Electronic Supplementary Information

Temperature- and pressure-dependent kinetics of the competing C–O bond fission reactions of dimethoxymethane

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Table S1 Conditions and first-order rate coefficients, k_{1+2}, for the decomposition of DMM at nominal pressures of 0.4 bar and 4.7 bar

T/K	p/bar	$[DMM]_0$/mol cm^{-3}	[Ar]/mol cm^{-3}	k_{1+2}/s^{-1}
1140	0.41	1.05×10^{-10}	4.31×10^{-6}	5
1140	0.42	1.05×10^{-10}	4.44×10^{-6}	17
1150	0.36	9.31×10^{-11}	3.81×10^{-6}	29
1170	0.43	1.07×10^{-10}	4.40×10^{-6}	7
1190	0.4	9.61×10^{-11}	4.06×10^{-6}	40
1200	0.42	1.03×10^{-10}	4.22×10^{-6}	7
1210	0.44	1.06×10^{-10}	4.35×10^{-6}	65
1230	0.41	9.75×10^{-11}	3.99×10^{-6}	102
1230	0.41	9.77×10^{-11}	4.01×10^{-6}	191
1230	0.38	9.19×10^{-11}	3.77×10^{-6}	290
1240	0.37	8.85×10^{-11}	3.62×10^{-6}	192
1240	0.4	9.43×10^{-11}	3.86×10^{-6}	296
1250	0.41	9.52×10^{-11}	3.89×10^{-6}	268
1250	0.4	9.20×10^{-11}	3.88×10^{-6}	138
1250	0.4	9.36×10^{-11}	3.84×10^{-6}	274
1250	0.4	9.41×10^{-11}	3.86×10^{-6}	164
1260	0.4	9.30×10^{-11}	3.81×10^{-6}	2130
1270	0.41	9.15×10^{-11}	3.86×10^{-6}	683
1280	0.43	9.79×10^{-11}	4.01×10^{-6}	626
1290	0.38	8.71×10^{-11}	3.57×10^{-6}	707
1300	0.39	8.80×10^{-11}	3.60×10^{-6}	737
1300	0.38	8.59×10^{-11}	3.51×10^{-6}	1270
1300	0.42	9.48×10^{-11}	3.88×10^{-6}	521
1310	0.4	8.89×10^{-11}	3.64×10^{-6}	1360
1320	0.41	8.86×10^{-11}	3.74×10^{-6}	1730

1320	0.41	9.12×10^{-11}	3.74×10^{-6}	2220
1330	0.41	9.04×10^{-11}	3.71×10^{-6}	3830
1340	0.4	8.86×10^{-11}	3.62×10^{-6}	1870
1340	0.38	8.33×10^{-11}	3.41×10^{-6}	2000
1360	0.41	8.90×10^{-11}	3.64×10^{-6}	2890
1370	0.4	8.56×10^{-11}	3.50×10^{-6}	1700
1370	0.42	9.09×10^{-11}	3.73×10^{-6}	260
1370	0.39	8.28×10^{-11}	3.39×10^{-6}	3750
1390	0.37	7.80×10^{-11}	3.20×10^{-6}	5390
1400	0.4	8.41×10^{-11}	3.44×10^{-6}	3420
1400	0.38	8.07×10^{-11}	3.30×10^{-6}	6520
1410	0.41	8.33×10^{-11}	3.52×10^{-6}	5260
1420	0.37	7.58×10^{-11}	3.10×10^{-6}	6090
1430	0.37	7.53×10^{-11}	3.08×10^{-6}	7560
1430	0.43	8.91×10^{-11}	3.65×10^{-6}	284
1450	0.39	7.91×10^{-11}	3.24×10^{-6}	8400
1470	0.38	7.49×10^{-11}	3.06×10^{-6}	9550
1470	0.38	7.70×10^{-11}	3.15×10^{-6}	8230
1470	0.4	8.02×10^{-11}	3.29×10^{-6}	7470
1470	0.4	7.91×10^{-11}	3.24×10^{-6}	7840
1500	0.39	7.62×10^{-11}	3.12×10^{-6}	14700
1530	0.39	7.55×10^{-11}	3.09×10^{-6}	14100
1550	0.39	7.47×10^{-11}	3.05×10^{-6}	14300
1550	0.41	7.85×10^{-11}	3.22×10^{-6}	14500
1560	0.4	7.55×10^{-11}	3.09×10^{-6}	41800
1160	4.76	1.11×10^{-10}	4.96×10^{-5}	106
1170	4.77	9.07×10^{-11}	4.90×10^{-5}	157
1200	4.71	8.76×10^{-11}	4.74×10^{-5}	318
1200	4.77	8.88×10^{-11}	4.80×10^{-5}	255

1210	4.75	9.26×10^{-11}	4.72×10^{-5}	355
1220	4.74	1.04×10^{-10}	4.67×10^{-5}	500
1240	4.81	1.04×10^{-10}	4.68×10^{-5}	681
1250	4.71	1.01×10^{-10}	4.52×10^{-5}	973
1250	4.81	8.60×10^{-11}	4.65×10^{-5}	756
1250	4.68	8.80×10^{-11}	4.49×10^{-5}	1020
1290	4.81	1.00×10^{-10}	4.49×10^{-5}	2120
1300	4.67	9.66×10^{-11}	4.33×10^{-5}	2920
1310	4.63	7.89×10^{-11}	4.26×10^{-5}	3730
1330	4.72	9.52×10^{-11}	4.27×10^{-5}	5690
1330	4.59	8.16×10^{-11}	4.16×10^{-5}	4520
1350	4.62	7.60×10^{-11}	4.11×10^{-5}	6960
1380	4.76	9.23×10^{-11}	4.14×10^{-5}	9670
1380	4.67	7.99×10^{-11}	4.08×10^{-5}	9880
1400	4.53	8.66×10^{-11}	3.88×10^{-5}	17000
1400	4.72	7.49×10^{-11}	4.05×10^{-5}	17500
1400	4.57	7.69×10^{-11}	3.92×10^{-5}	13800
1410	4.71	7.44×10^{-11}	4.02×10^{-5}	15500
1410	4.68	7.81×10^{-11}	3.98×10^{-5}	14500
1450	4.65	7.12×10^{-11}	3.85×10^{-5}	25500
1450	4.67	7.14×10^{-11}	3.86×10^{-5}	30900

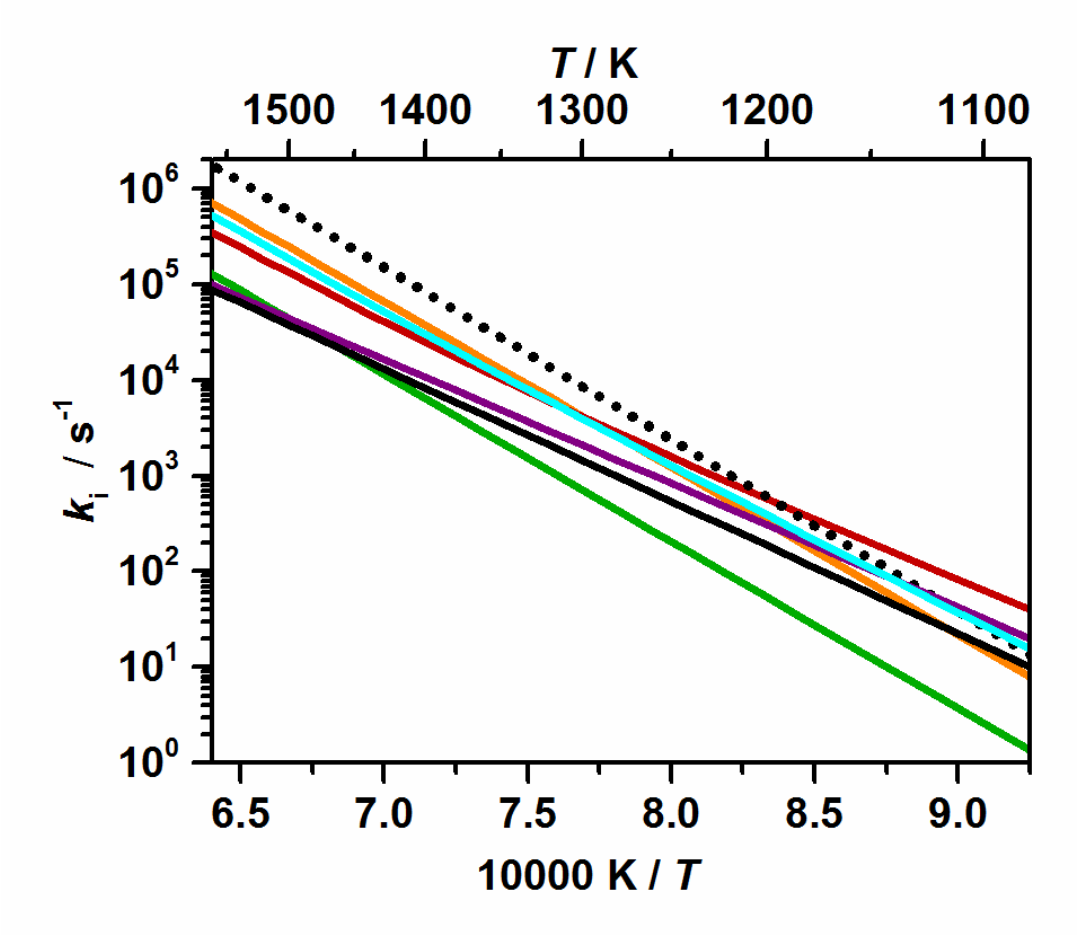

Figure S1 Comparison of rate coefficient expressions for the C–O bond-fission reactions of DMM at $p \sim 1$ bar; black solid line: $k_{1+2} = k_1 + k_2$ from this work, black dotted line: high-pressure limit $k_1^\infty + k_2^\infty$ from this work, purple: k_{1+2} from Peukert *et al.* [1], green: k_{1+2} from Marrodán *et al.* [2], orange: k_{1+2} from Vermeire *et al.* [3], red: $k_{1+2+3} = k_1 + k_2 + k_3$ from Sun *et al.* [4], cyan: $k_{1+2+3+4} = k_1 + k_2 + k_3 + k_4$ from Jacobs *et al.* [5].

References

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[5] S. Jacobs, M. Döntgen, A. B. S. Alquaity, W. A. Kopp, L. C. Kröger, U. Burke, H. Pitsch, K. Leonhard, H. J. Curran and K. A. Heufer, *Combust. Flame*, 2019, **205**, 522–533 (ref. [24] of the main text).

Table S2 Cartesian coordinates (in Å) of reactants and products in reactions (R1) to (R6) from B2PLYP-D3/def2-TZVPP calculations

		X	Y	Z
$CH_3OCH_2OCH_3$	C	0	0	0.930333
	H	-0.710583	0.551249	1.550536
	H	0.710583	-0.551249	1.550536
	O	0.77856	0.877733	0.165382
	C	0	1.813257	-0.566112
	H	-0.627951	2.404283	0.106697
	H	0.695755	2.47096	-1.077679
	H	-0.638367	1.316637	-1.296932
	O	-0.777856	-0.877733	0.165382
	C	0	-1.813257	-0.566112
	H	-0.695755	-2.47096	-1.077679
	H	0.638367	-1.316637	-1.296932
	H	0.627951	-2.404283	0.106697
CH_2OCH_3	C	-1.197182	0.228141	0.066537
	H	-1.122285	1.269323	-0.217793
	H	-2.120306	-0.317099	-0.029403
	O	-0.091787	-0.545475	-0.036932
	C	1.134078	0.169624	0.01265
	H	1.252195	0.661501	0.978753
	H	1.929449	-0.554277	-0.129647
	H	1.173867	0.917762	-0.781575
CH_3	C	0	0	0.000005
	H	0.106909	-1.070538	-0.00001
	H	-0.980569	0.442682	-0.00001
	H	0.87366	0.627853	-0.00001
OCH_2OCH_3	C	-0.750964	-0.453548	0.21654
	H	-1.327698	-1.344939	-0.064772
	H	-0.724972	-0.424171	1.326896
	O	-1.421129	0.65014	-0.149479
	O	0.530182	-0.62425	-0.309856
	C	1.438789	0.391561	0.090677
	H	2.398846	0.147674	-0.351772
	H	1.115256	1.37154	-0.259189
	H	1.539196	0.4146934	1.180211
OCH_3	C	0.575987	0.000001	-0.012789
	H	1.002502	0.904687	-0.456725
	H	0.867815	-0.000019	1.050778
	H	1.002499	-0.904673	-0.456754
	O	-0.791092	0	-0.007586
H_2CO	C	0	0.529073	0
	H	0.935705	1.112168	0
	H	-0.935705	1.112167	0
	O	0	-0.674846	0

Table S3 Rotational constants (in cm^{-1}) of reactants and products in reactions (R1) to (R6) from B2PLYP-D3/def2-TZVPP calculations

	A	B	C
$CH_3OCH_2OCH_3$	0,3440099	0.10905044	0.10239384
CH_2OCH_3	1.57726483	0.35886593	0.310781
CH_3	9.63400887	9.63396951	4.81699476
OCH_2OCH_3	0.62629194	0.19549291	0.16621966
OCH_3	5.292425335	0.93392643	0.928056369
H_2CO	9.55219894	1.29926084	1.14369855

Table S4 Harmonic wavenumbers (in cm^{-1}) of reactants and products in reactions (R1) to (R6) from B2PLYP-D3/def2-TZVPP calculations

$CH_3OCH_2OCH_3$	3158.2746, 3158.003, 3095.6578, 3095.3491, 3087.6616, 3032.8787, 3024.7457, 3023.7175, 1530.5627, 1522.806, 1517.3826, 1502.4537, 1501.7991, 1492.7256, 1479.6731, 1439.1076, 1345.6172, 1264.9865, 1222.258, 1188.8885, 1187.8252, 1169.7711, 1146.1054, 1074.4336, 950.9244, 936.9361, 608.0741, 455.1731, 322.3773, 224.3512, 157.9425, 133.9003, 93.4922
CH_2OCH_3	3293.6975, 3167.8444, 3140.9449, 3099.3261, 3035.2703, 1519.125, 1510.4072, 1504.5839, 1472.903, 1294.5564, 1262.0484, 1182.977, 1146.775, 968.6832, 587.0216, 434.3515, 302.2726, 165.1975
CH_3	3324.7538, 3324.7472, 3143.6574, 1429.3806, 1429.3734, 521.1626
OCH_2OCH_3	3166.0486, 3099.0609, 3020.4636, 2997.6555, 2851.4681, 1525.9739, 1503.2777, 1487.5821, 1390.5227, 1346.53, 1264.3748, 1193.3927, 1184.8951, 1123.6383, 1054.8563, 938.6581, 783.3246, 602.1616, 350.113, 190.1323, 133.6607
OCH_3	3064.9694, 3020.6753, 2943.2846, 1530.123, 1389.0458, 1386.9819, 1116.4847, 965.1717, 737.2354
H_2CO	2991.6966, 2929.1485, 1790.5879, 1545.3393, 1274.9597, 1208.5899

Table S5 'log *p*' parameterization of the pressure-dependent rate coefficients k_1 and k_2 in CHEMKIN-PRO format[a]

```
CH3OCH2OCH3=CH3+CH3OCH2          2.74E+108   -27.94  119635.52
        PLOG/ 1E-3   2.74E+108   -27.94  119635.52 /
        PLOG/ 1E-2   7.57E+111   -28.52  125253.35 /
        PLOG/ 1E-1   2.52E+113   -28.54  130279.60 /
        PLOG/ 4E-1   4.55E+112   -28.08  132480.52 /
        PLOG/ 1.0    1.422E+111  -27.49  133333.59 /
        PLOG/ 4.0    6.59E+106   -26.02  133278.13  /
        PLOG/ 1E+1   1.81E+102   -24.57  132048.95 /
        PLOG/ 1E+2   2.88E+83    -18.94  123350.93 /
        PLOG/ 1E+3   8.51E+55    -10.94  107037.16 /

CH3OCH2OCH3=CH3O+CH3OCH2         1.13E+108   -28.39   121297.17
        PLOG/ 1E-3   1.13E+108   -28.39   121297.17 /
        PLOG/ 1E-2   7.51E+118   -31.07   132923.31 /
        PLOG/ 1E-1   3.43E+114   -29.24   133132.81 /
        PLOG/ 4E-1   3.69E+114   -28.96   136015.54 /
        PLOG/ 1.0    4.98E+113   -28.53   137441.66 /
        PLOG/ 4.0    3.39E+110   -27.35   138466.60 /
        PLOG/ 1E+1   7.25E+106   -26.13   138085.96 /
        PLOG/ 1E+2   1.66E+90    -21.03   131634.45 /
        PLOG/ 1E+3   5.60E+62    -13.00   116148.55 /
```

[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