Electronic Supplementary Information

The unimolecular decomposition of dimethoxymethane: channel switching as a function of temperature and pressure

Tobias M. Pazdera, Johannes Wenz and Matthias Olzmann*

Institut für Physikalische Chemie, Karlsruher Institut für Technologie (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany. E-mail: matthias.olzmann@kit.edu

Fig. S1 Geometries of the stationary points for reactions (R1)–(R10); for Cartesian coordinates see Table S1.

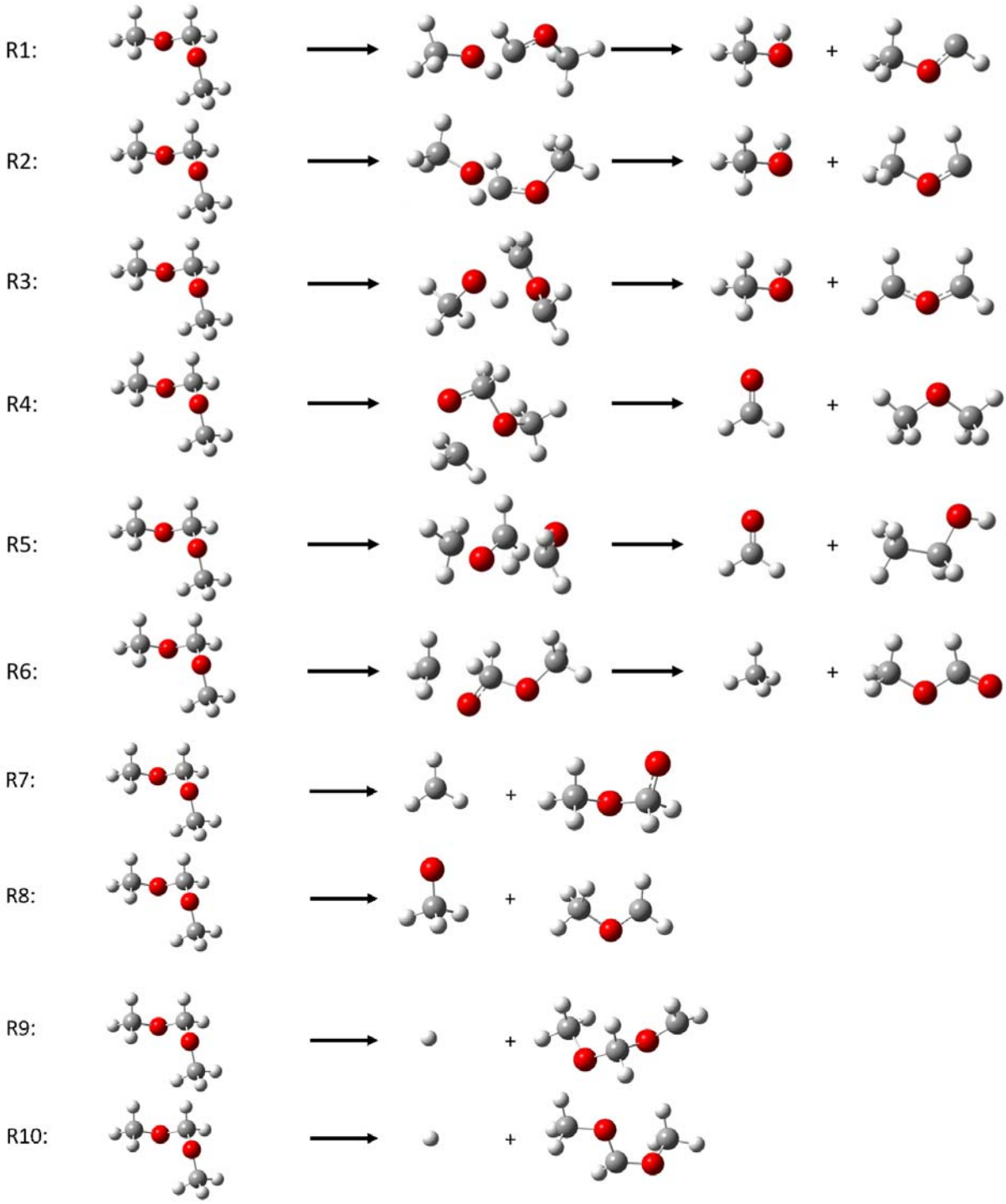

Table S1 Cartesian coordinates (in Å) of reactants, transition states and products in reactions (R1) to (R10) from B2PLYP-D3/def2-TZVPP calculations

Species	Atom	*x*	*y*	*z*
H	H	0	0	0
DMM	C	0.000000	0.000000	0.930333
	H	-0.710583	0.551249	1.550536
	H	0.710583	-0.551249	1.550536
	H	0.778560	0.877733	0.165382
	O	0.000000	1.813257	-0.566112
	C	-0.627951	2.404283	0.106697
	H	0.695755	2.470960	-1.077679
	H	-0.638367	1.316637	-1.296932
	O	-0.777856	-0.877733	0.165382
	C	0.000000	-1.813257	-0.566112
	H	-0.695755	-2.470960	-1.077679
	H	0.638367	-1.316637	-1.296932
	H	0.627951	-2.404283	0.106697
TS 1	C	2.107197	-0.635103	0.081258
	H	3.144398	-0.520570	-0.211867
	H	2.012311	-0.767226	1.155119
	H	1.646082	-1.465022	-0.445839
	O	1.428950	0.576590	-0.317320
	C	0.331928	0.844224	0.323587
	H	-0.431867	-0.083631	0.682999
	H	-0.112679	1.738198	-0.116794
	O	-1.176602	-0.649844	-0.107745
	C	-2.428397	-0.009736	-0.020506
	H	-2.723424	0.423354	-0.980888
	H	-3.193116	-0.728976	0.283606
	H	-2.424855	0.793589	0.728149
TS 2	O	-1.404860	-0.562673	-0.179294
	C	-2.198259	0.633165	-0.011476
	H	-1.828773	1.383776	-0.704653
	H	-3.223148	0.369770	-0.247072
	H	-2.116378	0.988686	1.013627
	C	-0.296928	-0.687663	0.486357
	H	0.757164	-0.955615	-0.174450
	H	-0.182893	0.076570	1.266266
	O	1.345220	-0.039178	-0.678277
	C	2.354541	0.331837	0.234488
	H	3.337169	0.160134	-0.210078
	H	2.272735	1.388713	0.504189
	H	2.305120	-0.261257	1.156521
TS 3	C	1.296067	-1.058241	0.121235
	H	1.763142	-1.714747	-0.604035

	H	1.944272	-0.919857	0.989526
	H	-0.220246	-0.770477	0.582806
	O	1.188303	0.241917	-0.560769
	C	0.668927	1.164236	0.128503
	H	0.315493	2.032022	-0.411712
	H	0.802605	1.200212	1.201158
	O	-1.028596	-0.043642	0.714102
	C	-1.885249	-0.212810	-0.399498
	H	-1.323878	-0.289531	-1.335538
	H	-2.478231	-1.123418	-0.288543
	H	-2.559275	0.640487	-0.461761
TS 4	C	-0.669550	1.433850	0.058662
	H	-0.799091	1.422453	1.127780
	H	-1.565939	1.603415	-0.509591
	H	0.174661	2.016727	-0.285941
	O	-1.579074	-0.451994	0.039644
	C	-0.434532	-1.084121	0.066182
	H	-0.037978	-1.370190	1.060646
	H	-0.329072	-1.918583	-0.641580
	O	0.532469	-0.030874	-0.432294
	C	1.838287	-0.004077	0.137720
	H	2.441140	-0.807813	-0.281451
	H	2.291381	0.948232	-0.127583
	H	1.792500	-0.105201	1.223534
TS 5	C	1.890134	-0.448376	0.000000
	H	2.398748	-0.779736	-0.915401
	H	0.894622	-1.135247	0.000006
	H	2.398750	-0.779724	0.915405
	O	1.453914	0.801443	-0.000007
	C	-0.428551	0.538634	-0.000003
	H	-0.478408	1.074804	0.936935
	H	-0.478410	1.074791	-0.936948
	O	-0.494525	-0.812432	0.000006
	C	-2.260587	0.011560	0.000003
	H	-2.516904	-0.512791	-0.906733
	H	-2.516902	-0.512779	0.906747
	H	-2.582581	1.047689	-0.000003
TS 6	C	-2.218793	0.410109	0.113140
	H	-3.101915	0.102973	-0.437159
	H	-2.360984	0.200896	1.174263
	H	-2.067673	1.482633	-0.026777
	O	-1.125100	-0.334468	-0.409964
	C	0.109546	-0.052022	0.148464
	H	-0.033902	0.493236	1.097513
	H	0.673493	0.825359	-0.491483
	O	0.924718	-1.076843	0.138347
	C	2.282525	0.651405	-0.076342

	H	2.209031	1.720106	0.086513
	H	2.719484	0.090520	0.730209
	H	2.525847	0.317812	-1.071710
***trans*-CH_3OCH**	C	-1.115824	0.134104	0.000000
	H	-1.625993	-0.222298	0.889572
	H	-1.019361	1.215252	-0.000009
	H	-1.625998	-0.222312	-0.889564
	O	0.208029	-0.448137	0.000000
	C	1.203381	0.384138	0.000000
	H	2.081777	-0.294998	0.000000
***cis*-CH_3OCH**	O	-0.208753	-0.499225	0.000000
	C	1.088304	0.159901	0.000000
	H	1.618454	-0.164819	0.889610
	H	1.618451	-0.164812	-0.889614
	H	0.940852	1.238183	0.000005
	C	-1.326940	0.147444	0.000000
	H	-1.075914	1.241174	0.000000
CH_2OCH_2	C	-1.184239	0.152124	0.000001
	H	-2.006038	-0.536439	-0.000009
	H	-1.269194	1.227732	0.000003
	O	0.000000	-0.401010	0.000000
	C	1.184239	0.152124	0.000005
	H	2.006039	-0.536438	-0.000010
	H	1.269192	1.227732	-0.000015
CH_3OCHO	C	1.674386	0.110268	-0.000005
	H	2.206498	-0.216103	-0.888796
	H	1.599975	1.197459	0.000133
	H	2.206598	-0.216320	0.888644
	O	0.379932	-0.496379	0.000007
	C	-0.692263	0.316153	0.000004
	H	-0.422223	1.383741	0.000016
	O	-1.815380	-0.092034	-0.000006
CH_3CH_2OH	C	0.081121	0.549331	-0.000002
	H	0.137658	1.191432	0.883883
	H	0.137654	1.191430	-0.883889
	C	-1.218063	-0.223388	0.000002
	H	-1.281918	-0.857036	-0.882537
	H	-1.281915	-0.857030	0.882546
	H	-2.066985	0.459028	0.000002
	O	1.149471	-0.395636	-0.000005
	H	1.981393	0.081607	0.000037
CH_2OCH_3	C	1.134078	0.169624	0.012650
	H	1.929449	-0.554279	-0.129635
	H	1.173871	0.917754	-0.781583
	H	1.252189	0.661511	0.978749
	O	-0.091787	-0.545476	-0.036932
	C	-1.197181	0.228141	0.066536

	H	-1.122284	1.269324	-0.217790
	H	-2.120307	-0.317098	-0.029403
OCH_2OCH_3	C	-1.438805	0.391556	0.090675
	H	-2.398844	0.147685	-0.351822
	H	-1.539261	0.414648	1.180207
	H	-1.115261	1.371553	-0.259140
	O	-0.530183	-0.624240	-0.309853
	C	0.750969	-0.453546	0.216539
	H	0.724983	-0.424210	1.326895
	H	1.327711	-1.344920	-0.064815
	O	1.421144	0.650138	-0.149473
$CH_2OCH_2OCH_3$	C	1.791307	-0.683221	0.145769
	H	2.822037	-0.679066	-0.192704
	H	1.766913	-0.777742	1.234904
	H	1.261848	-1.523654	-0.300302
	O	1.222806	0.555429	-0.261152
	C	-0.059012	0.747284	0.197604
	H	-0.133074	0.582960	1.281503
	H	-0.346733	1.765789	-0.056849
	O	-0.943741	-0.168107	-0.449954
	C	-2.158185	-0.293197	0.136923
	H	-2.811092	-0.990301	-0.358540
	H	-2.237085	-0.101752	1.199062
$CH_3OCHOCH_3$	C	-1.939941	0.577221	0.160741
	H	-2.950476	0.497278	-0.225758
	H	-1.965208	0.619189	1.251531
	H	-1.462093	1.473747	-0.229476
	O	-1.241582	-0.598919	-0.276725
	C	0.034607	-0.699135	0.141909
	H	0.203872	-0.943948	1.194446
	O	0.855337	0.256563	-0.378262
	C	2.185422	0.203227	0.119099
	H	2.668218	-0.730614	-0.168794
	H	2.717327	1.040268	-0.319789
	H	2.197789	0.295060	1.207245
CH_3OH	C	0.665271	-0.019931	0.000000
	H	1.080865	0.983508	0.000029
	H	1.026000	-0.542515	-0.888664
	H	1.025996	-0.542564	0.888637
	O	-0.748039	0.121758	0.000000
	H	-1.140175	-0.752909	0.000000
CH_3OCH_3	O	0.000000	0.592968	0.000000
	C	-1.167332	-0.196641	0.000000
	H	-2.018149	0.478591	0.000000
	H	-1.216560	-0.835308	0.888408
	H	-1.216560	-0.835309	-0.888408
	C	1.167332	-0.196641	0.000000

	H	1.216560	-0.835309	0.888408
	H	2.018149	0.478591	0.000000
	H	1.216560	-0.835308	-0.888408
CH_4	C	0.000000	0.000000	0.000000
	H	0.627265	0.627265	0.627265
	H	-0.627265	-0.627265	0.627265
	H	-0.627265	0.627265	-0.627265
	H	0.627265	-0.627265	-0.627265
H_2CO	C	0.000000	0.529073	0.000000
	H	0.935705	1.112168	0.000000
	H	-0.935705	1.112167	0.000000
	O	0.000000	-0.674846	0.000000
CH_3	C	0.000000	0.000000	0.000000
	H	-0.169549	1.062417	0.000000
	H	1.004854	-0.384375	0.000000
	H	-0.835306	-0.678042	0.000000
CH_3O	C	-0.575986	0.000001	-0.012768
	O	0.791092	0.000001	-0.007586
	H	-0.867817	-0.000044	1.050778
	H	-1.002505	0.904695	-0.456708
	H	-1.002499	-0.904662	-0.456775

Table S2 Unscaled harmonic wavenumbers (in cm^{-1}) and rotational constants (in cm^{-1}) of reactants, transition states and products in reactions (R1)–(R10) from B2PLYP-D3/def2-TZVPP calculations

Species	**Harmonic wavenumbers**	**Rotational constants**
H	-	-
DMM	93.49, 133.90, 157.94, 224.35, 322.38, 455.17, 608.07, 936.94, 950.92, 1074.43, 1146.11, 1169.77, 1187.83 1188.89, 1222.26, 1264.99, 1345.62, 1439.11, 1479.67, 1492.726, 1501.80, 1502.45, 1517.38, 1522.81, 1530.56, 3023.72, 3024.75, 3032.88, 3087.66, 3095.35, 3095.66, 3158.00, 3158.27	0.34401 0.10905 0.10239
TS 1	1265.10i, 74.82, 99.72, 101.17, 152.18, 208.03, 228.43, 504.00, 559.69, 936.83, 957.99, 1058.18, 1169.56, 1176.53, 1185.46, 1199.17, 1344.30, 1380.00, 1476.63, 1489.61, 1500.04, 1502.95, 1513.85, 1514.36, 1556.36, 1896.95, 2973.56, 3033.70, 3059.55, 3082.57, 3101.71, 3176.19, 3194.37	0.42728 0.07401 0.06645
TS 2	1280.22i, 77.10, 99.70, 136.26, 157.42, 195.01, 302.83, 498.54, 531.33, 930.62, 1000.26, 1053.43, 1170.07, 1171.93, 1178.71, 1190.96, 1333.24, 1381.69, 1476.85, 1487.02, 1497.32, 1504.09, 1513.71, 1514.16, 1528.88, 1928.37, 2980.92, 3012.55, 3041.75, 3069.58, 3070.31, 3160.25, 3188.89	0.43368 0.06938 0.06751
TS 3	795.84i, 79.58, 152.55, 159.45, 245.24, 394.60, 407.26, 501.45, 681.64, 751.11, 971.55, 1064.60, 1082.73, 1106.93, 1186.53, 1190.21, 1227.80, 1288.06, 1428.88, 1479.25,	0.26497 0.11175

	1485.56, 1506.90, 1517.11, 1586.11, 1599.62, 1702.97, 3013.90, 3052.62, 3069.90, 3109.80, 3136.80, 3178.83, 3264.13	0.09733
TS 4	663.92i, 116.56, 132.21, 139.54, 225.66, 333.34, 472.77, 534.61, 710.33, 844.28, 974.54, 1035.05, 1121.21, 1174.67, 1196.83, 1212.95, 1271.69, 1297.36, 1374.95, 1448.44, 1464.72, 1494.74, 1500.17, 1516.19, 1555.31, 2858.74, 2973.18, 3039.91, 3114.10, 3118.82, 3145.08, 3247.40, 3310.06	0.25591 0.14237 0.10026
TS 5	1182.08i, 124.66, 182.72, 270.08, 274.73, 359.76, 454.21, 472.61, 616.22, 912.35, 933.33, 1000.57, 1056.27, 1091.52, 1170.28, 1178.69, 1200.38, 1260.55, 1273.91, 1298.02, 1423.06, 1463.98, 1475.98, 1521.11, 1523.34, 1914.71, 2953.80, 3014.54, 3099.49, 3118.56, 3229.14, 3242.96, 3279.89	0.44257 0.09277 0.08043
TS 6	1798.87i, 83.04, 126.78, 194.81, 248.85, 281.04, 400.09, 455.48, 553.07, 800.21, 908.28, 987.35, 1072.42, 1117.21, 1177.15, 1201.18, 1229.08, 1249.18, 1375.44, 1420.61, 1437.09, 1481.24, 1484.74, 1510.28, 1511.68, 1978.31, 2895.09, 3032.27, 3096.18, 3107.25, 3165.01, 3262.28, 3312.67	0.40537 0.08314 0.07394
***trans*-CH_3OCH**	147.38, 520.70, 737.95, 924.63, 1177.59, 1199.42, 1351.46, 1430.04, 1475.85, 1504.06, 1511.09, 2882.28, 3079.00, 3176.96, 3186.14	1.99998 0.37231 0.33370
***cis*-CH_3OCH**	134.05, 541.15, 722.42, 874.84, 1169.39, 1175.99, 1337.35, 1439.54, 1485.63, 1492.14, 1509.88, 2744.27, 3064.31, 3167.06, 3182.93	1.83433 0.37657 0.33206
CH_2OCH_2	312.43, 436.80, 450.15, 547.80, 672.11, 1103.32, 1154.37, 1269.36, 1454.26, 1490.04, 1523.96, 3169.61, 3178.61, 3342.43, 3344.97	2.51487 0.37448 0.32594
CH_3OCHO	50.23, 191.98, 382.06, 642.42, 1033.19, 1037.88, 1124.86, 1188.71, 1272.23, 1417.50, 1497.63, 1500.85, 1529.67, 1822.16, 2986.62, 3061.24, 3143.65, 3162.83	1.62029 0.15598 0.14622
CH_3CH_2OH	238.59, 281.25, 418.90, 825.91, 907.19, 1045.60, 1111.24, 1189.34, 1277.31, 1311.12, 1415.29, 1464.34, 1495.98, 1514.26, 1542.31, 3013.98, 3044.02, 3063.09, 3136.37, 3142.22, 3859.50	1.17657 0.31378 0.27294
CH_2OCH_3	165.63, 302.42, 434.52, 587.09, 968.71, 1146.82, 1183.04, 1262.09, 1294.59, 1472.96, 1504.64, 1510.46, 1519.17, 3035.30, 3099.35, 3140.96, 3167.85, 3293.69	1.57726 0.35887 0.31078
OCH_2OCH_3	133.98, 190.46, 350.29, 602.21, 783.38, 938.68, 1054.87, 1123.66, 1184.97, 1193.45, 1264.43, 1346.58, 1390.57, 1487.65, 1503.34, 1526.02, 2851.52, 2997.64, 3020.48, 3099.09, 3166.03	0.62630 0.19549 0.16622
$CH_2OCH_2OCH_3$	61.61, 135.96, 186.60, 293.23, 346.56, 395.95, 565.21, 586.46, 952.59, 970.92, 1126.47, 1182.47, 1199.81, 1210.48, 1245.17, 1269.24, 1323.42, 1444.60, 1485.95, 1500.03, 1503.72, 1524.71, 1534.49, 2976.72, 3029.48, 3109.59, 3110.58, 3139.42, 3167.74, 3295.69	0.46069 0.09995 0.09106
$CH_3OCHOCH_3$	61.16, 97.11, 160.77, 174.65, 311.29, 361.70, 579.88, 875.89, 956.58, 1032.46, 1153.25, 1169.70, 1183.79, 1187.15, 1241.55, 1265.73, 1363.98, 1480.05, 1497.05, 1502.39,	0.53850 0.09258 0.08613

	1505.47, 1519.37, 1520.45, 3030.27, 3037.52, 3042.52, 3101.92, 3119.23, 3169.63, 3170.48	
CH_3OH	298.01, 1055.07, 1090.51, 1182.58, 1382.44, 1494.51, 1512.13, 1526.15, 3025.55, 3078.04, 3146.87, 3865.85	4.30422 0.82737 0.79864
CH_3OCH_3	212.46, 251.24, 416.28, 950.51, 1128.93, 1173.70, 1205.20, 1207.36, 1279.22, 1472.37, 1497.66, 1501.85, 1506.74, 1513.22, 1529.92, 2993.57, 3003.61, 3043.29, 3048.61, 3146.59, 3147.96	1.30810 0.33674 0.29792
CH_4	1353.67, 1353.67, 1353.67, 1574.66, 1574.66, 3055.68, 3168.26, 3168.26, 3168.26	5.31397 5.31397 5.31397
H_2CO	1208.59, 1274.97, 1545.35, 1790.59, 2929.16, 2991.70	9.55220 1.29926 1.14370
CH_3	521.16, 1429.38, 1429.38, 3143.69, 3324.78, 3324.78	9.63403 9.63403 4.81701
CH_3O	737.23, 965.19, 1116.49, 1387.00, 1389.06, 1530.14, 2943.30, 3020.68, 3064.97	5.29243 0.93393 0.92806

Table S3 'log *p*' parameterization of the rate coefficients of reactions (R1)–(R10) in OpenSMOKE++ (≡ CHEMKIN-PRO) format for T = 800–1800 K [a]

CH3OCH2OCH3=>CH3OH+trans-CH3OCH		1.39E+86	-22.49	95165.96
PLOG /	1.00E-05	1.39E+86	-22.49	95165.96 /
PLOG /	1.00E-04	1.39E+86	-22.12	98019.82 /
PLOG /	1.00E-03	1.39E+86	-21.77	101073.70 /
PLOG /	1.00E-02	1.39E+86	-21.46	104072.17 /
PLOG /	1.00E-01	1.39E+86	-21.18	107015.20 /
PLOG /	1.00E+00	1.39E+86	-20.92	109898.97 /
PLOG /	1.00E+01	1.39E+86	-20.69	112591.12 /
PLOG /	1.00E+02	1.63E+65	-14.54	101241.93 /
PLOG /	1.00E+03	1.91E+36	-6.18	84004.83 /
CH3OCH2OCH3=>CH3OH+ cis-CH3OCH		3.16E+84	-22.30	95249.75
PLOG /	1.00E-05	3.16E+84	-22.30	95249.75 /
PLOG /	1.00E-04	3.16E+84	-21.89	98142.26 /
PLOG /	1.00E-03	3.16E+84	-21.52	101272.56 /
PLOG /	1.00E-02	3.16E+84	-21.18	104392.10 /
PLOG /	1.00E-01	3.16E+84	-20.88	107509.39 /
PLOG /	1.00E+00	3.16E+84	-20.59	110614.06 /
PLOG /	1.00E+01	3.16E+84	-20.34	113546.97 /
PLOG /	1.00E+02	3.89E+67	-15.31	105043.26 /
PLOG /	1.00E+03	2.37E+38	-6.85	87783.74 /

```
CH3OCH2OCH3=> CH3OH+CH2OCH2          2.97E+83   -23.06    97453.11
PLOG /                 1.00E-05   2.97E+83   -23.06    97453.11 /
PLOG /                 1.00E-04   2.97E+83   -22.47   100516.32 /
PLOG /                 1.00E-03   2.97E+83   -21.97   103873.53 /
PLOG /                 1.00E-02   2.97E+83   -21.54   107340.60 /
PLOG /                 1.00E-01   2.97E+83   -21.14   110982.84 /
PLOG /                 1.00E+00   2.97E+83   -20.77   114799.58 /
PLOG /                 1.00E+01   2.97E+83   -20.43   118550.32 /
PLOG /                 1.00E+02   2.88E+75   -17.87   116632.62 /
PLOG /                 1.00E+03   7.72E+45    -9.26    99677.92 /

CH3OCH2OCH3=>CH2O+CH3OCH3            2.10E+85   -23.37    96856.03
PLOG /                 1.00E-05   2.10E+85   -23.37    96856.03 /
PLOG /                 1.00E-04   2.10E+85   -22.83   100084.06 /
PLOG /                 1.00E-03   2.10E+85   -22.37   103514.80 /
PLOG /                 1.00E-02   2.10E+85   -21.97   106965.97 /
PLOG /                 1.00E-01   2.10E+85   -21.60   110490.25 /
PLOG /                 1.00E+00   2.10E+85   -21.26   114081.34 /
PLOG /                 1.00E+01   2.10E+85   -20.95   117526.96 /
PLOG /                 1.00E+02   3.69E+68   -15.93   109588.92 /
PLOG /                 1.00E+03   1.25E+39    -7.37    92472.86 /

CH3OCH2OCH3=>CH2O+C2H5OH             2.01E+97   -32.82   120422.64
PLOG /                 1.00E-05   2.01E+97   -32.82   120422.64 /
PLOG /                 1.00E-04   2.01E+97   -31.48   122790.60 /
PLOG /                 1.00E-03   2.01E+97   -30.10   125148.30 /
PLOG /                 1.00E-02   2.01E+97   -28.68   127865.87 /
PLOG /                 1.00E-01   2.01E+97   -27.52   131676.58 /
PLOG /                 1.00E+00   2.01E+97   -26.60   136667.52 /
PLOG /                 1.00E+01   2.01E+97   -25.79   142784.55 /
PLOG /                 1.00E+02   1.55E+79   -19.96   137445.99 /
PLOG /                 1.00E+03   4.33E+48   -10.86   121954.78 /

CH3OCH2OCH3=>CH4+CH3OCHO             2.32E+106  -32.57   119956.04
PLOG /                 1.00E-05   2.32E+106  -32.57   119956.04 /
PLOG /                 1.00E-04   2.32E+106  -31.52   122824.38 /
PLOG /                 1.00E-03   2.32E+106  -30.53   126004.19 /
PLOG /                 1.00E-02   2.32E+106  -29.68   129466.70 /
PLOG /                 1.00E-01   2.32E+106  -28.93   133540.81 /
PLOG /                 1.00E+00   2.32E+106  -28.26   138460.75 /
PLOG /                 1.00E+01   2.32E+106  -27.64   144075.55 /
PLOG /                 1.00E+02   4.67E+78   -19.22   131624.43 /
PLOG /                 1.00E+03   1.97E+48   -10.24   115696.78 /

CH3OCH2OCH3=>CH3+CH3OCH2O            8.79E+95   -25.96   103268.59
PLOG /                 1.00E-05   8.79E+95   -25.96   103268.59 /
PLOG /                 1.00E-04   8.79E+95   -25.17   106770.72 /
PLOG /                 1.00E-03   8.79E+95   -24.58   110306.66 /
PLOG /                 1.00E-02   8.79E+95   -24.08   113903.17 /
PLOG /                 1.00E-01   8.79E+95   -23.65   117685.23 /
PLOG /                 1.00E+00   8.79E+95   -23.25   121649.92 /
```

PLOG /	1.00E+01	8.79E+95	-22.89	125519.72 /
PLOG /	1.00E+02	4.81E+62	-13.14	107187.88 /
PLOG /	1.00E+03	3.28E+47	-8.63	99609.87 /
CH3OCH2OCH3=>CH3O+CH3OCH2		2.11E+100	-28.38	108692.31
PLOG /	1.00E-05	2.11E+100	-28.38	108692.31 /
PLOG /	1.00E-04	2.11E+100	-27.18	112292.54 /
PLOG /	1.00E-03	2.11E+100	-26.40	115741.88 /
PLOG /	1.00E-02	2.11E+100	-25.80	119308.10 /
PLOG /	1.00E-01	2.11E+100	-25.28	123216.31 /
PLOG /	1.00E+00	2.11E+100	-24.81	127500.93 /
PLOG /	1.00E+01	2.11E+100	-24.40	131864.64 /
PLOG /	1.00E+02	1.49E+63	-13.48	111541.23 /
PLOG /	1.00E+03	8.73E+47	-8.92	104295.22 /
CH3OCH2OCH3=>H+CH3OCH2OCH2		5.29E+110	-35.77	121114.41
PLOG /	1.00E-05	5.29E+110	-35.77	121114.41 /
PLOG /	1.00E-04	5.29E+110	-32.96	123444.80 /
PLOG /	1.00E-03	5.29E+110	-31.19	126875.97 /
PLOG /	1.00E-02	5.29E+110	-30.07	130543.19 /
PLOG /	1.00E-01	5.29E+110	-29.23	134759.75 /
PLOG /	1.00E+00	5.29E+110	-28.52	139800.95 /
PLOG /	1.00E+01	5.29E+110	-27.88	145501.42 /
PLOG /	1.00E+02	1.18E+91	-21.74	138320.93 /
PLOG /	1.00E+03	9.09E+75	-17.10	132336.66 /
CH3OCH2OCH3=>H+CH3OCHOCH3		4.04E+116	-39.74	111213.50
PLOG /	1.00E-05	4.04E+116	-39.74	111213.50 /
PLOG /	1.00E-04	4.04E+116	-36.11	117893.11 /
PLOG /	1.00E-03	4.04E+116	-33.69	125144.37 /
PLOG /	1.00E-02	4.04E+116	-32.21	131126.72 /
PLOG /	1.00E-01	4.04E+116	-31.20	136452.78 /
PLOG /	1.00E+00	4.04E+116	-30.38	142150.83 /
PLOG /	1.00E+01	4.04E+116	-29.68	148365.75 /
PLOG /	1.00E+02	8.30E+96	-23.48	141611.96 /
PLOG /	1.00E+03	6.25E+81	-18.81	135861.51 /

[a] the notation is as follows:

first line:	reactant(s)=product(s)	dummy	dummy	dummy
next lines:	PLOG/pressure p_j	$B(p_j)$	$n(p_j)$	$C(p_j)$ /

for $k(T, p_j) = B(p_j)\, T^{n(p_j)} \exp(-C(p_j)/RT)$

units: $[k] = s^{-1}$, $[p_j]$ = bar, $[T]$ = K, $[C(p_j)]$ = cal mol^{-1}

The rate coefficient k for an arbitrary pressure p is obtained from the following interpolation:

$$\ln k(T, p) = \ln k(T, p_i) + \{\ln k(T, p_{i+1}) - \ln k(T, p_i)\} \frac{\ln p - \ln p_i}{\ln p_{i+1} - \ln p_i}$$

'PLOG' is the CHEMKIN keyword for this kind of representation

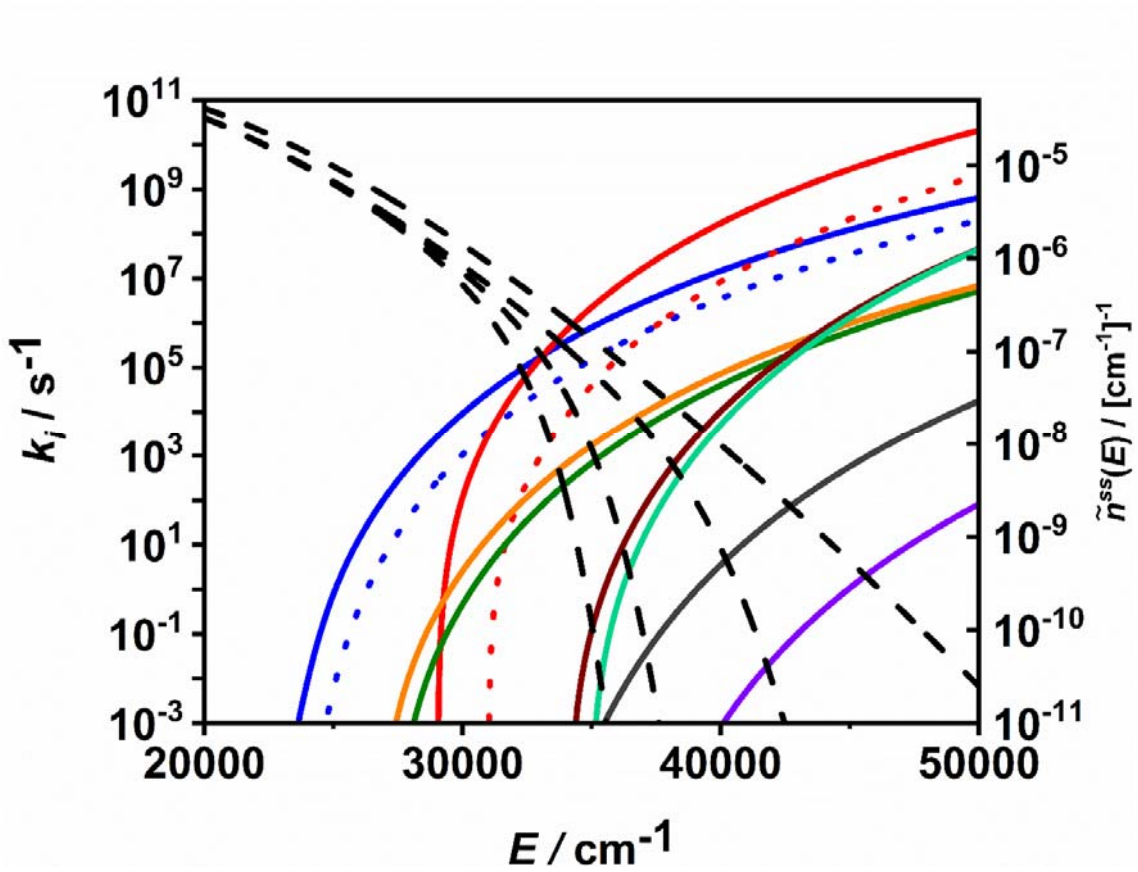

Fig. S2 Microcanonical rate coefficients of reactions (R1)–(R10) and normalized steady-state distributions of DMM at $T = 1300$ K and $p = 1$ mbar, $p = 10$ mbar, $p = 1$ bar and $p \rightarrow \infty$ (dashed lines, left to right). Order of $k_i(E)$ along the abscissa: (R1), (R2), (R4), (R3), (R7), (R8), R(9), (R10), (R6), (R5).

Table S4 Angular momentum-dependent threshold energies, $E_{01}(J)$ and $E_{07}(J)$, for the lowest molecular and radical channels, reactions (R1) and (R7), respectively

T/K	$\langle J \rangle_T$	$E_{01}(\langle J \rangle_T)$/kJ mol^{-1}	$E_{07}(\langle J \rangle_T)$/kJ mol^{-1}
0	0	289.9	343.7
800	71	294.2	346.0
1050	81	295.5	346.7
1300	90	296.8	347.4
1550	98	298.0	348.1
1800	106	299.4	348.8