"Gas Phase Fragmentation of η^2 Coordinated Aldehydes in $[VO_2(\eta^2\text{-OCHR})]^-$: Aldehyde Structure Dictates the Nature of the Products."

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OTHER CORRESPONDING DETAILS

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List of Supplementary Material:

- **Figures S1-S8**
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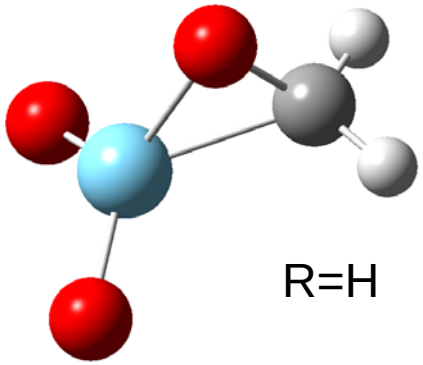
Figure S1: Structures of the stable isomers 3a and 3b of $[VO_2(\eta^2\text{-}OCHR)]^-$

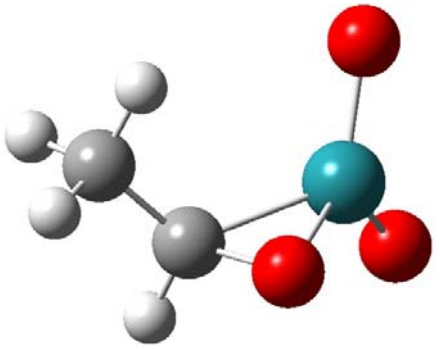


R=H

3a

V	-0.300371	0.000000	0.050848
O	-1.122807	-1.403657	-0.098010
O	1.405764	0.000000	0.765014
O	-1.122806	1.403657	-0.098010
C	1.595195	0.000000	-0.612434
H	2.028073	-0.918498	-1.023429
H	2.028073	0.918497	-1.023429

Sum of electronic and zero-point Energies= -336.874097
Sum of electronic and thermal Free Energies= -336.903390



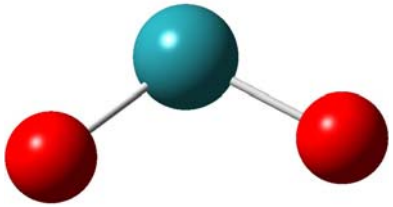
$R=CH_3$

3b: $[VO_2(\eta^2\text{-}OCHCH_3)]^-$

V	23.0	0.66336602	0.03514300	0.07554300
O	8.0	0.86005700	1.65789604	0.11275100
O	8.0	-0.72429198	-0.75528198	1.01826203
O	8.0	1.84871995	-0.88619298	-0.57132602
C	6.0	-1.22214198	-0.58084202	-0.26810300
C	6.0	-2.39395308	0.37052801	-0.40768099
H	1.0	-1.34927797	-1.52283502	-0.81775200
H	1.0	-3.30699301	-0.04217500	0.05119200
H	1.0	-2.17285800	1.32690203	0.07235900
H	1.0	-2.60759592	0.56034303	-1.46607602

Sum of electronic and zero-point Energies= -376.176349
Sum of electronic and thermal Free Energies= -376.207733

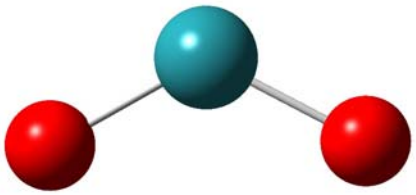
Figure S2: Structures of the stable isomers of $[V, O_2]^-$



5a: $^1[VO_2]^-$
ΔE = 0.68eV
ΔG = 0.71eV

V	23.0	0.00000000	0.00000000	0.38117000
O	8.0	0.00000000	1.32012606	-0.54793203
O	8.0	0.00000000	-1.32012606	-0.54793203

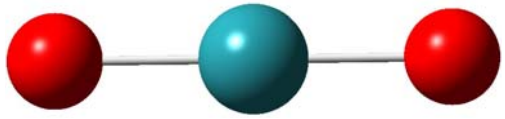
Sum of electronic and zero-point Energies= -222.244098
Sum of electronic and thermal Free Energies= -222.269238



5b: $^3[VO_2]^-$
ΔE = 0.00eV
ΔG = 0.00eV

V	23.0	0.00000000	0.00000000	0.32438201
O	8.0	0.00000000	1.44711697	-0.46629900
O	8.0	0.00000000	-1.44711697	-0.46629900

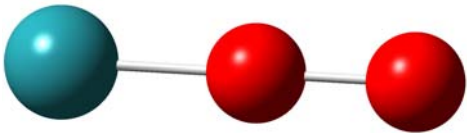
Sum of electronic and thermal Energies= -222.268936
Sum of electronic and thermal Free Energies= -222.295194



5c: $[VO_2]^-$ (O-V-O) linear
ΔE = 1.70eV
ΔG = 1.74eV

V	23.0	0.00000000	0.00000000	0.00000000
O	8.0	0.00000000	0.00000000	1.71492898
O	8.0	0.00000000	0.00000000	-1.71492898

Sum of electronic and thermal Energies= -222.206344
Sum of electronic and thermal Free Energies= -222.231138
Imaginary frequency= -182.802cm^{-1}, -182.802cm^{-1}

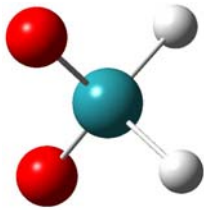


6: $[VO_2]^-$ (V-O-O) linear
ΔE = 6.45eV
ΔG = 6.50eV

O	8.0	0.00000000	0.00000000	-2.03995109
V	23.0	0.00000000	0.00000000	0.95074201
O	8.0	0.00000000	0.00000000	-0.69343102

Sum of electronic and zero-point Energies= -222.031938
Sum of electronic and thermal Free Energies= -222.056151

Figure S3: Structures of the stable isomers of [V, O_2, H_2]$^-$



7a: $[VO_2(H)_2]^-$

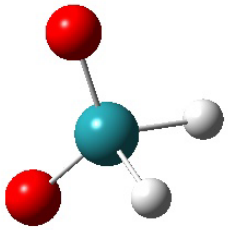
ΔE = 0.00eV

ΔG = 0.00eV

V	23.0	0.00000000	0.30031401	0.00000500
O	8.0	-1.34577096	-0.58824402	-0.00001000
O	8.0	1.34577096	-0.58824402	-0.00000900
H	1.0	0.00000100	1.25235605	-1.38053501
H	1.0	-0.00000100	1.25232005	1.38056898

Sum of electronic and zero-point Energies= -223.491124

Sum of electronic and thermal Free Energies= -223.517436



7b: $^3[VO_2(H)_2]^-$

ΔE = 2.44eV

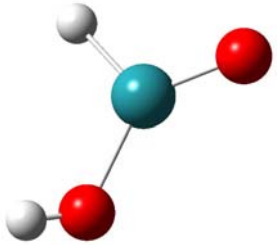
ΔG = 2.40eV

V	23.0	-0.00000400	0.27519801	0.00000400
O	8.0	-1.47495699	-0.56854898	-0.00001000
O	8.0	1.47496998	-0.56853998	-0.00000600
H	1.0	-0.00000900	1.38359499	-1.26284599
H	1.0	-0.00001000	1.38355994	1.26288402

Sum of electronic and zero-point Energies= -223.401327

Sum of electronic and thermal Free Energies= -223.429308

Imaginary frequency= -803.096cm^{-1}



8a: [VO(OH)(H)]$^-$

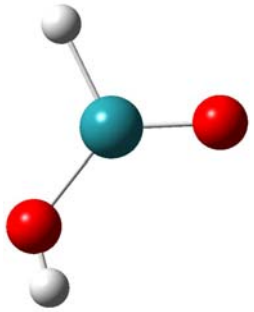
ΔE = 1.47eV

ΔG = 1.43eV

V	23.0	0.12892599	0.23277500	0.01015400
O	8.0	1.57383895	-0.51731098	0.00630700
O	8.0	-1.67500401	-0.38898301	-0.08183700
H	1.0	-2.37707996	-0.07364900	0.49576899
H	1.0	0.22110100	1.97016394	-0.12507100

Sum of electronic and zero-point Energies= -223.437251

Sum of electronic and thermal Free Energies= -223.464908



8b: $^3[VO(OH)(H)]^-$

ΔE = 0.15eV

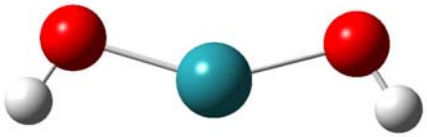
ΔG = 0.09eV

V	23.0	0.13453200	0.27216500	-0.00000300
O	8.0	1.49232304	-0.62944102	0.00000200
O	8.0	-1.67998302	-0.25716099	-0.00000700
H	1.0	-2.03837109	-1.14552498	0.00005900
H	1.0	0.44541201	1.97854495	0.00004100

Sum of electronic and zero-point Energies= -223.485498

Sum of electronic and thermal Free Energies= -223.513990

Figure S3-2: Structures of the stable isomers of $[V, O_2, H_2]^-$

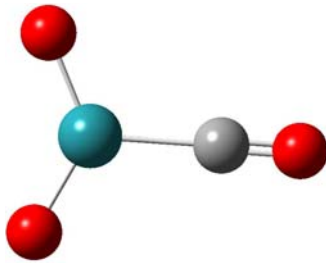


9: $[V(OH)(OH)]^-$
ΔE = 2.13eV
ΔG = 2.09eV

V	23.0	0.00000400	-0.17771301	-0.00006400
O	8.0	1.77029800	0.31694600	0.00002800
O	8.0	-1.77029896	0.31693900	0.00004400
H	1.0	2.31070304	-0.49186200	0.00050200
H	1.0	-2.31077600	-0.49181199	0.00040300

Sum of electronic and zero-point Energies= -223.412790
Sum of electronic and thermal Free Energies= -223.440451

Figure S4: Structures of the stable isomers of [V, O_3, C]$^-$



10a: $[VO_2(CO)]^-$

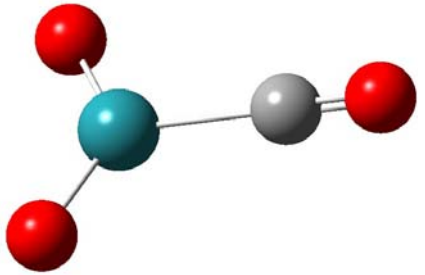
ΔE = 0.11eV

ΔG = +0.15eV

V	23.0	0.47216600	0.00001000	-0.00022200
O	8.0	1.19603705	1.48220801	0.00026900
O	8.0	1.19602001	-1.48218703	0.00026900
O	8.0	-2.64387989	0.00011800	0.00016300
C	6.0	-1.47420704	-0.00022500	-0.00008200

Sum of electronic and zero-point Energies= -335.655329

Sum of electronic and thermal Free Energies= -335.685617



10b: $^3[VO_2(CO)]^-$

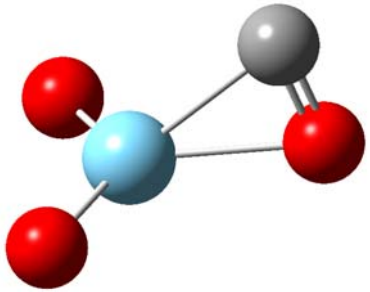
ΔE = +0.00eV

ΔG = +0.00eV

V	23.0	0.47216600	0.00001000	-0.00022200
O	8.0	1.19603705	1.48220801	0.00026900
O	8.0	1.19602001	-1.48218703	0.00026900
O	8.0	-2.64387989	0.00011800	0.00016300
C	6.0	-1.47420704	-0.00022500	-0.00008200

Sum of electronic and zero-point Energies= **-335.659250**

Sum of electronic and thermal Free Energies= -335.691080



11: $[VO_2(\eta^2\text{-}OC)]^-$

ΔE = +0.52eV

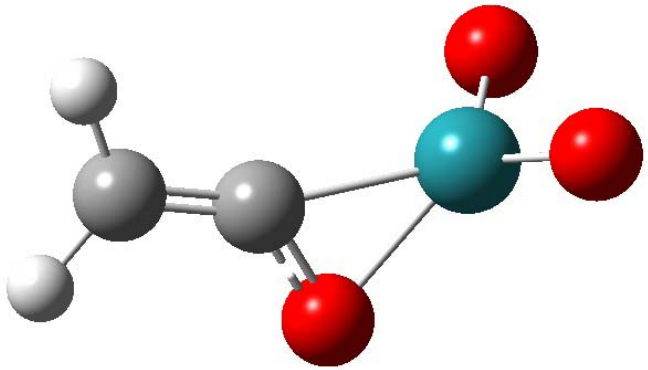
ΔG = +0.58eV

V	23.0	-0.06530100	0.26796600	0.00000000
O	8.0	-0.06530100	1.04649103	1.44482005
O	8.0	-0.06530100	1.04649103	-1.44482005
C	6.0	0.88052702	-1.55460894	0.00000000
O	8.0	-0.34205100	-1.69742703	0.00000000

Sum of electronic and zero-point Energies= -335.640280

Sum of electronic and thermal Free Energies= -335.669584

Figure S5: Structures of the stable isomers of [V, O_3, C_2, H_2]$^-$



12a: $[VO_2(\eta^2\text{-}OCCH_2)]^-$

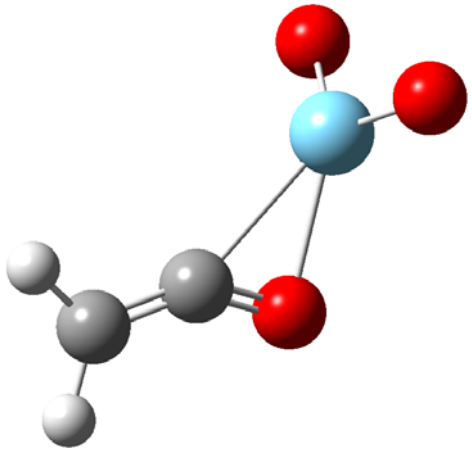
ΔE = +0.00eV

ΔG = +0.00eV

V	23.0	-0.62923199	0.00000000	0.04264500
O	8.0	-1.41035604	-1.38510001	-0.28706199
O	8.0	0.89458799	-0.00010500	1.15601599
O	8.0	-1.41028595	1.38517201	-0.28692999
C	6.0	1.34785700	-0.00000800	-0.09405500
C	6.0	2.59513211	0.00003000	-0.58247298
H	1.0	3.46323299	0.00000700	0.07421800
H	1.0	2.75959110	0.00013300	-1.65207005

Sum of electronic and zero-point Energies= -374.972802

Sum of electronic and thermal Free Energies= -375.003622



12b: $^3[VO_2(\eta^2\text{-}OCCH_2)]^-$

ΔE = +1.02eV

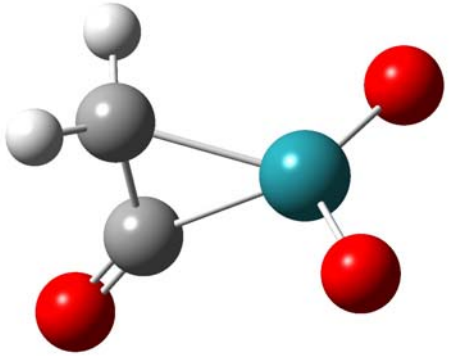
ΔG = +0.94eV

V	23.0	-0.71590298	0.00000000	-0.02824200
O	8.0	-1.52863598	-1.41156197	-0.20191200
O	8.0	1.01445198	-0.00000100	1.12753201
O	8.0	-1.52863503	1.41156197	-0.20191000
C	6.0	1.59838295	-0.00000100	0.02113200
C	6.0	2.77921104	0.00000100	-0.59623700
H	1.0	3.70088100	0.00000200	-0.01504900
H	1.0	2.84188390	0.00000100	-1.67443895

Sum of electronic and zero-point Energies= -374.935065

Sum of electronic and thermal Free Energies= -374.968944

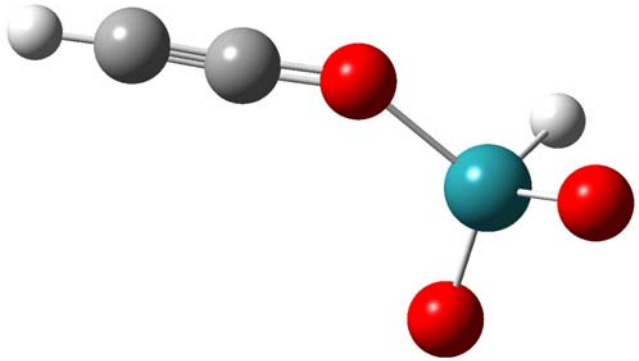
Figure S5-2: Structures of the stable isomers of $[V, O_3, C_2, H_2]^-$



13: $[VO_2(O)(CCH_2)]^-$
ΔE = +0.70eV
ΔG = +0.67eV

V	23.0	-0.62364501	0.01019700	0.04199600
O	8.0	-1.47490799	-1.22840595	-0.58573800
O	8.0	-1.29606605	1.48824799	0.12152600
C	6.0	1.39058197	-0.01980400	-0.23502199
O	8.0	2.43711495	0.30568600	-0.73640400
C	6.0	1.01748395	-0.50533599	1.14686596
H	1.0	1.55865705	-0.01189000	1.95278001
H	1.0	1.00763905	-1.59603703	1.21516395

Sum of electronic and zero-point Energies= -374.947101
Sum of electronic and thermal Free Energies= -374.979010

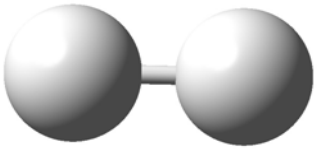


14: $[VO_2(H)(OCCH)]^-$
ΔE = +0.42eV
ΔG = +0.37eV

V	23.0	0.84892303	0.00696600	0.20043100
O	8.0	1.86695302	-1.02193999	-0.50168598
O	8.0	1.12092197	1.51933396	-0.26631701
H	1.0	1.30670905	-0.00158100	1.78363895
O	8.0	-0.95848900	-0.55996299	0.14054500
C	6.0	-2.14909601	-0.16964599	-0.01819500
C	6.0	-3.31067705	0.14736600	-0.16184200
H	1.0	-4.30838013	0.47559601	-0.29366300

Sum of electronic and zero-point Energies= -374.957063
Sum of electronic and thermal Free Energies= -374.989737

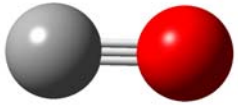
Figure S6: Structures of the stable neutrals



H_2

H	1.0	0.00000000	0.00000000	0.37207600
H	1.0	0.00000000	0.00000000	-0.37207600

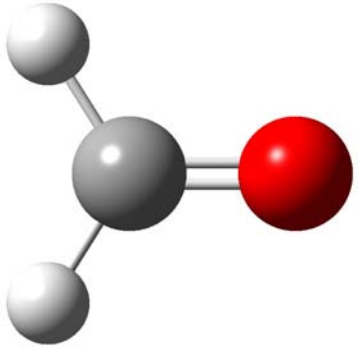
Sum of electronic and zero-point Energies= -1.169506
Sum of electronic and thermal Free Energies= -1.180997



CO

C	6.0	0.00000000	0.00000000	-0.64439303
O	8.0	0.00000000	0.00000000	0.48329499

Sum of electronic and zero-point Energies= -113.340707
Sum of electronic and thermal Free Energies= -113.363133

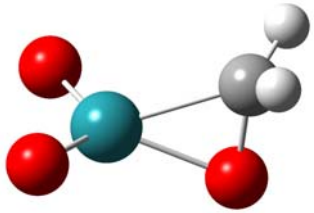


H_2CO

C	6.0	-0.52756798	0.00000000	0.00000600
O	8.0	0.67439002	0.00000000	-0.00000700
H	1.0	-1.11485398	0.93977898	-0.00000800
H	1.0	-1.11485398	-0.93977898	0.00003100

Sum of electronic and zero-point Energies= -114.515346
Sum of electronic and thermal Free Energies= -114.537004

Figure S7: Structures, energies and coordinates for ions on the Potential Energy Surface for the CID of $[VO_2(\eta^2\text{-}OCH_2)]^-$



3: $[VO_2(\eta^2\text{-}OCH_2)]^-$

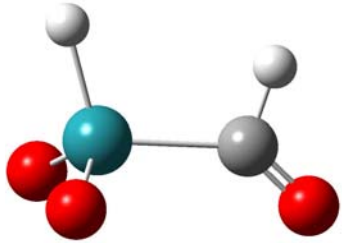
ΔE = 0.00eV

ΔG = 0.00eV

V	23.0	-0.30037099	0.00000000	0.05084800
O	8.0	-1.12280703	-1.40365696	-0.09801000
O	8.0	1.40576398	0.00000000	0.76501399
O	8.0	-1.12280595	1.40365696	-0.09801000
C	6.0	1.59519506	0.00000000	-0.61243403
H	1.0	2.02807307	-0.91849798	-1.02342904
H	1.0	2.02807307	0.91849703	-1.02342904

Sum of electronic and zero-point Energies= -336.874097

Sum of electronic and thermal Free Energies= -336.903390



15: $[VO_2(H)(CHO)]^-$

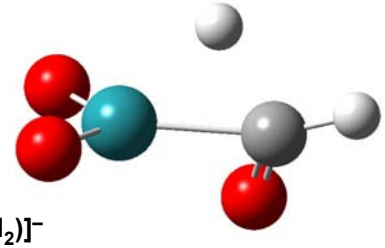
ΔE = +0.82eV

ΔG = +0.75eV

V	23.0	0.56068301	0.00000000	0.25172299
O	8.0	1.04508400	-1.35265303	-0.48119900
O	8.0	1.04508495	1.35265398	-0.48119599
O	8.0	-2.47608399	0.00000200	-0.42239100
C	6.0	-1.53196299	-0.00000200	0.33489001
H	1.0	1.16389704	-0.00000200	1.81708801
H	1.0	-1.78051996	-0.00000900	1.46223605

Sum of electronic and zero-point Energies= -336.843876

Sum of electronic and thermal Free Energies= -336.875752



TS3-15: $[VO_2(\eta^2\text{-}OCH_2)]^-$

ΔE = +1.76eV

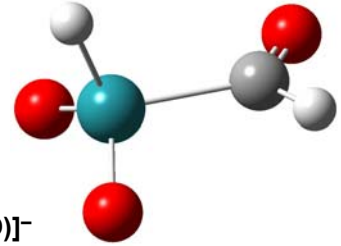
ΔG = +1.76eV

V	23.0	-0.32218000	-0.02927200	0.05720000
O	8.0	-0.85737401	1.52887106	0.10127300
O	8.0	1.64550900	0.28858301	-0.60351801
O	8.0	-1.39947104	-1.21519804	-0.23384300
C	6.0	1.53828001	-0.52031898	0.36706200
H	1.0	0.64245099	-0.08523100	1.51181400
H	1.0	2.42868590	-0.93765700	0.85892600

Sum of electronic and zero-point Energies= -336.809332

Sum of electronic and thermal Free Energies= -336.838799

Imaginary frequency= -731cm^{-1}



TS15-15': $[VO_2(H)(CHO)]^-$

ΔE = +0.90eV

ΔG = +0.89eV

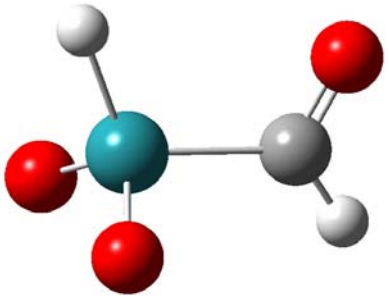
V	23.0	-0.52999198	0.01529100	0.25558800
O	8.0	-0.85937101	1.46110296	-0.37010801
O	8.0	-1.34811294	-1.17914701	-0.45594499
H	1.0	-0.87111402	0.01721300	1.89758098
C	6.0	1.52213800	-0.49992400	-0.03169800
O	8.0	2.47905803	0.24823099	-0.11881500
H	1.0	1.75550699	-1.61086500	-0.02696300

Sum of electronic and zero-point Energies= -336.840866

Sum of electronic and thermal Free Energies= -336.870731

Imaginary frequency= -104cm^{-1}

Figure S7-2: Structures, energies and coordinates for ions on the Potential Energy Surface for the CID of $[VO_2(\eta^2\text{-}OCH_2)]^-$



15': $[VO_2(H)(CHO)]^-$

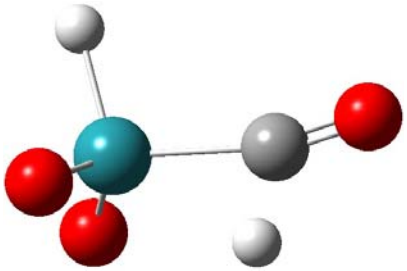
ΔE = +0.75eV

ΔG = +0.70eV

V	23.0	-0.20272499	0.47549900	0.00000000
O	8.0	0.41314501	1.11692905	1.34871995
O	8.0	0.41314501	1.11692905	-1.34871995
H	1.0	-1.85462499	0.73804802	0.00000000
C	6.0	0.41314501	-1.51267195	0.00000000
O	8.0	-0.50452000	-2.31914997	0.00000000
H	1.0	1.46427298	-1.91615105	0.00000000

Sum of electronic and zero-point Energies= -336.846658

Sum of electronic and thermal Free Energies= -336.877777



TS15'-16: $[VO_2(H)(CHO)]^-$

ΔE = +1.10eV

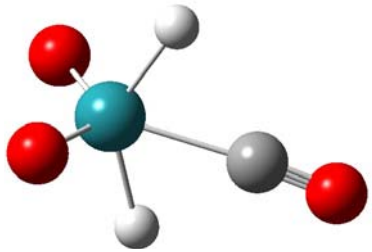
ΔG = +1.08eV

V	23.0	0.51643598	0.00000000	0.20925701
O	8.0	1.18221605	-1.38654804	-0.30457801
O	8.0	1.18220997	1.38655102	-0.30457801
O	8.0	-2.68240094	0.00000000	0.01453900
C	6.0	-1.48787796	-0.00000300	-0.11238400
H	1.0	0.67125201	0.00000000	1.85829997
H	1.0	-1.07821798	-0.00000400	-1.23997796

Sum of electronic and zero-point Energies= -336.833525

Sum of electronic and thermal Free Energies= -336.877777

Imaginary frequency= -430cm^{-1}



16: $[VO_2(H)_2(CO)]^-$

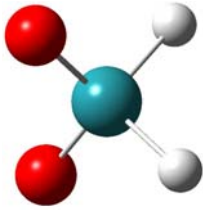
ΔE = +0.82eV

ΔG = +0.77eV

V	23.0	-0.47152400	0.00000000	0.03833800
O	8.0	-1.30422401	-1.39437401	-0.06576900
O	8.0	-1.30422294	1.39437401	-0.06576900
H	1.0	0.34610400	0.00000000	-1.44404495
C	6.0	1.58989406	0.00000000	0.05028900
O	8.0	2.73057699	0.00000000	-0.04156100
H	1.0	-0.01745000	0.00000000	1.64532900

Sum of electronic and zero-point Energies= -336.844024

Sum of electronic and thermal Free Energies= -336.875224



+ CO

7a: $[VO_2(H)_2]^-$

ΔE = +1.06eV

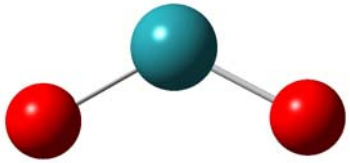
ΔG = +0.62eV

V	23.0	0.00000000	0.30031401	0.00000500
O	8.0	-1.34577096	-0.58824402	-0.00001000
O	8.0	1.34577096	-0.58824402	-0.00000900
H	1.0	0.00000100	1.25235605	-1.38053501
H	1.0	-0.00000100	1.25232005	1.38056898

Sum of electronic and zero-point Energies= -223.491124+ (-113.340707)

Sum of electronic and thermal Free Energies= -223.517436+(-113.363133)

Figure S7-3: Structures, energies and coordinates for ions on the Potential Energy Surface for the CID of $[VO_2(\eta^2\text{-}OCH_2)]^-$



+ H_2CO

5b: $^3[VO_2]^-$

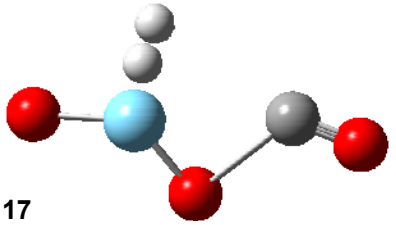
ΔE = +2.45eV

ΔG = +1.94eV

V	23.0	0.00000000	0.00000000	0.32438201
O	8.0	0.00000000	1.44711697	-0.46629900
O	8.0	0.00000000	-1.44711697	-0.46629900

Sum of electronic and zero-point Energies= -222.268936 + (-114.515346)

Sum of electronic and thermal Free Energies= -222.295194 + (-114.537004)



TS-16- 17

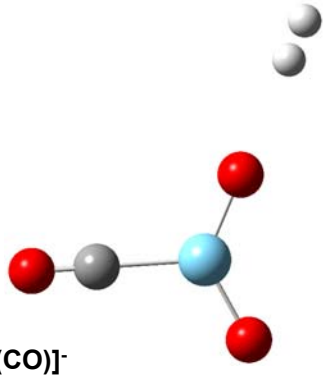
ΔE = +2.41eV

ΔG = +2.36eV

V	-0.712767	-0.125861	0.000023
O	-2.340102	-0.065146	-0.000053
O	0.187588	1.281811	0.000010
H	-0.396493	-1.767359	-0.479121
C	1.848202	-0.472194	-0.000021
O	2.914691	-0.058830	-0.000016
H	-0.396498	-1.767355	0.479195

Sum of electronic and zero-point Energies= -336.785653

Sum of electronic and thermal Free Energies= -336.816605



17: $[(H)_2VO_2(CO)]^-$

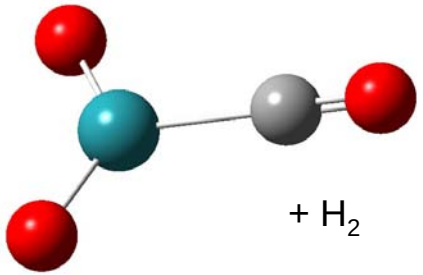
ΔE = +1.32eV

ΔG = +1.19eV

V	0.31860200	0.26035800	-0.00361600
O	1.50478100	-0.89425800	0.00081900
O	0.49099700	1.89862700	0.00571100
H	3.63781500	-2.98799100	0.00825900
C	-1.51619000	-0.38976900	-0.00233900
O	-2.61761300	-0.78044300	0.00373700
H	3.10616600	-2.45303300	0.00680600

Sum of electronic and zero-point Energies= -336.825431

Sum of electronic and thermal Free Energies= -336.859515



+ H_2

10b: $^3[VO_2(CO)]^-$

ΔE = +1.23eV

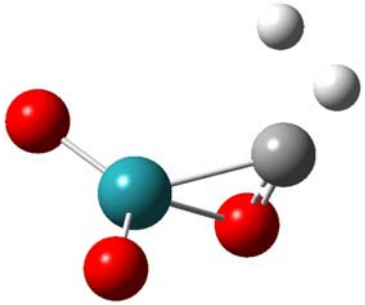
ΔG = +0.85eV

V	23.0	0.47216600	0.00001000	-0.00022200
O	8.0	1.19603705	1.48220801	0.00026900
O	8.0	1.19602001	-1.48218703	0.00026900
O	8.0	-2.64387989	0.00011800	0.00016300
C	6.0	-1.47420704	-0.00022500	-0.00008200

Sum of electronic and zero-point Energies= **-335.659250 + (-1.169506)**

Sum of electronic and thermal Free Energies= -335.691080**+ (-1.180997)**

Figure S7-4: Structures, energies and coordinates for ions on the Potential Energy Surface for the CID of $[VO_2(\eta^2\text{-}OCH_2)]^-$



TS3a-18:

ΔE = +3.04eV

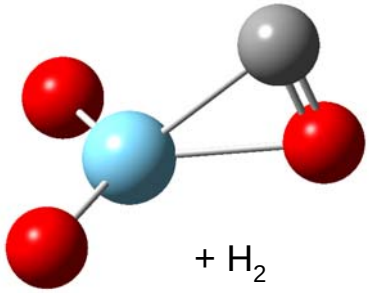
ΔE = +3.03eV

V	23.0	0.31677601	0.00892000	0.01016200
O	8.0	1.02950299	1.46219003	0.06313300
O	8.0	-1.42860103	-0.26399899	0.74933797
O	8.0	1.28117502	-1.28295505	-0.18904600
C	6.0	-1.60043001	-0.21975900	-0.53427899
H	1.0	-2.22825193	1.46123600	-1.00541699
H	1.0	-2.51163292	0.33028501	-1.01004303

Sum of electronic and zero-point Energies=-336.762219

Sum of electronic and thermal Free Energies=-336.791961

Imaginary frequency= -1227cm^{-1}



11: $[VO_2(\eta^2\text{-}OC)]^-$ + H_2

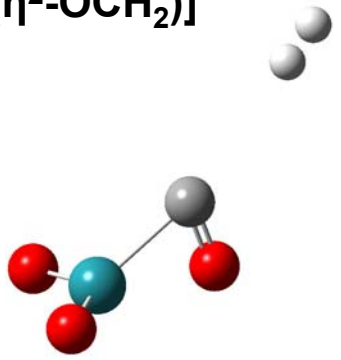
ΔE = +1.75eV

ΔG = +1.44eV

V	23.0	-0.06530100	0.26796600	0.00000000
O	8.0	-0.06530100	1.04649103	1.44482005
O	8.0	-0.06530100	1.04649103	-1.44482005
C	6.0	0.88052702	-1.55460894	0.00000000
O	8.0	-0.34205100	-1.69742703	0.00000000

Sum of electronic and zero-point Energies= -335.640280

Sum of electronic and thermal Free Energies= -335.669584



18: **$[VO_2(\eta^2\text{-}OC)(H)_2]^-$**

ΔE = +1.77eV

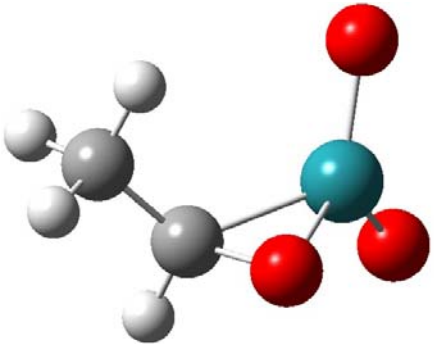
ΔE = +1.63eV

V	23.0	0.44668099	0.00351500	0.01941200
O	8.0	1.14894605	1.46511698	-0.22792400
O	8.0	-1.29825604	-0.04807800	0.96112603
O	8.0	1.20538497	-1.41973495	-0.27946201
C	6.0	-1.58998299	-0.03185300	-0.23510800
H	1.0	-4.94315720	0.08037200	-1.46194506
H	1.0	-4.23922014	0.05146100	-1.20380497

Sum of electronic and zero-point Energies=-336.809120

Sum of electronic and thermal Free Energies=-336.843397

Figure S8: Structures, energies and coordinates for ions on the Potential Energy Surface for the CID of $[VO_2(\eta^2\text{-}OCHCH_3)]^-$



3b: $[VO_2(\eta^2\text{-}OCHCH_3)]^-$

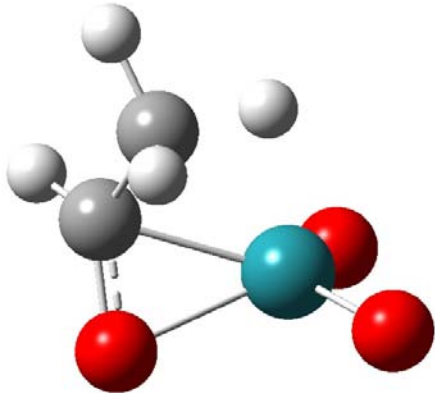
ΔE = +0.00eV

ΔG = +0.00eV

V	23.0	0.66336602	0.03514300	0.07554300
O	8.0	0.86005700	1.65789604	0.11275100
O	8.0	-0.72429198	-0.75528198	1.01826203
O	8.0	1.84871995	-0.88619298	-0.57132602
C	6.0	-1.22214198	-0.58084202	-0.26810300
C	6.0	-2.39395308	0.37052801	-0.40768099
H	1.0	-1.34927797	-1.52283502	-0.81775200
H	1.0	-3.30699301	-0.04217500	0.05119200
H	1.0	-2.17285800	1.32690203	0.07235900
H	1.0	-2.60759592	0.56034303	-1.46607602

Sum of electronic and zero-point Energies= -376.176349

Sum of electronic and thermal Free Energies= -376.207733



TS3b-19: $[VO_2(\eta^2\text{-}OCH_2CH_2)]^-$

ΔE = +1.06eV

ΔG = +1.09eV

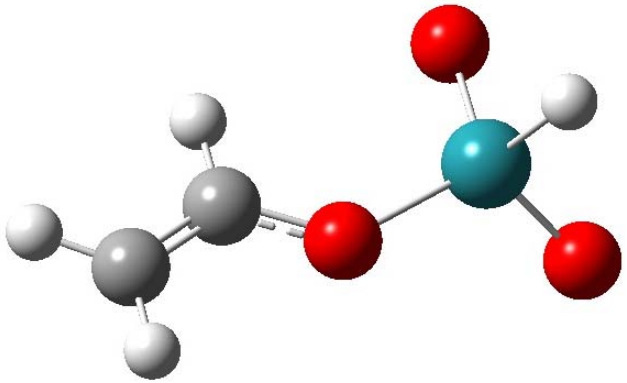
V	23.0	0.51077902	0.00307400	-0.02771600
O	8.0	1.60643601	-1.07023895	-0.59060502
O	8.0	0.97313100	1.54205000	0.36165300
C	6.0	-1.38216901	-0.64852101	0.07449100
O	8.0	-0.83297098	-0.50144601	1.28734601
C	6.0	-1.73633301	0.52337801	-0.79782897
H	1.0	-2.10570312	1.39853203	-0.25479901
H	1.0	-0.82289398	0.93023598	-1.36514699
H	1.0	-2.42470288	0.23643900	-1.59822500
H	1.0	-1.65637696	-1.64795804	-0.27149200

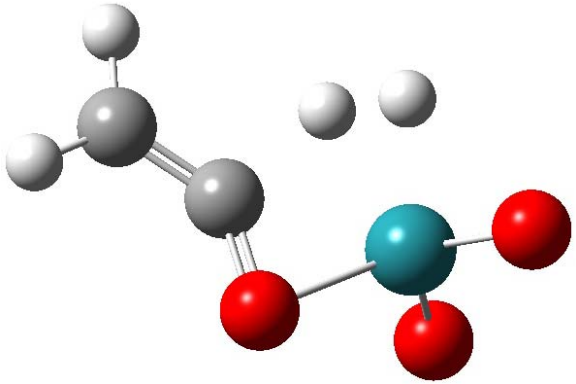
Sum of electronic and zero-point Energies= -376.137188

Sum of electronic and thermal Free Energies= -376.167673

Imaginary frequency= -286cm^{-1}

Figure S8-2: Structures, energies and coordinates for ions on the Potential Energy Surface for the CID of $[VO_2(\eta^2\text{-}OCHCH_3)]^-$





19: $[VO_2(H)(OCHCH_2)]^-$

ΔE = -0.35eV

ΔG = -0.39eV

V	23.0	0.92255598	-0.03237100	0.21440800
O	8.0	1.90654194	-1.08858800	-0.50571901
O	8.0	-0.88546997	-0.46279401	0.08674000
O	8.0	1.21488702	1.48923099	-0.23294000
C	6.0	-1.96610403	0.28267699	-0.12575600
C	6.0	-3.22998595	-0.16810100	-0.05761100
H	1.0	-1.77114296	1.33037198	-0.37271699
H	1.0	-4.05521202	0.50816202	-0.24353400
H	1.0	-3.44683290	-1.20185196	0.18631400
H	1.0	1.34326303	-0.08238800	1.81408703

Sum of electronic and zero-point Energies= -376.189172

Sum of electronic and thermal Free Energies= -376.222051

TS19-20 : $[VO_2(H_2)(OCCH_2)]^-$

ΔE = +1.08eV

ΔG = +1.10eV

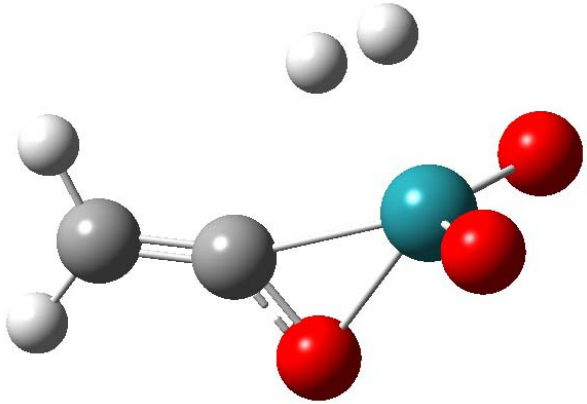
V	23.0	-0.64507902	0.00000000	-0.12015700
O	8.0	-1.48083496	-1.38844800	0.00647600
O	8.0	0.85145801	0.00000000	1.15453005
O	8.0	-1.48083496	1.38844800	0.00647700
C	6.0	1.44256401	0.00000000	0.01383900
C	6.0	2.72602892	0.00000000	-0.38948500
H	1.0	3.54055691	0.00000000	0.33094901
H	1.0	2.97263408	0.00000000	-1.44333005
H	1.0	-0.32023799	0.00000000	-1.82900703
H	1.0	0.51399899	0.00000000	-1.38098705

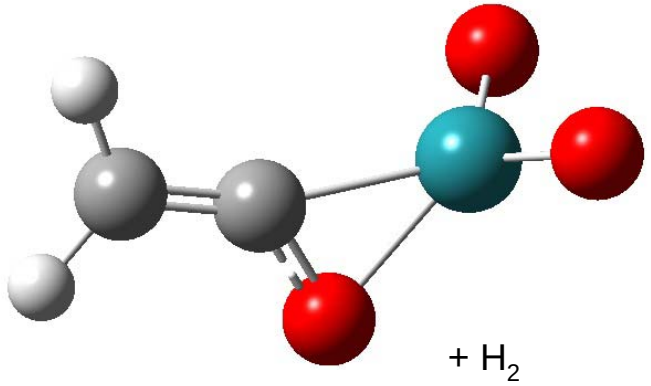
Sum of electronic and zero-point Energies= -376.136494

Sum of electronic and thermal Free Energies= -376.167421

Imaginary frequency= -700cm^{-1}

Figure S8-3: Structures, energies and coordinates for ions on the Potential Energy Surface for the CID of $[VO_2(\eta^2\text{-}OCHCH_3)]^-$





20: $[VO_2(H_2)(\eta^2\text{-}OCCH_2)]^-$

ΔE = +1.04eV

ΔG = +1.04eV

V	23.0	0.61478400	0.00001200	0.06788100
O	8.0	1.45167994	-1.39760494	0.00843400
O	8.0	-0.86995202	0.00006000	-1.16813803
O	8.0	1.45154798	1.39768398	0.00868600
C	6.0	-1.41341496	0.00008000	0.00965600
C	6.0	-2.68927789	-0.00008400	0.43667799
H	1.0	-3.52275109	-0.00025200	-0.26408601
H	1.0	-2.91466308	-0.00002200	1.49564505
H	1.0	0.71150202	-0.00115900	1.94458604
H	1.0	-0.06417300	0.00008500	1.79273605

Sum of electronic and zero-point Energies= -376.138001

Sum of electronic and thermal Free Energies= -376.169285

12a: $[VO_2(\eta^2\text{-}OCCH_2)]^-$ $+H_2$

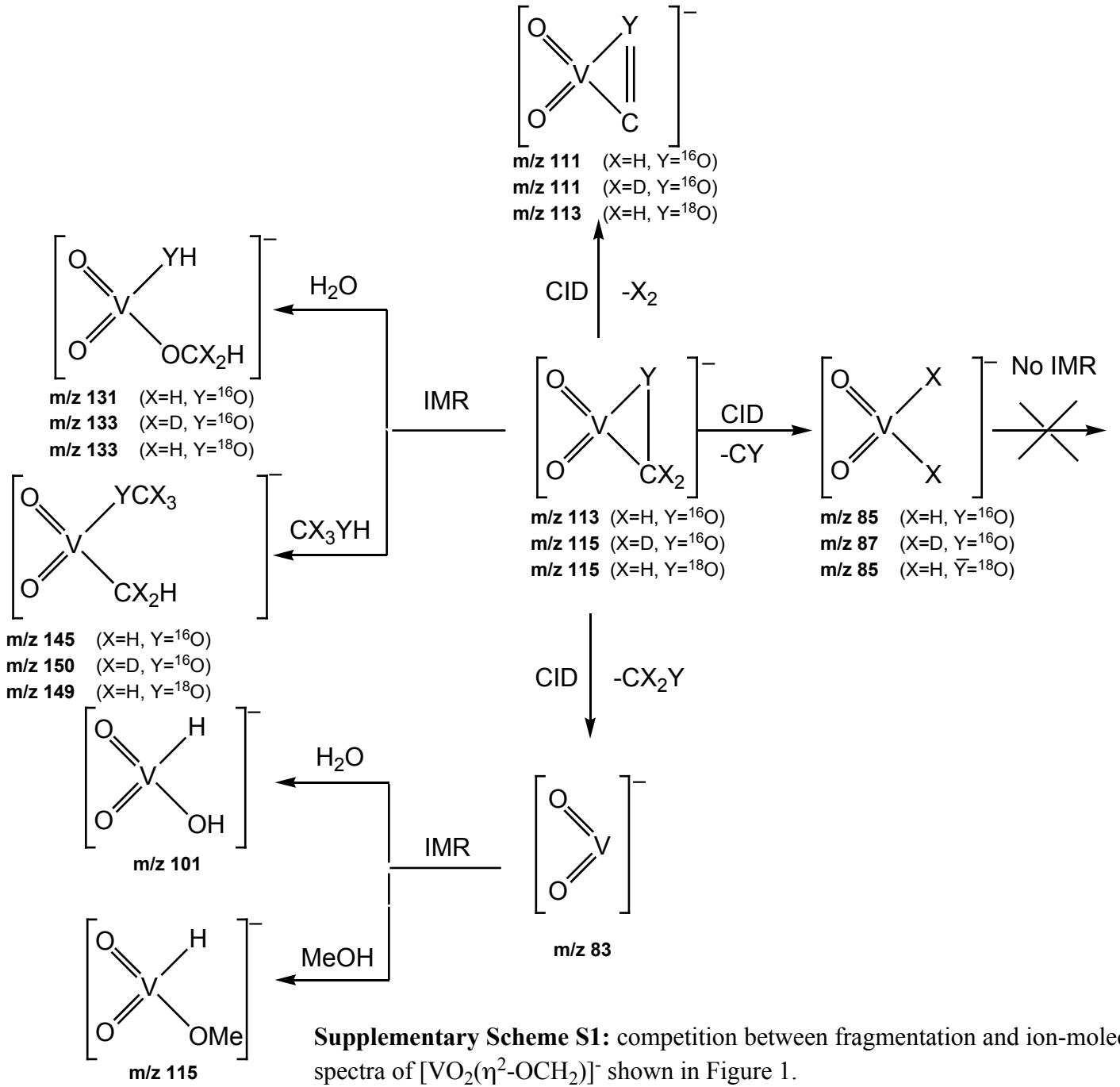
ΔE = +0.93eV

ΔG = +0.63eV

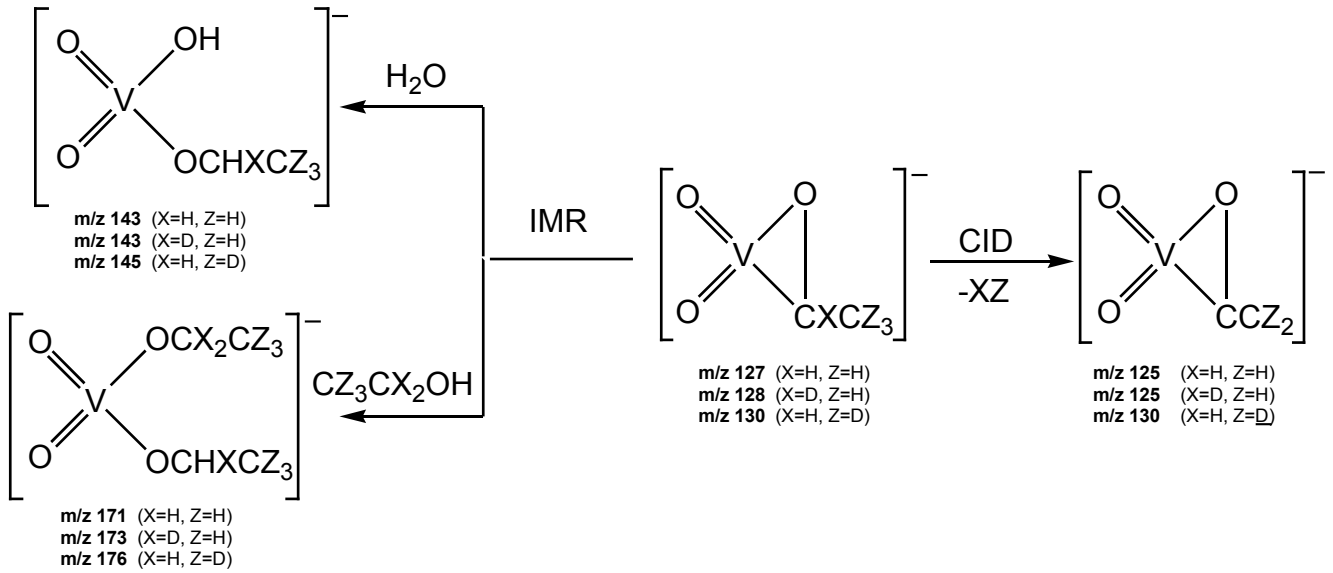
V	23.0	-0.62923199	0.00000000	0.04264500
O	8.0	-1.41035604	-1.38510001	-0.28706199
O	8.0	0.89458799	-0.00010500	1.15601599
O	8.0	-1.41028595	1.38517201	-0.28692999
C	6.0	1.34785700	-0.00000800	-0.09405500
C	6.0	2.59513211	0.00003000	-0.58247298
H	1.0	3.46323299	0.00000700	0.07421800
H	1.0	2.75959110	0.00013300	-1.65207005

Sum of electronic and zero-point Energies= -374.972802 **+ (-1.169506)**

Sum of electronic and thermal Free Energies= -375.003622 **+ (-1.180997)**



Supplementary Scheme S1: competition between fragmentation and ion-molecule reactions for CID spectra of $[VO_2(\eta^2\text{-}OCH_2)]^-$ shown in Figure 1.



Supplementary Scheme S2: competition between fragmentation and ion-molecule reactions for CID spectra of $[VO_2(\eta^2\text{-}OCHCH_3)]^-$ shown in Figure 2.