A Homolytic Oxy-Functionalization Mechanism: Intermolecular Hydrocarbyl Migration from M-R to Vanadate Oxo

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Computational details

The geometry optimizations and zero-point vibrational energy (ZPVE) were carried out with the B3LYP functional with the 6-31G** basis set[1-2] for all atoms except metals. For the metals, the core electrons were described by the Los Alamos angular momentum projected small-core effective core potential (ECP) using the double-ζ contraction of valence functions.[3]

Solvation energies were calculated using the Poisson-Boltzmann self-consistent polarizable continuum method implemented in Jaguar to represent cyclohexane (dielectric constant = 2.02 and effective radius = 2.78 Å).[4] The solvation calculations used the B3LYP/LACVP** level of theory and the gas-phase optimized structures. Single-point energy calculations were performed using the M06 functional with a larger basis set: metals were described with the triple-ζ contraction of Los Alamos valence functions augmented with two *f*-functions[5] and the core electrons were described by the same ECP. The other atoms were described with the 6-311++G** basis set.[6-7]

Unless otherwise noted, all energies discussed are free energies, calculated as

$$G_{298K} = E_{elec} + G_{solv} + ZPE + H_{vib} + \frac{n}{2}kT - T(S_{vib}) - T[0.54\times(S_{rot} + S_{trans} - 14.3) + 8.0],$$

where T = 298K and n = 12 accounts for the potential and kinetic energies of the translational and rotational modes. We followed the procedure proposed by Wertz[8] to handle the change of translational and rotational entropy when a solute is transferred from the gas phase into the solution phase. Wertz decomposed the solute solvation into three steps: (1) the solute is treated as an ideal gas and compressed from 1 atm (1 mol, 24.5 L) to 55.5 mol/L; (2) then the solute is transferred to a hypothetical 55.5 mol/L solution

which has the intermolecular interaction of a dilute solution; (3) then finally this hypothetical solution is diluted to 1M (1 mol, 1L). In the first step, due to the compression, the solute loses entropy of

$$\Delta S = 1.987 \times \ln\left(\frac{V_{final}}{V_{initial}}\right) = 1.987 \times \ln\left(\frac{\frac{1}{55.5}}{24.5}\right) = -14.3\,\text{e.u.}$$

In the second step, Wertz proposed that the solute loses 46% of its translational and rotational entropies, which means only 54% of translational and rotational entropy remains. In the third step, due to the expansion, the solute gains entropy of

$$\Delta S = 1.987 \times \ln\left(\frac{V_{final}}{V_{initial}}\right) = 1.987 \times \ln\left(\frac{1}{\frac{1}{55.5}}\right) = 8.0\,\text{e.u.}$$

Based on this, our solution phase librational entropies are derived from calculated gas phase translational and rotational entropies as

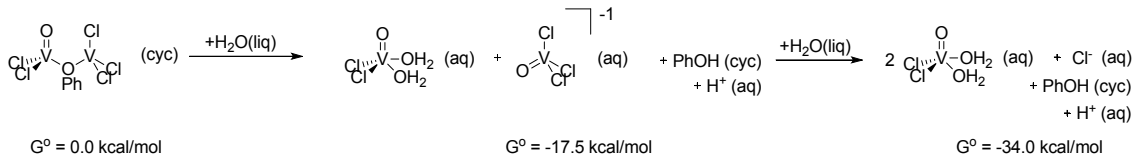
$$\left(S_{rot} + S_{trans} - 14.3\right) \times 0.54 + 8.0\,.$$

The combination of ideal gas translational entropy, the Wertz approximation and the continuum solvation free energies (which use the constant-concentration convention) results in computed free energies at standard (1M) concentration.

The imaginary frequencies of the transition states are:

-199.07 cm^{-1} for **1,4-TS**,
-306.10 cm^{-1} for **2,5-TS**,
-531.99 cm^{-1} for **3,6-TS**,
-264.54 cm^{-1} for **1,7-TS**,
-561.88 cm^{-1} for **1,7-TS-Me**,
-994.50 cm^{-1} for **1,7-TS'-Me**.

Reichle and Carrick (Ref 7) added 1N H_2SO_4 to quench their reaction and hydrolyze products, identifying most of the major product, phenol, in the cyclohexane layer. We have calculated ΔG for the formation of phenol and aquated vanadyl compounds from the dinuclear intermediate **7**, and find these reactions to be very exergonic even before hydrolyzing V-Cl bonds:



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Thermochemistry

Molecule	E(SCF)	G(solv)	ZPVE	H(vib)	S(vib)	S(trans+rot)	G	ΔG
1	-1298.6018	-2.3	60.8	4.8	30.9	73.3	-814839.3	0.0
1-Me	-1106.9693	-1.6	26.4	2.8	16.9	69.2	-694618.9	0.0
2	-2124.5917	-27.7	206.1	17.2	113.6	82.0	-1333049.6	0.0
3	-1548.1950	-6.0	187.1	11.8	74.9	79.6	-971346.0	0.0
4	-1298.6016	-5.1	60.9	4.4	33.4	73.9	-814843.2	-3.9
5	-2124.6755	-14.0	207.1	16.2	110.1	81.9	-1333087.5	-37.9
6	-1548.1589	-6.5	187.1	11.8	76.3	80.0	-971324.3	21.7
7	-2825.9613	-2.8	66.7	10.0	68.7	78.0	-1773273.6	-12.5
7-Me	-2634.3209	-3.1	33.9	8.1	56.1	76.1	-1653048.3	-7.7
VOCl3	-1527.3340	-0.4	5.0	2.3	13.9	70.2	-958421.7	
1,4-TS	-1298.5290	-5.5	59.2	4.8	31.4	73.3	-814798.7	40.7
2,5-TS	-2124.5601	-28.3	205.6	16.8	110.6	82.0	-1333030.5	19.1
3,6-TS	-1548.1091	-5.7	186.1	11.5	72.1	79.6	-971292.3	53.7
1,7-TS	-2825.9069	-3.3	64.9	9.3	67.1	78.1	-1773241.9	19.2
1,7-TS-Me	-2634.2613	-3.1	31.3	8.1	55.8	76.4	-1653013.3	27.3
1,7-TS'-Me	-2634.2411	-2.5	31.2	7.1	58.0	77.3	-1653002.0	38.7

Cartesian coordinates of optimized geometries (Å)

1

V1	-1.0086017315	-1.3302017285	0.0510976427
C2	-0.3236947584	-0.3153142321	1.5566025913
C3	-0.2808821503	-1.0183258882	2.7753799203
C4	0.1137598606	1.0173625258	1.4994541720
C5	0.1932974674	-0.3914092650	3.9184254222
H6	-0.6182692194	-2.0540622688	2.8303853473
C7	0.5875478728	1.6368610567	2.6467535703
H8	0.0778338132	1.5545068993	0.5542356368
C9	0.6255536601	0.9328089227	3.8500628748
H10	0.2279152251	-0.9289373899	4.8628948053
H11	0.9279990831	2.6687762838	2.6093508934
H12	0.9970304759	1.4225655711	4.7475774643
O13	-0.9327008702	-0.2811470570	-1.1024704999
Cl14	0.3015430504	-2.9825341315	-0.3234836283
Cl15	-3.0362506422	-1.8906326862	0.4530261700

1,4-TS

O1	0.0000000000	0.0000000000	0.0000000000
C2	0.0000000000	0.0000000000	2.1040160066
V3	1.4987622600	0.0000000000	0.6290979131
C4	-0.3944155849	1.2323695849	2.6484342827
C5	-0.3945954376	-1.2322538642	2.6485542567
C6	-0.9774197166	1.2201279020	3.9121922602
H7	-0.1846183936	2.1622606031	2.1322245909
C8	-0.9776018219	-1.2198396799	3.9123500753
H9	-0.1849785878	-2.1622097152	2.1323843242
C10	-1.2658919283	0.0001848235	4.5406703254
H11	-1.2229608602	2.1583017545	4.4005426935
H12	-1.2232926021	-2.1579885387	4.4006935080
H13	-1.7514823384	0.0002782064	5.5120844007
Cl14	2.6096215336	1.8979117153	0.7705435942
Cl15	2.6096437648	-1.8978855997	0.7705764872

4 (triplet state)

V1	-0.7370888966	3.8356009503	1.0859107698

Cl2	1.2084355029	3.9588911426	2.0405527119
Cl3	-0.9306240068	2.3800520834	-0.5112461321
O4	-2.0270976131	4.8766667614	1.6009075365
C5	-2.5738441124	5.8741850518	2.3331301955
C6	-1.8207241216	6.5004922121	3.3272639121
C7	-3.8894200664	6.2531981421	2.0708594512
C8	-2.4015406317	7.5217089879	4.0647408167
H9	-0.7963216241	6.1768589373	3.5031645282
C10	-4.4539516043	7.2777471438	2.8180902922
H11	-4.4412064244	5.7394497294	1.2881915570
C12	-3.7151246524	7.9124129125	3.8131731852
H13	-1.8245812902	8.0168997094	4.8419179447
H14	-5.4787241092	7.5828908532	2.6215781096
H15	-4.1635522063	8.7140187553	4.3947439205

2

Re1	0.1029553243	0.3436481572	0.5072996133
N2	-0.3718592327	-0.3942952005	2.4573272138
N3	2.1141723063	-0.1823149112	1.3483047325
N4	0.1376209196	-1.9174074502	0.1854267968
N5	0.1436358893	-1.4846770125	3.0623570172
N6	2.3916308000	-1.3059282609	2.0598086883
N7	0.6830977317	-2.8096560978	1.0409401172
B8	1.2741838671	-2.3025286396	2.3678425472
H9	1.6412110428	-3.2033152985	3.0687015984
C10	-1.2905629880	0.1495960553	3.2713989008
C11	3.2215392292	0.5711566678	1.3135875587
C12	-0.3427892457	-2.6027413830	-0.8556277543
C13	-0.4476277917	-1.6285417865	4.2542737457
C14	3.6700264482	-1.2534774364	2.4734676137
C15	0.5466758256	-4.0488303816	0.5410743603
C16	-1.3734116899	-0.6088508604	4.4310291665
C17	4.2374206344	-0.0784078044	2.0158606365
C18	-0.1049760839	-3.9644377437	-0.6779631691
H19	-2.0130985701	-0.4381962938	5.2840710534
H20	5.2488759001	0.2684163979	2.1678567502
H21	-0.3707567665	-4.7738611136	-1.3418180542
O22	-1.4918587762	0.2915090145	-0.0736791763

O23	0.3599216290	1.9331585680	1.0165404034
H24	-0.8209027291	-2.0776655818	-1.6736601266
H25	0.9221140520	-4.9020122405	1.0914099138
H26	-1.8231665564	1.0442132503	2.9727157891
H27	-0.1641608994	-2.4495115842	4.9001318571
H28	3.2273020790	1.5105443761	0.7540490558
H29	4.0790022517	-2.0611062755	3.0675702540
O30	0.8505268533	3.7471467223	-0.7603913461
S31	2.3113583151	3.9522976757	-0.8841319214
O32	3.1065483824	2.7105629774	-0.7911388808
O33	2.7203779050	4.8897490667	-1.9260554165
C34	2.7305991080	4.7809943810	0.6977197936
F35	2.4399526600	3.9746298776	1.7257700442
F36	2.0493736174	5.9093274772	0.8500231404
F37	4.0300650627	5.0597810417	0.7546293977
C38	1.1360807875	0.3244237954	-1.2761862274
C39	2.2173647745	-0.4927830320	-1.6259419272
C40	0.6672580478	1.3019980494	-2.1680778210
C41	2.8390606126	-0.3181082011	-2.8499811946
H42	2.5818980481	-1.2517037439	-0.9358851489
C43	1.3082020095	1.4693176622	-3.3914380585
H44	-0.1468408472	1.9703377137	-1.9048052698
C45	2.3910469823	0.6698533390	-3.7285174131
H46	3.6895571024	-0.9406488234	-3.1170680169
H47	0.9674022522	2.2546762016	-4.0613069091
H48	2.8985624827	0.8202255898	-4.6783866467

2,5-TS

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	2.0244650580
Re3	1.6899434659	0.0000000000	1.5651337933
N4	3.5061413626	-0.2971027270	2.7207986958
N5	2.8502379193	-0.9820826127	0.1113448608
N6	1.4616604472	-2.1418971186	2.3105226592
N7	4.2697995640	-1.4195985139	2.7025741126
N8	3.6947604468	-2.0328833832	0.3698526077
N9	2.4647012481	-3.0571724677	2.2845459197
B10	3.8523166165	-2.5988737376	1.7934501209

H11	4.6527941894	-3.4859113360	1.8288184539
C12	4.0760402615	0.5746939348	3.5717425654
C13	2.9704759436	-0.6571242311	-1.1962333920
C14	0.3879641973	-2.7412140069	2.8570070507
C15	5.3064230406	-1.2594037453	3.5452308865
C16	4.3260953808	-2.3583209707	-0.7705985312
C17	2.0280799798	-4.2197659872	2.8017711325
C18	5.2212212824	0.0017326872	4.1248502780
C19	3.9000217647	-1.5100049773	-1.7866371193
C20	0.6976309528	-4.0640315337	3.1782364553
H21	5.8994234763	0.4458081107	4.8366748670
H22	4.2266894168	-1.4983086747	-2.8146293010
H23	0.0488082557	-4.8045777746	3.6197019556
O24	2.1783314218	1.6139568190	1.5086528751
H25	-0.5322370930	-2.1882994431	2.9727937779
H26	2.6870784396	-5.0736078738	2.8647388573
H27	3.6440437754	1.5540494838	3.7155513272
H28	6.0331294260	-2.0487128057	3.6705105166
H29	2.4353262614	0.1924461383	-1.6210234171
H30	5.0377677203	-3.1714727383	-0.7799412880
O31	1.5757533733	3.5595019683	-0.5380400968
S32	2.2491505482	3.3015969810	-1.8398814629
O33	2.0008081639	1.9360457045	-2.3872608625
O34	2.1873176898	4.3925052426	-2.8215515204
C35	4.0454670838	3.2019574703	-1.3586268904
F36	4.2637552995	2.1400896885	-0.5405450888
F37	4.4477822761	4.3014568416	-0.7076021991
F38	4.8288467813	3.0398276856	-2.4372649627
C39	-0.4830404407	-1.2334454060	-0.4376739328
C40	-0.3681487801	1.2231583442	-0.5425547956
C41	-1.2977963145	-1.2341656782	-1.5683900478
H42	-0.2170593593	-2.1589929065	0.0587167310
C43	-1.1853970193	1.1863260066	-1.6772194028
H44	0.0330511330	2.1671080931	-0.1837942229
C45	-1.6489156949	-0.0266664853	-2.1838749440
H46	-1.6627141408	-2.1785451281	-1.9620243033
H47	-1.4395778572	2.1228571013	-2.1631359224
H48	-2.2919953782	-0.0358923535	-3.0589036633

5

Re1	-0.2391465087	-0.0828013042	-0.0658055433
N2	0.3653461124	0.1459184030	1.9725125702
N3	2.0412643882	-0.2087026592	-0.1087416403
N4	0.0282304718	-2.1367139280	0.0403304356
N5	1.1146980596	-0.7948940036	2.5947346399
N6	2.6991935161	-1.0540289662	0.7138565560
N7	0.8520711516	-2.7073946153	0.9562807350
B8	1.8723457521	-1.8437642957	1.7505046734
H9	2.5621760342	-2.5422188642	2.4413032953
C10	0.0147080942	1.0577197554	2.8795179148
C11	2.9499401724	0.4457795022	-0.8303747093
C12	-0.5458383837	-3.1156452056	-0.6685468064
C13	1.2447463784	-0.4607064584	3.8904825820
C14	4.0234578282	-0.9336716396	0.5090992335
C15	0.7918135316	-4.0381944092	0.8132445785
C16	0.5457728079	0.7109290198	4.1223578192
C17	4.2316033848	0.0143819636	-0.4774683717
C18	-0.1026279162	-4.3475797542	-0.2018534676
H19	0.4395738270	1.2412892747	5.0571229489
H20	5.1762022490	0.3507812236	-0.8792079206
H21	-0.3846673716	-5.3283695635	-0.5548563292
O22	-1.8367855824	-0.0681214510	0.4343119951
O23	0.2771826274	1.8898121034	-0.2650756719
S24	-0.3580465826	3.0991724881	-0.9979780299
O25	-1.8002328756	2.9801443052	-1.1000330066
O26	0.4501697947	3.5355695117	-2.1178088390
C27	-0.0663580375	4.3337963229	0.3320516983
F28	-0.7244959071	3.9841971888	1.4349770725
F29	1.2227241961	4.4269433961	0.6112071939
F30	-0.5130401847	5.5095021614	-0.0758711179
H31	-1.2351412846	-2.8627734343	-1.4636952110
H32	1.4020354873	-4.6774455431	1.4383622973
H33	-0.5956019521	1.9018736522	2.5839265630
H34	1.8365650942	-1.0787844026	4.5534184810
H35	2.6289409337	1.1926690875	-1.5496579942
H36	4.7213455752	-1.5296719137	1.0833156800

O37	-0.1294205805	-0.4483998749	-1.9691059427
C38	-0.1968835258	0.3928086685	-3.0335976503
C39	-1.3910780495	1.0382431315	-3.3486196543
C40	0.9200660682	0.5305261221	-3.8600527530
C41	-1.4544470187	1.8471631334	-4.4763268797
H42	-2.2483445703	0.9151120607	-2.6902006187
C43	0.8446511990	1.3462004638	-4.9808202486
H44	1.8294752236	-0.0118008152	-3.6065945980
C45	-0.3399998360	2.0083195329	-5.2918811723
H46	-2.3823747200	2.3644646775	-4.7097291371
H47	1.7183562780	1.4661548697	-5.6182364512
H48	-0.3921626563	2.6518566927	-6.1669605282

3

Re1	0.0694433662	0.1065614251	-0.0928596194
N2	-0.0492553819	-0.3750046710	1.9997503107
N3	2.1639806470	-0.2404692804	-0.0013594630
N4	0.2058432061	-2.2304767689	0.0199898634
N5	0.9021239059	-1.0920891049	2.6441047139
N6	2.7483942462	-1.0233430390	0.9370127605
N7	1.0468724244	-2.8333849307	0.8915538036
B8	1.8916829497	-1.9553686018	1.8285090396
H9	2.5929672268	-2.6094595809	2.5524642434
C10	-0.8755772682	0.1252622228	2.9223967383
C11	3.1393979969	0.3449364912	-0.7047589377
C12	-0.4575444618	-3.1954307270	-0.6155999073
C13	0.6663604014	-1.0464058734	3.9650951808
C14	4.0821540376	-0.9384679113	0.8103969421
C15	0.9120280718	-4.1689097915	0.8027730558
C16	-0.4541110361	-0.2654254312	4.1929817516
C17	4.3802892912	-0.0620165308	-0.2197265749
C18	-0.0445293627	-4.4487318357	-0.1560353732
H19	-0.9063495830	-0.0230332278	5.1433335306
H20	5.3572165077	0.2343844985	-0.5721923235
H21	-0.3940167355	-5.4194200793	-0.4762212915
O22	0.2681627165	1.7665913602	-0.0807817124
C23	0.0947454668	-0.3238139753	-2.1508561578
C24	-0.7895682708	0.3723316211	-2.9882630801

C25	-0.7116297607	0.2640120696	-4.3738838625
C26	0.2253337238	-0.5815143746	-4.9566033999
C27	1.0935719192	-1.3064131200	-4.1453624848
C28	1.0338697903	-1.1703203255	-2.7629577341
H29	-1.5491640981	1.0165564278	-2.5484590767
H30	-1.3989654737	0.8314681817	-4.9989422680
H31	0.2756842757	-0.6809354299	-6.0393634429
H32	1.8249212808	-1.9778488059	-4.5926660605
H33	1.7252390726	-1.7490823851	-2.1504705251
H34	-1.1909254475	-2.9334651206	-1.3685882205
H35	1.5078756996	-4.8203940738	1.4296509639
H36	-1.7210453387	0.7261706765	2.6109640500
H37	1.3095166292	-1.5850354864	4.6495679203
H38	2.8859040088	1.0202855195	-1.5125228085
H39	4.7252211988	-1.5194492599	1.4592082732
Cl40	-2.2877011525	-0.2122710251	-0.1350065322

3,6-TS

C1	-0.3087722128	0.0509073954	0.1599260246
O2	0.0153190602	-0.1206896191	1.8931852075
Re3	1.6945027502	-0.0120940909	1.3384808156
N4	3.5429212379	-0.0609252390	2.3640193597
N5	2.9166983608	-0.6846197456	-0.2623926081
N6	1.6789635880	-2.1610360732	1.7649676634
N7	4.4321922265	-1.0899106153	2.2456389315
N8	3.9004048422	-1.6181483909	-0.1289228880
N9	2.8109184239	-2.9080483834	1.6932218092
B10	4.1363757821	-2.2448973698	1.2628825034
H11	5.0335568202	-3.0383648959	1.2403643610
C12	4.0459863211	0.7995669187	3.2652174370
C13	2.8599490404	-0.3427113161	-1.5608081977
C14	0.7015972723	-2.9625147388	2.2156733764
C15	5.4721522836	-0.8774497501	3.0747444678
C16	4.4468270479	-1.8645890924	-1.3338539442
C17	2.5435978769	-4.1751062758	2.0845722388
C18	5.2657299087	0.3195414789	3.7503079693
C19	3.8151400214	-1.0646232842	-2.2805211797
C20	1.2032092248	-4.2544747248	2.4267182878

H21	5.9126862203	0.7814481810	4.4799626232
H22	4.0237903205	-1.0093746973	-3.3378136835
H23	0.6653960804	-5.1195014781	2.7835664952
C24	-0.9168920840	1.2769578283	-0.1390062655
C25	-1.8500719465	1.3376250376	-1.1745190647
C26	-2.2064172273	0.1831357569	-1.8750630785
C27	-1.6359672491	-1.0477684500	-1.5271991173
C28	-0.7124374210	-1.1282815871	-0.4892460125
H29	-0.6338514525	2.1678704256	0.4080023047
H30	-2.3031213841	2.2917637049	-1.4303307635
H31	-2.9359526693	0.2360162736	-2.6782828519
H32	-1.9173086531	-1.9496669086	-2.0648457009
H33	-0.2807278270	-2.0817416065	-0.2084397559
H34	-0.2882902797	-2.5603030845	2.3695365419
H35	3.3259508836	-4.9195588370	2.0913326770
H36	3.5095292384	1.7096573809	3.4873039366
H37	6.2861934250	-1.5861530688	3.1222403270
H38	2.1503198165	0.4027096756	-1.8860246638
H39	5.2438190151	-2.5868398010	-1.4354705278
Cl40	2.1096538325	2.3003330030	0.8898127523

6 (triplet state)

Re1	0.1308425803	-0.0059358567	0.6908362337
N2	0.0896436970	-1.3250811488	2.2901045818
N3	2.2431587374	-0.2715046937	0.7753047217
N4	0.1111646586	-1.8489081961	-0.3621394082
N5	0.9198043867	-2.3938942823	2.3871115579
N6	2.7860485639	-1.4939282171	0.9961432809
N7	0.9595072737	-2.8569916152	-0.0411163325
B8	1.8612491553	-2.7120006845	1.2027143664
H9	2.4993277785	-3.7098739565	1.4045291890
C10	-0.6408024525	-1.2806331325	3.4149176430
C11	3.2518883873	0.5973669499	0.6456836248
C12	-0.5595527641	-2.2254484745	-1.4582109798
C13	0.7143422931	-3.0087537613	3.5613782157
C14	4.1259426946	-1.3907042396	1.0000507393
C15	0.8245138364	-3.8532377500	-0.9316530456
C16	-0.2777513816	-2.3308016830	4.2535853688

C17	4.4700820132	-0.0673562145	0.7799915019
C18	-0.1403753310	-3.4933862046	-1.8577650537
H19	-0.6805332178	-2.5685255952	5.2270706191
H20	5.4632863560	0.3544746249	0.7274295621
H21	-0.4917925063	-4.0704275944	-2.7003874500
H22	-1.3060815915	-1.5626966506	-1.8779232468
H23	1.4262175969	-4.7486817451	-0.8409288793
H24	-1.3838934328	-0.5015897838	3.5362174002
H25	1.2897681476	-3.8876654635	3.8232964147
H26	3.0222845627	1.6406939541	0.4720679296
H27	4.7386596594	-2.2687202022	1.1609840431
Cl28	-2.1779735549	0.3319955390	0.3350619680
O29	0.6251904520	1.8736198005	0.6117800099
C30	-0.1289851615	2.9824404026	0.7947848779
C31	-0.8442084337	3.1792869572	1.9783036052
C32	-0.1293769058	3.9744983833	-0.1870417714
C33	-1.5548875269	4.3559797923	2.1712453160
H34	-0.8326006190	2.3932830974	2.7340378488
C35	-0.8476113000	5.1459523007	0.0152156635
H36	0.4340797188	3.8032043448	-1.1014524000
C37	-1.5620605040	5.3459446501	1.1928253043
H38	-2.1111714372	4.4988583881	3.0958983175
H39	-0.8481083308	5.9124327142	-0.7575489378
H40	-2.1229218222	6.2650801032	1.3459058798

VOCl3

V1	0.2585499669	0.0002759930	0.0000000000
Cl2	-0.4022733986	-1.0061240103	1.7418720384
Cl3	-0.4022733986	-1.0061240103	-1.7418720384
Cl4	-0.4024332702	2.0119537576	0.0000000000
O5	1.8152737140	-0.0002357084	0.0000000000

1,7-TS

V1	0.0000000000	0.0000000000	0.0000000000
C2	0.0000000000	0.0000000000	2.1219459270
O3	1.6324249718	0.0000000000	1.0859432683
C4	-0.1079194535	1.2339667540	2.7945964569

C5	-0.2246866376	-1.2240290252	2.7803526975
C6	-0.6279723370	1.2422975438	4.0816628067
H7	0.1644041369	2.1614057348	2.3010253241
C8	-0.7465623945	-1.1917855082	4.0694542755
H9	-0.0408295643	-2.1630315122	2.2714036650
C10	-0.9503825918	0.0335049007	4.7177040539
H11	-0.7723129287	2.1861578636	4.5983186717
H12	-0.9807994997	-2.1226934054	4.5765760000
H13	-1.3341288219	0.0470430411	5.7332824507
O14	-0.2333401742	-1.5164688318	-0.3006796470
Cl15	-1.9104842147	1.0375389601	-0.1278992745
Cl16	1.1793158097	0.8964178660	-1.6249684281
V17	3.2644195698	0.0279697697	1.6016487968
Cl18	4.5528229917	-1.0070903963	0.2551068432
Cl19	3.3434556002	-1.0014684122	3.4893872329
Cl20	3.8196316576	2.0834188409	1.8468442639

7

V1	0.0097577929	0.2653928479	-0.0314537537
C2	-0.0215947562	0.0080306397	2.8019494053
O3	0.8769846264	0.0345381537	1.7372871001
C4	-0.0951858238	1.1085726707	3.6463733183
C5	-0.8381615042	-1.1061868191	2.9487744699
C6	-1.0205262716	1.0814470272	4.6812332771
H7	0.5616863924	1.9604135663	3.4813080019
C8	-1.7614102209	-1.1110952505	3.9875100165
H9	-0.7394322636	-1.9417406791	2.2591895447
C10	-1.8512634865	-0.0238142702	4.8517584348
H11	-1.0948890236	1.9296696449	5.3565874837
H12	-2.4112558345	-1.9717697641	4.1216328879
H13	-2.5742134771	-0.0365450977	5.6633561722
O14	-0.3653033505	-1.1706507301	-0.5303357725
Cl15	-1.5053454239	1.8057467555	-0.1111947837
Cl16	2.0658662548	0.8553951920	-0.7631242383
V17	2.7429442824	-0.1032096431	1.7370535016
Cl18	3.7457146425	-1.6249424589	0.6638712775
Cl19	2.8588375551	-0.8915830186	3.7386601912
Cl20	3.7325016941	1.7596206726	2.0328231217

1-Me

V1	-1.0161310078	-1.3440117336	0.0360872784
O2	-0.9416471672	-0.2953303876	-1.1176325874
Cl3	0.3164374082	-2.9672170438	-0.3092364699
Cl4	-3.0318921423	-1.8702769657	0.4716120771
C5	-0.3212344697	-0.3187035577	1.5744276831
H6	-0.3378638325	-0.9871028586	2.4430080099
H7	0.6965098728	0.0047469665	1.3284074852
H8	-0.9717388914	0.5515875979	1.7173202506

1,7-TS-Me

V1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	1.9021751551
C3	2.0537951168	0.0000000000	1.5006733624
O4	0.2918227305	1.4707061025	-0.4623885454
Cl5	1.0914811657	-1.4716356412	-1.1786142885
Cl6	-2.1302351778	-0.4185539942	-0.1307064967
V7	-0.7660007824	-0.0362162658	3.4479992905
Cl8	-2.4451601910	1.2691009360	3.5746494912
Cl9	0.7171638246	0.6800052304	4.8468286496
Cl10	-1.2345927106	-2.0821269553	3.8621257182
H11	2.1927197371	-1.0653208187	1.6349247514
H12	2.4231624486	0.4380428325	0.5779592924
H13	2.1061602281	0.6307946469	2.3779584561

1,7-TS'-Me

V1	4.1504029446	-0.3011053542	1.2039665956
C2	1.9083388556	0.1393927268	1.7181092797
O3	0.0645261238	0.5284479936	2.1134561142
O4	4.6739844234	1.1744261542	1.1167730944
Cl5	4.8940789952	-1.3852387302	2.9103257294
Cl6	4.0759347676	-1.3083077214	-0.7000007218
V7	-0.7172971659	0.1075035863	3.4921578676
Cl8	-2.6819821329	0.9422165650	3.4942453643
Cl9	0.4674252514	0.8882519723	5.1059307562
Cl10	-0.7521647928	-2.0388625693	3.5316861684

H11	1.7347806920	-0.9327333245	1.7332824604
H12	1.8315839325	0.6847510215	0.7842102609
H13	2.2613291676	0.6517950815	2.6078730678

7-Me

V1	0.0469670155	-0.0030590212	-0.0136093373
O2	0.8509709477	0.0720930514	1.7859008900
O3	-0.3677364306	-1.5043148361	-0.1729131924
Cl4	-1.5224769080	1.4851612951	-0.1429764474
Cl5	2.0797404024	0.4511208410	-0.8812680092
V6	2.7111916842	0.0760960475	1.7661348544
Cl7	3.5917050208	-1.7314435702	1.0904164562
Cl8	2.9605588346	-0.2294505735	3.8963046349
Cl9	3.6829937619	1.9538320250	1.5975441113
C10	-0.0396294585	-0.2641511474	2.8667621529
H11	-1.0527808032	0.0314568045	2.5723253151
H12	0.0023695785	-1.3443346686	3.0390992705
H13	0.2589853566	0.2796012288	3.7654124541