Supplementary information to

Highly Correlated Ab Initio Thermodynamics of Oxymethylene Dimethyl Ethers (OME): Formation and Extension to the Liquid Phase

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1. Calculated CCSD(T) and MP2 energies.

All individual values contributing to the total energies of OME_n used to assess E_{comp} are compiled in S-Table 1.

S-Table 1: Components of the compound calculations to assess E_{comp} of OME_n (in Hartree).

n	$E_{CCSD(T)/A'VDZ}$	$E_{MP2/A'VDZ}$	$E_{MP2/A'VQZ}$	E_{comp}
FA	–114.242495	–114.216251	–114.348118	–114.374362
0	–154.640226	–154.586687	–154.781965	–154.835504
1	–268.908786	–268.830040	–269.158809	–269.237556
2	–383.176677	–383.072635	–383.534772	–383.638814
3	–497.444738	–497.315392	–497.910871	–498.040217
4	–611.712749	–611.558095	–612.286909	–612.441563
5	–725.980795	–725.800827	–726.662963	–726.842931
6	–840.248828	–840.043548	–841.039004	–841.244284
7	–954.516869	–954.286277	–955.415058	–955.64565

2. Benchmark 1: Several methods against CCSD(T)/A'VDZ – MP2(CBS) compound method

The method and basis set dependency of the general reaction 5 is exemplarily shown for OME5, i.e. reaction S1

$$5\ OME_1 \xrightarrow{\Delta E_{QM}} OME_5 + 4\ OME_0 \quad (S1)$$

is shown in S-Table 2.

S-Table 2: Method and basis set dependency of reaction S1.

	ΔE_{QM} kJ mol^{-1}	Δ fom ref. [kJ mol^{-1}]
BP86-D3(BJ)/def-TZVP	8.10	0.52
B3LYP-D3(BJ)/def2-TZVPP	6.85	–0.72
HF/A'VDZ	5.58	–1.99
HF/A'VTZ	5.98	–1.59
HF/A'VQZ	5.89	–1.68
HF/CBS(TZ,QZ)	5.86	–1.71
MP2/A'VDZ	6.89	–0.68
MP2/A'VTZ	8.34	0.77
MP2/A'VQZ	8.47	0.90
MP2/CBS(DZ,TZ,QZ)	8.51	0.93
MP2/CBS(TZ,QZ)	8.60	1.03
CCSD(T)/A'VDZ	5.86	–1.71
CCSD(T)/(DZ->QZ)	7.44	–0.13
CCSD(T)/(DZ->CBS(DZ,TZ,QZ))	7.48	–0.09
CCSD(T)/(DZ->CBS(TZ,QZ))	7.57(= ref.)	0.00

CBS(DZ, TZ, QZ) MP2 energies were extrapolated with X = 2 for DZ, 3 for TZ, 4 for QZ:

$$E_{MP2}(\infty) = E_{MP2}(X) + B \times \exp\big(-(X-1)\big) + C \times \exp(-(X-1)^2) \quad \text{(S2)}$$

(See ref. [1] for details)

CBS(TZ, QZ) HF and (MP2) correlation energies were extrapolated with X = 3 for TZ, 4 for QZ:

$$E_{HF}(\infty) = E_{HF}(X) + B \times X^{-5}$$
$$E_{correl}(\infty) = E_{correl}(X) + B \times X^{-3} \quad \text{(S3)}$$

(See ref. [2] for details)

3. Benchmark 2: CCSD(T)/(DZ->QZ) and W1 method

S-Table 3: W1[3] energetics calculated with Gaussian 03[4] (keyword: "w1u").

	W1-E_{QM}	W1-$H°$(298.15)	W1-$G°$(298.15)
OME_0	-155.090354	-155.006920	-155.037053
OME_1	-269.678875	-269.560080	-269.596967
OME_2	-384.266658	-384.112550	-384.155570
HCHO	-114.561056	-114.531117	-114.555929

Note: W1-E_{QM} was calculated via W1-E_{QM} = W1(0K) – E(ZPE)

A) Comparison of compound method and W1 for a non-isodesmic reaction.

$$OME_0 + HCHO \longrightarrow OME_1 \quad \text{(S4)}$$

S-Table 4: Energetics for reaction S4.

	ΔE_{QM} [kJ mol^{-1}]	$\Delta H°$(298.15 K) [kJ mol^{-1}]	$\Delta G°$(298.15 K) [kJ mol^{-1}]
MP2/A'VDZ	–68.43		
MP2/A'VQZ	–71.16		
CCSD(T)/A'VDZ	–75.42		
E_{comp}	–72.70	–58.89	–14.23
W1	–72.11	–57.87	–10.46
exp.		–55.50	–10.93

B) Comparison of compound method and W1 for an isodesmic reaction.

$$2\ OME_1 \xrightarrow{\Delta E_{QM}} OME_2 + OME_0 \quad (S5)$$

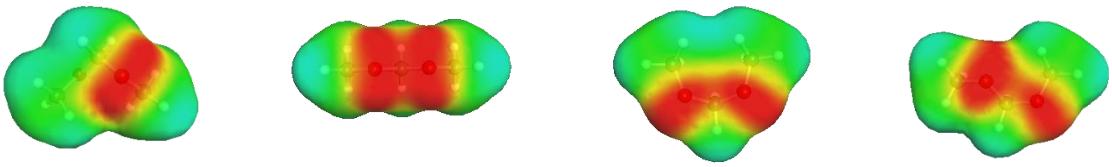
S-Table 5: Energetics for reaction S5.

	ΔE_{QM} [kJ mol^{-1}]	Δ fom ref. [kJ mol^{-1}]
MP2/A'VDZ	–1.99	–0.05
MP2/A'VQZ	–2.32	–0.38
CCSD(T)/A'VDZ	–1.76	0.18
E_{comp}	–2.08	–0.15
W1	–1.94 (= ref.)	0.00

4. COSMO-RS: Only lowest conformer against full conformer treatment.

Influence of energetically higher conformers on COSMO-RS[5] solvation thermodynamics of OME1. Version: COSMOthermX[6,7] C30_1501, BP86-D3/def2-TZVPD//BP86-D3/def-TZVP:

The four lowest energy conformers of OME1 (without enantiomers):



OME1_c0 OME1_c1 OME1_c2 OME1_c3

S-Table 6: Conformer ratio in gas and liquid phase (from COSMOTHERM[6,7] output).

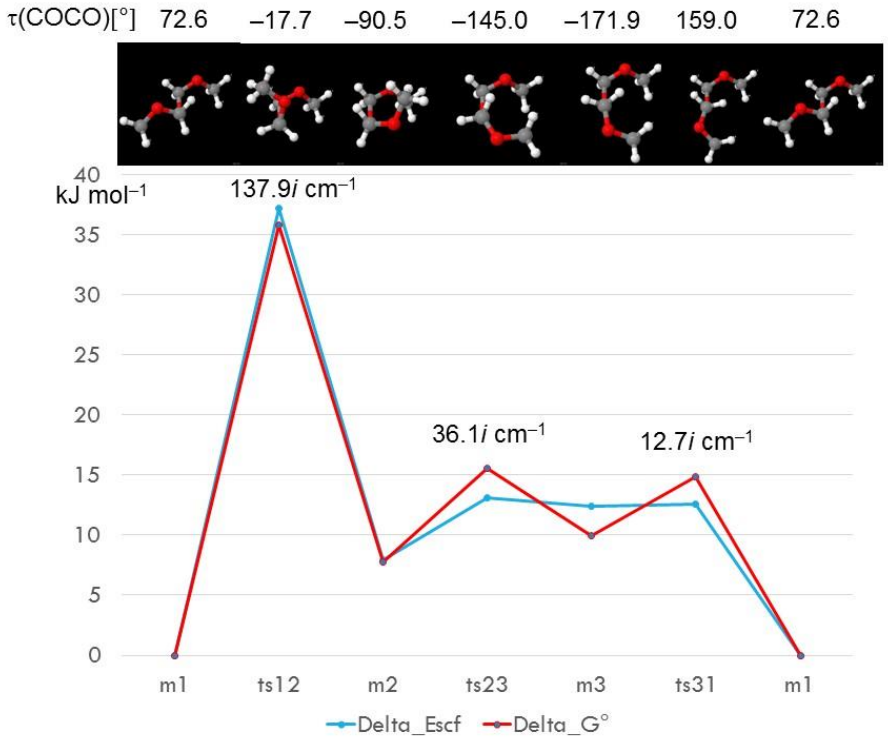
	%(gas)	%(liquid)
OME1_c0	98.789	97.461
OME1_c1	0.004	0.024
OME1_c2	0.432	1.152
OME1_c3	0.776	1.363

S-Table 7: Effect on higher conformer neglect.

	$\Delta_{vap}H°$ [kJ mol^{-1}]	$\Delta_{vap}G°$ [kJ mol^{-1}]
only OME1_c0	29.08	1.32
4 conformers	28.98	1.37

5. Internal rotation of OME2 C-O-bond.

Only minima and transition states were searched. Method: BP86-D3(BJ)/def-TZVP



S-Figure 1: Energy profile of rotation around one of the internal CO bonds in OME$_1$. Only minima and transition states were calculated.

S-Table 8: Details to S-Figure 1. Values in kJ mol^{-1}.

	ΔE_{scf}	$\Delta(E_{scf}$+ZPE)	ΔH°(298.15)	ΔG°(298.15)
m1	0.00	0.00	0.00	0.00
ts12	37.15	34.55	33.37	35.79
m2	7.92	7.62	7.45	7.75
ts23	13.09	11.99	9.97	15.57
m3	12.36	11.36	11.65	9.91
ts31	12.58	11.38	9.29	14.80
m1	0.00	0.00	0.00	0.00

Note: The calculated minimum 3 (m3) is extremely shallow, and due to the method and basis set error, it is unclear if it exists in reality.

6. B3LYP-D3(BJ)/def2-TZVPP cartesian coordinates in Å.

HCHO

C	0.00000	0.00000	-0.00626
O	0.00000	0.00000	1.19285
H	-0.93827	0.00000	-0.59330
H	0.93827	0.00000	-0.59330

OME_0

C	0.00000	-1.17210	0.04606
O	0.00000	0.00000	0.82911
C	0.00000	1.17210	0.04606
H	-0.89003	1.22714	-0.59402
H	0.89003	1.22714	-0.59402
H	0.00000	2.02077	0.72742
H	0.89003	-1.22714	-0.59402
H	-0.89003	-1.22714	-0.59402
H	0.00000	-2.02077	0.72742

OME_1

C	0.00000	-0.00000	-1.03229
H	0.89265	-0.11654	-1.65522
O	-0.07456	-1.17212	-0.26818
H	-0.89265	0.11654	-1.65522
O	0.07456	1.17212	-0.26818
C	1.28360	1.29588	0.46605
C	-1.28360	-1.29588	0.46605
H	1.24833	2.25626	0.97528
H	2.15046	1.27462	-0.20433
H	1.38964	0.49630	1.20256
H	-1.24833	-2.25626	0.97528
H	-2.15046	-1.27462	-0.20433
H	-1.38964	-0.49630	1.20256

OME_2

C	-2.53031	1.34531	0.10782
O	-1.44199	1.21491	-0.79528
H	-2.42284	2.24920	0.71819
H	-2.60781	0.48017	0.76971
H	-3.43295	1.42444	-0.49353
C	-0.19276	1.16962	-0.17096
H	0.54645	1.23120	-0.96992
O	0.00000	-0.00000	0.60047
H	-0.07362	1.99814	0.53373
C	0.19276	-1.16962	-0.17096
H	0.07362	-1.99814	0.53373
O	1.44199	-1.21491	-0.79528
H	-0.54645	-1.23120	-0.96992
C	2.53031	-1.34531	0.10782
H	3.43295	-1.42444	-0.49353
H	2.42284	-2.24920	0.71819
H	2.60781	-0.48017	0.76971

OME_3

C	-3.07636	2.06427	-0.56988
O	-1.79785	2.27400	0.01294
H	-3.09084	1.16671	-1.19169
H	-3.29061	2.93547	-1.18442
H	-3.84581	1.97066	0.20476
C	-1.40612	1.26267	0.89318
H	-0.50001	1.62095	1.38206
O	-1.17109	0.02560	0.24759
H	-2.18840	1.05415	1.62902
C	-0.00000	0.00000	-0.53761
H	-0.07619	-0.89478	-1.15476
O	1.17109	-0.02560	0.24759
H	0.07619	0.89478	-1.15476
C	1.40612	-1.26267	0.89318
O	1.79785	-2.27400	0.01294
H	0.50001	-1.62095	1.38206
H	2.18840	-1.05415	1.62902
C	3.07636	-2.06427	-0.56988
H	3.29061	-2.93547	-1.18442
H	3.84581	-1.97066	0.20476
H	3.09084	-1.16671	-1.19169

OME_4

C	-2.58768	1.32200	0.27903
O	-1.48999	1.13622	-0.59535
C	-0.23444	1.16154	0.04464
H	0.50327	1.25965	-0.75117
O	0.00000	-0.00000	0.81076
H	-0.16794	1.99469	0.74364
C	0.23444	-1.16154	0.04464
H	0.16794	-1.99469	0.74364
O	1.48999	-1.13622	-0.59535
H	-0.50327	-1.25965	-0.75117
C	2.58768	-1.32200	0.27903
O	2.69222	-2.63043	0.75540
H	2.49154	-0.68578	1.15897
H	3.46757	-1.04323	-0.30823
C	3.02483	-3.58159	-0.24607
H	3.13201	-4.54181	0.25294
H	3.97146	-3.31931	-0.73181
H	2.24504	-3.65108	-1.00736
O	-2.69222	2.63043	0.75540
H	-2.49154	0.68578	1.15897
H	-3.46757	1.04323	-0.30823
C	-3.02483	3.58159	-0.24607
H	-3.13201	4.54181	0.25294
H	-3.97146	3.31931	-0.73181
H	-2.24504	3.65108	-1.00736

OME_5

C	-3.25703	1.89152	-0.79603
O	-1.95481	2.13035	-0.29410
C	-1.49310	1.14323	0.59930
H	-0.61683	1.56902	1.08710

O	-1.16955	-0.06382	-0.05713
H	-2.25993	0.88578	1.32920
C	-0.00000	0.00000	-0.84277
H	-0.00799	-0.89774	-1.45992
O	1.16955	0.06382	-0.05713
H	0.00799	0.89774	-1.45992
C	1.49310	-1.14323	0.59930
O	1.95481	-2.13035	-0.29410
H	0.61683	-1.56902	1.08710
H	2.25993	-0.88578	1.32920
C	3.25703	-1.89152	-0.79603
O	-4.25552	2.08178	0.16114
H	-3.35559	0.86066	-1.13647
H	-3.37066	2.58934	-1.63080
C	-4.40785	3.43339	0.57162
H	-5.24323	3.46036	1.26725
H	-4.63149	4.07696	-0.28663
H	-3.50855	3.80546	1.06685
O	4.25552	-2.08178	0.16114
H	3.35559	-0.86066	-1.13647
H	3.37066	-2.58934	-1.63080
C	4.40785	-3.43339	0.57162
H	5.24323	-3.46036	1.26725
H	4.63149	-4.07696	-0.28663
H	3.50855	-3.80546	1.06685

OME_6

C	0.69405	-0.96029	0.17138
O	-0.17712	-1.87254	0.80131
C	-0.79128	-2.78950	-0.07916
O	0.11691	-3.74700	-0.57269
C	0.50933	-4.71692	0.38139
O	-0.50805	-5.62107	0.69226
O	0.00000	-0.00000	-0.59457
C	-0.69405	0.96029	0.17138
O	0.17712	1.87254	0.80131
C	0.79128	2.78950	-0.07916
O	-0.11691	3.74700	-0.57269
C	-0.50933	4.71692	0.38139
O	0.50805	5.62107	0.69226
C	0.86267	6.47947	-0.38302
C	-0.86267	-6.47947	-0.38302
H	1.35841	-1.47075	-0.52502
H	1.25883	-0.48664	0.97362
H	-1.19261	-2.28013	-0.95464
H	-1.58629	-3.26300	0.49593
H	0.79012	-4.24140	1.32126
H	1.36702	-5.22523	-0.06883
H	-1.25883	0.48664	0.97362
H	-1.35841	1.47075	-0.52502
H	1.19261	2.28013	-0.95464
H	1.58629	3.26300	0.49593
H	-0.79012	4.24140	1.32126
H	-1.36702	5.22523	-0.06883
H	1.61484	7.16707	-0.00370

H	-0.00719	7.04986	-0.72772
H	1.27290	5.91818	-1.22508
H	-1.61484	-7.16707	-0.00370
H	0.00719	-7.04986	-0.72772
H	-1.27290	-5.91818	-1.22508

OME_7

C	-0.00000	0.00000	-0.64740
O	-0.68339	0.95107	0.13871
C	0.15939	1.87144	0.79742
O	0.74154	2.79561	-0.09385
C	-0.16036	3.75353	-0.60629
O	-0.55135	4.69357	0.36750
O	0.68339	-0.95107	0.13871
C	-0.15939	-1.87144	0.79742
O	-0.74154	-2.79561	-0.09385
C	0.16036	-3.75353	-0.60629
O	0.55135	-4.69357	0.36750
C	-0.45766	-5.62725	0.70711
O	-0.70539	-6.55651	-0.30482
C	0.45766	5.62725	0.70711
O	0.70539	6.55651	-0.30482
C	-0.37250	7.45211	-0.53902
C	0.37250	-7.45211	-0.53902
H	0.76100	0.47650	-1.26442
H	-0.76100	-0.47650	-1.26442
H	0.99130	1.36174	1.28212
H	-0.46931	2.37642	1.52993
H	-1.07930	3.27929	-0.94932
H	0.36102	4.23744	-1.43150
H	-0.99130	-1.36174	1.28212
H	0.46931	-2.37642	1.52993
H	1.07930	-3.27929	-0.94932
H	-0.36102	-4.23744	-1.43150
H	-1.40488	-5.12052	0.89237
H	-0.09483	-6.11764	1.61517
H	1.40488	5.12052	0.89237
H	0.09483	6.11764	1.61517
H	-0.04029	8.15459	-1.29967
H	-0.62597	8.00183	0.37440
H	-1.26144	6.92535	-0.89215
H	0.04029	-8.15459	-1.29967
H	0.62597	-8.00183	0.37440
H	1.26144	-6.92535	-0.89215

References

1 K. A. Peterson, D. E. Woon and T. H. Dunning, *J. Chem. Phys.*, 1994, **100**, 7410–7415.

2 A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen and A. K. Wilson, *Chem. Phys. Lett.*, 1998, **286**, 243–252.

3 J. M. L. Martin and G. de Oliveira, *The Journal of Chemical Physics*, 1999, **111**, 1843–1856.

4 Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, Cheeseman, JR, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, A. Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision C.02*.

5 a) A. Klamt, *J. Phys. Chem.*, 1995, **99**, 2224–2235; b) A. Klamt, V. Jonas, T. Bürger and J. C. W. Lohrenz, *J. Phys. Chem. A*, 1998, **102**, 5074–5085.

6 F. Eckert and A. Klamt, *AIChE J.*, 2002, **48**, 369–385.

7 F. Eckert and A. Klamt, *COSMOTherm*, COSMOtherm, C3.0, release 1501, COSMOlogic GmbH & Co KG, http://www.cosmologic.de, 2015.