "C(O)C(O)C"
} constraints {
maximum length shortest + 3

rule CHscission only occurs with activation energy <= 180 kJ/mol
rule CHscission2 only occurs with activation energy <= 180 kJ/mol
rule CHscission3 only occurs with activation energy <= 180 kJ/mol
rule CHscission4 only occurs with activation energy <= 180 kJ/mol
rule CHscission5 only occurs with activation energy <= 180 kJ/mol
rule CHscission6 only occurs with activation energy <= 180 kJ/mol
rule CHscission7 only occurs with activation energy <= 180 kJ/mol

rule CHformation only occurs with activation energy <= 180 kJ/mol
rule CHformation2 only occurs with activation energy <= 180 kJ/mol
rule CHformation3 only occurs with activation energy <= 180 kJ/mol

rule OHadsorption2 only occurs with activation energy <= 180 kJ/mol
rule OHdesorption2 only occurs with activation energy <= 180 kJ/mol

rule OHscission only occurs with activation energy <= 180 kJ/mol
rule OHscission2 only occurs with activation energy <= 180 kJ/mol
rule OHscission3 only occurs with activation energy <= 180 kJ/mol
rule OHscission4 only occurs with activation energy <= 180 kJ/mol

rule COScission only occurs with activation energy <= 180 kJ/mol
rule COScission2 only occurs with activation energy <= 180 kJ/mol
rule COScission3 only occurs with activation energy <= 180 kJ/mol
rule COScission4 only occurs with activation energy <= 180 kJ/mol
rule COScission5 only occurs with activation energy <= 180 kJ/mol
rule COScission6 only occurs with activation energy <= 180 kJ/mol
rule COScission7 only occurs with activation energy <= 180 kJ/mol
rule COScission8 only occurs with activation energy <= 180 kJ/mol

} store in "To12propanediolwAE.txt"*/

//Pathway query to form Carbon Monoxide
find pathways to mol{
mol is "[C:]=O"
```

```
} constraints {
maximum length shortest + 3
contains <1 rule CCScissionToFormCOgas
contains <1 rule CCScissionToFormCOgas2
contains <1 rule CCScissionToFormCOgas3
contains <1 rule CCScissionToFormCOgas4

rule CHscission only occurs with activation energy <= 90 kJ/mol
rule CHscission2 only occurs with activation energy <= 90 kJ/mol
rule CHscission3 only occurs with activation energy <= 90 kJ/mol
rule CHscission4 only occurs with activation energy <= 90 kJ/mol
rule CHscission5 only occurs with activation energy <= 90 kJ/mol
rule CHscission6 only occurs with activation energy <= 90 kJ/mol
rule CHscission7 only occurs with activation energy <= 90 kJ/mol

rule CHformation only occurs with activation energy <= 90 kJ/mol
rule CHformation2 only occurs with activation energy <= 90 kJ/mol
rule CHformation3 only occurs with activation energy <= 90 kJ/mol

rule OHadsorption2 only occurs with activation energy <= 90 kJ/mol
rule OHdesorption2 only occurs with activation energy <= 90 kJ/mol

rule OHscission only occurs with activation energy <= 90 kJ/mol
rule OHscission2 only occurs with activation energy <= 90 kJ/mol
rule OHscission3 only occurs with activation energy <= 90 kJ/mol
rule OHscission4 only occurs with activation energy <= 90 kJ/mol

rule CCscission only occurs with activation energy <= 95 kJ/mol
rule CCscission2 only occurs with activation energy <= 95 kJ/mol
rule CCscission3 only occurs with activation energy <= 95 kJ/mol
rule CCscission4 only occurs with activation energy <= 95 kJ/mol
rule CCscission5 only occurs with activation energy <= 95 kJ/mol
rule CCscission6 only occurs with activation energy <= 95 kJ/mol
rule CCscission7 only occurs with activation energy <= 95 kJ/mol
rule CCscission8 only occurs with activation energy <= 95 kJ/mol
rule CCscission9 only occurs with activation energy <= 95 kJ/mol
rule CCscission10 only occurs with activation energy <= 95 kJ/mol
rule CCscission11 only occurs with activation energy <= 95 kJ/mol
rule CCscission12 only occurs with activation energy <= 95 kJ/mol

} store in "ToCOwAE.txt"

//Mechanisms query for Carbon Monoxide
find direct mechanisms to mol{
   mol is "[C:]=O"
  } constraints {
   maximum length 11
   contains <1 rule CHformation &&
   contains <1 rule CHformation2 &&
   contains <1 rule CHformation3 &&
   contains <1 rule OHformation &&
   contains <1 rule OHformation2 &&
   contains <1 rule OHformation3

   contains < 0 mol{
      mol is "OCC(O)CO"
   } in overall stoichiometry

   contains > 2 mol {
     mol is "[C:]=O"
   } in overall stoichiometry
```

```
  } store in "CODirectMechsFromGlycerol.txt"
```

S9. Kinetics file (for calculating activation barriers)

```
import "glycerol_decomposition_GA_final.txt"

kinetics OHadsorption{

  sticking factor A 1.0 L/mol/s Ea 0.0 kJ/mol n 0.0
}

kinetics OHadsorption2{

  sticking factor A 1.0 (L/mol)^2/s Ea 0.0 kJ/mol n 0.0
}

kinetics OHdesorption{
  use reverse of OHadsorption
}

kinetics OHdesorption2{
  use reverse of OHadsorption
}

kinetics OHdesorption3{
  use reverse of OHadsorption
}


kinetics CHscission{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 1.02, b = 1.06*96.45 kJ/mol ) n 0.0
}

//the only difference between this and the prev is that here C is bonded to a weakly bound O
kinetics CHscission2{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 1.02, b = 1.06*96.45 kJ/mol ) n 0.0
}

//CH scission where the C-O surface ring is adjacent to the central C
kinetics CHscission3{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 1.02, b = 1.06*96.45 kJ/mol ) n 0.0
}

//CH scission where the carbon of C-O surface ring is central
kinetics CHscission4{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 1.02, b = 1.06*96.45 kJ/mol ) n 0.0
}

//CH scission where there the central C is connected to an oxygen that is weakly bonded, and also connected to to C-
O surface ring
kinetics CHscission5{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 1.02, b = 1.06*96.45 kJ/mol ) n 0.0
}

//CH scission where central C is both a part of C-O surface ring and is bonded to an O which is weakly bonded
kinetics CHscission6{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 1.02, b = 1.06*96.45 kJ/mol ) n 0.0
}

kinetics CHscission7{
```

```
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 1.02, b = 1.06*96.45 kJ/mol ) n 0.0
}

kinetics CCscission{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

//CC scission where one of hte carbon is bonded to an oxygen that is weakly bound to the surface
kinetics CCscission2{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

//CC scission where both carbon atoms are bonded to oxygen atoms that are weakly bonded to the surface
kinetics CCscission3{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

//CC scission where one the central Cs is bonded to a surface C-O ring
kinetics CCscission4{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}


kinetics CCscission5{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

//both CC carbons are part of C-O rings
kinetics CCscission6{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}


//CC-O scission
kinetics CCscission7{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

//(O_)CCC-O scission
kinetics CCscission8{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

//CC(O_)C-O scission
kinetics CCscission9{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

//(O_)CC(O_)C-O
kinetics CCscission10{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

//(O_)CC-O
kinetics CCscission11{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

//(O-C)C(O_)C-O
kinetics CCscission12{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}
```

```
kinetics CCScissionToFormCOgas{
  A 1.0e13 1/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

kinetics CCScissionToFormCOgas2{
  A 1.0e13 1/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

kinetics CCScissionToFormCOgas3{
  A 1.0e13 1/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}

kinetics CCScissionToFormCOgas4{
  A 1.0e13 1/s Ea from BEP (a = 0.66, b = 1.59*96.45 kJ/mol ) n 0.0
}



kinetics OHscission{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.86, b = 0.56*96.45 kJ/mol ) n 0.0
}

kinetics OHscission2{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.86, b = 0.56*96.45 kJ/mol ) n 0.0
}

kinetics OHscission3{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.86, b = 0.56*96.45 kJ/mol ) n 0.0
}


kinetics OHscission4{
  A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.86, b = 0.56*96.45 kJ/mol ) n 0.0
}

kinetics HHscission{
  sticking factor A 0.1 (L/mol)^2/s Ea 0.0 kJ/mol n 0.0

}

kinetics CHformation{
  use reverse of CHscission
}

kinetics CHformation2{
  //A 1.0e13 L/mol/s Ea from BEP (a = .02, b = 1.06*96.45 kJ/mol ) n 0.0
  use reverse of CHscission
}

kinetics CHformation3{
  //A 1.0e13 L/mol/s Ea from BEP (a = .02, b = 1.06*96.45 kJ/mol ) n 0.0
  use reverse of CHscission
}

kinetics HHformation{
  //A 1.0e13 L/mol/s Ea 0.0 kJ/mol n 0.0
  use reverse of HHscission
}

kinetics OHformation{
```

```
 // A 1.0e13 L/mol/s Ea from BEP (a = -0.14, b = 0.56*96.45 kJ/mol ) n 0.0
 use reverse of OHscission
}

kinetics OHformation2{
  //A 1.0e13 L/mol/s Ea from BEP (a = -0.14, b = 0.56*96.45 kJ/mol ) n 0.0
  use reverse of OHscission
}

kinetics OHformation3{
  //A 1.0e13 L/mol/s Ea from BEP (a = -0.14, b = 0.56*96.45 kJ/mol ) n 0.0
  use reverse of OHscission
}


kinetics CdoubleCFormation{
  //A 1.0e13 1/s Ea 0.0 kJ/mol n 0.0
  use reverse of OHscission
}

kinetics CdoubleOFormation{
  A 1.0e13 1/s Ea from BEP (a = 1.02, b = 1.06*96.45 kJ/mol ) n 0.0
}

kinetics CdoubleOFromCOH{
  A 1.0e13 1/s Ea from BEP (a = 0.86, b = 0.56*96.45 kJ/mol ) n 0.0
}

kinetics CarbonMonoxideFormation{
  A 1.0e13 1/s Ea 0.0 kJ/mol n 0.0
  //use reverse of CarbonMonoxideAdsorption
}
/*
kinetics CarbonMonoxideAdsorption{
  sticking factor A 0.8 (L/mol)^2/s Ea 0.0 kJ/mol n 0.0
}*/


kinetics COScission{
  define COvalue: A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.84, b = 1.87*96.45 kJ/mol ) n 0.0
  define COHvalue: A 1.0e13 (L/mol)^2/s Ea from BEP (a = 0.69, b = 1.43*96.45 kJ/mol ) n 0.0
  if product mol any (mol is "[{M}]O")
   { use COHvalue}
  use COvalue
}

kinetics COScission2{
   if product mol any (mol is "[{M}]O")
   { use COScission.COHvalue}
  use COScission.COvalue
}

kinetics COScission3{
   if product mol any (mol is "[{M}]O")
   { use COScission.COHvalue}
  use COScission.COvalue
}

kinetics COScission4{
   if product mol any (mol is "[{M}]O")
   { use COScission.COHvalue}
  use COScission.COvalue
```

```
}

kinetics COScission5{
   if product mol any (mol is "[{M}]O")
   { use COScission.COHvalue}
  use COScission.COvalue
}

kinetics COScission6{
   if product mol any (mol is "[{M}]O")
   { use COScission.COHvalue}
  use COScission.COvalue
}

kinetics COScission7{
   if product mol any (mol is "[{M}]O")
   { use COScission.COHvalue}
  use COScission.COvalue
}

kinetics COScission8{
   if product mol any (mol is "[{M}]O")
   { use COScission.COHvalue}
  use COScission.COvalue
}
```

S10. Group additivity file

```
import "glycerol_decomposition_GA_final.txt"

define composite atom Zeo, HTA


group additivity {

//C(H)(H)(H)(H) - Methane -- taken from NIST (Rln12 added to entropy)
fragment {
   C labeled c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   H labeled h3 single bond to c1
   H labeled h4 single bond to c1
} enthalpy -74.87 kJ/mol entropy 209.37 J/mol/K cp (298=> 35.69 J/mol/K, 400=> 40.63 J/mol/K, 500=> 46.63
J/mol/K, 600=> 52.74 J/mol/K, 800=> 64.08 J/mol/K, 1000=> 73.75 J/mol/K, 1500=> 90.86 J/mol/K)

//C(C)(H)(H)(H)   -42.9   127.12   25.31  32.07   38.44   44.06   53.36   60.63   72.47
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   H labeled h3 single bond to c1
   } enthalpy -42.9 kJ/mol entropy 127.12 cp (298=>25.31, 400=>32.07, 500=>38.44, 600=>44.06, 800=>53.36,
1000=>60.63, 1500=>72.47)

//C(C)(C)(H)(H)   -20.5   39.96   25.05   30.11   35.05   39.40   46.39   51.60   59.63
fragment {
   C labeled c1
   C labeled c2 single bond to c1
```

```
   C labeled c3 single bond to c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   } enthalpy -20.5 kJ/mol entropy 39.96 cp (298=>25.05, 400=>30.11, 500=>35.05 , 600=>39.40, 800=>46.39,
1000=>51.60, 1500=>59.63)

//C(C)(C)(C)(H)   -6.9   -48.97   21.44 27.27   31.71   35.10   39.83   42.89   47.01
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 single bond to c1
   C labeled c4 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy -6.9 kJ/mol entropy -48.97 cp (298=>21.44, 400=>27.27, 500=>31.71, 600=>35.10, 800=>39.83,
1000=>42.89, 1500=>47.01)

//C(C)(C)(C)(C)   3.9   -148.25   17.53   24.47   29.01   31.78   34.22   34.72   33.79
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 single bond to c1
   C labeled c4 single bond to c1
   C labeled c5 single bond to c1
   } enthalpy 3.9 kJ/mol entropy -148.25 cp (298=>17.53, 400=>24.47, 500=>29.01, 600=>31.78, 800=>34.22,
1000=>34.72, 1500=>33.79)

//C(=C)(H)(H)   25.1   115.76   20.59   25.93   30.75   34.87   41.44   46.45   54.57
fragment {
   C labeled c1
   C labeled c2 double bond to c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   } enthalpy 25.1 kJ/mol entropy 115.76 cp(298=>20.59, 400=>25.93, 500=>30.75, 600=>34.87, 800=>41.44,
1000=>46.45, 1500=>54.57)

//C(=C)(C)(H)   37.1   32.91   18.44   21.74   25.02   27.96   32.65   36.06   41.17
fragment {
   C labeled c1
   C labeled c2 double bond to c1
   C labeled c3 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy 37.1 kJ/mol entropy 32.91 cp (298=>18.44, 400=>21.74, 500=>25.02, 600=>27.96, 800=>32.65,
1000=>36.06, 1500=>41.17)

//C(=C)(C)(C)   45.3   -55.9   19.58   21.71   23.12   24.25   25.94   27.02   28.35
fragment {
   C labeled c1
   C labeled c2 double bond to c1
   C labeled c3 single bond to c1
   C labeled c4 single bond to c1
   } enthalpy 45.3 kJ/mol entropy -55.9 cp(298=>19.58, 400=>21.71, 500=>23.12, 600=>24.25, 800=>25.94,
1000=>27.02, 1500=>28.35)

//C(=C)(C=C)(H)   30.4   25.73   18.10   24.14   29.11   32.72   37.14   39.66   43.06
fragment {
   C labeled c1
   C labeled c2 double bond to c1
   C labeled c3 single bond to c1
   C labeled c4 double bond to c3
   H labeled h1 single bond to c1
   } enthalpy 30.4 kJ/mol entropy 25.73 cp(298=>18.10, 400=>24.14, 500=>29.11, 600=>32.72, 800=>37.14,
1000=>39.66, 1500=>43.06)
```

```
//C(=C)(C=C)(C)   40.0   -62.49   18.57   23.97   26.76   28.02   28.75   28.88   28.97
fragment {
   C labeled c1
   C labeled c2 double bond to c1
   C labeled c3 single bond to c1
   C labeled c4 double bond to c3
   C labeled c5 single bond to c1
   } enthalpy 40.0 kJ/mol entropy -62.9  cp(298=>18.57, 400=>23.97, 500=>26.76, 600=>28.02, 800=>28.75,
1000=>28.88, 1500=>28.97)

//C(=C)(C=C)(C=C)   46.9   -49.16   18.68   19.20   18.83   18.80   20.02   21.79   25.04
fragment {
   C labeled c1
   C labeled c2 double bond to c1
   C labeled c3 single bond to c1
   C labeled c4 double bond to c3
   C labeled c5 single bond to c1
   C labeled c6 double bond to c5
   } enthalpy 46.9 kJ/mol entropy -49.16  cp(298=>18.68, 400=>19.20, 500=>18.83, 600=>18.80, 800=>20.02,
1000=>21.79, 1500=>25.04)

//C(=C)(=C)   141.3   25.58   15.24   17.29   18.73   19.79   21.26   22.24   23.53
fragment {
   C labeled c1
   C labeled c2 double bond to c1
   C labeled c3 double bond to c1
   } enthalpy 141.3 kJ/mol entropy 25.58  cp(298=>15.24, 400=>17.29, 500=>18.73, 600=>19.79, 800=>21.26,
1000=>22.24, 1500=>23.53)

//C(C=C)(H)(H)(H)   -42.9   127.20   24.95   31.78   38.21   43.88   53.23   60.51   72.28
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   H labeled h3 single bond to c1
   } enthalpy -42.9 kJ/mol entropy 127.20 cp(298=>24.95, 400=>31.78, 500=>38.21, 600=>43.88, 800=>53.23,
1000=>60.51, 1500=>72.28)

//C(C=C)(C)(H)(H)   -18.9   41.91   21.93   28.33   33.87   38.47   45.63   50.93   59.18
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   } enthalpy -18.9 kJ/mol entropy 41.91  cp(298=>21.93, 400=>28.33, 500=>33.87, 600=>38.47, 800=>45.63,
1000=>50.93, 1500=>59.18)

//C(C=C)(C)(C)(H)   -3.9   -49.65   24.94   30.73   35.02   38.03   41.77   44.07   47.41
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy -3.9 kJ/mol entropy -49.65  cp(298=>24.94, 400=>30.73, 500=> 35.02, 600=>38.03, 800=>41.77,
1000=>44.07, 1500=>47.41)
```

```
//C(C=C)(C)(C)(C)   7.1   -142.15   20.74   27.75   32.02   34.38   36.03   36.13   35.39
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 single bond to c1
   C labeled c6 single bond to c1
   } enthalpy 7.1 kJ/mol entropy -142.15  cp(298=>20.74, 400=>27.75, 500=>32.02, 600=>34.38, 800=>36.03,
1000=>36.13, 1500=>35.39)

//C(C=C)(C=C)(H)(H)   -17.1   39.93   24.30   30.13   35.27   39.52   46.13   51.10   59.04
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 double bond to c4
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   } enthalpy -17.1 kJ/mol entropy 39.93 cp(298=>24.30, 400=>30.13, 500=>35.27, 600=>39.52, 800=>46.13,
1000=>51.10, 1500=>59.04)

//C(C=C)(C=C)(C)(H)   0.4   -51.11   24.80   31.62   35.72   38.31   41.49   43.59   46.92
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 double bond to c4
   C labeled c6 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy 0.4 kJ/mol entropy -51.11  cp(298=>24.80, 400=>31.62, 500=>35.72, 600=>38.31, 800=>41.49,
1000=>43.59, 1500=>46.92)

//C(C=C)(C=C)(C)(C)   13.8   -144.37   21.40   28.46   32.44   34.57   36.03   36.05   35.17
fragment {
    C labeled c1
            C labeled c2 single bond to c1
            C labeled c3 double bond to c2
            C labeled c4 single bond to c1
            C labeled c5 double bond to c4
            C labeled c6 single bond to c1
            C labeled c7 single bond to c1
            } enthalpy 13.8 kJ/mol entropy -144.37  cp(298=>21.40,400=>28.46, 500=>32.44, 600=>34.57, 800=>36.03,
1000=>36.05, 1500=>35.17)

//C(C=C)(C=C)(C=C)(H)   4.1   -47.09   22.35   29.28   33.54   36.30   39.83   42.21   45.98
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 double bond to c4
   C labeled c6 single bond to c1
   C labeled c7 double bond to c6
   H labeled h1 single bond to c1
   } enthalpy 4.1 kJ/mol entropy -47.09  cp(298=>22.35, 400=>29.28, 500=>33.54, 600=>36.30, 800=>39.83,
1000=>42.21, 1500=>45.98)

//C(C=C)(C=C)(C=C)(C)   15.3   -157.02   22.88   35.05   40.76   42.57   41.76   39.80   36.50
```

```
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 double bond to c4
   C labeled c6 single bond to c1
   C labeled c7 double bond to c6
   C labeled c8 single bond to c1
   } enthalpy 15.3 kJ/mol entropy -157.02  cp(298=>22.88, 400=>35.05, 500=>40.76, 600=>42.57, 800=>41.76,
1000=>39.80, 1500=>36.50)

//C(C=C)(C=C)(C=C)(C=C)   22.3   -160.76   27.84   39.77   45.02   46.17   44.10   41.24   36.90
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 double bond to c4
   C labeled c6 single bond to c1
   C labeled c7 double bond to c6
   C labeled c8 single bond to c1
   C labeled c9 double bond to c8
   } enthalpy 22.3 kJ/mol entropy -160.76  cp(298=>27.84, 400=>39.77, 500=>45.02, 600=>46.17, 800=>44.10,
1000=>41.24, 1500=>36.90)


//cH   13.8   0.0
fragment {
  c labeled c1
  H labeled h1 single bond to c1
  c labeled c2 aromatic bond to c1
  c labeled c3 aromatic bond to c1
  } enthalpy 13.8 kJ/mol entropy 48.22 cp(298=>13.62, 400=> 18.63, 500=>22.9, 600=>26.35, 800=>31.41,
1000=>34.92, 1500=>40.12)


//cC   24.4   0.0
fragment {
  c labeled c1
  C labeled c2 single bond to c1
  c labeled c3 aromatic bond to c1
  c labeled c4 aromatic bond to c1
  } enthalpy 24.4 kJ/mol entropy -33.23 cp (298=>10.3, 400=>13.56, 500=> 16.42, 600=> 18.77, 800=> 22.05,
1000=> 24.04, 1500=>26.38)

//c(C=C)   24.0   0.0
fragment {
  c labeled c1
  C labeled c2 single bond to c1
  C labeled c5 double bond to c2
  c labeled c3 aromatic bond to c1
  c labeled c4 aromatic bond to c1
  } enthalpy 24.0 kJ/mol entropy -31.53 cp(298=>12.15, 400=> 14.72, 500=> 16.64, 600=> 18.34, 800=> 21.19,
1000=> 23.24, 1500=> 25.93)

//C(c)(H)(H)(H)   -42.9   0.0
fragment {
  C labeled c1
  c labeled c2 single bond to c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
```

```
  H labeled h3 single bond to c1
  } enthalpy -42.9 kJ/mol entropy 127.2  cp(298=>24.95, 400=>31.78, 500=> 38.21, 600=> 43.88, 800=> 53.23,
1000=> 60.51, 1500=> 72.28)

//C(c)(C)(H)(H)   -21.2   0.0
fragment {
  C labeled c1
  c labeled c2 single bond to c1
  C labeled c3 single bond to c1
  H labeled h2 single bond to c1
  H labeled h3 single bond to c1
  } enthalpy -21.2 kJ/mol entropy 39.5 cp(298=> 24.73, 400=> 30.33, 500=> 35.46, 600=> 39.81, 800=>46.59,
1000=> 51.64, 1500=> 59.55)

//C(c)(C)(C)(H)   -4.7   0.0
fragment {
  C labeled c1
  c labeled c2 single bond to c1
  C labeled c3 single bond to c1
  C labeled c4 single bond to c1
  H labeled h3 single bond to c1
  } enthalpy -4.7 kJ/mol entropy -51.95 cp(298=>24.68, 400=> 30.18, 500=> 34.20, 600=> 37.10, 800=> 40.95,
1000=> 43.47, 1500=> 47.15)

//C(c)(C)(C)(C)   11.1   0.0
fragment {
  C labeled c1
  c labeled c2 single bond to c1
  C labeled c3 single bond to c1
  C labeled c4 single bond to c1
  C labeled c5 single bond to c1
  } enthalpy 11.1 kJ/mol entropy -144.1 cp(298=>22.7, 400=> 28.58, 500=> 31.96, 600=> 33.75, 800=> 34.96,
1000=> 35.04, 1500=> 34.54)

//C(c)(C=C)(H)(H)   -19.8   0.0
fragment {
  C labeled c1
  c labeled c2 single bond to c1
  C labeled c3 single bond to c1
  C labeled c4 double bond to c3
  H labeled h2 single bond to c1
  H labeled h3 single bond to c1
  } enthalpy -19.8 kJ/mol entropy 39.4  cp(298=>23.74, 400=> 30.65, 500=> 36.11, 600=> 40.40, 800=> 46.89,
1000=> 51.72, 1500=> 59.39)

//C(c)(C=C)(C)(H)   -3.8   0.0
fragment {
  C labeled c1
  c labeled c2 single bond to c1
  C labeled c3 single bond to c1
  C labeled c4 double bond to c3
  C labeled c5 single bond to c1
  H labeled h1 single bond to c1
  } enthalpy -3.8 kJ/mol entropy -46.68 cp(298=> 21.06, 400=> 27.35, 500=> 31.9, 600=> 35.1, 800=> 39.22, 1000=>
41.76, 1500=> 45.0)

//C(=C)(c)(H)   30.4   0.0
fragment {
  C labeled c1
  C labeled c2 double bond to c1
  c labeled c3 single bond to c1
  H labeled h1 single bond to c1
```

```
  } enthalpy 30.4 kJ/mol entropy 25.73 cp (298=>18.1, 400=>24.14, 500=> 29.11, 600=> 32.72, 800=> 37.14, 1000=>
39.66, 1500=> 43.06)
//C(=C)(c)(C)   41.5   0.0
fragment {
  C labeled c1
  C labeled c2 double bond to c1
  c labeled c3 single bond to c1
  C labeled c4 single bond to c1
  } enthalpy 41.5 kJ/mol entropy -59.73 cp(298=> 16.35, 400=>20.32, 500=> 23.19, 600=> 25.12, 800=> 27.09,
1000=> 27.83, 1500=> 28.13)

//C(=C)(c)(C=C)   31.6   0.0
fragment {
  C labeled c1
  C labeled c2 double bond to c1
  c labeled c3 single bond to c1
  C labeled c4 single bond to c1
  C labeled c5 double bond to c4
  } enthalpy 31.6 kJ/mol entropy -75.23 cp(298=>23.23, 400=> 28.96, 500=> 31.20, 600=> 31.85, 800=> 31.56,
1000=> 30.76, 1500=> 28.87)

//C(=O)(H)(H) -- taken from NIST
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  } enthalpy -115.9 kJ/mol entropy 213.18 cp(298=>35.39, 400=>39.24, 500=>43.74, 600=>48.18,
800=>55.94,1000=>61.95, 1500=>71.15)

//C(=O)(C)(C)   -132.4642   62.7418   23.408   26.334   29.678   32.604   37.202   40.128   43.89
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  } enthalpy -132.4642 kJ/mol entropy 62.7418 cp(298=>23.408, 400=>26.334, 500=>29.678, 600=>32.604,
800=>37.202,1000=>40.128, 1500=>43.89)

//C(=O)(C)(H)   -123.1846   145.882   29.26   32.604   36.784   40.546   46.816   50.996   58.102
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  C labeled c2 single bond to c1
  H labeled h1 single bond to c1
  } enthalpy -123.1846 kJ/mol entropy 145.882 cp (298=>29.26, 400=>32.604, 500=>36.784, 600=>40.546,
800=>46.816, 1000=>50.996, 1500=>58.102)


//C(=O)(C)(O)   -145.7148   63.2852   23.0736   25.2472   28.424   31.9352   37.2438   41.7582   48.2372
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  C labeled c2 single bond to c1
  O labeled 02 single bond to c1
  } enthalpy -145.7148 kJ/mol entropy 63.2852 cp (298=>23.0736, 400=> 25.2472, 500=> 28.424, 600=> 31.9352,
800=> 37.2438, 1000=> 41.7582, 1500=> 48.2372)


//C(=O)(C=O)(H)   -105.2942   89.034   30.1796   35.5718   40.6714   45.0186   51.1632   54.8834   59.356
fragment {
  C labeled c1
```

O labeled o1 double bond to c1
C labeled c2 single bond to c1
O labeled o2 double bond to c2
H labeled h1 single bond to c1
} enthalpy -105.2942 kJ/mol entropy 89.034 cp(298=> 30.1796, 400=> 35.5718, 500=> 40.6714, 600=> 45.0186, 800=> 51.1632, 1000=> 54.8834, 1500=> 59.356)

//C(=O)(H)(O) -134.4288 146.0074 28.5912 32.0606 36.8258 42.0508 50.0346 55.6776 62.6582
fragment {
C labeled c1
O labeled o1 double bond to c1
H labeled h1 single bond to c1
O labeled o2 single bond to c1 } enthalpy -134.4288 kJ/mol entropy 146.0074 cp(298=> 28.5912, 400=> 32.0606, 500=> 36.8258, 600=> 42.0508, 800=> 50.0346, 1000=> 55.6776, 1500=> 62.6582)

//O(C)(C) -96.8924 38.0798 11.9548 10.3246 10.7008 11.6622 13.6686 15.3406 17.138
fragment {
O labeled o1
C labeled c1 single bond to o1
C labeled c2 single bond to o1
} enthalpy -96.8924 kJ/mol entropy 38.0798 cp (298=>11.9548, 400=> 10.3246, 5000=> 10.7008, 600=> 11.6622, 800=> 13.6686, 1000=> 15.3406, 1500=> 17.138)

//O(C)(C=O) -181.5374 20.6074 11.2024 13.5432 15.7586 17.2216 19.8968 21.2762 21.318
fragment {
O labeled o1
C labeled c1 single bond to o1
C labeled c2 single bond to o1
O labeled o2 double bond to c2
} enthalpy -181.5374 kJ/mol entropy 20.6074 cp(298=> 11.2024, 400=> 13.5432, 500=> 15.7586, 600=> 17.2216, 800=> 19.8968, 1000=> 21.2762, 1500=> 21.318)

//O(C)(H) -158.2548 123.101 17.347 17.556 18.9772 20.6492 23.7006 26.334 30.7648
fragment {
O labeled o1
C labeled c1 single bond to o1
H labeled h1 single bond to o1
} enthalpy -158.2548 kJ/mol entropy 123.101 cp(298=> 17.347, 400=> 17.556, 500=>18.9772, 600=> 20.6492, 800=> 23.7006, 1000=> 26.334, 1500=> 30.7648)

//O(C)(O) -18.9772 35.53 13.376 14.212 15.048 15.884 17.138 17.556 17.556
fragment {
O labeled o1
C labeled c1 single bond to o1
O labeled o2 single bond to o1
} enthalpy -18.9772 kJ/mol entropy 35.53 cp(298=>13.376, 400=>14.212, 500=>15.048, 600=>15.884, 800=> 17.138, 1000=> 17.556, 1500=> 17.556)

//O(C=O)(H) -241.5622 102.41 15.884 20.9 24.244 26.334 30.096 32.604 38.874
fragment {
O labeled o1
C labeled c1 single bond to o1
O labeled o2 double bond to c1
H labeled h1 single bond to o1
} enthalpy -241.5622 kJ/mol entropy 102.41 cp(298=> 15.884, 400=> 20.9, 500=> 24.244, 600=> 26.334, 800=> 30.096, 1000=> 32.604, 1500=>38.874)

//C(C)(C)(C)(O) -29.3854 -144.0428 21.2344 28.3404 32.8548 35.0702 36.0734 35.53 33.649
fragment {
C labeled c1
C labeled c2 single bond to c1

```
  C labeled c3 single bond to c1
  C labeled c4 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy  -29.3854 kJ/mol entropy -144.0428 cp(298=> 21.2344, 400=> 28.3404, 500=> 32.8548, 600=> 35.0702,
800=> 36.0734, 1000=>35.53, 1500=> 33.649)

//C(C)(C)(H)(O)   -31.0156   -51.7484   21.0254   28.1732   33.649   37.4946   42.0926   44.6842   47.6102
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  H labeled h1 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy -31.0156 kJ/mol entropy -51.7484 cp(298=> 21.0254, 400=> 28.1732, 500=> 33.649, 600=> 37.4946,
800=> 42.0926, 1000=> 44.6842, 1500=> 47.6102)

//C(C)(C=O)(H)(H)   -21.9868   40.128   25.916   32.186   36.366   39.71   46.398   50.996   59.356
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  O labeled o1 double bond to c3
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  } enthalpy -21.9868 kJ/mol entropy 40.128 cp(298=> 25.916, 400=> 32.186, 500=> 36.366, 600=> 39.71, 800=>
46.398, 1000=> 50.996, 1500=> 59.356)

//C(C)(H)(H)(O)   -33.1056   38.038   22.4466   29.2182   35.1538   40.0444   47.443   52.668   60.401
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy -33.1056 kJ/mol entropy 38.038 cp(298=> 22.4466, 400=> 29.2182, 500=> 35.1538, 600=> 40.0444,
800=> 47.443, 1000=> 52.668, 1500=>60.401)

//C(C=O)(H)(H)(H)   -43.0958   127.1138   25.8742   32.7712   39.292   45.1022   54.4236   61.7386   73.4844
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  O labeled o1 double bond to c2
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  H labeled h3 single bond to c1
  } enthalpy -43.0958 kJ/mol entropy 127.1138 cp(298=> 25.8742, 400=> 32.7712, 500=> 39.292, 600=> 45.1022,
800=> 54.4236, 1000=> 61.7386, 1500=> 73.4844)

//C(H)(H)(H)(O)   -41.8   127.1138   25.8742   32.7712   39.292   45.1022   54.4236   61.7386   73.4844
fragment {
  C labeled c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  H labeled h3 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy -41.8 kJ/mol entropy 127.1138 cp (298=> 25.8742, 400=> 32.7712, 500=> 39.292, 600=> 45.1022,
800=> 54.4236, 1000=> 61.7386, 1500=>73.4844)

//C(=C)(H)(O)  35.948        25.916   20.064   27.17   31.768   35.112   38.038   40.128   43.89
fragment {
  C labeled c1
  C labeled c2 double bond to c1
```

H labeled h1 single bond to c1
O labeled o1 single bond to c1
} enthalpy 35.948 kJ/mol entropy 25.916 cp (298=> 20.064, 400=> 27.17, 500=> 31.768, 600=> 35.112, 800=> 38.038, 1000=>40.128, 1500=> 43.89)

//C(C)(C)(C=O)(C=O) 9.4886 -141.9528 29.2182 33.1474 33.8162 34.067 33.6072 33.7744 32.0606
fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
C labeled c4 single bond to c1
O labeled o1 double bond to c1
C labeled c5 single bond to c1
O labeled o2 double bond to c1
} enthalpy 9.4886 kJ/mol entropy -141.9528 cp (298=> 29.2182, 400=> 33.1474, 500=> 33.8162, 600=> 34.067, 800=>33.6072, 1000=> 33.7744, 1500=>32.0606)

//C(C)(C)(C=O)(H) -6.9806 -49.3658 24.8292 31.1828 35.1538 37.8708 41.9672 44.308 48.1118
fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
C labeled c4 single bond to c1
O labeled o1 double bond to c4
H labeled h1 single bond to c1
} enthalpy -6.9806 kJ/mol entropy -49.3658 cp (298=> 24.8292, 400=> 31.1828, 500=> 35.1538, 600=> 37.8708, 800=> 41.9672, 1000=> 44.308, 1500=> 48.1118)

//C(C)(C)(C=O)(O) -19.1444 -156.541 30.8066 41.8836 46.189 47.3176 46.0218 43.9736 39.4592
fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
C labeled c4 single bond to c1
O labeled o1 double bond to c4
O labeled o2 single bond to c1
} enthalpy -19.1444 kJ/mol entropy -156.541 cp (298=> 30.8066, 400=> 41.8836, 500=> 46.189, 600=> 47.3176, 800=> 46.0218, 1000=> 43.9736, 1500=> 39.4592)

//C(C)(C=O)(C=O)(H) 2.7588 -53.295 27.9642 33.6072 36.4496 38.5396 41.0894 43.3884 44.2244
fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
O labeled o1 double bond to c3
C labeled c4 single bond to c1
O labeled o2 double bond to c4
H labeled h1 single bond to c1
} enthalpy 2.7588 kJ/mol entropy -53.295 cp (298=> 27.9642, 400=> 33.6072, 500=> 36.4496, 600=> 38.5396, 800=> 41.0894, 1000=> 43.3884, 1500=> 44.2244)

//C(C)(C=O)(C=O)(C) -2.926 -161.557 31.6844 42.218 46.4816 48.4044 48.697 47.4848 41.2148
fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
O labeled o1 double bond to c3
C labeled c4 single bond to c1
O labeled o2 double bond to c4
C labeled c5 single bond to c1

} enthalpy -2.926 kJ/mol entropy -161.557 cp (298=> 31.6844, 400=> 42.218, 500=> 46.4816, 600=> 48.4044, 800=> 48.697, 1000=> 47.4848, 1500=> 41.2148)

//C(C)(C=O)(H)(O) -20.4402 -67.4652 29.0928 40.5042 46.1054 48.7388 50.3272 50.9542 50.4526
fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
O labeled o1 double bond to c3
H labeled h1 single bond to c1
O labeled o2 single bond to c1
} enthalpy -20.4402 kJ/mol entropy -67.4652 cp (298=> 29.0928, 400=> 40.5042, 500=> 46.1054, 600=> 48.7388, 800=> 50.3272, 1000=> 50.9542, 1500=>50.4526)

//C(C)(C=O)(O)(O) -56.5136 -153.6986 30.0542 41.5492 45.7292 46.9832 45.9382 44.0154 40.9222
fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
O labeled o1 double bond to c3
O labeled o2 single bond to c1
O labeled o3 single bond to c1
} enthalpy -56.5136 kJ/mol entropy -153.6986 cp(298=> 30.0542, 400=> 41.5492, 500=> 45.7292, 600=> 46.9832, 800=> 45.9382, 1000=> 44.0154, 1500=> 40.9222)

//C(C=O)(H)(H)(O) -22.9482 30.7648 27.9642 39.083 46.0636 50.6198 55.5522 58.52 62.5746
fragment {
C labeled c1
C labeled c2 single bond to c1
O labeled o1 double bond to c2
H labeled h1 single bond to c1
H labeled h2 single bond to c1
O labeled o2 single bond to c1
} enthalpy -22.9482 kJ/mol entropy 30.7648 cp (298=> 27.9642, 400=> 39.083, 500=> 46.0636, 600=> 50.6198, 800=> 55.5522, 1000=> 58.52, 1500=> 62.5746)

//C(H)(H)(O)(O) -75.2818 11.9966 29.0928 47.7774 59.356 65.208 68.4684 68.4266 68.8446
fragment {
C labeled c1
H labeled h1 single bond to c1
H labeled h2 single bond to c1
O labeled o1 single bond to c1
O labeled o2 single bond to c1
} enthalpy -75.2818 kJ/mol entropy 11.9966 cp (298=> 29.0928, 400=> 47.7774, 500=> 59.356, 600=> 65.208, 800=> 68.4684, 1000=> 68.4266, 1500=> 68.8446)

//C(H)(O)(O)(O) -128.0334 -63.5778 31.1828 42.7614 47.861 50.2018 52.2082 53.0442 54.5908
fragment {
C labeled c1
H labeled h1 single bond to c1
O labeled o1 single bond to c1
O labeled o2 single bond to c1
O labeled o3 single bond to c1
} enthalpy -128.0334 kJ/mol entropy -63.5778 cp (298=> 31.1828, 400=> 42.7614, 500=> 47.861, 600=> 50.2018, 800=> 52.2082, 1000=> 53.0442, 1500=> 54.5908)

//C(O)(O)(O)(O) -201.5596 -191.862 33.231 55.3014 63.4942 64.581 59.774 54.0056 46.3144
fragment {
C labeled c1
O labeled o1 single bond to c1
O labeled o2 single bond to c1
O labeled o3 single bond to c1

O labeled o4 single bond to c1
} enthalpy -201.5596 kJ/mol entropy -191.862 cp (298=> 33.231, 400=> 55.3014, 500=> 63.4942, 600=> 64.581, 800=> 59.774, 1000=> 54.0056, 1500=> 46.3144)

//C(=C)(C)(C=O) 46.0636 -64.581 19.7714 26.0832 30.305 33.1056 35.5718 35.0284 28.5076
fragment {
C labeled c1
C labeled c2 double bond to c1
C labeled c3 single bond to c1
C labeled c4 single bond to c1
O labeled o1 double bond to c4
} enthalpy 46.0636 kJ/mol entropy -64.581 cp (298=> 19.7714, 400=> 26.0832, 500=> 30.305, 600=> 33.1056, 800=> 35.5718, 1000=> 35.0284, 1500=> 28.5076)

//C(=C)(C)(O) 37.3692 -55.5104 19.228 24.2858 27.2118 29.1764 29.9288 30.1796 30.514
fragment {
C labeled c1
C labeled c2 double bond to c1
C labeled c3 single bond to c1
O labeled o1 single bond to c1
} enthalpy 37.3692 kJ/mol entropy -55.5104 cp (298=> 19.228, 400=> 24.2858, 500=> 27.2118, 600=> 29.1764, 800=> 29.9288, 1000=> 30.1796, 1500=> 30.514)

//C(=C)(C=O)(H) 42.3852 20.2312 21.945 28.842 34.1924 38.247 42.9286 44.517 41.9254
fragment {
C labeled c1
C labeled c2 double bond to c1
C labeled c3 single bond to c1
O labeled o1 double bond to c3
H labeled h1 single bond to c1
} enthalpy 42.3852 kJ/mol entropy 20.2312 cp (298=> 21.945, 400=> 28.842, 500=> 34.1924, 600=> 38.247, 800=> 42.9286, 1000=> 44.517, 1500=> 41.9254)

//C(=C)(C=O)(O) 47.0668 -68.9282 15.5914 22.4884 26.5012 29.8034 33.9416 36.5332 34.2342
fragment {
C labeled c1
C labeled c2 double bond to c1
C labeled c3 single bond to c1
O labeled o1 double bond to c3
O labeled o2 single bond to c1
} enthalpy 47.0668 kJ/mol entropy -68.9282 cp (298=> 15.5914, 400=> 22.4884, 500=> 26.5012, 600=> 29.8034, 800=>33.9416, 1000=> 36.5332, 1500=> 34.2342)

//C(=O)(C)(C=C) -136.7278 65.7514 24.9964 25.5816 27.0864 28.6748 32.186 36.1152 45.0186
fragment {
C labeled c1
O labeled o1 double bond to c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
C labeled c4 double bond to c3
} enthalpy -136.7278 kJ/mol entropy 65.7514 cp (298=> 24.9964, 400=> 25.5816, 500=> 27.0864, 600=> 28.6748, 800=> 32.186, 1000=> 36.1152, 1500=> 45.0186)

//C(=O)(C)(C=O) -124.8984 3.6366 28.1732 32.2278 36.2824 39.501 43.0958 44.6842 44.4334
fragment {
C labeled c1
O labeled o1 double bond to c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
O labeled o2 double bond to c3
} enthalpy -124.8984 kJ/mol entropy 3.6366 cp(298=> 28.1732, 400=> 32.2278, 500=>36.2824, 600=> 39.501, 800=> 43.0958, 1000=>44.6842, 1500=>44.4334)

```
//C(=O)(C=C)(H)   -134.387   144.8788   27.2118   30.1796   33.5236   36.7422   42.9286   48.8224   61.9058
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  C labeled c2 single bond to c1
  C labeled c3 double bond to c1
  H labeled h1 single bond to c1
  } enthalpy -134.387 kJ/mol entropy 144.8788 cp (298=> 27.2118, 400=> 30.1796, 500=> 33.5236, 600=> 36.7422,
800=> 42.9286, 1000=> 48.8224, 1500=> 61.9058)

  //C(=O)(C=C)(O)   -145.7148   63.2852   23.0736   25.2472   28.424   31.9352   37.2438   41.7582   48.2372
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  C labeled c2 single bond to c1
  C labeled c3 double bond to c1
  O labeled o2 single bond to c1
  } enthalpy -145.7148 kJ/mol entropy 63.2852 cp (298=> 23.0736, 400=> 25.2472, 500=> 28.424, 600=> 31.9352,
800=> 37.2438, 1000=> 41.7582, 1500=> 48.2372)

//C(=O)(C=O)(C=O)   -91.751   176.0616   30.8902   31.3918   30.723   30.305   31.6008   33.7744   39.6264
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  C labeled c2 single bond to c1
  O labeled o2 double bond to c2
  C labeled c3 single bond to c1
  O labeled o3 double bond to c3
  } enthalpy -91.751 kJ/mol entropy 176.0616 cp (298=> 30.8902, 400=> 31.3918, 500=> 30.723, 600=> 30.305,
800=> 31.6008, 1000=> 33.7744, 1500=> 39.6264)

//C(=O)(O)(O)   -125.5672   65.5424   27.7134   32.3114   36.4496   40.3788   44.2244   46.2726   43.0958
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  O labeled o2 single bond to c1
  O labeled o3 single bond to c1
  } enthalpy -125.5672 kJ/mol entropy 65.5424 cp (298=> 27.7134, 400=> 32.3114, 500=> 36.4496, 600=> 40.3788,
800=> 44.2244, 1000=> 46.2726, 1500=> 43.0958)

//O(C=C)(H)   -185.801   114.4484   21.8196   24.4112   26.2086   27.17   29.678   31.2664   33.5236
fragment {
  O labeled o1
  C labeled c1 single bond to o1
  C labeled c2 double bond to c1
  H labeled h1 single bond to o1
  } enthalpy -185.801 kJ/mol entropy 114.4484 cp (298=> 21.8196, 400=> 24.4112, 500=> 26.2086, 600=> 27.17,
800=> 29.678, 1000=> 31.2664, 1500=> 33.5236)

//O(=C)   0.0   0.0
fragment {
  O labeled o1
  C labeled c1 double bond to o1
  } enthalpy 0.0 kJ/mol entropy 0.0 cp (298=>0.0, 400=> 0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)

//O(=C=O)   0.0   0.0
fragment {
   O labeled o1
   C labeled c1 double bond to o1
   O labeled o2 double bond to c1
   } enthalpy 0.0 kJ/mol entropy 0.0 cp(298=> 0.0, 400=>0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)
```

```
//H   0.0   130.68   28.8495   29.1816   29.2618   29.3246   29.6250   30.2041   32.29921242 -- taken from NIST (but Rln2 added to entropy
fragment {
   H labeled h1
   } enthalpy 0.0 kJ/mol entropy 136.44 cp(298=>28.8495, 400=>29.1816, 500=>29.2618,600=>29.3246, 800=>29.6250, 1000=>30.2041, 1500=>32.2992)


//C(=O)(=O)   -393.51   213.79   37.2175   41.3360   44.6146   47.3173   51.4390   54.3017   58.7272 -- taken from NIST (but Rln2 added to entropy
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  O labeled o2 double bond to c1
  } enthalpy -393.51 kJ/mol entropy 213.79 cp (298=>37.2175, 400=> 41.3360, 500=> 44.6146, 600=> 47.3173, 800=> 51.4390, 1000=> 54.3017, 1500=> 58.7272)

//O   -241.82   188.84   33.5974   34.2631   35.2184   36.3179   38.7365   41.2656   47.1086 --Rln2 added to entropy
fragment {
  O labeled o1
  } enthalpy -241.82 kJ/mol entropy 194.2 cp (298=> 33.5974, 400=> 34.2631, 500=> 35.2184, 600=> 36.3179, 800=> 38.7365, 1000=> 41.2656, 1500=> 47.1086)

// N -- taken from NIST, entropy and cp are half its value. Entropy increased by Rln2
fragment {
  N labeled n1
  N labeled n2 triple bond to n1
  } enthalpy 0.0 kJ/mol entropy 104.443 cp(298=>29.12, 400=> 29.25, 500=> 29.58, 600=>30.10, 800=>31.44, 1000=>32.69, 1500=>34.85)

//values taken from Benson's book

fragment {
  O labeled o1
  c labeled c1 single bond to o1
  H labeled h1 single bond to o1
  } enthalpy -37.9 kcal/mol entropy 29.1 cal/mol/K cp (298=> 4.3 cal/mol/K , 400=> 4.5 cal/mol/K , 500=> 4.8 cal/mol/K, 600=> 5.2 cal/mol/K , 800=> 6.0 cal/mol/K , 1000=> 6.6 cal/mol/K, 1500=> 6.6 cal/mol/K )

//O(c)C -- taken from Benson, entropy and cp same as OC(C) in Benson's
fragment {
  O labeled o1
  c labeled c1 single bond to o1
  C labeled c2 single bond to o1
  } enthalpy -22.6 kcal/mol entropy 8.68 cal/mol/K  cp (298=> 3.4 cal/mol/K , 400=> 3.7 cal/mol/K , 500=> 3.7 cal/mol/K, 600=> 3.8 cal/mol/K , 800=> 4.4 cal/mol/K , 1000=> 4.6 cal/mol/K, 1500=> 4.6 cal/mol/K )

  //c(O) -- taken from Benson
fragment {
  c labeled c1
  O labeled o1 single bond to c1
  c labeled c2 aromatic bond to c1
  c labeled c3 aromatic bond to c1
  } enthalpy -1.8 kcal/mol entropy 10.2 cal/mol/K  cp (298=> 3.9 cal/mol/K , 400=> 5.3 cal/mol/K , 500=> 6.2 cal/mol/K, 600=> 6.6 cal/mol/K , 800=> 6.9 cal/mol/K , 1000=> 6.9 cal/mol/K, 1500=> 6.9 cal/mol/K )

  //cC=O taken same as C(=C)(C=O)C
fragment {
   c labeled c1
   c labeled c2 aromatic bond to c1
   c labeled c3 aromatic bond to c1
```

```
   C labeled c4 single bond to c1
   O labeled o1 double bond to c4
   } enthalpy 46.0636 kJ/mol entropy -64.581 cp (298=> 19.7714, 400=> 26.0832, 500=> 30.305, 600=> 33.1056,
800=> 35.5718, 1000=> 35.0284, 1500=> 28.5076)

//C(=O)cH --taken same as C(=O)(C=C)H

fragment {
  C labeled c1
  O labeled o1 double bond to c1
  c labeled c2 single bond to c1
  H labeled h1 single bond to c1
  } enthalpy -134.387 kJ/mol entropy 144.8788 cp (298=> 27.2118, 400=> 30.1796, 500=> 33.5236, 600=> 36.7422,
800=> 42.9286, 1000=> 48.8224, 1500=> 61.9058)

  // C(=O)cC --enthalpy from benson, taken to be same as C(=O)(C)(C=C)

  fragment {
    C labeled c1
            O labeled o1 double bond to c1
            c labeled c2 single bond to c1
            C labeled c3 single bond to c1
            } enthalpy -157.168 kJ/mol entropy 65.7514 cp (298=> 24.9964, 400=> 25.5816, 500=> 27.0864, 600=>
28.6748, 800=> 32.186, 1000=> 36.1152, 1500=> 45.0186)


            // C(=O)cO -- from benson only for enthalpy, taken same as C(=O)(C=C)O for evertything else
            fragment {
              C labeled c1
              O labeled o1 double bond to c1
              c labeled c2 single bond to c1
              O labeled o2 single bond to c1
              } enthalpy -192.28 kJ/mol entropy 63.2852 cp (298=> 23.0736, 400=> 25.2472, 500=> 28.424, 600=>
31.9352, 800=> 37.2438, 1000=> 41.7582, 1500=> 48.2372)


  //C(=O)cc -- enthalpy from Bensons's, everthying else from C(=O)(C=C)(C)

  fragment {
    C labeled c1
            O labeled o1 double bond to c1
            c labeled c2 single bond to c1
            c labeled c3 single bond to c1
            } enthalpy -163.468 kJ/mol entropy 65.7514 cp (298=> 24.9964, 400=> 25.5816, 500=> 27.0864, 600=>
28.6748, 800=> 32.186, 1000=> 36.1152, 1500=> 45.0186)

//o(c)(c)
fragment {
  o labeled o1
  c labeled c1 aromatic bond to o1
  c labeled c2 aromatic bond to o1
  } enthalpy -97.9377 kJ/mol entropy 86.587 cp (298=> 6.623, 400=> 2.486, 500=> 1.07, 600=> 1.9945, 800=> 6.41,
1000=> 8.634, 1500=> 10.353)

//c(c)(o)(C)
fragment {
  c labeled c1
  c labeled c2 aromatic bond to c1
  o labeled o1 aromatic bond to c1
  C labeled c3 single bond to c1
  } enthalpy 15.275 kJ/mol entropy -37.913 cp (298=> 13.991, 400=> 17.539, 500=> 20.241, 600=> 22.115, 800=>
24.567, 1000=> 26.075, 1500=> 27.598)
```

```
//c(c)o
fragment {
  c labeled c1
  c labeled c2 aromatic bond to c1
  o labeled o1 aromatic bond to c1
  H labeled h1 single bond to c1
  } enthalpy 16.479            kJ/mol entropy 46.972 cp (298=> 14.41, 400=> 19.48, 500=> 23.71, 600=> 27.06, 800=>
31.97, 1000=> 35.35, 1500=> 40.38)

//C(O)(c)(H)(H) --taken from Benson, cp values that of C(O)(C)(H)(H) from Benson
fragment {
  C labeled c1
  c labeled c2 single bond to c1
  O labeled o1 single bond to c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  } enthalpy -6.6 kcal/mol entropy 9.7 cal/mol/K cp(298=> 4.99 cal/mol/K ,400=> 6.85 cal/mol/K ,500=> 8.3 cal/mol/K
,600=> 9.43 cal/mol/K,800=> 11.11 cal/mol/K, 1000=> 12.33 cal/mol/K, 1500=> 12.33 cal/mol/K)


fragment {
    C: labeled c1
            O labeled o1 double bond to c1
            } enthalpy -110.53 kJ/mol entropy 197.66 cp(298=>29.15 ,400=>29.30, 500=>29.82 ,600=> 30.47, 800=>
31.88, 1000=> 33.18, 1500=> 35.22)

fragment {
    O labeled o1
    C: labeled c1 double bond to o1
   } enthalpy 0.0 kJ/mol entropy  0.0  cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)


//C(C)(H)(O)(O) taken same as CH2O2 from above-- Benson's book has very close dHf for both.
fragment {
  C labeled c1
  H labeled h1 single bond to c1
  C labeled c2 single bond to c1
  O labeled o1 single bond to c1
  O labeled o2 single bond to c1
  } enthalpy -75.2818 kJ/mol entropy 11.9966 cp (298=> 29.0928, 400=> 47.7774, 500=> 59.356, 600=> 65.208,
800=> 68.4684, 1000=> 68.4266, 1500=> 68.8446)


//C(c)(O)(C) taken to be same as C(C)(C)(O)(H)
fragment {
  C labeled c1
  c labeled c2 single bond to c1
  C labeled c3 single bond to c1
  H labeled h1 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy -31.0156 kJ/mol entropy -51.7484 cp(298=> 21.0254, 400=> 28.1732, 500=> 33.649, 600=> 37.4946,
800=> 42.0926, 1000=> 44.6842, 1500=> 47.6102)


  //radical groups

//'H.' - hydrogen atom

fragment {
   H. labeled h1
```

} enthalpy 217.998 kJ/mol entropy 114.717 cp(298=> 20.79, 400=> 20.79, 500=>20.79, 600=>20.79, 800=>20.79, 1000=>20.79, 1500=>20.79)

// 'C.'(H)(H)(H) -- taken from NIST, the entropy value is subtracted by Rln6 because the group additivity algo will add this symmetry correction
fragment {
C. labeled c1
H labeled h1 single bond to c1
H labeled h2 single bond to c1
H labeled h3 single bond to c1
} enthalpy 145.69 kJ/mol entropy 179.27 cp(298=>38.68, 400=>42.05, 500=>45.23, 600=>48.28, 800=>53.94, 1000=>58.94, 1500=>68.17)

// 'C.'(C)(H)(H)
fragment {
C. labeled c1
C labeled c2 single bond to c1
H labeled h1 single bond to c1
H labeled h2 single bond to c1
} enthalpy 168.0 kJ/mol entropy 139.01 cp(298=>22.79, 400=>27.81, 500=>32.10, 600=>35.67, 800=>41.33, 1000=>45.76, 1500=>53.10)

fragment {
C. labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
H labeled h1 single bond to c1
} enthalpy 177.3 kJ/mol entropy 56.57 cp(298=>18.53, 400=>21.25, 500=>24.24, 600=>26.99, 800=>31.4, 1000=>34.71, 1500=>39.53)

fragment {
C. labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
C labeled c4 single bond to c1
} enthalpy 184.5 kJ/mol entropy -22.82 cp(298=>11.49, 400=>13.96, 500=>16.76, 600=>19.19, 800=>22.54, 1000=>24.46, 1500=>26.39)

fragment {
C. labeled c1
C labeled c2 single bond to c1
C labeled c3 double bond to c2
H labeled h1 single bond to c1
H labeled h2 single bond to c1
} enthalpy 107.0 kJ/mol entropy 117.96 cp(298=>21.40, 400=>28.87, 500=>34.63, 600=>38.99, 800=>45.28, 1000=>49.87, 1500=>57.25)

fragment {
C. labeled c1
C labeled c2 single bond to c1
C labeled c3 double bond to c2
C labeled c4 single bond to c1
H labeled h1 single bond to c1
} enthalpy 115.2 kJ/mol entropy 35.99 cp(298=>18.28, 400=>23.44, 500=>27.72, 600=>31.02, 800=>35.66, 1000=>38.81, 1500=>43.43)

fragment {
C. labeled c1
C labeled c2 single bond to c1
C labeled c3 double bond to c2
C labeled c4 single bond to c1

```
   C labeled c5 single bond to c1
   } enthalpy 127.5 kJ/mol entropy -46.53  cp(298=>13.09, 400=>16.90, 500=>20.15, 600=>22.68, 800=>25.96,
1000=>27.80, 1500=>29.76)

fragment {
   C. labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 double bond to c4
   H labeled h1 single bond to c1
   } enthalpy 76.5 kJ/mol entropy 16.49  cp(298=>17.36, 400=>25.75, 500=>31.54, 600=>35.44, 800=>40.27,
1000=>43.29, 1500=>47.62)

fragment {
   C. labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 double bond to c4
   C labeled c6 single bond to c1
   } enthalpy 86.7 kJ/mol entropy -71.99  cp(298=>12.47, 400=>21.07, 500=>26.66, 600=>30.09, 800=>33.32,
1000=>34.48, 1500=>35.06)

fragment {
   C. labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 double bond to c4
   C labeled c6 single bond to c1
   C labeled c7 double bond to c6
   } enthalpy 71.4 kJ/mol entropy -79.68  cp(298=>13.98, 400=>23.08, 500=>28.62, 600=>31.85, 800=>34.95,
1000=>36.29, 1500=>37.56)

fragment {
   C. labeled c1
   C labeled c2 double bond to c1
   H labeled h1 single bond to c1
   } enthalpy 275.8 kJ/mol entropy 121.36  cp(298=>20.59, 400=>23.57, 500=>25.74, 600=>27.44, 800=>30.14,
1000=>32.31, 1500=>35.96)

fragment {
   C. labeled c1
   C labeled c2 double bond to c1
   C labeled c3 single bond to c1
   } enthalpy 273.2 kJ/mol entropy 41.33  cp(298=>16.74, 400=>17.40, 500=>18.26, 600=>19.11, 800=>20.49,
1000=>21.39, 1500=>22.40)

fragment {
   C. labeled c1
   C labeled c2 double bond to c1
   C labeled c3 single bond to c1
   C labeled c4 double bond to c3
   } enthalpy 234.9 kJ/mol entropy 37.49  cp(298=>16.93, 400=>17.91, 500=>18.53, 600=>19.28, 800=>21.01,
1000=>22.54, 1500=>24.73)


//Groups with non-central radicals

//C('C.')(H)(H)(H)   -42.9   127.12   25.31  32.07   38.44   44.06   53.36   60.63   72.47
fragment {
```

```
   C labeled c1
   C. labeled c2 single bond to c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   H labeled h3 single bond to c1
   } enthalpy -42.9 kJ/mol entropy 127.12 cp (298=>25.31, 400=>32.07, 500=>38.44, 600=>44.06, 800=>53.36,
1000=>60.63, 1500=>72.47)

//C('C.')(C)(H)(H)   -20.5   39.96   25.05   30.11   35.05   39.40   46.39   51.60   59.63
fragment {
   C labeled c1
   C. labeled c2 single bond to c1
   C labeled c3 single bond to c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   } enthalpy -20.5 kJ/mol entropy 39.96 cp (298=>25.05, 400=>30.11, 500=>35.05 , 600=>39.40, 800=>46.39,
1000=>51.60, 1500=>59.63)

//C('C.')(C)(C)(H)   -6.9   -48.97   21.44 27.27   31.71   35.10   39.83   42.89   47.01
fragment {
   C labeled c1
   C. labeled c2 single bond to c1
   C labeled c3 single bond to c1
   C labeled c4 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy -6.9 kJ/mol entropy -48.97 cp (298=>21.44, 400=>27.27, 500=>31.71, 600=>35.10, 800=>39.83,
1000=>42.89, 1500=>47.01)

//C('C.')(C)(C)(C)   3.9   -148.25   17.53   24.47   29.01   31.78   34.22   34.72   33.79
fragment {
   C labeled c1
   C. labeled c2 single bond to c1
   C labeled c3 single bond to c1
   C labeled c4 single bond to c1
   C labeled c5 single bond to c1
   } enthalpy 3.9 kJ/mol entropy -148.25 cp (298=>17.53, 400=>24.47, 500=>29.01, 600=>31.78, 800=>34.22,
1000=>34.72, 1500=>33.79)

//C(=C)('C.')(H)   37.1   32.91   18.44   21.74   25.02   27.96   32.65   36.06   41.17
fragment {
   C labeled c1
   C labeled c2 double bond to c1
   C. labeled c3 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy 37.1 kJ/mol entropy 32.91 cp (298=>18.44, 400=>21.74, 500=>25.02, 600=>27.96, 800=>32.65,
1000=>36.06, 1500=>41.17)

//C(=C)('C.')(C)   45.3   -55.9   19.58   21.71   23.12   24.25   25.94   27.02   28.35
fragment {
   C labeled c1
   C labeled c2 double bond to c1
   C. labeled c3 single bond to c1
   C labeled c4 single bond to c1
   } enthalpy 45.3 kJ/mol entropy -55.9 cp(298=>19.58, 400=>21.71, 500=>23.12, 600=>24.25, 800=>25.94,
1000=>27.02, 1500=>28.35)

//C(=C)(C=C)('C.')   40.0   -62.49   18.57   23.97   26.76   28.02   28.75   28.88   28.97
fragment {
   C labeled c1
   C labeled c2 double bond to c1
   C labeled c3 single bond to c1
   C labeled c4 double bond to c3
```

```
   C. labeled c5 single bond to c1
   } enthalpy 40.0 kJ/mol entropy -62.9  cp(298=>18.57, 400=>23.97, 500=>26.76, 600=>28.02, 800=>28.75,
1000=>28.88, 1500=>28.97)

//C(C=C)('C.')(H)(H)   -18.9   41.91   21.93   28.33   33.87   38.47   45.63   50.93   59.18
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C. labeled c4 single bond to c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   } enthalpy -18.9 kJ/mol entropy 41.91  cp(298=>21.93, 400=>28.33, 500=>33.87, 600=>38.47, 800=>45.63,
1000=>50.93, 1500=>59.18)

//C(C=C)('C.')(C)(H)   -3.9   -49.65   24.94   30.73   35.02   38.03   41.77   44.07   47.41
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C. labeled c4 single bond to c1
   C labeled c5 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy -3.9 kJ/mol entropy -49.65  cp(298=>24.94, 400=>30.73, 500=> 35.02, 600=>38.03, 800=>41.77,
1000=>44.07, 1500=>47.41)

//C(C=C)('C.')(C)(C)   7.1   -142.15   20.74   27.75   32.02   34.38   36.03   36.13   35.39
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C. labeled c4 single bond to c1
   C labeled c5 single bond to c1
   C labeled c6 single bond to c1
   } enthalpy 7.1 kJ/mol entropy -142.15  cp(298=>20.74, 400=>27.75, 500=>32.02, 600=>34.38, 800=>36.03,
1000=>36.13, 1500=>35.39)

//C(C=C)(C=C)('C.')(H)   0.4   -51.11   24.80   31.62   35.72   38.31   41.49   43.59   46.92
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 double bond to c4
   C. labeled c6 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy 0.4 kJ/mol entropy -51.11  cp(298=>24.80, 400=>31.62, 500=>35.72, 600=>38.31, 800=>41.49,
1000=>43.59, 1500=>46.92)

//C(C=C)(C=C)('C.')(C)   13.8   -144.37   21.40   28.46   32.44   34.57   36.03   36.05   35.17
fragment {
    C labeled c1
          C labeled c2 single bond to c1
          C labeled c4 single bond to c1
          C labeled c3 double bond to c2
          C labeled c5 double bond to c4
          C. labeled c6 single bond to c1
          C labeled c7 single bond to c1
          } enthalpy 13.8 kJ/mol entropy -144.37  cp(298=>21.40,400=>28.46, 500=>32.44, 600=>34.57, 800=>36.03,
1000=>36.05, 1500=>35.17)

//C(C=C)(C=C)(C=C)('C.')   15.3   -157.02   22.88   35.05   40.76   42.57   41.76   39.80   36.50
```

```
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 double bond to c4
   C labeled c6 single bond to c1
   C labeled c7 double bond to c6
   C. labeled c8 single bond to c1
   } enthalpy 15.3 kJ/mol entropy -157.02  cp(298=>22.88, 400=>35.05, 500=>40.76, 600=>42.57, 800=>41.76,
1000=>39.80, 1500=>36.50)



//Surface species

//C(C)(H)(M)(O)
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  H labeled h1 single bond to c1
  M labeled m1 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy -18.3 kcal/mol entropy -3.3 cal/mol/K cp(298=>6.3 cal/mol/K, 400=>8.6 cal/mol/K, 500=>10.1 cal/mol/K ,
600=>11.1 cal/mol/K, 800=>12.4 cal/mol/K, 1000=>13.1 cal/mol/K, 1500=>13.1 cal/mol/K )

//C(C)(M)(M)(O)
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  M labeled m1 single bond to c1
  M labeled m2 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy -13.8 kcal/mol entropy -6.7 cal/mol/K cp(298=>5.7 cal/mol/K, 400=>7.5 cal/mol/K, 500=>8.5 cal/mol/K ,
600=>9.1 cal/mol/K, 800=>9.6 cal/mol/K, 1000=>9.9 cal/mol/K, 1500=>9.9 cal/mol/K )

//C(=O)(C)(M)
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  M labeled m1 single bond to c1
  O labeled o1 double bond to c1
  } enthalpy -46.5 kcal/mol entropy 7.6 cal/mol/K cp(298=>8.0 cal/mol/K, 400=>9.2 cal/mol/K, 500=>10.1 cal/mol/K,
600=>10.8 cal/mol/K, 800=>11.6 cal/mol/K, 1000=>12.1 cal/mol/K, 1500=>12.1 cal/mol/K )

//C(=O)(H)(M)
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  M labeled m1 single bond to c1
  H labeled h1 single bond to c1
  } enthalpy -43.3 kcal/mol entropy 12.2 cal/mol/K cp(298=> 9.6 cal/mol/K, 400=> 11.0  cal/mol/K, 500=> 12.1
cal/mol/K, 600=> 12.9 cal/mol/K, 800=> 14.2 cal/mol/K, 1000=> 15.0 cal/mol/K, 1500=> 15.0 cal/mol/K)

//C(C)(C)(M)(O)
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  M labeled m1 single bond to c1
  O labeled o1 single bond to c1
```

```
  } enthalpy -12.7  kcal/mol entropy -2.0 cal/mol/K cp(298=>7.1 cal/mol/K, 400=> 9.1  cal/mol/K, 500=> 10.4
cal/mol/K, 600=>11.1 cal/mol/K, 800=>11.7 cal/mol/K, 1000=>12.0 cal/mol/K, 1500=>12.0 cal/mol/K )

//C(H)(H)(M)(O)
fragment {
  C labeled c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  M labeled m1 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy -11.4  kcal/mol entropy 1.7 cal/mol/K cp(298=>6.4 cal/mol/K, 400=> 8.5  cal/mol/K, 500=> 10.1  cal/mol/K,
600=>11.4 cal/mol/K, 800=>13.0 cal/mol/K, 1000=>14.3 cal/mol/K, 1500=>14.3 cal/mol/K )

//M
fragment {
   M labeled m1
   } enthalpy 0.0 kJ/mol entropy 0.0 cp(298=>0.0, 400=>0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)

//M(C)
fragment {
   M labeled m1
   C labeled c1 single bond to m1
   } enthalpy 0.0 kJ/mol entropy 0.0 cp(298=>0.0, 400=>0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)

//M(O)
fragment {
   M labeled m1
   O labeled o1 single bond to m1
   } enthalpy 0.0 kJ/mol entropy 0.0 cp(298=>0.0, 400=>0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)

//M(_O)
fragment {
   M labeled m1
   O labeled o1 partial bond to m1
   } enthalpy 0.0 kJ/mol entropy 0.0 cp(298=>0.0, 400=>0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)


//C(H)(M)(M)(O)
fragment {
  C labeled c1
  H labeled h1 single bond to c1
  M labeled m1 single bond to c1
  M labeled m2 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy -3.4  kcal/mol entropy -2.1 cal/mol/K cp(298=>5.3 cal/mol/K, 400=> 6.7  cal/mol/K, 500=> 7.7  cal/mol/K,
600=>8.5 cal/mol/K, 800=>9.4 cal/mol/K, 1000=>10.0 cal/mol/K, 1500=>10.0 cal/mol/K )

//C(H3)M
fragment {
   C labeled c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   H labeled h3 single bond to c1
   M labeled m2 single bond to c1
   } enthalpy -12.3 kcal/mol entropy 11.0 cal/mol/K cp(298=> 9.1 cal/mol/K, 400=> 11.1 cal/mol/K, 500=> 12.7
cal/mol/K, 600=> 13.9 cal/mol/K, 800=> 16.0 cal/mol/K, 1000=> 17.5 cal/mol/K, 1500=> 17.5 cal/mol/K)

//C(H2)(M2)
fragment {
   C labeled c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
```

```
   M labeled m1 single bond to c1
   M labeled m2 single bond to c1
   } enthalpy -1.2 kcal/mol entropy 6.8 cal/mol/K cp(298=> 7.6 cal/mol/K, 400=> 9.3 cal/mol/K, 500=> 10.6 cal/mol/K,
600=> 11.5 cal/mol/K, 800=> 12.8 cal/mol/K, 1000=>13.9 cal/mol/K, 1500=> 13.9 cal/mol/K)

//C(H)(M3)
 fragment {
   C labeled c1
   H labeled h1 single bond to c1
   M labeled m1 single bond to c1
   M labeled m2 single bond to c1
   M labeled m3 single bond to c1
   } enthalpy -3.8 kcal/mol entropy 5.1  cal/mol/K cp(298=> 6.3 cal/mol/K, 400=>7.5 cal/mol/K, 500=> 8.2 cal/mol/K,
600=>8.7 cal/mol/K, 800=>9.4 cal/mol/K, 1000=>9.9 cal/mol/K, 1500=> 9.9 cal/mol/K)

//C.(M3) or C(M4)
fragment {
  C labeled c1
  M labeled m1 single bond to c1
  M labeled m2 single bond to c1
  M labeled m3 single bond to c1
  M labeled m4 single bond to c1
  } enthalpy 18.9 kcal/mol entropy  4.4 cal/mol/K cp(298=> 4.6 cal/mol/K, 400=> 5.1 cal/mol/K, 500=> 5.4 cal/mol/K,
600=> 5.5 cal/mol/K, 800=>5.7 cal/mol/K, 1000=>5.8 cal/mol/K, 1500=>5.8 cal/mol/K)

//O(C)(M)
fragment {
  O labeled o1
  C labeled c1 single bond to o1
  M labeled m1 single bond to o1
  } enthalpy -24.7 kcal/mol entropy  6.7 cal/mol/K cp(298=> 4.3 cal/mol/K, 400=> 4.6 cal/mol/K, 500=> 4.9 cal/mol/K,
600=> 5.3 cal/mol/K, 800=>5.7 cal/mol/K, 1000=>5.8 cal/mol/K, 1500=>5.8 cal/mol/K)

//O(_M)(C)(H)
fragment {
  O labeled o1
  C labeled c1 single bond to o1
  H labeled h1 single bond to o1
  M labeled m2 partial bond to o1
  } enthalpy -42.9 kcal/mol entropy  12.5 cal/mol/K cp(298=> 7.1 cal/mol/K, 400=> 7.7 cal/mol/K, 500=> 8.4 cal/mol/K,
600=> 8.9 cal/mol/K, 800=> 9.7 cal/mol/K, 1000=> 10.3 cal/mol/K, 1500=> 10.3 cal/mol/K)

//C(M3)(O)
fragment {
  C labeled c1
  M labeled m1 single bond to c1
  M labeled m2 single bond to c1
  M labeled m3 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy -8.0 kcal/mol entropy  -5.3 cal/mol/K cp(298=> 5.2 cal/mol/K, 400=> 6.4 cal/mol/K, 500=> 7.1 cal/mol/K,
600=> 7.5 cal/mol/K, 800=> 7.8 cal/mol/K, 1000=> 7.9 cal/mol/K, 1500=> 7.9 cal/mol/K)

//C(=O)(M2)
fragment {
  C labeled c1
  O labeled o1 double bond to c1
  M labeled m1 single bond to c1
  M labeled m2 single bond to c1
  } enthalpy -56.4 kcal/mol entropy 10.9 cal/mol/K cp(298=> 8.4 cal/mol/K, 400=> 9.1 cal/mol/K, 500=> 9.5 cal/mol/K,
600=> 9.9 cal/mol/K, 800=> 10.4 cal/mol/K, 1000=> 10.8 cal/mol/K, 1500=> 11.3 cal/mol/K)

//C(C)(H)(H)(M)
```

```
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  M labeled m1 single bond to c1
  } enthalpy -8.4 kcal/mol entropy 3.2 cal/mol/K cp(298=>6.6 cal/mol/K, 400=>8.6 cal/mol/K, 500=>10.2 cal/mol/K ,
600=>11.5 cal/mol/K, 800=>13.3 cal/mol/K, 1000=>14.6 cal/mol/K, 1500=>14.6 cal/mol/K )

//C(C)(H)(M)(M)
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  H labeled h1 single bond to c1
  M labeled m1 single bond to c1
  M labeled m2 single bond to c1
} enthalpy 3.6 kcal/mol entropy 1.6 cal/mol/K cp(298=>5.3 cal/mol/K, 400=>6.9 cal/mol/K, 500=>8.0 cal/mol/K ,
600=>8.8 cal/mol/K, 800=>9.8 cal/mol/K, 1000=>10.6 cal/mol/K, 1500=>10.6 cal/mol/K )

//C(C)(C)(H)(M)
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  H labeled h1 single bond to c1
  M labeled m1 single bond to c1
} enthalpy -6.7 kcal/mol entropy 3.1 cal/mol/K cp(298=>6.7 cal/mol/K, 400=>8.5 cal/mol/K, 500=>9.8 cal/mol/K ,
600=>10.8 cal/mol/K, 800=>12.1 cal/mol/K, 1000=>13.0 cal/mol/K, 1500=>13.0 cal/mol/K )

//C(C)(C)(M)(M)
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  M labeled m1 single bond to c1
  M labeled m2 single bond to c1
} enthalpy 3.7 kcal/mol entropy 1.1 cal/mol/K cp(298=>6.9 cal/mol/K, 400=>8.2 cal/mol/K, 500=>9.1 cal/mol/K ,
600=>9.7 cal/mol/K, 800=>10.4 cal/mol/K, 1000=>10.7 cal/mol/K, 1500=>10.7 cal/mol/K )


//C(C)(C)(C)(M)
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  C labeled c4 single bond to c1
  M labeled m1 single bond to c1
} enthalpy 0.2 kcal/mol entropy 0.2 cal/mol/K cp(298=>5.5 cal/mol/K, 400=>6.8 cal/mol/K, 500=>7.8 cal/mol/K ,
600=>8.3 cal/mol/K, 800=>9.0 cal/mol/K, 1000=>9.3 cal/mol/K, 1500=>9.3 cal/mol/K )

//C(C)(M)(M)(M)
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  M labeled m1 single bond to c1
  M labeled m2 single bond to c1
  M labeled m3 single bond to c1
} enthalpy 6.2 kcal/mol entropy -2.3 cal/mol/K cp(298=>5.1 cal/mol/K, 400=>6.5 cal/mol/K, 500=>7.3 cal/mol/K ,
600=>7.9 cal/mol/K, 800=>8.5 cal/mol/K, 1000=>8.8 cal/mol/K, 1500=>8.8 cal/mol/K )

/*
```

```
//O(M) -- obtained from BE of O(M) (Grabow et al JPCC 2008), entropy change calculated from free radical value - translational entropy, and Cp = Cvib
fragment {
  O labeled o1
  H labeled h1 single bond to o1
  M labeled m1 single bond to o1
} enthalpy -163.83 kJ/mol entropy 39.56 cp(298=> 7.32, 400=>7.32, 500=>20.3, 600=>7.32, 800=>7.32, 1000=>7.32, 1500=>7.32)

//O(M)(M) -- obtained using the same method as above

fragment {
  O labeled o1
  M labeled m1 single bond to o1
  M labeled m2 single bond to o1
 } enthalpy -110.69 kJ/mol entropy 17.66 cp(298=> 18.5, 400=>18.5, 500=>18.5, 600=>18.5, 800=>18.5, 1000=>18.5, 1500=>18.5)

*/
//O(M) -- obtained from Salccioli ACS Catal 2011
fragment {
  O labeled o1
  H labeled h1 single bond to o1
  M labeled m1 single bond to o1
} enthalpy -38.9 kcal/mol entropy 9.5 cal/mol/K cp(298=>1.4 cal/mol/K, 400=>4.3 cal/mol/K, 500=>6.3 cal/mol/K , 600=>7.5 cal/mol/K, 800=>8.3 cal/mol/K, 1000=>8.8 cal/mol/K, 1500=>9.3 cal/mol/K )


//O(M)(M) -- obtained using the same source as above

fragment {
  O labeled o1
  M labeled m1 single bond to o1
  M labeled m2 single bond to o1
} enthalpy -31.3 kcal/mol entropy 6.5 cal/mol/K cp(298=>1.0 cal/mol/K, 400=>3.0 cal/mol/K, 500=>4.6 cal/mol/K , 600=>5.2 cal/mol/K, 800=>5.5 cal/mol/K, 1000=>5.7 cal/mol/K, 1500=>5.8 cal/mol/K )


 //O_{M}

 fragment {
   O labeled o1
   H labeled h1 single bond to o1
   H labeled h2 single bond to o1
   M labeled m1 partial bond to o1
 } enthalpy -63.1 kcal/mol entropy 16.4 cal/mol/K cp(298=>2.1 cal/mol/K, 400=>6.4 cal/mol/K, 500=>8.9 cal/mol/K , 600=>10.3 cal/mol/K, 800=>11.1 cal/mol/K, 1000=>11.7 cal/mol/K, 1500=>12.6 cal/mol/K )


// C(C)(C=O)(H)(M)

fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 single bond to c1
   O labeled o1 double bond to c3
   H labeled h1 single bond to c1
   M labeled m1 single bond to c1
} enthalpy -5.6 kcal/mol entropy 2.0 cal/mol/K cp(298=> 6.7 cal/mol/K, 400=>8.6 cal/mol/K, 500=>9.9 cal/mol/K , 600=>10.3 cal/mol/K, 800=>11.1 cal/mol/K, 1000=>11.7 cal/mol/K, 1500=>11.7cal/mol/K )

// C(C)(C=O)(M)(M)
```

fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
O labeled o1 double bond to c3
M labeled m1 single bond to c1
M labeled m2 single bond to c1
} enthalpy -0.1 kcal/mol entropy -1.4 cal/mol/K cp(298=> 5.5 cal/mol/K, 400=>6.8 cal/mol/K, 500=>7.6 cal/mol/K , 600=>8.1 cal/mol/K, 800=>8.6 cal/mol/K, 1000=>8.9 cal/mol/K, 1500=>8.9 cal/mol/K)

//C(C)(C)(C=O)(M)

fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c1
C labeled c4 single bond to c1
O labeled o1 double bond to c4
M labeled m1 single bond to c1
} enthalpy -5.4 kcal/mol entropy -4.3 cal/mol/K cp(298=> 6.3 cal/mol/K, 400=>8.0 cal/mol/K, 500=>9.0 cal/mol/K , 600=>9.7 cal/mol/K, 800=>10.5 cal/mol/K, 1000=>10.9 cal/mol/K, 1500=>10.9 cal/mol/K)

//C(C=O)(H)(M)(O)

fragment {
C labeled c1
C labeled c2 single bond to c1
O labeled o1 double bond to c2
H labeled h1 single bond to c1
M labeled m1 single bond to c1
O labeled o2 single bond to c1
} enthalpy -17.9 kcal/mol entropy -4.0 cal/mol/K cp(298=> 6.5 cal/mol/K, 400=>8.7 cal/mol/K, 500=>10.2 cal/mol/K , 600=>11.2 cal/mol/K, 800=>12.3 cal/mol/K, 1000=>13.1 cal/mol/K, 1500=>13.1 cal/mol/K)

//C(CO)(H)(M)(M) enthalpy -1.4 kcal/mol entropy 0.0 cal/mol/K cp(298=> 5.7 cal/mol/K, 400=> 7.4 cal/mol/K, 500=> 8.5 cal/mol/K , 600=> 9.4 cal/mol/K, 800=> 10.4 cal/mol/K, 1000=> 11.1 cal/mol/K, 1000=> 11.1 cal/mol/K
fragment {
C labeled c1
C labeled c2 single bond to c1
O labeled o1 double bond to c2
H labeled h1 single bond to c1
M labeled m1 single bond to c1
M labeled m2 single bond to c1
} enthalpy -1.4 kcal/mol entropy 0.0 cal/mol/K cp(298=> 5.7 cal/mol/K, 400=> 7.4 cal/mol/K, 500=> 8.5 cal/mol/K , 600=> 9.4 cal/mol/K, 800=> 10.4 cal/mol/K, 1000=> 11.1 cal/mol/K, 1000=> 11.1 cal/mol/K)

//C(CO)(H)(H)(M) enthalpy -8.8 kcal/mol entropy 4.2 cal/mol/K cp(298=> 7.0 cal/mol/K, 400=> 9.0 cal/mol/K, 500=> 10.5 cal/mol/K , 600=> 11.7 cal/mol/K, 800=> 13.3 cal/mol/K, 1000=> 14.6 cal/mol/K, 1500=> 14.6 cal/mol/K
fragment {
C labeled c1
C labeled c2 single bond to c1
O labeled o1 double bond to c2
H labeled h1 single bond to c1
H labeled h2 single bond to c1
M labeled m1 single bond to c1
} enthalpy -8.8 kcal/mol entropy 4.2 cal/mol/K cp(298=> 7.0 cal/mol/K, 400=> 9.0 cal/mol/K, 500=> 10.5 cal/mol/K , 600=> 11.7 cal/mol/K, 800=> 13.3 cal/mol/K, 1000=> 14.6 cal/mol/K, 1500=> 14.6 cal/mol/K)

//C(CO)(M)(M)(O) enthalpy -16.7 kcal/mol entropy -8.6 cal/mol/K cp(298=> 5.9 cal/mol/K, 400=> 7.9 cal/mol/K, 500=> 9.0 cal/mol/K , 600=> 9.6 cal/mol/K, 800=> 10.2 cal/mol/K, 1000=> 10.5 cal/mol/K, 1500=> 10.5 cal/mol/K

```
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   O labeled o1 double bond to c2
   M labeled m1 single bond to c1
   M labeled m2 single bond to c1
   O labeled o2 single bond to c1
} enthalpy -16.7 kcal/mol entropy -8.6 cal/mol/K cp(298=>  5.9 cal/mol/K, 400=>  7.9  cal/mol/K, 500=> 9.0 cal/mol/K ,
600=>  9.6 cal/mol/K, 800=>  10.2  cal/mol/K, 1000=> 10.5 cal/mol/K, 1500=> 10.5 cal/mol/K)

//C(CO)(M)(M)(M)  enthalpy 2.3 kcal/mol entropy -3.5 cal/mol/K cp(298=> 5.6 cal/mol/K, 400=>  6.8  cal/mol/K, 500=>
7.6 cal/mol/K , 600=> 8.0 cal/mol/K, 800=>  8.4 cal/mol/K, 1000=>  8.6  cal/mol/K, 1500=> 8.6  cal/mol/K

fragment {
   C labeled c1
   C labeled c2 single bond to c1
   O labeled o1 double bond to c2
   M labeled m1 single bond to c1
   M labeled m2 single bond to c1
   M labeled m3 single bond to c1
 } enthalpy 2.3 kcal/mol entropy -3.5 cal/mol/K cp(298=> 5.6 cal/mol/K, 400=>  6.8  cal/mol/K, 500=> 7.6 cal/mol/K ,
600=> 8.0 cal/mol/K, 800=>  8.4 cal/mol/K, 1000=>  8.6  cal/mol/K, 1500=> 8.6  cal/mol/K)

//C(=O)(C=O)(M)

fragment {
   C labeled c1
   O labeled o1 double bond to c1
   C labeled c2 single bond to c1
   O labeled o2 double bond to c2
   M labeled m1 single bond to c1
 } enthalpy -44.2 kcal/mol entropy 7.0 cal/mol/K cp(298=> 8.6 cal/mol/K, 400=> 9.8 cal/mol/K, 500=> 10.6 cal/mol/K,
600=> 11.2 cal/mol/K, 800=> 12.0 cal/mol/K, 1000=> 12.5 cal/mol/K, 1500=> 12.5 cal/mol/K)



//Zeolites

fragment {
  Zeo labeled z1
  H labeled h1 single bond to z1
} enthalpy 0.0 kJ/mol entropy 0.0 cp(298=>0.0, 400=>0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)

fragment {
  HTA labeled h1
  H labeled h2 single bond to h1
} enthalpy 0.0 kJ/mol entropy 0.0 cp(298=>0.0, 400=>0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)

fragment {
  HTA labeled h1
  Zeo labeled z1 single bond to h1
} enthalpy 0.0 kJ/mol entropy 0.0 cp(298=>0.0, 400=>0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)

fragment {
  Zeo labeled z1
  HTA labeled h1 single bond to z1
} enthalpy 0.0 kJ/mol entropy 0.0 cp(298=>0.0, 400=>0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)

fragment {
  Zeo labeled z1
  C labeled c1 single bond to z1
} enthalpy 0.0 kJ/mol entropy 0.0 cp(298=>0.0, 400=>0.0, 500=>0.0, 600=>0.0, 800=>0.0, 1000=>0.0, 1500=>0.0)
```

```
//Treating C-Zeo fragments like C-H fragments and then accounting for corrections in group corrections!

//C(H)(H)(H)(Zeo) - Methane -- taken from NIST
fragment {
   C labeled c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   H labeled h3 single bond to c1
   Zeo labeled z1 single bond to c1
} enthalpy -74.87 kJ/mol entropy 188.66 J/mol/K cp (298=> 35.69 J/mol/K, 400=> 40.63 J/mol/K, 500=> 46.63
J/mol/K, 600=> 52.74 J/mol/K, 800=> 64.08 J/mol/K, 1000=> 73.75 J/mol/K, 1500=> 90.86 J/mol/K)


//C(C)(H)(H)(Zeo)   -42.9   127.12   25.31  32.07   38.44   44.06   53.36   60.63   72.47
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   Zeo labeled z1 single bond to c1
   } enthalpy -42.9 kJ/mol entropy 127.12 cp (298=>25.31, 400=>32.07, 500=>38.44, 600=>44.06, 800=>53.36,
1000=>60.63, 1500=>72.47)

//C(C)(C)(H)(Zeo)   -20.5   39.96   25.05   30.11   35.05   39.40   46.39   51.60   59.63
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 single bond to c1
   H labeled h1 single bond to c1
   Zeo labeled z1 single bond to c1
   } enthalpy -20.5 kJ/mol entropy 39.96 cp (298=>25.05, 400=>30.11, 500=>35.05 , 600=>39.40, 800=>46.39,
1000=>51.60, 1500=>59.63)

//C(C)(C)(C)(Zeo)   -6.9   -48.97   21.44 27.27   31.71   35.10   39.83   42.89   47.01
fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 single bond to c1
   C labeled c4 single bond to c1
   Zeo labeled z1 single bond to c1
   } enthalpy -6.9 kJ/mol entropy -48.97 cp (298=>21.44, 400=>27.27, 500=>31.71, 600=>35.10, 800=>39.83,
1000=>42.89, 1500=>47.01)




}
```

S11. Group corrections file

```
import "glycerol_decomposition_GA_final.txt"
define composite atom Zeo, HTA

define characteristic acyclicMol on Molecule {
   ! Molecule is cyclic
}

define characteristic surfaceSpecies on Molecule{
```

```
  fragment  f{
    M labeled m1}
  Molecule contains >=1 of f
}

define characteristic gasPhaseSpecies on Molecule{
   ! Molecule is surfaceSpecies
}

define characteristic PrimaryAlkoxide on Molecule {
   fragment f{
      Zeo labeled z1
            C labeled c1 single bond to z1 {! connected to >1 C with single bond}
   }
   Molecule contains >=1 of f
}

define characteristic SecondaryTwoAlkoxide on Molecule {
    fragment f{
              C labeled c1 {connected to 2 C with single bond}
                    C labeled c2 single bond to c1 {! connected to >1 C with single bond}
                    Zeo labeled z1 single bond to c1
           }
           Molecule contains >=1 of f
}

define characteristic SecondaryInternalAlkoxide on Molecule {
    fragment f{
              C labeled c1 {connected to 2 C with single bond}
                    C labeled c2 single bond to c1 {connected to >1 C with single bond}
                    C labeled c3 single bond to c1 {connected to >1 C with single bond}
                    Zeo labeled z1 single bond to c1
           }
           Molecule contains >=1 of f
}

define characteristic TertiaryAlkoxide on Molecule {
   fragment f{
      C labeled c1 {connected to 3 C with single bond}
            Zeo labeled z1 single bond to c1
   }
   Molecule contains >=1 of f
}


group corrections {
//C[|C|==3]C[|C|==2]   2.9   -0.7   -0.9   -1.08   -1.10   -1.01   -0.76   -0.56   -0.35
gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 3 C with single bond}
   nonringatom C labeled c2 single bond to c1 {connected to 2 C with single bond}
   } enthalpy 2.9 kJ/mol entropy  -0.7  cp(298=>-0.9, 400=>-1.08, 500=>-1.10, 600=>-1.01, 800=>-0.76, 1000=>-0.56,
1500=>-0.35)

//C[|C|=2]C[|C|=4]   5.8   -1.4   -1.8   -2.16   -2.20   -2.02   -1.52   -1.12   -0.70
gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 2 C with single bond}
   nonringatom C labeled c2 single bond to c1 {connected to 4 C with single bond}
   } enthalpy 5.8 kJ/mol  entropy -1.4  cp (298=> -1.8, 400=>-2.16, 500=>-2.20, 600=>-2.02, 800=>-1.52, 1000=>-
1.12, 1500=>-0.70)

   //C[|C|=3]C[|C|=3]
gasPhaseSpecies fragment {
```

```
   nonringatom C labeled c1 {connected to 3 C with single bond}
   nonringatom C labeled c2 single bond to c1 {connected to 3 C with single bond}
   } enthalpy 8.7 kJ/mol  entropy -2.1  cp (298=> -2.7, 400=>-3.24, 500=>-3.30, 600=>-3.03, 800=>-2.28, 1000=>-
1.68, 1500=>-1.05)

//C[|C|=3]C[|C|=4]   14.5   -3.5   -4.5   -5.40   -5.50   -5.05   -3.80   -2.8   -1.75
gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 3 C with single bond}
   nonringatom C labeled c2 single bond to c1{connected to 4 C with single bond}
   } enthalpy 14.5 kJ/mol entropy -3.5  cp(298=>-4.5, 400=>-5.40, 500=>-5.50, 600=>-5.05, 800=>-3.80, 1000=>-2.8,
1500=>-1.75)

//C[|C|=4]C[|C|=4]   23.2   -5.6   -7.2   -8.64   -8.80   -8.08   -6.08   -4.48   -2.8
gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 4 C with single bond}
   nonringatom C labeled c2 single bond to c1 {connected to 4 C with single bond}
   } enthalpy 23.2 kJ/mol entropy -5.6  cp(298=>-7.2, 400=>-8.64, 500=>-8.80, 600=>-8.08, 800=>-6.08, 1000=>-4.48,
1500=>-2.8)

//C[|C|=4]CC[|C|=3]   7.1   2.72   -1.42   -0.18   0.55   0.83   0.67   0.18   -0.99
 gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 4 C with single bond}
   nonringatom C labeled c2 single bond to c1
   nonringatom C labeled c3 single bond to c2 {connected to 3C with single bond}
   } enthalpy 7.1 kJ/mol entropy 2.72 cp (298=>-1.42, 400=>-0.18, 500=>0.55, 600=>0.83, 800=>0.67, 1000=>0.18,
1500=>-0.99)

//C[|C|=4]CC[|C|=4]   14.2   5.44   -2.84   -0.36   1.10   1.66   1.34   0.36   -1.98
gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 4 C with single bond}
   nonringatom C labeled c2 single bond to c1
   nonringatom C labeled c3 single bond to c2 {connected to 4 C with single bond}
   } enthalpy 14.2 kJ/mol entropy 5.44 cp(298=>-2.84, 400=>-0.36, 500=>1.10, 600=>1.66, 800=>1.34, 1000=>0.36,
1500=>-1.98)

//C[|=C|=1][|C|==2]C[|C|==3]   2.9   -0.7   -0.9   -1.08   -1.10   -1.01   -0.76   -0.56   -0.35
gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 1 C with double bond, connected to 2 C with single bond}
   nonringatom C labeled c2 single bond to c1 {connected to 3 C with single bond}
   } enthalpy 2.9 kJ/mol entropy -0.7 cp(298=>-0.9, 400=>-1.08, 500=>-1.10, 600=>-1.01, 800=>-0.76, 1000=>-0.56,
1500=>-0.35)

//C[|=C|=1][|C|==2]C[|C|==4]   5.8   -1.4   -1.8   -2.16   -2.20   -2.02   -1.52   -1.12   -0.70
gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 1 C with double bond, connected to 2 C with single bond}
   nonringatom C labeled c2 single bond to c1 {connected to 4 C with single bond}
   } enthalpy 5.8 kJ/mol entropy -1.4   cp( 298=>-1.8, 400=>-2.16, 500=>-2.20, 600=>-2.02, 800=>-1.52, 1000=>-1.12,
1500=>-0.70)

//cyclic group corrections   -- taken from Benson's book

gasPhaseSpecies fragment {
 C labeled c1
 C labeled c2 single bond to c1
 C labeled c3 single bond to c2
 ringbond c3 single bond to c1
 } enthalpy 27.6 kcal/mol entropy 32.1 cal/mol/K cp(298=>-3.05 cal/mol/K, 400=>-2.53 cal/mol/K,  500=> -2.10
cal/mol/K, 600=> -1.90 cal/mol/K, 800=>-1.77 cal/mol/K, 1000=>-1.62 cal/mol/K, 1500=>-1.52 cal/mol/K)

gasPhaseSpecies fragment {
 C labeled c1
 C labeled c2 single bond to c1
```

C labeled c3 double bond to c2
ringbond c3 single bond to c1
} enthalpy 53.7 kcal/mol entropy 33.6 cal/mol/K cp(298=>-3.05 cal/mol/K, 400=>-2.53 cal/mol/K, 500=> -2.10 cal/mol/K, 600=> -1.90 cal/mol/K, 800=>-1.77 cal/mol/K, 1000=>-1.62 cal/mol/K, 1500=>-1.52 cal/mol/K)

gasPhaseSpecies fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c2
C labeled c4 single bond to c3
ringbond c1 single bond to c3
} enthalpy 26.2 kcal/mol entropy 29.8 cal/mol/K cp(298=>-4.61 cal/mol/K, 400=> -3.89 cal/mol/K, 500=> -3.14 cal/mol/K, 600=>-2.64 cal/mol/K, 800=> -1.88 cal/mol/K, 1000=>-1.38 cal/mol/K, 1500=> -0.67 cal/mol/K)

gasPhaseSpecies fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 double bond to c2
C labeled c4 single bond to c3
ringbond c1 single bond to c4
} enthalpy 29.8 kcal/mol entropy 29.0 cal/mol/K cp(298=>-2.53 cal/mol/K, 400=> -2.19 cal/mol/K, 500=> -1.89 cal/mol/K, 600=>-1.68 cal/mol/K, 800=> -1.48 cal/mol/K, 1000=>-1.33 cal/mol/K, 1500=> -1.22 cal/mol/K)

gasPhaseSpecies fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c2
C labeled c4 single bond to c3
C labeled c5 single bond to c4
ringbond c1 single bond to c5
} enthalpy 6.3 kcal/mol entropy 27.3 cal/mol/K cp(298=>-7.5 cal/mol/K, 400=>-6.49 cal/mol/K, 500=>-5.4 cal/mol/K, 600=>-4.37 cal/mol/K, 800=> -2.93 cal/mol/K, 1000=>-1.93 cal/mol/K, 1500=>-0.37 cal/mol/K)

gasPhaseSpecies fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 double bond to c2
C labeled c4 single bond to c3
C labeled c5 single bond to c4
ringbond c1 single bond to c5
} enthalpy 5.9 kcal/mol entropy 25.8 cal/mol/K cp(298=>-5.98 cal/mol/K, 400=>-5.35 cal/mol/K, 500=>-4.89 cal/mol/K, 600=>-4.14 cal/mol/K, 800=> -2.93 cal/mol/K, 1000=>-2.26 cal/mol/K, 1500=>-1.08 cal/mol/K)

gasPhaseSpecies fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 double bond to c2
C labeled c4 single bond to c3
C labeled c5 double bond to c4
ringbond c1 single bond to c5
} enthalpy 6.0 kcal/mol entropy 25.8 cal/mol/K cp(298=>-5.98 cal/mol/K, 400=>-5.35 cal/mol/K, 500=>-4.89 cal/mol/K, 600=>-4.14 cal/mol/K, 800=> -2.93 cal/mol/K, 1000=>-2.26 cal/mol/K, 1500=>-1.08 cal/mol/K)

gasPhaseSpecies fragment {
C labeled c1
C labeled c2 single bond to c1
C labeled c3 single bond to c2
C labeled c4 single bond to c3
C labeled c5 single bond to c4
C labeled c6 single bond to c5
ringbond c1 single bond to c6

```
 } enthalpy 0.0 kJ/mol entropy 18.8 cal/mol/K cp(298=> -6.4 cal/mol/K, 400=> -4.6 cal/mol/K, 500=> -3.3 cal/mol/K,
600=> -1.6 cal/mol/K, 800=> 0.82 cal/mol/K, 1000=> 1.98 cal/mol/K, 1500=> 3.19 cal/mol/K)

gasPhaseSpecies fragment {
 C labeled c1
 C labeled c2 single bond to c1
 C labeled c3 double bond to c2
 C labeled c4 single bond to c3
 C labeled c5 single bond to c4
 C labeled c6 single bond to c5
 ringbond c1 single bond to c6
 } enthalpy 1.4 kcal/mol entropy 21.5 cal/mol/K cp(298=> -4.28 cal/mol/K, 400=> -3.04 cal/mol/K, 500=> -1.98
cal/mol/K, 600=> -1.43 cal/mol/K, 800=> -0.29 cal/mol/K, 1000=> 0.08 cal/mol/K, 1500=> 0.81 cal/mol/K)


 //for entropy adding the difference between cyclohexene and cyclohexane to cyclohexane
gasPhaseSpecies fragment {
 C labeled c1
 C labeled c2 single bond to c1
 C labeled c3 double bond to c2
 C labeled c4 single bond to c3
 C labeled c5 double bond to c4
 C labeled c6 single bond to c5
 ringbond c1 single bond to c6
 } enthalpy 4.8 kcal/mol entropy 24.2 cal/mol/K cp(298=> -2.16 cal/mol/K, 400=> -1.48 cal/mol/K, 500=> -0.66
cal/mol/K, 600=> -1.26 cal/mol/K, 800=> -1.4 cal/mol/K, 1000=> -1.82 cal/mol/K, 1500=> -1.57 cal/mol/K)


 gasPhaseSpecies fragment {
 C labeled c1
 C labeled c2 single bond to c1
 C labeled c3 double bond to c2
 C labeled c4 single bond to c3
 C labeled c5 single bond to c4
 C labeled c6 double bond to c5
 ringbond c1 single bond to c6
 } enthalpy 0.5 kcal/mol entropy 24.2 cal/mol/K cp(298=> -2.16 cal/mol/K, 400=> -1.48 cal/mol/K, 500=> -0.66
cal/mol/K, 600=> -1.26 cal/mol/K, 800=> -1.4 cal/mol/K, 1000=> -1.82 cal/mol/K, 1500=> -1.57 cal/mol/K)

//Radical group 1

fragment {
   nonringatom C. labeled c1 {connected to 3 C with single bond}
   nonringatom C labeled c2 single bond to c1 {connected to 2 C with single bond}
   } enthalpy 1.8 kJ/mol entropy  0.82  cp(298=>-0.93, 400=>-0.73, 500=>-0.7, 600=>-0.71, 800=>-0.69, 1000=>-0.63,
1500=>-0.47)

fragment {
   nonringatom C labeled c1 {connected to 3 C with single bond}
   nonringatom C. labeled c2 single bond to c1 {connected to 2 C with single bond}
   } enthalpy 1.8 kJ/mol entropy  0.82  cp(298=>-0.93, 400=>-0.73, 500=>-0.7, 600=>-0.71, 800=>-0.69, 1000=>-0.63,
1500=>-0.47)

fragment {
   nonringatom C. labeled c1 {connected to 2 C with single bond}
   nonringatom C labeled c2 single bond to c1 {connected to 4 C with single bond}
   } enthalpy 3.6 kJ/mol entropy  1.64  cp(298=>-1.86, 400=>-1.46, 500=>-1.4, 600=>-1.42, 800=>-1.38, 1000=>-1.26,
1500=>-0.94)

 fragment {
   nonringatom C. labeled c1 {connected to 3 C with single bond}
   nonringatom C labeled c2 single bond to c1 {connected to 3 C with single bond}
```

```
  } enthalpy 5.4 kJ/mol entropy  2.46  cp(298=>-2.79, 400=>-2.19, 500=>-2.1, 600=>-2.13, 800=>-2.07, 1000=>-1.89,
1500=>-1.41)

fragment {
  nonringatom C. labeled c1 {connected to 3 C with single bond}
  nonringatom C labeled c2 single bond to c1{connected to 4 C with single bond}
  } enthalpy 9.0 kJ/mol entropy  4.10  cp(298=>-4.65, 400=>-3.65, 500=>-3.5, 600=>-3.55, 800=>-3.45, 1000=>-3.15,
1500=>-2.35)

//Radical group 2

//S-T
fragment {
  nonringatom C. labeled c1
  nonringatom C labeled c2 single bond to c1 {connected to 2 C with single bond}
  nonringatom C labeled c3 single bond to c2 {connected to 3 C with single bond}
  } enthalpy 0.7 kJ/mol entropy -0.87  cp (298=>0.53, 400=>0.59, 500=>0.61, 600=>0.59, 800=>0.49, 1000=>0.38,
1500=>0.25) //1 RG2 only
//S-T
fragment {
  nonringatom C. labeled c1
  nonringatom C labeled c2 single bond to c1 {connected to 3 C with single bond}
  nonringatom C labeled c3 single bond to c2 {connected to 2 C with single bond}
  } enthalpy 0.7 kJ/mol entropy -0.87  cp (298=>0.53, 400=>0.59, 500=>0.61, 600=>0.59, 800=>0.49, 1000=>0.38,
1500=>0.25) //1 RG2 only

//S-Q
fragment {
  nonringatom C. labeled c1
  nonringatom C labeled c2 single bond to c1 {connected to 2 C with single bond}
  nonringatom C labeled c3 single bond to c2 {connected to 4 C with single bond}
  } enthalpy 1.4 kJ/mol entropy -1.74  cp (298=>1.06, 400=>1.18, 500=>1.22, 600=>1.18, 800=>0.98, 1000=>0.76,
1500=>0.50) //2 RG2 only

//S-Q
fragment {
  nonringatom C. labeled c1
  nonringatom C labeled c2 single bond to c1 {connected to 4 C with single bond}
  nonringatom C labeled c3 single bond to c2 {connected to 2 C with single bond}
  } enthalpy 3.6 kJ/mol entropy -1.55  cp (298=>-0.37, 400=>-0.49, 500=>-0.49, 600=>-0.42, 800=>-0.27, 1000=>-
0.18, 1500=>-0.1) //1 RG2 and 1 AG

//T-T
fragment {
  nonringatom C. labeled c1
  nonringatom C labeled c2 single bond to c1 {connected to 3 C with single bond}
  nonringatom C labeled c3 single bond to c2 {connected to 3 C with single bond}
  } enthalpy 4.3 kJ/mol entropy -2.44  cp (298=>0.16, 400=>0.10, 500=>0.12, 600=>0.17, 800=>0.22, 1000=>0.2,
1500=>0.15)  //2 RG2 and 1 AG

//T-Q
fragment {
  nonringatom C. labeled c1
  nonringatom C labeled c2 single bond to c1 {connected to 4 C with single bond}
  nonringatom C labeled c3 single bond to c2 {connected to 3 C with single bond}
  } enthalpy 10.1 kJ/mol entropy -3.84  cp (298=>-1.64, 400=>-2.06, 500=>-2.08, 600=>-1.85, 800=>-0.32, 1000=>-
0.92, 1500=>-0.55)  //2 RG2 and 3 AG

//T-Q
fragment {
  nonringatom C. labeled c1
  nonringatom C labeled c2 single bond to c1 {connected to 3 C with single bond}
```

```
   nonringatom C labeled c3 single bond to c2 {connected to 4 C with single bond}
   } enthalpy 7.9 kJ/mol entropy -3.99  cp (298=>-0.21, 400=>-0.39, 500=>-0.37, 600=>-0.25, 800=>-0.05,
1000=>0.02, 1500=>0.05) //3 RG2 and 2 AG

//Q-Q
fragment {
   nonringatom C. labeled c1
   nonringatom C labeled c2 single bond to c1 {connected to 4 C with single bond}
   nonringatom C labeled c3 single bond to c2 {connected to 4 C with single bond}
   } enthalpy 16.6 kJ/mol entropy -6.09  cp (298=>-2.91, 400=>-3.63, 500=>-3.67, 600=>-3.28, 800=>-1.35, 1000=>-
1.66, 1500=>-1.0) //3 RG2 and 5 AG

//ortho substitutions
gasPhaseSpecies fragment {
  nonringatom C labeled c1
  c labeled c2 single bond to c1
  c labeled c3 aromatic bond to c2
  nonringatom  C labeled c4 single bond to c3
  } enthalpy 0.0 kJ/mol entropy -5.73 cp (298=>3.23, 400=>2.36, 500=>1.97, 600=>1.79, 800=>1.65, 1000=>1.53,
1500=>1.08)

//C[|C|=1]C(O)CO[|H|=1]   -8.3182   -2.2572   3.5112   2.8842   2.5498   2.299   2.1318   1.5884   -0.5016
gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 1 C with single bond}
   nonringatom C labeled c2 single bond to c1
   nonringatom O labeled o1 single bond to c2
   nonringatom C labeled c3 single bond to c2
   nonringatom O labeled o2 single bond to c3 {connected to 1 H with single bond}
   } enthalpy -8.3182 kJ/mol entropy -2.2572 cp(298=>3.5112, 400=>2.8842, 500=>2.5498, 600=>2.299,
800=>2.1318, 1000=>1.5884, 1500=>-0.5016)

//C[|C|=1]C(O)CC[|C|=1]   1.5884   0.7942   0.5016   0.0836   0.1672   0.1672   0.209   -0.1672   -3.3858
gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 1 C with single bond}
   nonringatom C labeled c2 single bond to c1
   nonringatom O labeled o1 single bond to c2
   nonringatom C labeled c3 single bond to c2
   nonringatom C labeled c4 single bond to c3 {connected to 1 C with single bond}
   } enthalpy 1.5884 kJ/mol entropy  0.7942  cp(298=>0.5016, 400=>0.0836, 500=>0.1672, 600=>0.1672,
800=>0.209, 1000=>-0.1672, 1500=>-3.3858)

//C[|C|=1]C[|C|=2]C(O)CO[|H|=1]   -9.7394   -8.9452   5.8938   3.0096   2.0064   1.8392   1.5884   2.2154   0.836
gasPhaseSpecies fragment {
   nonringatom C labeled c1 {connected to 1 C with single bond}
   nonringatom C labeled c2 single bond to c1 {connected to 2 C with single bond}
   nonringatom C labeled c3 single bond to c2
   nonringatom O labeled o1 single bond to c3
   nonringatom C labeled c4 single bond to c3
   nonringatom O labeled o2 single bond to c4 {connected to 1 H with single bond}
   } enthalpy -9.7394 kJ/mol entropy -8.9452 cp(298=> 5.8938, 400=>3.0096, 500=>2.0064, 600=>1.8392,
800=>1.5884, 1000=>2.2154, 1500=>0.836)

//C[|C|=1]OCO[|H|=1]   2.2572   -1.2958   1.0032   1.0868   1.672   2.2572   3.135   3.0096   1.881

gasPhaseSpecies fragment {
  nonringatom C labeled c1 {connected to 1 C with single bond}
  nonringatom O labeled o1 single bond to c1
  nonringatom C labeled c2 single bond to o1
  nonringatom O labeled o2 single bond to c2 {connected to 1 H with single bond}
  } enthalpy 2.2572 kJ/mol entropy -1.2958 cp(298=>1.0032, 400=>1.0868, 500=>1.672, 600=>2.2572, 800=>3.135,
1000=>3.0096, 1500=>1.881)
```

```
//C[|C|=1]OCOC[|C|=1]  4.0964  12.2056  -5.1414  -3.6366  -2.4244  -1.9646  -2.1318  -2.3408  -1.672
gasPhaseSpecies fragment {
  nonringatom C labeled c1 {connected to 1 C with single bond}
  nonringatom O labeled o1 single bond to c1
  nonringatom C labeled c2 single bond to o1
  nonringatom O labeled o2 single bond to c2 {connected to 1 C with single bond}
  } enthalpy 4.0964 kJ/mol entropy 12.2056 cp(298=>-5.1414, 400=>-3.6366, 500=>-2.4244, 600=>-1.9646, 800=>-
2.1318, 1000=>-2.3408, 1500=>-1.672)

//C[|H|=3]C[|H|=2]OCO[|H|]  4.8488  -13.8358  12.958  14.9226  14.5882  13.3342  10.3246  7.8166  4.5144
gasPhaseSpecies fragment {
  nonringatom C labeled c1 {connected to 3 H with single bond}
  nonringatom C labeled c2 single bond to c1 {connected to 2 H with single bond}
  nonringatom O labeled o1 single bond to c2
  nonringatom C labeled c3 single bond to o1
  nonringatom O labeled o2 single bond to c3 {connected to 1 H with single bond}
  } enthalpy 4.8488 kJ/mol entropy -13.8358 cp(298=> 12.958, 400=> 14.9226, 500=> 14.5882, 600=>13.3342,
800=>10.3246, 1000=>7.8166, 1500=>4.5144)

//O[|H|=1]C[|H|=2]OCC[|H|=3]  9.6558  5.7266  2.6752  -2.8842  -7.7748  -10.1992  -9.9066  -7.524  -3.4694
gasPhaseSpecies fragment {
  nonringatom O labeled o1 {connected to 1 H with single bond}
  nonringatom C labeled c1 single bond to o1 {connected to 2 H with single bond}
  nonringatom O labeled o2 single bond to c1
  nonringatom C labeled c2 single bond to o2
  nonringatom C labeled c3 single bond to c2 {connected to 3 H with single bond}
  } enthalpy 9.6558 kJ/mol entropy 5.7266 cp(298=> 2.6752, 400=> -2.8842, 500=>-7.7748, 600=>-10.1992, 800=>-
9.9066, 1000=>-7.524, 1500=>-3.4694)

//C[|H|=3]C(O)CO[|H|]  -6.1028  -5.8938  -0.5434  -1.045  -1.0868  -0.7942  0.5852  1.3376  0.0418
gasPhaseSpecies fragment {
  nonringatom C labeled c1 {connected to 3 H with single bond}
  nonringatom C labeled c2 single bond to c1
  nonringatom O labeled o1 single bond to c2
  nonringatom C labeled c3 single bond to c2
  nonringatom O labeled o2 single bond to c3 {connected to 1 H with single bond}
  } enthalpy -6.1028 kJ/mol entropy -5.8938 cp(298=> -0.5434, 400=>-1.045, 500=> -1.0868, 600=>-0.7942, 800=>
0.5852, 1000=> 1.3376, 1500=> 0.0418)

//C[|H|=3]C[|H|=2]C(O)CO[|H|]  -10.1156  -18.4338  3.1768  1.254  1.5466  2.8424  4.807  6.5208  4.6398
gasPhaseSpecies fragment {
  nonringatom C labeled c1 {connected to 3 H with single bond}
  nonringatom C labeled c2 single bond to c1 {connected to 2 H with single bond}
  nonringatom C labeled c3 single bond to c2
  nonringatom O labeled o1 single bond to c3
  nonringatom C labeled c4 single bond to c3
  nonringatom O labeled o2 single bond to c4 {connected to 1 H with single bond}
  } enthalpy -10.1156 kJ/mol entropy -18.4338 cp(298=> 3.1768, 400=> 1.254, 500=>1.5466, 600=>2.8424,
800=>4.807, 1000=>6.5208, 1500=>4.6398)


//C[|H|=3]C=CO[|H|=1]  7.3568  5.0578  -4.2636  -5.9356  -6.2282  -5.8102  -4.5144  -3.344  -5.9774
gasPhaseSpecies fragment {
  nonringatom C labeled c1 {connected to 3 H with single bond}
  nonringatom C labeled c2 single bond to c1
  nonringatom C labeled c3 double bond to c2
  nonringatom O labeled o1 single bond to c3 {connected to 1 H with single bond}
  } enthalpy 7.3568 kJ/mol entropy 5.0578 cp(298=> -4.2636, 400=> -5.9356, 500=> -6.2282, 600=> -5.8102, 800=> -
4.5144, 1000=>-3.344, 1500=> -5.9774)
//O[|H|=1]CC=O  -13.8776  -13.4596  -3.3022  -0.7106  2.1736  4.5144  6.9388  7.315  4.9742
gasPhaseSpecies fragment {
  nonringatom O labeled o1 {connected to 1 H with single bond}
```

```
  nonringatom C labeled c1 single bond to o1
  nonringatom C labeled c2 single bond to c1
  nonringatom O labeled o2 double bond to c2
  } enthalpy -13.8776 kJ/mol entropy -13.4596 cp(298=>-3.3022, 400=>-0.7106, 500=>2.1736, 600=>4.5144,
800=>6.9388, 1000=>7.315, 1500=>4.9742)

//O[|H|=1]CCOC   -11.1606   -23.2408   -0.5016   4.9742   9.7394   12.9162   14.7136   13.2088   8.36
gasPhaseSpecies fragment {
  nonringatom O labeled o1 {connected to 1 H with single bond}
  nonringatom C labeled c1 single bond to o1
  nonringatom C labeled c2 single bond to c1
  nonringatom O labeled o2 single bond to c2
  nonringatom C labeled c3 single bond to o1
  } enthalpy -11.1606 kJ/mol entropy -23.2408 cp(298=> -0.5016, 400=>4.9742, 500=> 9.7394, 600=> 12.9162,
800=> 14.7136, 1000=>13.2088, 1500=>8.36)


//cyclic ethers and oxygenates correction

gasPhaseSpecies fragment {
  O labeled o1
  C labeled c1 single bond to o1
  C labeled c2 single bond to c1
  ringbond c2 single bond to o1
  } enthalpy 26.9 kcal/mol entropy 30.5 cal/mol/K cp(298=>  -2.0  cal/mol/K, 400=> -2.8 cal/mol/K, 500=> -3.0
cal/mol/K, 600=> -2.6 cal/mol/K, 800=> -2.3 cal/mol/K, 1000=> -2.3 cal/mol/K, 1500=> -2.3 cal/mol/K)

gasPhaseSpecies fragment {
  O labeled o1
  C labeled c1 single bond to o1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c2
  ringbond c3 single bond to o1
  } enthalpy 25.7 kcal/mol entropy 26.1 cal/mol/K cp(298=>  -4.6  cal/mol/K, 400=> -5.0 cal/mol/K, 500=> -4.2
cal/mol/K, 600=> -3.5 cal/mol/K, 800=> -2.6 cal/mol/K, 1000=> 0.2 cal/mol/K, 1500=> 0.2 cal/mol/K)


//tetrahydrofuran correction -- enthalpy taken from Benson's, others taken from Benson's for cyclopentane

gasPhaseSpecies fragment {
  O labeled o1
  C labeled c1 single bond to o1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c2
  C labeled c4 single bond to c3
  ringbond c4 single bond to o1
  } enthalpy 6.0 kcal/mol entropy 27.3 cal/mol/K cp(298=> -7.5 cal/mol/K, 400=> -6.49 cal/mol/K, 500=> -5.4
cal/mol/K, 600=> -4.37 cal/mol/K, 800=> -2.93 cal/mol/K, 1000=> -2.26 cal/mol/K, 1500=> -2.26 cal/mol/K)



 // H(M)  -- surface Hydrogen

 fragment {
   M labeled m1
   H labeled h1 single bond to m1
 } enthalpy -10.0 kcal/mol  entropy  12.5 cal/mol/K  cp(298=> 3.3 cal/mol/K, 400=> 3.6 cal/mol/K, 500=> 3.9 cal/mol/K,
600=>4.1 cal/mol/K, 800=>4.5 cal/mol/K, 1000=>4.9 cal/mol/K, 1500=>5.4 cal/mol/K)


//Surface partial bonds corrections
```

```
//C(C)(H)(H)(O_M)  wrt C(C)(H)(H)(O) in nonsurface corrections in JPCC 2012
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  O labeled o1 single bond to c1
  M labeled m1 partial bond to o1
  } enthalpy -5.016 kJ/mol entropy -9.196 cp(298=> -2.926, 400=> -3.334, 500=> -2.508, 600=> -2.09, 800=> -1.672,
1000=> -1.254, 1500=> -1.254)

//C(C)(C)(H)(O_M)  wrt C(C)(C)(H)(O) in nonsurface corrections in JPCC 2012
fragment {
  C labeled c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  H labeled h1 single bond to c1
  O labeled o1 single bond to c1
  M labeled m1 partial bond to o1
  } enthalpy -12.54 kJ/mol entropy -3.762 cp(298=> 3.344, 400=> 3.762, 500=> 3.344, 600=> 5.016, 800=> 6.27,
1000=> 7.524, 1500=> 7.524)

//C(H)(H)(O)(O_M) wrt C(H)(H)(O)(O) in gas phase additivities
fragment {
  C labeled c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  O labeled o1 single bond to c1
  O labeled o2 single bond to c1
  M labeled m1 partial bond to o2
  } enthalpy -7.4822 kJ/mol entropy -14.0866 cp(298=> -11.1188, 400=> -20.6074, 500=> -25.916, 600=> -26.752,
800=> -23.3244, 1000=> -18.2666, 1500=> -18.6846)



//nonsurface corrections

//C(C)(C=O)(H)(H)   -21.9868   40.128   25.916   32.186   36.366   39.71   46.398   50.996   59.356
surfaceSpecies fragment {
  C labeled c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  O labeled o1 double bond to c3
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  } enthalpy 0.0 kJ/mol entropy -4.18 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(C)(H)(H)(O)   -33.1056   38.038   22.4466   29.2182   35.1538   40.0444   47.443   52.668   60.401
surfaceSpecies fragment {
  C labeled c1
  C labeled c2 single bond to c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy 0.0 kJ/mol entropy -13.79  cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(C)(H)(H)(H)   -42.9   127.12   25.31  32.07   38.44   44.06   53.36   60.63   72.47
surfaceSpecies fragment {
   C labeled c1
   C labeled c2 single bond to c1
```

```
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   H labeled h3 single bond to c1
   }enthalpy 0.0 kJ/mol entropy -89.5  cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(C)(C)(C=O)(H)   -6.9806   -49.3658   24.8292   31.1828   35.1538   37.8708   41.9672   44.308   48.1118
surfaceSpecies fragment {
  C labeled c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  C labeled c4 single bond to c1
  O labeled o1 double bond to c4
  H labeled h1 single bond to c1
  } enthalpy 0.0 kJ/mol entropy 80.29  cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(C=C)(C)(C)(H)   -3.9   -49.65   24.94   30.73   35.02   38.03   41.77   44.07   47.41
surfaceSpecies fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 double bond to c2
   C labeled c4 single bond to c1
   C labeled c5 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy 0.0 kJ/mol entropy 73.89  cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(C)(C)(H)(O)   -31.0156   -51.7484   21.0254   28.1732   33.649   37.4946   42.0926   44.6842   47.6102
surfaceSpecies fragment {
  C labeled c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  H labeled h1 single bond to c1
  O labeled o1 single bond to c1
  }enthalpy 0.0 kJ/mol entropy 71.81  cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(C)(C)(H)(H)   -20.5   39.96   25.05   30.11   35.05   39.40   46.39   51.60   59.63
surfaceSpecies fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 single bond to c1
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   } enthalpy 0.0 kJ/mol entropy -2.34  cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(C)(C)(C)(H)   -6.9   -48.97   21.44 27.27   31.71   35.10   39.83   42.89   47.01
surfaceSpecies fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 single bond to c1
   C labeled c4 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy 0.0 kJ/mol entropy 76.14  cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(C)(C)(C)(O)   -29.3854   -144.0428   21.2344   28.3404   32.8548   35.0702   36.0734   35.53   33.649
surfaceSpecies fragment {
  C labeled c1
  C labeled c2 single bond to c1
```

```
  C labeled c3 single bond to c1
  C labeled c4 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy 0.0 kJ/mol entropy 136.1 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(C)(C)(C)(C)   3.9   -148.25   17.53   24.47   29.01   31.78   34.22   34.72   33.79
surfaceSpecies fragment {
   C labeled c1
   C labeled c2 single bond to c1
   C labeled c3 single bond to c1
   C labeled c4 single bond to c1
   C labeled c5 single bond to c1
   } enthalpy 0.0 kJ/mol entropy 146.16 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(=O)(C)(H)   -123.1846   145.882   29.26   32.604   36.784   40.546   46.816   50.996   58.102
surfaceSpecies fragment {
  C labeled c1
  O labeled o1 double bond to c1
  C labeled c2 single bond to c1
  H labeled h1 single bond to c1
  } enthalpy 0.0 kJ/mol entropy -73.57 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(=O)(C)(O)   -145.7148   63.2852   23.0736   25.2472   28.424   31.9352   37.2438   41.7582   48.2372
surfaceSpecies fragment {
  C labeled c1
  O labeled o1 double bond to c1
  C labeled c2 single bond to c1
  O labeled 02 single bond to c1
  } enthalpy 0.0 kJ/mol entropy -16.0512 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(=O)(C)(C)   -132.4642   62.7418   23.408   26.334   29.678   32.604   37.202   40.128   43.89
surfaceSpecies fragment {
  C labeled c1
  O labeled o1 double bond to c1
  C labeled c2 single bond to c1
  C labeled c3 single bond to c1
  } enthalpy 0.0 kJ/mol entropy -0.0418 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(=C)(C)(H)   37.1   32.91   18.44   21.74   25.02   27.96   32.65   36.06   41.17
surfaceSpecies fragment {
   C labeled c1 {connected to 1 C with double bond}
   C labeled c3 single bond to c1
   H labeled h1 single bond to c1
   } enthalpy 0.0 kJ/mol entropy 5.128 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(=C)(C)(C)   45.3   -55.9   19.58   21.71   23.12   24.25   25.94   27.02   28.35
surfaceSpecies fragment {
   C labeled c1 {connected to 1 C with double bond}
   C labeled c3 single bond to c1
   C labeled c4 single bond to c1
   } enthalpy 0.0 kJ/mol entropy 82.65 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//C(=C)(H)(H)   25.1   115.76   20.59   25.93   30.75   34.87   41.44   46.45   54.57
surfaceSpecies fragment {
   C labeled c1 {connected to 1 C with double bond}
```

```
   H labeled h1 single bond to c1
   H labeled h2 single bond to c1
   } enthalpy 0.0 kJ/mol entropy -81.066 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//O(C)(H)   -158.2548   123.101   17.347   17.556   18.9772   20.6492   23.7006   26.334   30.7648
surfaceSpecies fragment {
  O labeled o1 {! connected to >=1 M with partial bond}
  C labeled c1 single bond to o1
  H labeled h1 single bond to o1
  } enthalpy 0.0 kJ/mol entropy -63.745 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//O(C)(C)   -96.8924   38.0798   11.9548   10.3246   10.7008   11.6622   13.6686   15.3406   17.138
surfaceSpecies fragment {
  O labeled o1  {! connected to >=1 M with partial bond}
  C labeled c1 single bond to o1
  C labeled c2 single bond to o1
  } enthalpy 0.0 kJ/mol entropy -2.968 cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)


//C(H)(H)(H)(O)   -41.8   127.1138   25.8742   32.7712   39.292   45.1022   54.4236   61.7386   73.4844
//This contribution is calculated from CH3OM species given in Salciccioli ACS Catal. oaoer
surfaceSpecies fragment {
  C labeled c1
  H labeled h1 single bond to c1
  H labeled h2 single bond to c1
  H labeled h3 single bond to c1
  O labeled o1 single bond to c1
  } enthalpy 0.0 kJ/mol entropy -80.2978  cp(298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0,
1500=>0.0)

//correction for C(C)(COwk)(H)(M) wrt C(C)(CO)(H)(M)
//the correction is 15.9       -2.3       -2.7       -3         -3.2       -3.3       -3.3       -3.4

surfaceSpecies fragment {
   C labeled c1
   O labeled o1 double bond to c1
   H labeled h1 single bond to c1
   C labeled c2 single bond to c1 {connected to 2 C with single bond, connected to 1 M with single bond, connected to
1 H with single bond}
} enthalpy 15.9     kcal/mol entropy -2.3 cal/mol/K cp (298=>-2.7 cal/mol/K, 400=> -3 cal/mol/K, 500=> -3.2 cal/mol/K,
600=> -3.3 cal/mol/K, 800=> -3.3 cal/mol/K, 1000=> -9.3 cal/mol/K, 1500=> -9.3 cal/mol/K)

//correction for C-(C)(COwk)(H)2 wrt C-(C)(CO)(H)2
//the correction is 0.5        -2.4       -1         -0.8       -0.3       0.2        0.6        0.9

surfaceSpecies fragment {
   C labeled c1
   O labeled o1 double bond to c1
   H labeled h1 single bond to c1
   C labeled c2 single bond to c1 {connected to 2 C with single bond, connected to 2 H with single bond}
} enthalpy 0.5       kcal/mol entropy -2.4 cal/mol/K cp (298=>-1.0 cal/mol/K, 400=> -0.8 cal/mol/K, 500=> -0.3
cal/mol/K, 600=> 0.2 cal/mol/K, 800=> 0.6 cal/mol/K, 1000=> 0.9 cal/mol/K, 1500=> 0.9 cal/mol/K)

//the correction for C-(C)(COwk)(M)2 wrt C-(C)(CO)(M)2
//the correction is 18.3       -3.8       -2.7       -2.9       -3         -3.1       -3.2       -3.3

surfaceSpecies fragment {
   C labeled c1
   O labeled o1 double bond to c1
```

```
   H labeled h1 single bond to c1
   C labeled c2 single bond to c1 {connected to 2 C with single bond, connected to 2 M with single bond}
} enthalpy 18.3     kcal/mol entropy -3.8 cal/mol/K cp (298=>-2.7 cal/mol/K, 400=> -2.9 cal/mol/K, 500=> -3.0
cal/mol/K, 600=> -3.1 cal/mol/K, 800=> -3.2 cal/mol/K, 1000=> -3.3 cal/mol/K, 1500=> -3.3 cal/mol/K)

//the correction for C(C)(C)(COwk)(H)
// correction is -10.1574      61.4878  -4.7652  -4.4308  -2.5498  -1.0868  1.5048   2.926     -0.8778

surfaceSpecies fragment {
   C labeled c1
   O labeled o1 double bond to c1
   H labeled h1 single bond to c1
  C labeled c2 single bond to c1 {connected to 3 C with single bond, connected to 1 H with single bond}
} enthalpy -10.1574 kJ/mol entropy 61.4878  cp(298=> -4.7652, 400=> -4.430, 500=> -2.5498, 600=> -1.0868, 800=>
1.5048, 1000=> 2.926, 1500=>-0.8778)


  // the correction for C-(C)2(COwk)(M) wrt C-(C)2(CO)(M)
  // the correction is 17.5     1.5         -2.1        -2.4        -2.5        -2.6        -2.7        -2.9        -2.9

surfaceSpecies fragment {
   C labeled c1
   O labeled o1 double bond to c1
   H labeled h1 single bond to c1
  C labeled c2 single bond to c1 {connected to 3 C with single bond, connected to 1 M with single bond}
} enthalpy 17.5     kcal/mol entropy 1.5 cal/mol/K cp (298=>-2.1 cal/mol/K, 400=> -2.4 cal/mol/K, 500=> -2.5
cal/mol/K, 600=> -2.6 cal/mol/K, 800=> -2.7 cal/mol/K, 1000=> -2.9 cal/mol/K, 1500=> -2.9 cal/mol/K)

//the correction for C-(COwk)(H)(M)(O)  wrt C-(CO)(H)(M)(O)
// the correction is 14.2       -2          -2.6        -2.9        -3.3        -3.4        -3.6        -3.7        -3.7

surfaceSpecies fragment {
   C labeled c1
   O labeled o1 double bond to c1
   H labeled h1 single bond to c1
  C labeled c2 single bond to c1 {connected to 1 C with single bond, connected to 1 M with single bond, connected to
1 H with single bond, connected to 1 O with single bond}
} enthalpy 14.2     kcal/mol entropy -2.0 cal/mol/K cp (298=>-2.6 cal/mol/K, 400=> -2.9 cal/mol/K, 500=> -3.3
cal/mol/K, 600=> -3.4 cal/mol/K, 800=> -3.6 cal/mol/K, 1000=> -3.7 cal/mol/K, 1500=> -3.7 cal/mol/K)

//the correction for C-(COwk)(H)(M)2 wrt C-(CO)(H)(M)2
//the correction is 12.4       -3.5        -3.1        -3.4        -3.5        -3.7        -3.8        -3.9        -3.9

surfaceSpecies fragment {
   C labeled c1
   O labeled o1 double bond to c1
   H labeled h1 single bond to c1
  C labeled c2 single bond to c1 {connected to 1 C with single bond, connected to 2 M with single bond, connected to
1 H with single bond}
}  enthalpy 12.4 kcal/mol entropy -3.5 cal/mol/K cp (298=>-3.1 cal/mol/K, 400=> -3.4 cal/mol/K, 500=> -3.5 cal/mol/K,
600=> -3.7 cal/mol/K, 800=> -3.8 cal/mol/K, 1000=> -3.9 cal/mol/K, 1500=> -3.9 cal/mol/K)


//correctiong for C-(COwk)(H)2(M) wrt C-(CO)(H)2(M)
//the correction is 13.4       -2.6        -2.5        -2.8        -3          -3.1        -3.3        -3.4        -3.4

surfaceSpecies fragment {
   C labeled c1
   O labeled o1 double bond to c1
   H labeled h1 single bond to c1
   C labeled c2 single bond to c1 {connected to 1 C with single bond, connected to 1 M with single bond, connected to
2 H with single bond}
```

} enthalpy 13.4 kcal/mol entropy -2.6 cal/mol/K cp (298=>-2.5 cal/mol/K, 400=> -2.8 cal/mol/K, 500=> -3.0 cal/mol/K, 600=> -3.1 cal/mol/K, 800=> -3.3 cal/mol/K, 1000=> -3.4 cal/mol/K, 1500=> -3.4 cal/mol/K)

// correction for C-(COwk)(M)2(O) wrt C-(CO)(M)2(O)
//the correction is 13.3 -3.4 -3.1 -3.6 -3.9 -4 -4.2 -4.3 -4.3

surfaceSpecies fragment {
C labeled c1
O labeled o1 double bond to c1
H labeled h1 single bond to c1
C labeled c2 single bond to c1 {connected to 1 C with single bond, connected to 2 M with single bond, connected to 1 O with single bond}
}enthalpy 13.3 kcal/mol entropy -3.4 cal/mol/K cp (298=>-3.1 cal/mol/K, 400=> -3.6 cal/mol/K, 500=> -3.9 cal/mol/K, 600=> -4.0 cal/mol/K, 800=> -4.2 cal/mol/K, 1000=> -4.3 cal/mol/K, 1500=> -4.3 cal/mol/K)

// correction for COwk-(C)(H) wrt CO-(C)(H)
//the correction is -14 -0.4 3.7 4.4 4.7 4.8 4.9 4.9 4.9
surfaceSpecies fragment {
C labeled c1
O labeled o1 double bond to c1
H labeled h1 single bond to c1
C labeled c2 single bond to c1
} enthalpy -14.0 kcal/mol entropy -0.4 cal/mol/K cp (298=>3.7 cal/mol/K, 400=> 4.4 cal/mol/K, 500=> 4.7 cal/mol/K, 600=> -4.8 cal/mol/K, 800=> 4.9 cal/mol/K, 1000=> 4.9 cal/mol/K, 1500=> 4.9 cal/mol/K)

//Surface ring corrections

//C(M3)C(M3) 0 1 25.3 10.6 -4.9 -6.4 -7.5 -8.3 -9 -9.3
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1 {connected to 3 M with single bond}
} enthalpy 25.3 kcal/mol entropy 10.6 cal/mol/K cp (298=>-4.9 cal/mol/K, 400=> -6.4 cal/mol/K, 600=> -7.5 cal/mol/K, 800=> -8.3 cal/mol/K, 1000=> -9.0 cal/mol/K, 1500=> -9.3 cal/mol/K)

//C(M3)C(M2) 54.75 0.6958 17.6046 7.3758 -3.4096 -4.4533 -5.2188 -5.7754 -6.2625 -6.4713
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1 {connected to 2 M with single bond}
} enthalpy 17.6046 kcal/mol entropy 7.3758 cal/mol/K cp (298=>-3.4096 cal/mol/K, 400=> -4.4533 cal/mol/K, 600=> -5.2188 cal/mol/K, 800=> -5.7754 cal/mol/K, 1000=> -6.2625 cal/mol/K, 1500=> -6.4713 cal/mol/K)

//C(M3)C(M) 70.5 0.6083 15.3908 6.4483 -2.9808 -3.8933 -4.5625 -5.0492 -5.4750 -5.6575
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1 {connected to 1 M with single bond, !connected to >=1 any atom with strong bond}
} enthalpy 15.3908 kcal/mol entropy 6.4483 cal/mol/K cp (298=> -2.9808 cal/mol/K, 400=> -3.8933 cal/mol/K, 500=> -4.5625 cal/mol/K, 600=> -5.0492 cal/mol/K, 800=> -5.4750 cal/mol/K, 1000=> -5.6575 cal/mol/K, 1500=> -5.6575 cal/mol/K)

//C(M3)O(M) 70.5 0.6083 15.3908 6.4483 -2.9808 -3.8933 -4.5625 -5.0492 -5.4750 -5.6575
fragment {
C labeled c1 {connected to 3 M with single bond}
O labeled o1 single bond to c1 {connected to 1 M with single bond}
} enthalpy 15.3908 kcal/mol entropy 6.4483 cal/mol/K cp (298=> -2.9808 cal/mol/K, 400=> -3.8933 cal/mol/K, 500=> -4.5625 cal/mol/K, 600=> -5.0492 cal/mol/K, 800=> -5.4750 cal/mol/K, 1000=> -5.6575 cal/mol/K, 1500=> -5.6575 cal/mol/K)

//C(M3)C(=O)(M) 60 0.6667 16.8667 7.0667 -3.2667 -4.2667 -5.0000 -5.5333 -6.0000 -6.2000

fragment {
  C labeled c1 {connected to 3 M with single bond}
  C labeled c2 single bond to c1 {connected to 1 M with single bond}
  O labeled o1 double bond to c2
} enthalpy 16.8667 kcal/mol entropy 7.0667 cal/mol/K cp (298=> -3.2667 cal/mol/K, 400=> -4.2667 cal/mol/K, 500=> -5.0000 cal/mol/K, 600=> -5.5333 cal/mol/K, 800=> -6.0000 cal/mol/K, 1000=> -6.2000 cal/mol/K, 1500=> -6.2 cal/mol/K)

//C(M2)C(M) 125.25 0.3042 7.6954 3.2242 -1.4904 -1.9467 -2.2813 -2.5246 -2.7375 -2.8288
fragment {
  C labeled c1 {connected to 2 M with single bond}
  C labeled c2 single bond to c1{connected to 1 M with single bond, !connected to >=1 any atom with strong bond}
} enthalpy 7.6954 kcal/mol entropy 3.2242 cal/mol/K cp (298=> -1.4904 cal/mol/K, 400=> -1.9467 cal/mol/K, 500=> -2.2813 cal/mol/K, 600=> -2.5246 cal/mol/K, 800=> -2.7375 cal/mol/K, 1000=> -2.8288 cal/mol/K, 1500=> -2.82875 cal/mol/K)

//C(M2)O(M) 125.25 0.3042 7.6954 3.2242 -1.4904 -1.9467 -2.2813 -2.5246 -2.7375 -2.8288
fragment {
  C labeled c1 {connected to 2 M with single bond}
  O labeled o1 single bond to c1{connected to 1 M with single bond}
} enthalpy 7.6954 kcal/mol entropy 3.2242 cal/mol/K cp (298=> -1.4904 cal/mol/K, 400=> -1.9467 cal/mol/K, 500=> -2.2813 cal/mol/K, 600=> -2.5246 cal/mol/K, 800=> -2.7375 cal/mol/K, 1000=> -2.8288 cal/mol/K, 1500=> -2.82875 cal/mol/K)

//C(M2)C(=O)(M) 114.75 0.3625 9.1713 3.8425 -1.7763 -2.3200 -2.7188 -3.0088 -3.2625 -3.3713
fragment {
 C labeled c1 {connected to 2 M with single bond}
 C labeled c2 single bond to c1
 O labeled o1 double bond to c2 {connected to 1 M with single bond}
} enthalpy 9.1713 kcal/mol entropy 3.8425 cal/mol/K cp (298=> -1.7763 cal/mol/K, 400=> -2.3200 cal/mol/K, 500=> -2.7188 cal/mol/K, 600=> -3.0088 cal/mol/K, 800=> -3.2625 cal/mol/K, 1000=> -3.3713 cal/mol/K, 1500=> -3.37125 cal/mol/K)

//C(M2)C(M2) 109.5 0.3917 9.9092 4.1517 -1.9192 -2.5067 -2.9375 -3.2508 -3.5250 -3.6425
fragment {
  C labeled c1 {connected to 2 M with single bond}
  C labeled c2 single bond to c1 {connected to 2 M with single bond}
} enthalpy 9.9092 kcal/mol entropy 4.1517 cal/mol/K cp (298=> -1.9192 cal/mol/K, 400=> -2.5067 cal/mol/K, 500=> -2.9375 cal/mol/K, 600=> -3.2508 cal/mol/K, 800=> -3.5250 cal/mol/K, 1000=> -3.6425 cal/mol/K, 1500=> -3.6425 cal/mol/K)

//C(M)C(M) 141 0.2167 5.4817 2.2967 -1.0617 -1.3867 -1.6250 -1.7983 -1.9500 -2.0150
fragment {
  C labeled c1 {connected to 1 M with single bond, !connected to >=1 any atom with strong bond}
  C labeled c2 single bond to c1 {connected to 1 M with single bond, !connected to >=1 any atom with strong bond}
} enthalpy 5.4817 kcal/mol entropy 2.2967 cal/mol/K cp (298=> -1.0617 cal/mol/K, 400=> -1.3867 cal/mol/K, 500=> -1.6250 cal/mol/K, 600=> -1.7983 cal/mol/K, 800=> -1.9500 cal/mol/K, 1000=> -2.0150 cal/mol/K, 1500=> -2.015 cal/mol/K)

//C(M)O(M) 141 0.2167 5.4817 2.2967 -1.0617 -1.3867 -1.6250 -1.7983 -1.9500 -2.0150
fragment {
  C labeled c1 {connected to 1 M with single bond, !connected to >=1 any atom with strong bond}
  O labeled o1 single bond to c1 {connected to 1 M with single bond}
} enthalpy 5.4817 kcal/mol entropy 2.2967 cal/mol/K cp (298=> -1.0617 cal/mol/K, 400=> -1.3867 cal/mol/K, 500=> -1.6250 cal/mol/K, 600=> -1.7983 cal/mol/K, 800=> -1.9500 cal/mol/K, 1000=> -2.0150 cal/mol/K, 1500=> -2.015 cal/mol/K)

```
//C(M)C(=O)(M)   130.5    0.2750   6.9575   2.9150   -1.3475  -1.7600  -2.0625  -2.2825  -2.4750  -2.5575
fragment {
  C labeled c1 {connected to 1 M with single bond, !connected to >=1 any atom with strong bond}
  C labeled c2 single bond to c1 {connected to 1 M with single bond}
  O labeled o1 double bond to c2
} enthalpy          6.9575   kcal/mol entropy  2.9150    cal/mol/K          cp (298=>          -1.3475   cal/mol/K, 400=>
          -1.7600   cal/mol/K, 500=> -2.0625   cal/mol/K, 600=> -2.2825   cal/mol/K, 800=> -2.4750   cal/mol/K,
1000=>  -2.5575   cal/mol/K, 1500=>           -2.5575 cal/mol/K)


//O(M)O(M)        141      0.2167   5.4817   2.2967   -1.0617  -1.3867  -1.6250  -1.7983  -1.9500  -2.0150
fragment {
  O labeled o1 {connected to 1 M with single bond}
  O labeled o2 single bond to o1 {connected to 1 M with single bond}
} enthalpy          5.4817   kcal/mol entropy  2.2967    cal/mol/K          cp (298=>          -1.0617   cal/mol/K, 400=>
          -1.3867   cal/mol/K, 500=> -1.6250   cal/mol/K, 600=> -1.7983   cal/mol/K, 800=> -1.9500   cal/mol/K,
1000=>  -2.0150   cal/mol/K, 1500=>           -2.015 cal/mol/K)


//O(M)C(=O)M     130.5    0.2750   6.9575   2.9150   -1.3475  -1.7600  -2.0625  -2.2825  -2.4750  -2.5575
fragment {
  O labeled o1 {connected to 1 M with single bond}
  C labeled c1 single bond to o1 {connected to 1 M with single bond}
  O labeled o2 double bond to c1
} enthalpy          6.9575   kcal/mol entropy  2.9150    cal/mol/K          cp (298=>          -1.3475   cal/mol/K, 400=>
          -1.7600   cal/mol/K, 500=> -2.0625   cal/mol/K, 600=> -2.2825   cal/mol/K, 800=> -2.4750   cal/mol/K,
1000=>  -2.5575   cal/mol/K, 1500=>           -2.5575 cal/mol/K)

//C(=O)(M)C(=O)(M)        120      0.3333   8.4333   3.5333   -1.6333  -2.1333  -2.5000  -2.7667  -3.0000  -3.1000
fragment {
  C labeled c1 {connected to 1 M with single bond}
  O labeled o1 double bond to c1
  C labeled c2 single bond to c1 {connected to 1 M with single bond}
  O labeled o2 double bond to c2
} enthalpy          8.4333   kcal/mol entropy  3.5333    cal/mol/K          cp (298=>          -1.6333   cal/mol/K, 400=>
          -2.1333   cal/mol/K, 500=> -2.5000   cal/mol/K, 600=> -2.7667   cal/mol/K, 800=> -3.0000   cal/mol/K,
1000=>  -3.1000   cal/mol/K, 1500=>           -3.1 cal/mol/K)


//C(M)(M)C(=O)C(M)(M)     169.5    0.0583   1.4758   0.6183   -0.2858  -0.3733  -0.4375  -0.4842  -0.5250  -0.5425
fragment {
  C labeled c1 {connected to 2 M with single bond}
  C labeled c2 single bond to c1
  O labeled o1 double bond to c2
  C labeled c3 single bond to c2 {connected to 2 M with single bond}
} enthalpy          1.4758   kcal/mol entropy  0.6183    cal/mol/K          cp (298=>          -0.2858   cal/mol/K, 400=>
          -0.3733   cal/mol/K, 500=> -0.4375   cal/mol/K, 600=> -0.4842   cal/mol/K, 800=> -0.5250   cal/mol/K,
1000=>  -0.5425   cal/mol/K, 1500=>           -0.5425 cal/mol/K)


//C(M)(M)C(=O)C(=O)(M)  174.75   0.0292   0.7379   0.3092   -0.1429  -0.1867  -0.2188  -0.2421  -0.2625  -0.2713
fragment {
  C labeled c1 {connected to 2 M with single bond}
  C labeled c2 single bond to c1
  O labeled o1 double bond to c2
  C labeled c3 single bond to c2 {connected to 1 M with single bond}
  O labeled o2 double bond to c3
```

} enthalpy 0.7379 kcal/mol entropy 0.3092 cal/mol/K cp (298=> -0.1429 cal/mol/K, 400=> -0.1867 cal/mol/K, 500=> -0.2188 cal/mol/K, 600=> -0.2421 cal/mol/K, 800=> -0.2625 cal/mol/K, 1000=> -0.2713 cal/mol/K, 1500=> -0.27125 cal/mol/K)

//C(M)(M)(M)CC(M)(M)(M) 70.5 0.6083 15.3908 6.4483 -2.9808 -3.8933 -4.5625 -5.0492 -5.4750 -5.6575
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1 {!connected to >=1 any atom with strong bond}
C labeled c3 single bond to c2 {connected to 3 M with single bond}
} enthalpy 15.3908 kcal/mol entropy 6.4483 cal/mol/K cp (298=> -2.9808 cal/mol/K, 400=> -3.8933 cal/mol/K, 500=> -4.5625 cal/mol/K, 600=> -5.0492 cal/mol/K, 800=> -5.4750 cal/mol/K, 1000=> -5.6575 cal/mol/K, 1500=> -5.6575 cal/mol/K)

//C(M)(M)(M)OC(M)(M)(M) 70.5 0.6083 15.3908 6.4483 -2.9808 -3.8933 -4.5625 -5.0492 -5.4750 -5.6575
fragment {
C labeled c1 {connected to 3 M with single bond}
O labeled c2 single bond to c1
C labeled c3 single bond to c2 {connected to 3 M with single bond}
} enthalpy 15.3908 kcal/mol entropy 6.4483 cal/mol/K cp (298=> -2.9808 cal/mol/K, 400=> -3.8933 cal/mol/K, 500=> -4.5625 cal/mol/K, 600=> -5.0492 cal/mol/K, 800=> -5.4750 cal/mol/K, 1000=> -5.6575 cal/mol/K, 1500=> -5.6575 cal/mol/K)

//C(M)(M)(M)C(=O)C(M)(M)(M) 60 0.6667 16.8667 7.0667 -3.2667 -4.2667 -5.0000 -5.5333 -6.0000 -6.2000
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1
O labeled o1 double bond to c2
C labeled c3 single bond to c2 {connected to 3 M with single bond}
} enthalpy 16.8667 kcal/mol entropy 7.0667 cal/mol/K cp (298=> -3.2667 cal/mol/K, 400=> -4.2667 cal/mol/K, 500=> -5.0000 cal/mol/K, 600=> -5.5333 cal/mol/K, 800=> -6.0000 cal/mol/K, 1000=> -6.2000 cal/mol/K, 1500=> -6.2 cal/mol/K)

//C(M)(M)(M)CC(M)(M) 125.25 0.3042 7.6954 3.2242 -1.4904 -1.9467 -2.2813 -2.5246 -2.7375 -2.8288
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1 {!connected to >=1 any atom with strong bond}
C labeled c3 single bond to c2 {connected to 2 M with single bond}
} enthalpy 7.6954 kcal/mol entropy 3.2242 cal/mol/K cp (298=> -1.4904 cal/mol/K, 400=> -1.9467 cal/mol/K, 500=> -2.2813 cal/mol/K, 600=> -2.5246 cal/mol/K, 800=> -2.7375 cal/mol/K, 1000=> -2.8288 cal/mol/K, 1500=> -2.82875 cal/mol/K)

//C(M)(M)(M)C(=O)C(M)(M) 114.75 0.3625 9.1713 3.8425 -1.7763 -2.3200 -2.7188 -3.0088 -3.2625 -3.3713
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1
O labeled o1 double bond to c2
C labeled c3 single bond to c2 {connected to 2 M with single bond}
} enthalpy 9.1713 kcal/mol entropy 3.8425 cal/mol/K cp (298=> -1.7763 cal/mol/K, 400=> -2.3200 cal/mol/K, 500=> -2.7188 cal/mol/K, 600=> -3.0088 cal/mol/K, 800=> -3.2625 cal/mol/K, 1000=> -3.3713 cal/mol/K, 1500=> -3.37125 cal/mol/K)

//C(M)(M)(M)CC(M) 141 0.2167 5.4817 2.2967 -1.0617 -1.3867 -1.6250 -1.7983 -1.9500 -2.0150
fragment {
C labeled c1 {connected to 3 M with single bond}

C labeled c2 single bond to c1 {!connected to >=1 any atom with strong bond}
C labeled c3 single bond to c2 {connected to 1 M with single bond, !connected to >=1 any atom with strong bond}
} enthalpy 5.4817 kcal/mol entropy 2.2967 cal/mol/K cp (298=> -1.0617 cal/mol/K, 400=> -1.3867 cal/mol/K, 500=> -1.6250 cal/mol/K, 600=> -1.7983 cal/mol/K, 800=> -1.9500 cal/mol/K, 1000=> -2.0150 cal/mol/K, 1500=> -2.015 cal/mol/K)

//C(M)(M)(M)OC(M) 141 0.2167 5.4817 2.2967 -1.0617 -1.3867 -1.6250 -1.7983 -1.9500 -2.0150
fragment {
C labeled c1 {connected to 3 M with single bond}
O labeled o1 single bond to c1
C labeled c3 single bond to o1 {connected to 1 M with single bond, !connected to >=1 any atom with strong bond}
} enthalpy 5.4817 kcal/mol entropy 2.2967 cal/mol/K cp (298=> -1.0617 cal/mol/K, 400=> -1.3867 cal/mol/K, 500=> -1.6250 cal/mol/K, 600=> -1.7983 cal/mol/K, 800=> -1.9500 cal/mol/K, 1000=> -2.0150 cal/mol/K, 1500=> -2.015 cal/mol/K)

//C(M)(M)(M)C(=O)C(M) 130.5 0.2750 6.9575 2.9150 -1.3475 -1.7600 -2.0625 -2.2825 -2.4750 -2.5575
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1
O labeled o1 double bond to c2
C labeled c3 single bond to c2 {connected to 1 M with single bond, !connected to >=1 any atom with strong bond}
} enthalpy 6.9575 kcal/mol entropy 2.9150 cal/mol/K cp (298=> -1.3475 cal/mol/K, 400=> -1.7600 cal/mol/K, 500=> -2.0625 cal/mol/K, 600=> -2.2825 cal/mol/K, 800=> -2.4750 cal/mol/K, 1000=> -2.5575 cal/mol/K, 1500=> -2.5575 cal/mol/K)

//C(M)(M)(M)CO(M) 141 0.2167 5.4817 2.2967 -1.0617 -1.3867 -1.6250 -1.7983 -1.9500 -2.0150
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1 {!connected to >=1 any atom with strong bond}
O labeled o1 single bond to c2 {connected to 1 M with single bond}
} enthalpy 5.4817 kcal/mol entropy 2.2967 cal/mol/K cp (298=> -1.0617 cal/mol/K, 400=> -1.3867 cal/mol/K, 500=> -1.6250 cal/mol/K, 600=> -1.7983 cal/mol/K, 800=> -1.9500 cal/mol/K, 1000=> -2.0150 cal/mol/K, 1500=> -2.015 cal/mol/K)

//C(M)(M)(M)OO(M) 141 0.2167 5.4817 2.2967 -1.0617 -1.3867 -1.6250 -1.7983 -1.9500 -2.0150
fragment {
C labeled c1 {connected to 3 M with single bond}
O labeled o1 single bond to c1
O labeled o2 single bond to o1 {connected to 1 M with single bond}
} enthalpy 5.4817 kcal/mol entropy 2.2967 cal/mol/K cp (298=> -1.0617 cal/mol/K, 400=> -1.3867 cal/mol/K, 500=> -1.6250 cal/mol/K, 600=> -1.7983 cal/mol/K, 800=> -1.9500 cal/mol/K, 1000=> -2.0150 cal/mol/K, 1500=> -2.015 cal/mol/K)

//C(M)(M)(M)C(=O)O(M) 130.5 0.2750 6.9575 2.9150 -1.3475 -1.7600 -2.0625 -2.2825 -2.4750 -2.5575
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1
O labeled o1 double bond to c2
O labeled o2 single bond to c2 {connected to 1 M with single bond}
} enthalpy 6.9575 kcal/mol entropy 2.9150 cal/mol/K cp (298=> -1.3475 cal/mol/K, 400=> -1.7600 cal/mol/K, 500=> -2.0625 cal/mol/K, 600=> -2.2825 cal/mol/K, 800=> -2.4750 cal/mol/K, 1000=> -2.5575 cal/mol/K, 1500=> -2.5575 cal/mol/K)

//C(M)(M)(M)OC(=O)(M) 130.5 0.2750 6.9575 2.9150 -1.3475 -1.7600 -2.0625 -2.2825 -2.4750 -2.5575
fragment {
C labeled c1 {connected to 3 M with single bond}
O labeled o1 single bond to c1

```
  C labeled c2 single bond to o1 {connected to 1 M with single bond}
  O labeled o2 double bond to c2
} enthalpy          6.9575   kcal/mol entropy  2.9150    cal/mol/K          cp (298=>         -1.3475   cal/mol/K, 400=>
          -1.7600   cal/mol/K, 500=> -2.0625   cal/mol/K, 600=> -2.2825   cal/mol/K, 800=> -2.4750   cal/mol/K,
1000=>  -2.5575   cal/mol/K, 1500=>          -2.5575 cal/mol/K)


//C(M)(M)(M)C(=O)C(=O)(M)          120       0.3333   8.4333   3.5333   -1.6333  -2.1333  -2.5000  -2.7667  -3.0000
          -3.1000
fragment {
  C labeled c1 {connected to 3 M with single bond}
  C labeled c2 single bond to c1
  O labeled o1 double bond to c2
  C labeled c3 single bond to c2 {connected to 1 M with single bond}
  O labeled o2 double bond to c3
} enthalpy          8.4333   kcal/mol entropy  3.5333    cal/mol/K          cp (298=>         -1.6333   cal/mol/K, 400=>
          -2.1333   cal/mol/K, 500=> -2.5000   cal/mol/K, 600=> -2.7667   cal/mol/K, 800=> -3.0000   cal/mol/K,
1000=>  -3.1000   cal/mol/K, 1500=>          -3.1 cal/mol/K)

//C(M)(M)(M)CCC(M)(M)(M)           141       0.2167   5.4817   2.2967   -1.0617  -1.3867  -1.6250  -1.7983  -1.9500
          -2.0150
fragment {
  C labeled c1 {connected to 3 M with single bond}
  C labeled c2 single bond to c1 {!connected to >=1 any atom with strong bond}
  C labeled c3 single bond to c2 {!connected to >=1 any atom with strong bond}
  C labeled c4 single bond to c3 {connected to 3 M with single bond}
} enthalpy          5.4817   kcal/mol entropy  2.2967    cal/mol/K          cp (298=>         -1.0617   cal/mol/K, 400=>
          -1.3867   cal/mol/K, 500=> -1.6250   cal/mol/K, 600=> -1.7983   cal/mol/K, 800=> -1.9500   cal/mol/K,
1000=>  -2.0150   cal/mol/K, 1500=>          -2.015 cal/mol/K)


//C(M)(M)(M)COC(M)(M)(M)           141       0.2167   5.4817   2.2967   -1.0617  -1.3867  -1.6250  -1.7983  -1.9500
          -2.0150
fragment {
  C labeled c1 {connected to 3 M with single bond}
  C labeled c2 single bond to c1 {!connected to >=1 any atom with strong bond}
  O labeled o1 single bond to c2
  C labeled c4 single bond to o1 {connected to 3 M with single bond}
} enthalpy          5.4817   kcal/mol entropy  2.2967    cal/mol/K          cp (298=>         -1.0617   cal/mol/K, 400=>
          -1.3867   cal/mol/K, 500=> -1.6250   cal/mol/K, 600=> -1.7983   cal/mol/K, 800=> -1.9500   cal/mol/K,
1000=>  -2.0150   cal/mol/K, 1500=>          -2.015 cal/mol/K)


//C(M)(M)(M)CC(=O)C(M)(M)(M)       130.5     0.2750   6.9575   2.9150   -1.3475  -1.7600  -2.0625  -2.2825  -2.4750
          -2.5575
fragment {
  C labeled c1 {connected to 3 M with single bond}
  C labeled c2 single bond to c1 {!connected to >=1 any atom with strong bond}
  C labeled c3 single bond to c2
  O labeled o1 double bond to c3
  C labeled c4 single bond to c3 {connected to 3 M with single bond}
} enthalpy          6.9575   kcal/mol entropy  2.9150    cal/mol/K          cp (298=>         -1.3475   cal/mol/K, 400=>
          -1.7600   cal/mol/K, 500=> -2.0625   cal/mol/K, 600=> -2.2825   cal/mol/K, 800=> -2.4750   cal/mol/K,
1000=>  -2.5575   cal/mol/K, 1500=>          -2.5575 cal/mol/K)

//C(M)(M)(M)OOC(M)(M)(M)           141       0.2167   5.4817   2.2967   -1.0617  -1.3867  -1.6250  -1.7983  -1.9500
          -2.0150
fragment {
  C labeled c1 {connected to 3 M with single bond}
  O labeled o1 single bond to c1
  O labeled o2 single bond to o1
  C labeled c2 single bond to o2 {connected to 3 M with single bond}
```

} enthalpy 5.4817 kcal/mol entropy 2.2967 cal/mol/K cp (298=> -1.0617 cal/mol/K, 400=> -1.3867 cal/mol/K, 500=> -1.6250 cal/mol/K, 600=> -1.7983 cal/mol/K, 800=> -1.9500 cal/mol/K, 1000=> -2.0150 cal/mol/K, 1500=> -2.015 cal/mol/K)

//C(M)(M)(M)OC(=O)C(M)(M)(M) 130.5 0.2750 6.9575 2.9150 -1.3475 -1.7600 -2.0625 -2.2825 -2.4750 -2.5575
fragment {
C labeled c1 {connected to 3 M with single bond}
O labeled o1 single bond to c1
C labeled c2 single bond to o1
O labeled o2 double bond to c2
C labeled c3 single bond to c2 {connected to 3 M with single bond}
} enthalpy 6.9575 kcal/mol entropy 2.9150 cal/mol/K cp (298=> -1.3475 cal/mol/K, 400=> -1.7600 cal/mol/K, 500=> -2.0625 cal/mol/K, 600=> -2.2825 cal/mol/K, 800=> -2.4750 cal/mol/K, 1000=> -2.5575 cal/mol/K, 1500=> -2.5575 cal/mol/K)

//C(M)(M)(M)C(=O)C(=O)C(M)(M)(M) 120 0.3333 8.4333 3.5333 -1.6333 -2.1333 -2.5000 -2.7667 -3.0000 -3.1000
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1
O labeled o1 double bond to c2
C labeled c3 single bond to c2
O labeled o2 double bond to c3
C labeled c4 single bond to c3 {connected to 3 M with single bond}
} enthalpy 8.4333 kcal/mol entropy 3.5333 cal/mol/K cp (298=> -1.6333 cal/mol/K, 400=> -2.1333 cal/mol/K, 500=> -2.5000 cal/mol/K, 600=> -2.7667 cal/mol/K, 800=> -3.0000 cal/mol/K, 1000=> -3.1000 cal/mol/K, 1500=> -3.1 cal/mol/K)

//C(M)(M)(M)C(=O)C(=O)C(M)(M) 174.75 0.0292 0.7379 0.3092 -0.1429 -0.1867 -0.2188 -0.2421 -0.2625 -0.2713
fragment {
C labeled c1 {connected to 3 M with single bond}
C labeled c2 single bond to c1
O labeled o1 double bond to c2
C labeled c3 single bond to c2
O labeled o2 double bond to c3
C labeled c4 single bond to c3 {connected to 2 M with single bond}
} enthalpy 0.7379 kcal/mol entropy 0.3092 cal/mol/K cp (298=> -0.1429 cal/mol/K, 400=> -0.1867 cal/mol/K, 500=> -0.2188 cal/mol/K, 600=> -0.2421 cal/mol/K, 800=> -0.2625 cal/mol/K, 1000=> -0.2713 cal/mol/K, 1500=> -0.27125 cal/mol/K)

//----------

//Zeolite corrections
//The corrections are of the form alpha*CN + beta. The first four provide the alpha values, the next four are for the beta.
//Because alpha is to be multiplied by CN, the fragment found is a C atom in thefirs four. Since beta is a constant to be added once to all species, we find zeo (which will occur only once)

PrimaryAlkoxide fragment {
C labeled c1
} enthalpy -4.5257 kJ/mol entropy -9.4955 cp (298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0, 1500=> 0.0)

SecondaryTwoAlkoxide fragment {
C labeled c1
} enthalpy -4.5257 kJ/mol entropy -9.4955 cp (298=> 0.0, 400=> 0.0, 500=> 0.0, 600=> 0.0, 800=> 0.0, 1000=> 0.0, 1500=> 0.0)

```
SecondaryInternalAlkoxide fragment {
    C labeled c1
} enthalpy -9.19 kJ/mol entropy -9.4955 cp (298=>      0.0, 400=>          0.0, 500=>          0.0, 600=>          0.0,
800=>    0.0, 1000=> 0.0, 1500=>    0.0)


TertiaryAlkoxide fragment {
    C labeled c1
} enthalpy 20.813 kJ/mol entropy -9.4955 cp (298=>    0.0, 400=>          0.0, 500=>          0.0, 600=>          0.0,
800=>    0.0, 1000=> 0.0, 1500=>    0.0)


PrimaryAlkoxide fragment {
   Zeo labeled z1
 } enthalpy 27.55 kJ/mol entropy -156.72 cp (298=>     0.0, 400=>          0.0, 500=>          0.0, 600=>          0.0,
800=>    0.0, 1000=> 0.0, 1500=>    0.0)


 SecondaryTwoAlkoxide fragment {
   Zeo labeled z1
} enthalpy 8.3581 kJ/mol entropy -156.72 cp (298=>    0.0, 400=>          0.0, 500=>          0.0, 600=>          0.0,
800=>    0.0, 1000=> 0.0, 1500=>    0.0)

SecondaryInternalAlkoxide fragment {
   Zeo labeled z1
} enthalpy 24.66 kJ/mol entropy -156.72 cp (298=>      0.0, 400=>          0.0, 500=>          0.0, 600=>          0.0,
800=>    0.0, 1000=> 0.0, 1500=>    0.0)


TertiaryAlkoxide fragment {
  Zeo labeled z1
} enthalpy -56.524 kJ/mol entropy -156.72 cp (298=>   0.0, 400=>          0.0, 500=>          0.0, 600=>          0.0,
800=>    0.0, 1000=> 0.0, 1500=>    0.0)



//-------------------------------------------------------------------------------------------------------------

/*


//Non-Pt metal linear scaling corrections

//enthalpy correction is Gamma*(BE of C/H/O on Metal - BE of C/H/O on Pt)

//C-M bonded species
fragment {
  C labeled c1 {connected to 4 M with single bond}
} enthalpy -1.0*(-16.8)  entropy        0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  C labeled c1 {connected to 3 M with single bond}
} enthalpy -0.75*(-16.8)  entropy       0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  C labeled c1 {connected to 2 M with single bond}
```

```
} enthalpy -0.5*(-16.8)  entropy       0.0         cp (298=>         0.0, 400=>         0.0, 500=>         0.0, 600=>
            0.0, 800=>         0.0, 1000=> 0.0, 1500=>   0.0)


fragment {
  C labeled c1 {connected to 1 M with single bond}
} enthalpy -0.25*(-16.8)  entropy      0.0         cp (298=>         0.0, 400=>         0.0, 500=>         0.0, 600=>
            0.0, 800=>         0.0, 1000=> 0.0, 1500=>   0.0)

// O-M bonded species
fragment {
  O labeled o1 {connected to 2 M with single bond}
} enthalpy -1.0*(121.8)  entropy       0.0         cp (298=>         0.0, 400=>         0.0, 500=>         0.0, 600=>
            0.0, 800=>         0.0, 1000=> 0.0, 1500=>   0.0)

fragment {
  O labeled o1 {connected to 1 M with single bond}
} enthalpy -0.5*(121.8)  entropy       0.0         cp (298=>         0.0, 400=>         0.0, 500=>         0.0, 600=>
            0.0, 800=>         0.0, 1000=> 0.0, 1500=>   0.0)


//H-M bonded species
 fragment {
   M labeled m1
   H labeled h1 single bond to m1
 } enthalpy -1.0*(19.7)  entropy       0.0         cp (298=>         0.0, 400=>         0.0, 500=>         0.0, 600=>
            0.0, 800=>         0.0, 1000=> 0.0, 1500=>   0.0)


 //O_Pt interactions

 fragment {
    O labeled o1 {connected to 1 H with single bond, connected to 1 M with partial bond}
  } enthalpy -0.1*(121.8)  entropy      0.0         cp (298=>         0.0, 400=>         0.0, 500=>         0.0, 600=>
            0.0, 800=>         0.0, 1000=> 0.0, 1500=>   0.0)



//Aldehyde interaction

fragment {
 O labeled o1
 C labeled c1 double bond to o1 {connected to 1 H with single bond, ! connected to >=1 M with any bond}
 C labeled c2 single bond to c1
 M labeled m1 single bond to c2
} enthalpy -0.1*(121.8)  entropy       0.0         cp (298=>         0.0, 400=>         0.0, 500=>         0.0, 600=>
            0.0, 800=>         0.0, 1000=> 0.0, 1500=>   0.0)

*/
/*
//New set of linear scaling corrections

//C-M bonded species
fragment {
  C labeled c1 {connected to 4 M with single bond}
} enthalpy -1.0*(-16.8)  entropy       0.0         cp (298=>         0.0, 400=>         0.0, 500=>         0.0, 600=>
            0.0, 800=>         0.0, 1000=> 0.0, 1500=>   0.0)

fragment {
  C labeled c1 {connected to 3 M with single bond, !connected to >=1 O with any bond}
} enthalpy -0.82*(-16.8) entropy       0.0         cp (298=>         0.0, 400=>         0.0, 500=>         0.0, 600=>
            0.0, 800=>         0.0, 1000=> 0.0, 1500=>   0.0)
```

```
fragment {
   C labeled c1 {connected to 3 M with single bond, connected to 1 O with single bond}
} enthalpy -0.66*(-16.8) entropy       0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  C labeled c1 {connected to 2 M with single bond, ! connected to >=1 O with any bond}
} enthalpy -0.57*(-16.8) entropy       0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  C labeled c1 {connected to 2 M with single bond, connected to 1 O with single bond}
} enthalpy -0.72*(-16.8) entropy       0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  C labeled c1 {connected to 2 M with single bond, connected to 1 O with double bond}
} enthalpy -0.42*(-16.8) entropy       0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  C labeled c1 {connected to 1 M with single bond, ! connected to >=1 O with any bond}
} enthalpy -0.45*(-16.8) entropy       0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  C labeled c1 {connected to 1 M with single bond, connected to 1 O with single bond}
  O labeled o1 single bond to c1 {! connected to >=1 M with any single bond}
} enthalpy -0.42*(-16.8) entropy       0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  C labeled c1 {connected to 1 M with single bond, connected to 1 O with double bond}
} enthalpy -0.66*(-16.8) entropy       0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  C labeled c1 {connected to 1 M with single bond, connected to 1 O with single bond}
  O labeled o1 single bond to c1 {connected to 1 M with single bond}
} enthalpy -0.26*(-16.8) entropy       0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)


// O-M bonded species
fragment {
  O labeled o1 {connected to 2 M with single bond}
} enthalpy -1.0*(121.8)  entropy       0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  O labeled o1 {connected to 1 M with single bond, connected to 1 H with single bond}
} enthalpy -0.37*(121.8)  entropy      0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

fragment {
  O labeled o1 {connected to 1 M with single bond, connected to 1 C with single bond}
  C labeled c1 {! connected to >=1 M with single bond} //the case of it being connected to M has already been taken
care of with an earlier CH2O fragment
} enthalpy -0.37*(121.8)  entropy      0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)
```

```
/H-M bonded species
 fragment {
   M labeled m1
   H labeled h1 single bond to m1
 } enthalpy -1.0*(19.7)  entropy        0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)


 //O_Pt interactions

 fragment {
    O labeled o1 {connected to 1 H with single bond, connected to 1 M with partial bond}
  } enthalpy -0.14*(121.8)  entropy    0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)


//Aldehyde interaction

fragment {
 O labeled o1
 C labeled c1 double bond to o1 {connected to 1 H with single bond, ! connected to >=1 M with any bond}
 C labeled c2 single bond to c1
 M labeled m1 single bond to c2
} enthalpy -0.1*(121.8)  entropy        0.0          cp (298=>          0.0, 400=>          0.0, 500=>          0.0, 600=>
            0.0, 800=>          0.0, 1000=> 0.0, 1500=>    0.0)

*/

}
```

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