Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Unimolecular Decomposition of 2,5-dimethylfuran:

a Theoretical Chemical Kinetic Study

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Table S1: Geometries optimized at the B3LYP/cbsb7 level of theory unless specified otherwise. (Angstroms)

M1

6	-1.108078	-0.003479	0.000009
6	-0.717983	1.298413	-0.000073
6	0.717983	1.298413	0.000059
6	1.108078	-0.003479	0.000000
8	0.000000	-0.811533	-0.000082
1	-1.370778	2.157278	-0.000106
1	1.370778	2.157278	0.000130
6	-2.430059	-0.683482	0.000052
1	-2.551859	-1.319291	-0.882798
1	-2.551816	-1.319283	0.882916
1	-3.229615	0.058716	0.000067
6	2.430059	-0.683482	0.000017
1	2.551871	-1.319248	-0.882864
1	3.229615	0.058716	0.000082
1	2.551804	-1.319327	0.882850

M2

6	1.096208	-0.176264	-0.000175
6	-0.015316	-0.960168	-0.000161
6	-1.156448	-0.081027	0.000121
6	-0.639208	1.174576	0.000031
8	0.728941	1.139505	-0.000082
1	-0.030518	-2.039658	-0.000135
6	2.555139	-0.463427	0.000130
1	3.043959	-0.038435	-0.882192
1	3.043231	-0.039238	0.883241
1	2.723228	-1.541205	-0.000318
1	-1.083723	2.155887	0.000028
6	-2.602338	-0.473006	0.000062
1	-2.853008	-1.071790	0.881354
1	-3.250199	0.406336	-0.000207
1	-2.852723	-1.072042	-0.881164

M3

6	-1.141090	-0.129102	0.139061
6	0.009464	0.678641	-0.395398
6	1.030249	1.245364	0.573976
6	1.427059	0.218516	-0.086615
8	-1.035582	-0.812405	1.136878
1	-0.190121	1.210343	-1.328312
1	1.162532	2.002291	1.326027
6	-2.439443	-0.048293	-0.643019
1	-3.196929	-0.669382	-0.167042
1	-2.787848	0.988555	-0.693783
1	-2.282593	-0.381207	-1.674443
6	2.392550	-0.843464	-0.423719
1	2.611687	-0.843620	-1.495837
1	3.326649	-0.716993	0.127581
1	1.968543	-1.820708	-0.174929

M4

6	1.481529	.197035	-.010683
6	.385065	-.824130	-.059557
6	-.866008	-.503171	-.290045
6	-2.097437	-.157448	-.521073
8	1.282929	1.380677	-.174554
1	.656119	-1.865039	.102967
6	2.868749	-.357505	.260276
1	3.145169	-1.084588	-.510249
1	3.590869	.457172	.273518
1	2.887078	-.883570	1.220362
6	-3.105558	.225191	.533887
1	-3.457081	1.248044	.368278
1	-3.978971	-.432816	.489030
1	-2.676361	.166346	1.534298
1	-2.428292	-.130795	-1.558599

M5

6	-1.518729	-0.039713	0.000021
6	-0.410026	-1.029462	0.001979
6	0.932202	-0.885485	0.001305
6	1.760747	0.308307	-0.001522
8	-2.661671	-0.461982	-0.003381
1	-0.804305	-2.040996	0.003436
1	1.503771	-1.812218	0.002900
6	-1.263754	1.457112	0.002402
1	-2.227018	1.965273	0.005347
1	-0.693368	1.758288	0.885374
1	-0.697998	1.761123	-0.882680
6	3.098815	0.246793	-0.001066
1	3.622916	-0.703741	0.001572
1	3.708387	1.142315	-0.003276
1	1.285456	1.280500	-0.004341

M6

6	-1.202968	-0.048340	-0.000005
8	-0.590753	-1.270547	-0.000080
6	1.903800	0.227021	0.000004
6	0.996251	1.178105	-0.000067
6	-0.460145	1.072200	0.000012
1	1.380304	2.197765	-0.000258
1	-1.000379	2.010501	0.000077
6	-2.702104	-0.062134	0.000067
1	-3.108219	0.948879	0.000120
1	-3.088105	-0.584116	-0.884494
1	-3.088022	-0.584177	0.884629
6	2.857435	-0.658666	0.000072
1	3.267136	-1.054819	0.925907
1	-1.257329	-1.963685	-0.000146
1	3.267021	-1.055088	-0.925698

M7

6	-.905058	.104600	.010746
6	-.192982	1.240336	.161668
6	1.243673	1.202813	-.067873
6	1.874948	.022458	-.105326
8	-.295352	-1.090858	-.231993
1	-.706705	2.177006	.329389
1	1.769820	2.130109	-.267849
6	2.393469	-.010088	-.024741
1	2.707100	-.443262	-.980108
1	2.751742	-.678629	.764052
1	2.865191	.965837	.091960
6	1.071333	-1.204143	.225774
1	1.046447	-1.381019	1.314294
1	1.459093	-2.102125	-.255330
1	2.927520	-.076907	-.341956

M8

6	1.581410	-0.305499	0.208082
6	0.637799	0.563551	-0.171048
6	-0.820632	0.421821	-0.026424
6	-1.379330	-0.771888	-0.037784
8	-1.880215	-1.823681	-0.061864
1	0.943972	1.492333	-0.652412
6	3.050731	-0.124321	-0.029398
1	3.613914	-0.169419	0.909565
1	3.451039	-0.917080	-0.672326
1	3.264247	0.834320	-0.508714
6	-1.697159	1.655178	0.104962
1	-1.534785	2.326744	-0.744557
1	-2.758476	1.402246	0.129592
1	-1.460160	2.205539	1.020797
1	1.285055	-1.218286	0.722632

M9

6	1.678073	-0.759576	-0.106268
6	0.790674	0.432906	0.044776
6	-0.484885	0.257452	0.312714
6	-1.742555	0.052524	0.571656
8	1.342577	-1.914692	-0.010834
6	-2.826828	-0.125933	-0.462650
1	-3.300953	-1.105547	-0.348825
1	-3.607133	0.631508	-0.338512
1	-2.427727	-0.052090	-1.474523
1	-2.043068	-0.007415	1.617475
1	2.736548	-0.492854	-0.327144
6	1.433246	1.794724	-0.119269
1	2.232124	1.940553	0.615310
1	1.881164	1.898729	-1.113024
1	0.702077	2.592078	0.010166

M10

6	1.247774	-0.100842	0.187753
6	0.781957	0.292492	1.320339
6	-0.236563	0.278768	0.182191
6	-1.210486	-0.848132	0.182141
8	-2.316505	-0.807949	-0.303367
1	0.911494	0.562525	2.354282
6	2.340314	-0.528009	-0.708426
1	2.115010	-1.500443	-1.156266
1	2.456159	0.184717	-1.530871
1	3.288362	-0.598282	-0.170732
1	-0.832265	-1.769340	0.684608
6	-0.727245	1.560220	-0.470818
1	-1.021526	1.383573	-1.508884
1	-1.609613	1.946607	0.046972
1	0.049919	2.327260	-0.451253

M11

6	1.062546	-1.091325	-0.000219
6	-0.245738	-0.723131	0.000040
6	-0.245738	0.723112	0.000001
6	1.062514	1.091352	0.000198
8	1.879263	-0.000007	-0.000058
1	1.556335	2.049060	0.000335
6	-1.445806	1.619754	-0.000018
1	-2.073594	1.449691	0.880773
1	-1.152069	2.671571	-0.000041
1	-2.073623	1.449654	-0.880782
1	1.556233	-2.049093	-0.000407
6	-1.445775	-1.619740	0.000063
1	-2.073565	-1.449767	0.880850
1	-2.073680	-1.449632	-0.880615
1	-1.152155	-2.671559	-0.000040

CA1

6	-1.060405	-.198174	-.030053
6	-.016377	-.959127	-.326890
6	1.191985	-.064952	-.429634
6	.666665	1.328652	-.120571
8	-.624301	1.177061	.082274
1	-.035594	-2.028534	-.473728
1	1.537682	.002916	-1.474618
6	-2.508132	-.408719	.205775
1	-2.790191	-.060157	1.203816
1	-3.103437	.156644	-.517503
1	-2.762113	-1.465705	.118299
6	2.400594	-.437397	.448393
1	2.804618	-1.409907	.158164
1	3.185026	.313896	.344414
1	2.112432	-.487340	1.500848

CA2 [B3LYP/6-311+G(2d,p)]

6	-1.026913	-0.022257	-0.006199
6	-0.574702	1.300120	0.152879
6	0.786365	1.394374	-0.093166
6	1.201665	0.048127	-0.433765
8	-0.101284	-0.864855	-0.340154
1	-1.241109	2.106482	0.433681
6	-2.408624	-0.550349	0.154851
1	-2.748849	-0.993182	-0.784543
1	-2.420840	-1.341568	0.908210
1	-3.097621	0.239666	0.449696
6	2.246582	-0.623592	0.435655
1	2.373792	-1.668829	0.152272
1	3.195730	-0.102350	0.310965
1	1.963296	-0.567895	1.487830
1	1.439644	-0.032024	-1.498415

CA3 [B3LYP/6-311+G(2d,p)]

6	0.555612	1.131786	0.103603
6	1.094485	-0.152441	-0.028349
6	0.070664	-1.037289	-0.372992
6	-1.132845	-0.240535	-0.459773
8	-0.714356	1.252260	-0.103499
6	-2.294033	-0.580800	0.455212
1	-3.083383	0.166697	0.372528
1	-2.692458	-1.554428	0.170419
1	-1.960276	-0.638280	1.492250
1	-1.450980	-0.125692	-1.500563
1	1.080384	2.049845	0.357558
6	2.546824	-0.483871	0.177108
1	2.990683	-0.871443	-0.742438
1	3.124911	0.389943	0.488971
1	2.661724	-1.255812	0.940415

CA4

6	1.643818	0.306241	0.253868
6	0.195826	0.741641	0.423914
6	-0.632938	-0.475518	0.063659
6	0.236404	-1.430805	-0.235277
8	1.581829	-0.956978	-0.113608
1	0.144754	-2.461129	-0.540809
6	-2.125035	-0.548759	0.070509
1	-2.557617	0.181762	-0.620843
1	-2.483734	-1.538737	-0.217763
1	-2.523674	-0.320323	1.064606
6	-0.114125	2.034856	-0.350726
1	-0.010694	1.874974	-1.426576
1	-1.131909	2.377596	-0.150908
1	0.582596	2.820906	-0.056474
1	0.101948	0.954848	1.501942

B1

6	1.721144	0.035001	-0.247305
6	0.527715	-0.078169	0.262140
6	-0.733338	0.441677	-0.420786
6	-1.839438	-0.619071	-0.408392
8	-1.901383	-1.603572	0.237037
1	0.355887	-0.575107	1.224710
1	-0.521608	0.663782	-1.468887
6	3.137645	-0.231362	0.026006
1	3.585025	-0.860713	-0.749472
1	3.714636	0.698045	0.066578
1	3.262920	-0.745059	0.991722
6	-1.296734	1.712602	0.252012
1	-0.559022	2.513604	0.184212
1	-2.218326	2.038085	-0.235668
1	-1.510413	1.531882	1.308452

B2

6	-1.165800	-0.206440	-0.000088
6	-0.486880	1.079347	0.000045
6	0.914164	1.332715	0.000186
6	1.966287	0.499349	0.000098
8	-0.578716	-1.286163	-0.000185
1	-1.124106	1.958964	0.000056
1	1.166798	2.396121	0.000352
6	-2.688287	-0.158341	-0.000072
1	-3.077309	-1.175444	-0.000513
1	-3.060865	0.372888	0.881393
1	-3.060917	0.373708	-0.881015
6	2.458672	-0.871530	0.000007
1	1.623303	-1.580841	-0.001017
1	3.087844	-1.053015	-0.879810
1	3.086045	-1.053681	0.880982

B3

6	-1.246016	-0.587959	-0.053773
6	-0.056027	0.210246	-0.076925
6	1.142778	-0.418963	-0.005213
1	-0.067663	1.309700	-0.132191
1	1.106827	-1.505237	0.035634
6	-2.492110	0.211803	0.031946
1	-3.321322	-0.258170	-0.506067
1	-2.780188	0.133930	1.095389
1	-2.432615	1.286554	-0.216435
6	2.479644	0.232861	0.034272
1	3.004955	-0.036641	0.958261
1	3.104992	-0.138098	-0.786244
1	2.415411	1.320029	-0.030187

C6H7O

6	-1.044960	0.005233	-0.000076
6	-0.598785	1.304412	-0.000208
6	0.808829	1.262767	0.000218
6	1.182026	-0.095457	-0.000047
8	0.017230	-0.853711	-0.000207
1	-1.227145	2.181567	-0.000295
1	1.494008	2.095345	0.000252
6	-2.396372	-0.605289	0.000176
1	-2.543978	-1.238044	-0.881416
1	-2.544196	-1.236890	0.882578
1	-3.161508	0.172185	-0.000434
6	2.396156	-0.734033	0.000065
1	3.309713	-0.157425	0.000262
1	2.453904	-1.812854	-0.000062

M2-R1

6	-1.185422	-0.200722	0.000123
6	-0.010215	-0.975920	0.000050
6	1.089239	-0.088047	-0.000128
6	0.546514	1.173526	-0.000170
8	-0.813425	1.135454	0.000154
1	0.020476	-2.054741	0.000069
6	-2.520696	-0.522414	-0.000027
1	0.991703	2.155227	-0.000013
6	2.547450	-0.434863	0.000015
1	2.813693	-1.026204	-0.880986
1	3.167965	0.463699	-0.000841
1	2.813788	-1.024637	0.882066
1	-3.274218	0.251966	-0.000386
1	-2.827222	-1.558307	-0.000325

M2-R2

6	-1.032171	-0.176943	0.000009
6	0.053527	-0.981626	0.000052
6	1.234180	-0.130260	-0.000062
6	0.718411	1.163559	0.000039
8	-0.643674	1.145113	0.000065
1	0.046277	-2.060546	0.000080
6	-2.496652	-0.427082	0.000001
1	-2.971043	0.012721	0.882657
1	-2.971043	0.012740	-0.882646
1	-2.693555	-1.499700	-0.000008
1	1.182188	2.135551	0.000067
6	2.577561	-0.517248	-0.000111
1	3.371380	0.218325	-0.000143
1	2.856042	-1.562385	-0.000089

TS_M1_CA2

6	1.091054	-0.004836	-0.017956
6	0.716654	1.301665	-0.054288
6	-0.735929	1.413055	-0.067656
6	-1.106585	0.050274	0.092773
8	0.003779	-0.818706	0.085319
1	1.403881	2.134448	-0.104850
1	-1.173834	0.795345	1.095441
6	2.414469	-0.682745	-0.027464
1	2.565220	-1.248933	0.896463
1	2.482066	-1.389144	-0.859767
1	3.214453	0.051647	-0.122897
6	-2.423095	-0.639223	-0.105591
1	-2.543571	-1.482400	0.577734
1	-3.231255	0.075601	0.045846
1	-2.486605	-1.016047	-1.129439

TS_CA2_M4 [B3LYP/6-311+G(2d,p)]

6	-1.027415	-0.035139	-0.009142
6	-0.565445	1.294137	0.152288
6	0.787348	1.385160	-0.095941
6	1.234721	0.068764	-0.437141
8	-0.126231	-0.887835	-0.341752
1	-1.231748	2.100618	0.433439
6	-2.423878	-0.527246	0.158121
1	-2.779911	-0.955496	-0.782097
1	-2.451496	-1.322752	0.906296
1	-3.091299	0.278190	0.461314
6	2.255649	-0.621536	0.440089
1	2.362502	-1.669559	0.159724
1	3.217946	-0.122767	0.318810
1	1.968543	-0.555057	1.490445
1	1.449430	-0.035333	-1.503561

TS_CA2_M2

6	-1.006415	0.105492	-0.020526
6	-0.212341	1.180921	-0.229720
6	1.117540	0.743586	-0.682790
6	0.981710	-0.640613	-0.541721
8	-0.297623	-1.064912	-0.201500
1	-0.536378	2.208726	-0.141333
6	-2.437643	-0.060789	0.343693
1	-2.978599	-0.602652	-0.438089
1	-2.537575	-0.635498	1.269248
1	-2.907442	0.913223	0.482981
6	2.056082	0.008856	0.809763
1	1.610196	-0.645969	1.565514
1	3.049714	-0.313988	0.517756
1	2.093824	1.017898	1.204258
1	1.593660	-1.447166	-0.920534

TS_ M4 → 1,2-butadiene + CH2CO

6	-1.570926	0.346728	-0.117778
6	-0.449230	-0.850135	-0.331958
6	0.814694	-0.683593	0.054894
6	2.023945	-0.444814	0.459477
8	-1.240860	1.487468	0.080046
6	-2.768709	-0.376694	0.121336
1	-1.300628	-1.107531	0.605303
1	-3.656010	0.149889	0.460529
1	-2.928741	-1.294458	-0.432277
6	3.005141	0.469316	-0.238906
1	3.324083	1.263641	0.441933
1	3.897370	-0.087331	-0.541185
1	2.560045	0.929277	-1.120658
1	2.365634	-0.933913	1.372652
1	-0.664368	-1.584156	-1.109054

TS_ M4 → 2,3-pentadiene + CO

6	1.224226	.536338	-.337651
6	.685562	-.665362	-.765884
6	-.706186	-.527369	-1.172527
6	-1.781263	-.117738	-.508319
8	1.352701	1.642035	-.019953
6	1.284356	-1.134424	.997468
1	2.324007	-1.447815	.924797
1	1.128864	-.413582	1.797846
1	.608245	-1.978910	1.108879
6	-1.951166	.361592	.917993
1	-2.250701	1.416259	.935599
1	-2.747909	-.198177	1.420152
1	-1.043291	.263859	1.513913
1	-2.715417	-.116012	-1.075531
1	1.341416	-1.380119	-1.252513

TS_ M4 → 3-methylbuta-1,2-diene + CO

6	-1.432428	.021723	.085805
6	-.766347	1.329114	-.037883
6	.531421	1.352657	-.292389
6	1.222556	.132339	-.443272
8	-2.467285	-.440788	.323129
1	-1.459707	2.149735	.114393
6	.067640	-1.429237	-.328008
6	2.323624	-.147363	.575051
1	2.751611	-1.142877	.441320
1	3.122032	.588189	.457700
1	1.938489	-.064983	1.593966
1	1.558331	-.028188	-1.470383
1	.999794	-1.936435	-.602724
1	-.214693	-1.865529	.631800
1	-.636369	-1.729007	-1.106921

TS_ M4 → 1-butyne + CH2CO

6	-1.612599	0.333249	-0.052983
6	-0.463707	-1.404025	-0.257880
6	0.685163	-1.107259	0.120155
6	1.549267	-0.110718	0.561850
8	-2.712909	-0.068454	0.073008
1	-1.146140	-2.177304	-0.546046
6	-0.732356	1.399484	-0.067087
1	0.565265	0.770149	0.451951
1	-0.303623	1.644926	-1.033476
1	-1.020242	2.239195	0.556497
6	2.708654	0.353993	-0.311196
1	3.064984	1.332166	0.022299
1	3.551973	-0.340448	-0.264516
1	2.402100	0.437780	-1.356559
1	1.782421	-0.147177	1.628631

TS_M1_CA1

6	1.003773	.100833	-.010266
6	.226758	1.204147	-.084956
6	-1.074615	.713546	-.501684
6	-1.017940	-.691573	-.736484
8	.291433	-1.022781	-.336862
1	.521378	2.219258	.128300
1	-1.879963	1.331172	-.874996
6	2.435851	-.101736	.332130
1	2.535218	-.760918	1.199400
1	2.957521	-.581056	-.501238
1	2.922051	.848615	.553787
6	-2.031261	-.227379	.817484
1	-1.592707	-1.064444	1.350132
1	-2.015388	.651649	1.466655
1	-3.034976	-.449058	.475514

TS_CA1_M2

6	-1.087665	-0.175277	0.001312
6	0.002813	-0.962362	-0.085294
6	1.144954	-0.051377	-0.087337
6	0.657616	1.306643	0.056353
8	-0.720141	1.149709	0.027923
1	0.021906	-2.039444	-0.140644
1	1.119552	0.692737	-1.100102
6	-2.546381	-0.455197	0.051077
1	-2.985152	-0.021249	0.953954
1	-3.054455	-0.006131	-0.807121
1	-2.734943	-1.529048	0.048423
6	2.585756	-0.441933	0.111817
1	2.906050	-1.208690	-0.597525
1	3.230149	0.433044	0.011577
1	2.715463	-0.841878	1.120486

TS_CA1_B1 [MP2/6-31G(d')]

6	-1.188423	-.288551	-.049007
6	-.110224	-.902092	-.377158
6	1.215060	-.123672	-.468120
6	.831198	1.303651	-.145693
8	-.323320	1.527225	.122121
1	-.042547	-1.970756	-.591681
1	1.608823	-.153278	-1.497221
6	-2.630992	-.413264	.211413
1	-2.862265	-.088773	1.233777
1	-3.198395	.229573	-.473189
1	-2.984444	-1.448991	.088127
6	2.285787	-.648933	.501054
1	2.518687	-1.697346	.278561
1	3.208445	-.063483	.415611
1	1.923813	-.587579	1.534123

TS_CA1_pC3H4+methylketene

6	-1.312788	-.603021	-.065800
6	-.228965	-1.143692	-.340847
6	1.356671	-.012193	-.448758
6	.784226	1.235601	-.176758
8	-.316101	1.585841	.068119
1	.212103	-2.100341	-.561593
1	1.642064	-.091209	-1.500804
6	-2.694012	-.249513	.237420
1	-2.768179	.227504	1.218970
1	-3.084108	.462409	-.495684
1	-3.350035	-1.129464	.237769
6	2.406404	-.552092	.511788
1	2.541020	-1.621135	.330942
1	3.375270	-.067042	.374710
1	2.091462	-.417985	1.548464

TS_ B1 → propyne + methylketene

6	-1.669622	-0.717462	-0.162705
6	-0.430100	-0.865616	-0.231073
6	0.677015	0.456397	0.428192
6	1.997978	-0.040912	0.284146
8	2.563882	-0.987158	-0.124979
1	0.269467	-1.618034	-0.585414
1	0.424689	0.493232	1.490052
6	-2.981548	-0.152399	0.125526
1	-3.471420	0.182442	-0.794353
1	-3.637733	-0.897510	0.588267
1	-2.935640	0.707233	0.809556
6	0.392076	1.774769	-0.292061
1	-0.677206	1.981135	-0.239673
1	0.927932	2.609290	0.164254
1	0.674063	1.710820	-1.345007

TS_B1_B3+CO

6	1.765227	0.012446	-0.300634
6	0.603406	0.286807	0.267322
6	-0.603241	0.678410	-0.449683
6	-1.706843	-1.030199	-0.584118
8	-1.859376	-1.641527	0.378039
1	0.507924	0.180884	1.356596
1	-0.463328	0.846323	-1.512856
6	3.153030	-0.275833	0.070957
1	3.521551	-1.190854	-0.403926
1	3.817760	0.539195	-0.237304
1	3.254786	-0.390923	1.161614
6	-1.586828	1.597370	0.228974
1	-1.188168	2.618385	0.274903
1	-2.533871	1.638442	-0.314999
1	-1.790151	1.276754	1.254753

TS_B3_C5H8-12

6	-1.471861	.674951	-.162976
6	-.151080	.890141	.040362
6	.719464	-.230923	-.276058
1	.289501	1.816238	.402314
1	.565217	-.695170	-1.248036
6	-1.843756	-.644769	.140782
1	-1.883710	-.873853	1.211296
1	-2.618198	-1.168866	-.420687
1	-.545286	-1.108430	.080970
6	2.169308	-.229283	.135357
1	2.538895	-1.257913	.184519
1	2.803507	.296037	-.590277
1	2.317621	.231248	1.115094

TS_B3_C5H8-13

6	-.776232	-.148589	-.372717
6	.063353	.891618	.008108
6	1.420624	.583983	.042796
1	-.313327	1.897320	.195810
1	2.204121	1.332545	-.021310
6	-2.179472	-.255363	.097161
1	-2.851572	-.640192	-.675554
1	-2.181063	-1.012705	.896533
1	-2.598166	.662767	.534749
6	1.661132	-.836907	.051016
1	2.606378	-1.185271	-.368107
1	1.445436	-1.357866	.984447
1	.551768	-1.105053	-.504750

TS_M1_B2

6	1.137663	-.184663	-.037982
6	.527212	1.126065	.057746
6	-.864786	1.331418	-.030366
6	-1.851586	.431900	-.204898
8	.473735	-1.200375	-.238076
1	1.167652	1.999133	.122157
1	-1.173083	2.378422	-.099825
6	2.649079	-.261474	.120666
1	2.945589	-1.303002	.237637
1	3.136424	.146830	-.771228
1	2.995688	.321792	.977980
6	-2.435659	-.842777	.193738
1	-1.903280	-1.322860	1.020522
1	-3.484578	-.688867	.481792
1	-2.445829	-1.531250	-.657852

TS_B2_M3

6	-1.399539	-0.071085	0.042574
6	-0.031671	0.179611	-0.399919
6	0.894823	-0.892054	-0.499090
6	1.961544	-0.472438	0.177850
8	-1.772419	-1.179578	0.404406
1	0.300654	1.194446	-0.579846
1	0.605897	-1.919174	-0.700140
6	-2.362599	1.107336	-0.019930
1	-2.223748	1.704440	-0.924870
1	-3.385333	0.734962	0.025905
1	-2.188490	1.764482	0.839230
6	2.871290	0.669416	0.246490
1	2.659367	1.482626	-0.463566
1	2.933856	1.067742	1.262905
1	3.874054	0.282381	0.017289

TS_B2_M5

6	-1.215286	-0.204489	-0.023696
6	-0.425361	1.028024	0.091803
6	0.924331	1.123123	-0.066524
6	1.869207	0.152347	-0.493035
8	-0.730504	-1.310366	-0.219941
1	-0.971258	1.946216	0.280264
1	1.344667	2.127201	0.002271
6	-2.722607	-0.035804	0.115082
1	-2.973967	0.476360	1.049115
1	-3.112480	0.577259	-0.704131
1	-3.199959	-1.014412	0.092329
6	2.567598	-0.694581	0.345479
1	2.353999	-0.813113	1.414141
1	3.285476	-1.397705	-0.074873
1	3.130252	0.369401	-0.114239

TS_B2_M6

6	1.098888	-0.141670	0.005629
8	0.447315	-1.204274	-0.120757
6	-1.799486	0.322618	-0.374501
6	-0.896356	1.279125	-0.015724
6	0.482041	1.142281	0.104908
1	-1.336334	2.276210	0.041855
1	1.088916	2.029452	0.217781
6	2.611575	-0.232167	0.032713
1	3.088807	0.716723	0.282838
1	2.915290	-0.996350	0.751799
1	2.964986	-0.555346	-0.951224
6	-2.402920	-0.778637	0.204416
1	-3.085984	-1.386882	-0.385519
1	-1.256572	-1.134684	-0.025844
1	-2.520076	-0.864227	1.289730

TS_M5_M7

6	.940142	-.087283	-.102082
6	.225508	1.111397	-.395316
6	-1.095161	1.257664	.044292
6	-1.889083	.147738	.324885
8	.427190	-1.229587	.064885
1	.820630	2.000754	-.560780
1	-1.434287	2.253333	.322841
6	2.420705	.021122	.201653
1	2.562434	.061819	1.286270
1	2.945923	-.859662	-.170239
1	2.855607	.921040	-.235743
6	-1.504424	-1.060793	-.253405
1	-1.216993	-1.062599	-1.297773
1	-1.887932	-2.004168	.118886
1	-2.649024	.187110	1.097300

TS_M6_C6H6+H2O

6	1.299562	0.147151	-0.100738
8	0.643806	-1.257758	-0.237413
6	-1.816868	0.240718	0.067621
6	-0.972274	1.246183	-0.021018
6	0.482327	1.215089	-0.116486
1	-1.414366	2.240795	0.006518
1	0.983058	2.175462	-0.134456
6	2.615115	-0.236522	0.233376
1	3.202383	0.456694	0.825388
1	1.531142	-1.484420	0.416039
1	3.181774	-0.757968	-0.539079
6	-2.657672	-0.759947	0.096712
1	-3.100477	-1.158999	-0.814735
1	-0.256225	-1.308573	0.152082
1	-2.978878	-1.216952	1.030745

TS_M2_CA3

6	0.636689	1.144244	0.031023
6	1.156233	-0.108971	0.013945
6	0.052466	-1.073146	0.005672
6	-1.073633	-0.208438	-0.103749
8	-0.718500	1.153230	-0.047994
1	-0.699728	-0.761471	-1.144227
6	-2.532738	-0.471292	0.122984
1	-3.157428	0.162587	-0.509419
1	-2.748106	-1.519804	-0.079854
1	-2.781212	-0.266192	1.167120
6	2.607969	-0.481153	0.049516
1	3.253238	0.397671	0.128798
1	2.815788	-1.137396	0.898793
1	2.887593	-1.031286	-0.853813
1	1.095937	2.122587	0.060201

TS_CA3_M9 [B3LYP/6-311+G(2d,p)]

6	0.558192	1.137137	0.100564
6	1.088926	-0.161105	-0.028533
6	0.065721	-1.033865	-0.372391
6	-1.140136	-0.273270	-0.469001
8	-0.698431	1.286014	-0.101649
6	-2.295408	-0.579601	0.459656
1	-3.068212	0.185028	0.380752
1	-2.721484	-1.544705	0.183648
1	-1.952095	-0.641793	1.493178
1	-1.455774	-0.125441	-1.505260
1	1.112751	2.039515	0.352664
6	2.541106	-0.494747	0.178684
1	2.990522	-0.872026	-0.742547
1	3.116503	0.377044	0.501265
1	2.654829	-1.273027	0.935621

TS_M9_2-pentyne+CO

6	0.735754	1.072944	-0.084019
6	0.687598	-0.674830	-0.057112
6	-0.540677	-0.940488	-0.303386
6	-1.599599	-0.048337	-0.527186
8	1.667410	1.741781	0.077365
6	-2.728106	0.086109	0.487677
1	-2.337827	0.093792	1.507565
1	-3.280701	1.013630	0.319073
1	-3.434600	-0.743759	0.400853
1	-1.951232	0.000587	-1.561991
1	-0.777459	0.985981	-0.401313
6	2.008620	-1.308194	0.202168
1	2.734006	-1.028314	-0.567167
1	2.415267	-0.985583	1.164805
1	1.911723	-2.393800	0.210399

TS_CA3_M11

6	-0.461256	1.204329	0.322987
6	-0.917984	0.005772	-0.098546
6	0.191192	-0.701463	-0.779711
6	1.251325	0.177319	-0.528652
8	0.883020	1.369025	0.080022
6	1.424953	-1.283027	0.561913
1	1.733598	-0.687911	1.426846
1	0.649210	-1.973624	0.874828
1	2.248843	-1.832446	0.119322
1	-0.936996	2.045901	0.805351
6	-2.314362	-0.522356	0.018540
1	-2.336519	-1.437121	0.620867
1	-2.990115	0.202457	0.479848
1	-2.707870	-0.784715	-0.967171
1	2.232478	0.231816	-0.979249

TS_M2_CA4

6	0.455849	1.219421	-0.296778
6	0.930529	0.012843	0.076261
6	-0.240165	-0.641078	0.651807
6	-1.359021	0.240279	0.657765
8	-0.871279	1.372314	-0.020718
1	-0.207498	-1.542560	1.249921
6	-1.550774	-1.178733	-0.594352
1	-1.972202	-0.487590	-1.316147
1	-0.815155	-1.810407	-1.100319
1	-2.314753	-1.774967	-0.110666
1	0.946516	2.066108	-0.756002
6	2.312391	-0.543669	-0.072415
1	2.323117	-1.421440	-0.727894
1	2.993790	0.195561	-0.498998
1	2.723561	-0.857601	0.892121

TS_CA4_M11

6	-1.117135	1.016614	-0.065252
6	0.199628	0.747376	0.013453
6	0.256184	-0.718995	0.075767
6	-1.087564	-1.255215	-0.022421
8	-1.879604	-0.118119	-0.032651
1	-0.324183	-1.152996	1.112855
6	1.496380	-1.555955	-0.090996
1	2.288240	-1.270507	0.605672
1	1.257273	-2.611220	0.049511
1	1.883288	-1.432836	-1.106042
1	-1.657919	1.949171	-0.133529
6	1.353193	1.700628	0.028503
1	1.934614	1.610391	0.951740
1	2.039034	1.511339	-0.803383
1	1.012368	2.734887	-0.049947

TS_CA4_pC3H4+CH3CHCO

6	**-0.139586**	**-1.729682**	**-0.341471**
6	**-0.810471**	**-0.731238**	**-0.017032**
6	**0.320621**	**0.815455**	**0.446496**
6	**1.590850**	**0.236322**	**0.310809**
8	**1.931472**	**-0.842631**	**-0.030337**
1	**0.077743**	**0.981015**	**1.499977**
6	**-0.010789**	**2.006806**	**-0.443605**
1	**-1.074655**	**2.235954**	**-0.368162**
1	**0.539915**	**2.901149**	**-0.144367**
1	**0.223208**	**1.788300**	**-1.487649**
1	**0.177361**	**-2.699228**	**-0.644042**
6	**-2.220113**	**-0.268550**	**0.169074**
1	**-2.356864**	**0.251519**	**1.122254**
1	**-2.516382**	**0.424618**	**-0.623728**
1	**-2.905166**	**-1.116955**	**0.142781**

Table S2: Hindrance potentials and barrier heights for the set of reference molecules and radicals calculated at the B3LYP/6-31+G(d,p) level of theory.

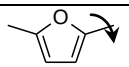
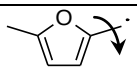
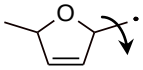
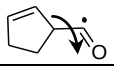
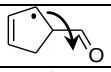
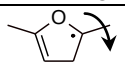
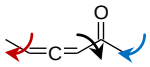
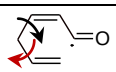
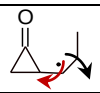
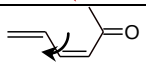
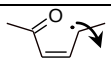
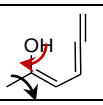
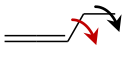
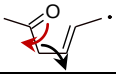
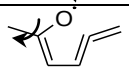
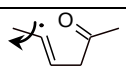
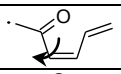
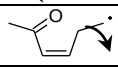
Species	Rotation characteristics		
	V (kcal/mol)	# minima	symmetry
	1.25	3	3
	19	2	2
	2.96	1	1
	0.96	2	2
	1.41	2	1
	4.42	3	3
	3.1	1	1
	3.05	2	1
	1.4	3	3
	3.93	2	1
	6.3	1	1
	0.73	3	3
	1.2	3	3
	7.04	1	1
	1.5	3	3
	0.71	3	3
	2.77	1	1
	2.32	2	1
	3.16	1	1
	3.17	2	1
	10	1	1
	0.36	3	3
	2.42	3	3
	8.77	1	1
	3.09	3	3
	1.66	3	1
	5.09	1	1
	2.17	1	1
	0.2	3	3
	0.27	3	3
	6.18	1	1
	0.47	2	2

Table S3: Zero-point corrected energies at the CBS-QB3 level of theory.

Name	E (0K) CBS-QB3
M1	-308.112744
M2	-308.108787
M3	-308.042442
M4	-308.066250
M5	-308.080865
M6	-308.046407
M7	-308.083655
M8	-308.075018
M9	-308.058926
M10	-308.038292
M11	-308.104954
CA1	-308.017603
CA2	-308.019253
CA3	-308.011074
CA4	-308.012896
B1	-307.970926
B2	-307.985878
B3	-194.795153
C_6H_7O	-307.478627
M2-R1	-307.473833
M2-R2	-307.467661
TS_M1_CA2	-307.983271
TS_CA2_M4	-308.018912
TS_CA2_M2	-307.978963
TS_ M4_1,2-butadiene+CH2CO	-307.94322
TS_ M4_2,3-pentadiene +CO	-307.925002
TS_ M4_3-methylbuta-1,2-diene +CO	-307.942578
TS_ M4_1-butyne+CH2CO	-307.958898
TS_M1_CA1	-307.983271
TS_CA1_M2	-308.005649
TS_CA1_B1	-307.970129
TS_CA1_pC3H4+methylketene	-307.970376
TS_ B1_propyne +methylketene	-307.945083
TS_B1_B3+CO	-307.954292
TS_B3_C5H8-12	-307.936286
TS_B3_C5H8-13	-307.960106
TS_M1_B2	-307.983564
TS_B2_M3	-307.983378
TS_B2_M5	-307.968640
TS_B2_M6	-307.982351
TS_M5_M7	-308.047809
TS_M6_C6H6+H2O	-307.92204
TS_M2_CA3	-307.997449
TS_CA3_M9	-308.011074
TS_M9_2-pentyne+CO	-307.997254
TS_CA3_M11	-307.974985
TS_M2_CA4	-307.976863
TS_CA4_M11	-308.000137
TS_CA4_pC3H4+CH3CHCO	-307.964714

Table S4: Isodesmic reactions used to compute the enthalpies of formation.

Values on the first line below a given isodesmic reactions are enthalpies at 298 K (in Hartree) computed at the CBS-QB3 level of theory.
Experimental data (2nd line below each isodesmic reaction, in kcal mol^{-1}) are taken from NIST chemistry webbook (http://webbook.nist.gov/chemistry/). If not known calculated at the CBS-QB3 level of theory with the atomization energy method.

DMF (M1)						**DMF**
DMF +	2*CH4 =	ethoxyethane	1,3-butadiene			DHf mean
-308.104743	-80.812346	-233.20586	-155.661311	31.3		**-30.0**
	-17.89	-60.28	26	**-29.8**		
DMF +	C2H6 =	THF	1,3-butadiene			
-308.104743	-79.626126	-232.017501	-155.661311	32.7		
	-20	-44.03	26	**-30.7**		
DMF +	CH4 =	DME	cyclopentadiene			
-308.104743	-40.406173	-154.746927	-193.707639	35.4		
	-17.89	-43.99	31.89	**-29.6**		
DMF +	C2H6 =	Furan	iC4H10			
-308.104743	-79.626126	-229.63842	-158.077841	9.2		
	-20	-8.3	-32.42	**-29.9**		
DMF-2,4 (M2)						**DMF-2,4 (M2)**
DMF, 2-4 +	2*CH4 =	ethoxyethane	1,3-butadiene			DHf mean
-308.100721	-80.812346	-233.20586	-155.661311	28.8		**-27.5**
	-17.89	-60.28	26	**-27.3**		
DMF, 2-4 +	C2H6 =	THF	1,3-butadiene			
-308.100721	-79.626126	-232.017501	-155.661311	30.1		
	-20	-44.03	26	**-28.2**		
DMF, 2-4 +	CH4 =	DME	cyclopentadiene			
-308.100721	-40.406173	-154.746927	-193.707639	32.8		
	-17.89	-43.99	31.89	**-27.0**		
DMF, 2-4 +	C2H6 =	Furan	iC4H10			
-308.100721	-79.626126	-229.63842	-158.077841	6.6		
	-20	-8.3	-32.42	**-27.4**		

vinylcyclopropylcarbinyl (M3)						**vinylcyclopropyl**
Dfurop +	CH4 =	2,3-pentadiene	acetaldehyde			DHf mean
-308.033251	-40.406173	-194.869283	-153.577614	-4.7		**14.2**
	-17.89	31.79	-40.8	**13.6**		
Dfurop +	C2H6 =	2,3-pentadiene	acetone			
-308.033251	-79.626126	-194.869283	-192.813157	-14.5		
	-20	31.79	-52.23	**14.0**		
Dfurop +	2*CH4 =	allene	acetone + C2H6			
-308.033251	-80.812346	-116.415548	-272.439283	-5.8		
	-35.78	45.7	-72.23	**15.0**		

dimethyl_furop (M4)						dimethyl_furop
Dfurop +	CH4 =	2,3-pentadiene	acetaldehyde			DHf mean
-308.056827	-40.406173	-194.869283	-153.577614	10.1		**-0.6**
	-17.89	31.79	-40.8	**-1.2**		
Dfurop +	C2H6 =	2,3-pentadiene	acetone			
-308.056827	-79.626126	-194.869283	-192.813157	0.3		
	-20	31.79	-52.23	**-0.8**		
Dfurop +	2*CH4 =	allene	acetone + C2H6			
-308.056827	-80.812346	-116.415548	-272.439283	9.0		
	-35.78	45.7	-72.23	**0.2**		

dimethyl_furop_13 (M5)						dimethyl_furop 13
Dfurop +	CH4 =	2,3-pentadiene	acetaldehyde			DHf mean
-308.072087	-40.406173	-194.869283	-153.577614	19.7		**-10.2**
	-17.89	31.79	-40.8	**-10.8**		
Dfurop +	C2H6 =	2,3-pentadiene	acetone			
-308.072087	-79.626126	-194.869283	-192.813157	9.9		
	-20	31.79	-52.23	**-10.3**		
Dfurop +	2*CH4 =	allene	acetone + C2H6			
-308.072087	-80.812346	-116.415548	-272.439283	18.6		
	-35.78	45.7	-72.23	**-9.4**		

CH2CCHCHC(OH)CH3 (M6)						CH2CCHCHC(OH)
Dfurop +	2*CH4 =	1,2-butadiene	ethanol + ethylene			DHf mean
-308.037059	-80.812346	-155.642326	-233.17753	18.5		**12.3**
	-35.78	38.8	-43.46	**12.5**		
M6 +	2*CH4 =	allene	ethanol + propene			
-308.037059	-80.812346	-116.415548	-272.406059	17.4		
	-35.78	45.7	-51.121	**12.9**		
M6 +	2*CH4 =	1,2-butadiene	methanol + propene			
-308.037059	-80.812346	-155.642326	-233.176853	19.0		
	-35.78	38.8	-44.121	**11.5**		

C6H8O# (M7)						C6H8O#
C6H8O# +	2*CH4 =	ethoxyethane	1,3-butadiene			DHf mean
-308.076159	-80.812346	-233.20586	-155.661311	13.4		**-12.1**
	-17.89	-60.28	26	**-11.9**		
C6H8O# +	C2H6 =	THF	1,3-butadiene			
-308.076159	-79.626126	-232.017501	-155.661311	14.7		
	-20	-44.03	26	**-12.8**		
C6H8O# +	CH4 =	DME	cyclopentadiene			
-308.076159	-40.406173	-154.746927	-193.707639	17.4		
	-17.89	-43.99	31.89	**-11.6**		
C6H8O# +	C2H6 =	Furan	iC4H10			
-308.076159	-79.626126	-229.63842	-158.077841	-8.8		
	-20	-8.3	-32.42	**-11.9**		

M8						M8
C6H6O	2*CH4 =	divinylether	2-butene			DHf mean
-306.880407	-80.812346	-230.790263	-156.869284	20.8		**9.8**
	-35.78	-3.03	-2.58	**9.3**		
C6H6O	2*CH4 =	1,3,5-hexatriene	DME			
-306.880407	-80.812346	-232.911445	-154.746927	21.6		
	-35.78	40.1	-43.99	**10.3**		
M9						**M9**
C6H6O	3*CH4 =	acetone	1,3-butadiene + C2H6			DHf mean
-306.902026	-121.218519	-192.813157	-235.287437	12.5		**-5.2**
	-53.67	-52.23	6	**-5.1**		
C6H6O	3*CH4 =	acetone	1,3-pentadiene			
-306.902026	-80.812346	-192.813157	-194.890151	6.9		
	-35.78	-52.23	18.11	**-5.3**		
						0
M10						**M10**
C6H6O	2*CH4 =	1,3,5-hexatriene	DME			DHf mean
-306.861848	-80.812346	-232.911445	-154.746927	9.9		**21.5**
	-35.78	40.1	-43.99	**22.0**		
C6H6O	2*CH4 =	divinylether	2-butene			
-306.861848	-80.812346	-230.790263	-156.869284	9.2		
	-35.78	-3.03	-2.58	**21.0**		

DMF (M11)						DMF (M11)
DMF +	2*CH4 =	ethoxyethane	1,3-butadiene			DHf mean
-308.096962	-80.812346	-233.20586	-155.661311	26.4		**-25.1**
	-17.89	-60.28	26	**-24.9**		
DMF +	C2H6 =	THF	1,3-butadiene			
-308.096962	-79.626126	-232.017501	-155.661311	27.8		
	-20	-44.03	26	**-25.8**		
DMF +	CH4 =	DME	cyclopentadiene			
-308.096962	-40.406173	-154.746927	-193.707639	30.5		
	-17.89	-43.99	31.89	**-24.7**		
DMF +	C2H6 =	Furan	iC4H10			
-308.096962	-79.626126	-229.63842	-158.077841	4.3		
	-20	-8.3	-32.42	**-25.0**		

alpha carbene (CA1)						alpha carbene
alpha carbene +	4*CH4 =	DME + propene +	C4H10 + CH2(singulet)			DHf mean
-308.009472	-161.624692	-272.388104	-197.131379	72.0		**30.8**
	-71.56	-39.111	70.34	**30.8**		
alpha carbene +	2*CH4 =	THF + CH2(singulet)	propene			
-308.009472	-80.812346	-271.071039	-117.641177	68.8		
	-35.78	58.73	4.879	**30.6**		
alpha carbene +	3*CH4 =	ethoxyethane + CH2	1-butene			
-308.009472	-121.218519	-272.259398	-156.86502	65.0		
	-53.67	42.48	-0.15	**31.0**		

beta carbene (CA2)						beta carbene (CA
beta carbene +	4*CH4 =	DME + propene +	C4H10 + CH2(singulet)			DHf mean
-308.010862	-161.624692	-272.388104	-197.131379	72.8		**29.9**
	-71.56	-39.111	70.34	**30.0**		
beta carbene +	2*CH4 =	THF + CH2(singulet)	propene			
-308.010862	-80.812346	-271.071039	-117.641177	69.6		
	-35.78	58.73	4.879	**29.7**		
beta carbene +	3*CH4 =	ethoxyethane + CH2	1-butene			
-308.010862	-121.218519	-272.259398	-156.86502	65.9		
	-53.67	42.48	-0.15	**30.1**		

alpha carbene (CA3)						alpha carbene (C
alpha carbene +	4*CH4 =	DME + propene +	C4H10 + CH2(singulet)			DHf mean
-308.0025917	-161.624692	-272.388104	-197.131379	67.6		**35.1**
	-71.56	-39.111	70.34	**35.1**		
alpha carbene +	2*CH4 =	THF + CH2(singulet)	propene			
-308.0025917	-80.812346	-271.071039	-117.641177	64.5		
	-35.78	58.73	4.879	**34.9**		
alpha carbene +	3*CH4 =	ethoxyethane + CH2	1-butene			
-308.0025917	-121.218519	-272.259398	-156.86502	60.7		
	-53.67	42.48	-0.15	**35.3**		
alpha carbene (CA4)						alpha carbene (C
alpha carbene +	4*CH4 =	DME + propene +	C4H10 + CH2(singulet)			DHf mean
-308.004771	-161.624692	-272.388104	-197.131379	69.0		**33.8**
	-71.56	-39.111	70.34	**33.8**		
alpha carbene +	2*CH4 =	THF + CH2(singulet)	propene			
-308.004771	-80.812346	-271.071039	-117.641177	65.8		
	-35.78	58.73	4.879	**33.6**		
alpha carbene +	3*CH4 =	ethoxyethane + CH2	1-butene			
-308.004771	-121.218519	-272.259398	-156.86502	62.0		
	-53.67	42.48	-0.15	**34.0**		

birad_alpha_c (B1)						**birad_alpha_c**
birad_alpha_c +	3*CH4 =	CHO + C2H3	iC4H10 + C2H6			DHf mean
-307.9610634	-121.218519	-191.439892	-237.703967	22.4		**59.9**
	-53.67	81.4	-52.42	**60.2**		
birad_alpha_c +	2*CH4 =	C2H3O + C2H3	iC4H10			
-307.961063	-80.812346	-230.676066	-158.077841	12.2		
	-35.78	68.1	-32.42	**59.2**		
birad_alpha_c +	2*CH4 =	CHO + C2H3	2-methyl-butane			
-307.961063	-80.812346	-191.439892	-197.301421	20.1		
	-35.78	81.4	-36.73	**60.3**		
birad_C5 (B3)						**birad_C5**
birad_C5	2*CH4 =	iC3H7 + C2H3	C2H6			DHf mean
-194.787313	-80.812346	-195.934173	-79.626126	24.7		83.4
	-35.78	93	-20	**84.1**		
birad_C5	CH4 + C2H4 =	C3H5 + C2H3	propane			
-194.787313	-118.818821	-194.743654	-118.850345	0.0		
	-5.35	111.9	-25.02	**92.2**		
birad_C5	2*CH4 =	C2H3+ C2H5	propane			
-194.787313	-80.812346	-156.705551	-118.850345	27.5		
	-35.78	99.4	-25.02	**82.7**		

DMF_birad (B2)						**DMF_birad (B2)**
birad_alpha_c +	3*CH4 =	CHO + C2H3	iC4H10 + C2H6			DHf mean
-307.9759698	-121.218519	-191.439892	-237.703967	31.8		**50.7**
	-53.67	81.4	-52.42	**50.9**		
birad_alpha_c +	2*CH4 =	i-propenyl + C2H6	CH3COCH2			
-307.9759698	-80.812346	-196.598449	-192.162382	17.2		
	-35.78	40.4	-8.6	**50.3**		
birad_alpha_c +	2*CH4 =	CHO + C2H3	2-methyl-butane			
-307.9759698	-80.812346	-191.439892	-197.301421	29.5		
	-35.78	81.4	-36.73	**51.0**		
birad_alpha_c +	2*CH4 =	acetone	C4H10 + CH2(singulet)			
-307.9759698	-80.812346	-192.813157	-195.918558	35.5		
	-35.78	-52.23	102.61	**50.6**		

DMF_RY (R1)						**DMF_RY (R1)**
C6H7O	CH4 =	furan	n-propyl			DHf mean
-307.471026	-40.406173	-229.63842	-118.189706	30.8		**2.7**
	-17.89	-8.23	23.9	**2.8**		
C6H7O	2*CH4 =	furan	C2H6 + C2H5			
-307.471026	-80.812346	-229.63842	-158.592742	32.8		
	-35.78	-8.23	8.4	**3.2**		
C6H7O	3*CH4 =	CH3OCH3	C3H7+C4H6			
-307.471026	-121.218519	-154.746927	-273.851017	57.5		
	-53.67	-43.99	49.9	**2.1**		

M2-R1						M2-R1
C6H7O	CH4 =	furan	n-propyl			DHf mean
-307.466152	-40.406173	-229.63842	-118.189706	27.7		**5.7**
	-17.89	-8.23	23.9	**5.8**		
C6H7O	2*CH4 =	furan	C2H6 + C2H5			
-307.466152	-80.812346	-229.63842	-158.592742	29.7		
	-35.78	-8.23	8.4	**6.2**		
C6H7O	3*CH4 =	CH3OCH3	C3H7+C4H6			
-307.466152	-121.218519	-154.746927	-273.851017	54.4		
	-53.67	-43.99	49.9	**5.2**		

M2-R2						M2-R2
C6H7O	CH4 =	furan	n-propyl			DHf mean
-307.459947	-40.406173	-229.63842	-118.189706	23.8		**9.6**
	-17.89	-8.23	23.9	**9.7**		
C6H7O	2*CH4 =	furan	C2H6 + C2H5			
-307.459947	-80.812346	-229.63842	-158.592742	25.8		
	-35.78	-8.23	8.4	**10.1**		
C6H7O	3*CH4 =	CH3OCH3	C3H7+C4H6			
-307.459947	-121.218519	-154.746927	-273.851017	50.5		
	-53.67	-43.99	49.9	**9.1**		

Table S5: High-pressure limit rate expressions for DMF decomposition pathways (reverse direction), with tight transition state structures on the PES, computed using CBS-QB3 and TST/HR/Eckart methods.

	$k_\infty = A\,T^n\,e^{-E/RT}$			
Reaction	A	n	E	T (K)
M1 ⇆ CA2	2.25×10^{11}	0.458	8816	500 - 2000
CA2 ⇆ M4	9.94×10^{10}	-0.046	30892	500 - 2000
CA2 ⇆ M2	1.48×10^{11}	0.772	82474	500 - 2000
M1 ⇆ CA1	5.16×10^{10}	0.600	20658	500 - 2000
CA1 ⇆ M2	2.37×10^{12}	0.272	7795	500 - 2000
CA1 ⇆ B1	4.70×10^{09}	0.342	610	500 - 2000
M1 ⇆ B2	3.15×10^{12}	0.091	1973	500 - 2000
B2 ⇆ M3	7.73×10^{11}	0.144	37848	500 - 2000
B2 ⇆ M5	1.90×10^{11}	0.611	70510	500 - 2000
B2 ⇆ M6	7.18×10^{11}	0.095	39695	500 - 2000
M3 ⇆ M2	4.93×10^{10}	1.471	83667	500 - 2000
M5 ⇆ M7	2.06×10^{12}	0.260	22672	500 - 2000
M2 ⇆ CA3	4.32×10^{11}	0.244	7016	500 - 2000
CA3 ⇆ M9	2.94×10^{09}	0.421	30504	500 - 2000
CA3 ⇆ M11	1.54×10^{11}	0.786	82578	500 - 2000
M2 ⇆ CA4	1.57×10^{11}	0.382	21617	500 - 2000
CA4 ⇆ M11	4.71×10^{11}	0.686	66425	500 - 2000

Table S6: NASA polynomials and reaction mechanism in CHEMKIN format.

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! Please cite this work as
! Unimolecular decomposition of 2,5-dimethylfuran: a theoretical study
! B. Sirjean and R. Fournet, PCCP, x, xx-xx, 2012
!
!
! *************************
!           MECHANISM OF DMF
! *************************
! Detailed chemical structures can be found in PES schemes
!
!
ELEMENTS
H O C AR
END

SPECIES

!*DMF initiation species !
M1              ! 2,5-DMF
R1C6H7O         ! C6H7O
R1H
CA2
M4              ! ch3/ch//c//ch/c(/ch3)//o
C4H5-1s                         ! ch///c/ch(.)/ch3
R14CH3CO        ! .c(//o)/ch3
M2              ! 2,4-DMF
CA3
CA4
M8
M9
M10
M11
M2-R1
M2-R2
CH2COZ
C4H6-12
C5H8-23
C5H8-2
C5H7-2s
B2CO
CH3CH3CHCCH
C4H6-1
CA1
B1
M3
M5
M6
M7
pC3H4               !ch///c/ch3
B2
B3
C5H8            ! ch2//ch/ch2/ch//ch2                   1,3-pentadiene
CH3CHCO
C5H8-12                     ! ch2//c//ch/ch2/ch3
C6H6-l2         ! ch2//c//ch/ch//c//ch2
H2O
R5CHO
M5F-2yl
```

R4CH3
nC4H5
M6-RY
R2OH
C4H4
AR

EnD

THERMO ALL
  300.000 1000.000 5000.000

!*Especes ajoutées*!
R1H   l 6/94H   1   0   0   0g   200.000 6000.00 1000.00   1
 0.25000000e+01 0.00000000e+00 0.00000000e+00 0.00000000e+00 0.00000000e+00   2
 0.25473660e+05-0.44668285e+00 0.25000000e+01 0.00000000e+00 0.00000000e+00   3
 0.00000000e+00 0.00000000e+00 0.25473660e+05-0.44668285e+00 0.26219035e+05   4
H2O   l 5/89H   2 O 1   0   0g   200.000 6000.00 1000.00   1
 0.26770389e+01 0.29731816e-02-0.77376889e-06 0.94433514e-10-0.42689991e-14   2
-0.29885894e+05 0.68825500e+01 0.41986352e+01-0.20364017e-02 0.65203416e-05   3
-0.54879269e-08 0.17719680e-11-0.30293726e+05-0.84900901e+00-0.29084817e+05   4
AR   g 5/97AR 1 0   0   0g   200.000 6000.00 1000.00   1
 2.50000000e+00 0.00000000e+00 0.00000000e+00 0.00000000e+00 0.00000000e+00   2
-7.45375000e+02 4.37967491e+00 2.50000000e+00 0.00000000e+00 0.00000000e+00   3
 0.00000000e+00 0.00000000e+00-7.45375000e+02 4.37967491e+00 0.00000000e+00   4
B2CO   rus 79C   1O   1   0   0g   200.000 6000.00 1000.00   1
 0.30484859e+01 0.13517281e-02-0.48579405e-06 0.78853644e-10-0.46980746e-14   2
-0.14266117e+05 0.60170977e+01 0.35795335e+01-0.61035369e-03 0.10168143e-05   3
 0.90700586e-09-0.90442449e-12-0.14344086e+05 0.35084093e+01-0.13293628e+05   4
R14CH3CO   iu2/03C 2 H 3 O 1   0 g   200.000 6000.00 1000.00   1
 0.53137165e+01 0.91737793e-02-0.33220386e-05 0.53947456e-09-0.32452368e-13   2
-0.36450414e+04-0.16757558e+01 0.40358705e+01 0.87729487e-03 0.30710010e-04   3
-0.39247565e-07 0.15296869e-10-0.26820738e+04 0.78617682e+01-0.12388039e+04   4
CH2COZ   g 4/02C 2 H 2 O 1   0 g   200.000 6000.00 1000.00   1
 5.75871449e+00 6.35124053e-03-2.25955361e-06 3.62321512e-10-2.15855515e-14   2
-8.08533464e+03-4.96490444e+00 2.13241136e+00 1.81319455e-02-1.74093315e-05   3
 9.35336040e-09-2.01724844e-12-7.14808520e+03 1.33807969e+01-5.84267744e+03   4
pC3H4   t 2/90H 4 C 3   0   0 g   200.000 6000.00 1000.00   1
 0.60252400e+01 0.11336542e-01-0.40223391e-05 0.64376063e-09-0.38299635e-13   2
 0.19620942e+05-0.86043785e+01 0.26803869e+01 0.15799651e-01 0.25070596e-05   3
-0.13657623e-07 0.66154285e-11 0.20802374e+05 0.98769351e+01 0.22302059e+05   4
C4H5-1s   H   5C   4   0   0g   300.00   5000.00 1000.00   1 BS-CBSQB3
 7.69293940E+00 1.54258422E-02-5.90706254E-06 1.04195983E-09-6.93720612E-14   2
 3.51003630E+04-1.31002920E+01 1.61027097E+00 3.28109340E-02-2.45693748E-05   3
 9.62797991E-09-1.32525965E-12 3.68073742E+04 1.83050762E+01   4
C4H6-12   0C   4H   6   G 0300.00   5000.00 1000.00   1
  .88417616E+01 .15843917E-01 -.53288832E-05 .83887475E-09 -.50956042E-13   2
  .15358018E+05 -.21569241E+02 .13161099E+01 .32781690E-01 -.17367984E-04   3
  .31549054E-08 .24441525E-12 .17789736E+05 .18652039E+02   4
C4H6-1   0C   4H   6   G 0300.00   5000.00 1000.00   1
 0.83276472E+01 0.16502315E-01-0.56312797E-05 0.89907620E-09-0.55341236E-13   2
 0.16017064E+05-0.18720215E+02 0.14775175E+01 0.33041432E-01-0.18198547E-04   3
 0.32913221E-08 0.41783853E-12 0.18094027E+05 0.17427605E+02   4
C5H8   C   5H   8O   0   G   0300.00   5000.00 1000.00   1
 0.11670992E+02 0.23878116E-01-0.88798688E-05 0.15070004E-08-0.96833511E-13   2
 0.29606875E+04-0.38388065E+02 0.36735153E+01 0.31901374E-01-0.40754057E-05   3
-0.44839923E-08 0.10373115E-11 0.66159673E+04 0.81445122E+01   4
CH3CHCO   H   4C   3O   1   0g   300.00   5000.00 1000.00   1
 6.41142736E+00 1.41180512E-02-5.47884915E-06 9.75510219E-10-6.53860403E-14   2
-1.12002860E+04-6.98716513E+00 2.51775679E+00 1.97247469E-02-9.91194448E-07   3

-1.03311292E-08 5.01227079E-12-9.80356352E+03 1.45477165E+01 4
C5H8-12 C 5H 8O 0 G 0300.00 5000.00 1000.00 1
0.11842818E+02 0.20301070E-01-0.67252231E-05 0.10506498E-08-0.63661506E-13 2
0.11569117E+05-0.36193130E+02 0.63297063E+00 0.46450026E-01-0.26112299E-04 3
0.50091677E-08 0.41070825E-12 0.15082342E+05 0.23348232E+02 4
!*DMF UNIMOLECULAR INITIATION MECHANISM* (CBSQB3)!
M1 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.17792073E+01 2.85086757E-02-1.11333319E-05 1.99173491E-09-1.33982691E-13 2
-2.11130695E+04-3.67325928E+01 8.03526924E-01 4.43305994E-02 4.19434117E-06 3
-3.49560899E-08 1.65826978E-11-1.72836857E+04 2.37121051E+01 4
M2 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.17507214E+01 2.85323202E-02-1.11416636E-05 1.99310905E-09-1.34069370E-13 2
-1.98398788E+04-3.65534702E+01 9.81305762E-01 4.35634382E-02 5.29256086E-06 3
-3.56109186E-08 1.67166549E-11-1.60529620E+04 2.28891553E+01 4
M3 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.33637948E+01 2.66475885E-02-1.04353326E-05 1.87050464E-09-1.26004554E-13 2
7.79505289E+02-4.03490571E+01 2.20408315E+00 4.54691495E-02-3.65339547E-06 3
-2.60382230E-08 1.32832060E-11 4.54429462E+03 2.04549946E+01 4
M4 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.31123130E+01 2.70313492E-02-1.06211461E-05 1.90792098E-09-1.28711095E-13 2
-6.55772052E+03-3.82463856E+01 3.36118275E+00 4.09374257E-02 1.79956683E-06 3
-2.81171725E-08 1.32619168E-11-3.09098365E+03 1.56332033E+01 4
M5 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.34841494E+01 2.75330271E-02-1.10218444E-05 2.00315143E-09-1.36182468E-13 2
-1.17105735E+04-4.26388201E+01 1.31598715E+00 4.83574977E-02-5.70561360E-06 3
-2.51806416E-08 1.30096836E-11-7.58148485E+03 2.36822304E+01 4
M6 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.45828789E+01 2.64245517E-02-1.05619757E-05 1.91683361E-09-1.30156786E-13 2
-5.05932212E+02-4.90023566E+01 1.02464106E+00 6.19095416E-02-4.29604761E-05 3
1.23389598E-08-1.45838728E-13 3.48728924E+03 2.18751820E+01 4
M7 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.19191145E+01 2.89417030E-02-1.13280633E-05 2.02982515E-09-1.36703699E-13 2
-1.22651167E+04-3.84602626E+01-1.46577596E+00 5.47640541E-02-1.25343839E-05 3
-2.22277640E-08 1.28296891E-11-7.93858593E+03 3.35998913E+01 4
B1 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.33151102E+01 2.59331531E-02-1.00721885E-05 1.79442506E-09-1.20329254E-13 2
2.40892087E+04-3.65954916E+01 3.12513494E+00 4.97413502E-02-2.50097914E-05 3
-9.36720293E-10 3.87705127E-12 2.72211969E+04 1.73463453E+01 4
B2 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.28206882E+01 2.75323852E-02-1.07507929E-05 1.92287141E-09-1.29319876E-13 2
1.92845044E+04-3.72127261E+01 2.01893495E+00 4.69414201E-02-8.16937445E-06 3
-2.06827232E-08 1.12307238E-11 2.28819680E+04 2.13761859E+01 4
B3 H 8C 5 0 0g 300.00 5000.00 1000.00 1
9.11031421E+00 2.52020877E-02-9.79174291E-06 1.74487806E-09-1.17026079E-13 2
3.72747279E+04-2.01230216E+01 3.30831606E+00 2.62103782E-02 2.02169381E-05 3
-4.03405157E-08 1.67057182E-11 3.97102828E+04 1.37465455E+01 4
CA1 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.23306693E+01 2.80240728E-02-1.09529356E-05 1.96050516E-09-1.31929906E-13 2
9.32988826E+03-3.81797710E+01 2.78627324E-01 4.93474491E-02-5.90684405E-06 3
-2.65692544E-08 1.40238496E-11 1.33200215E+04 2.71740101E+01 4
CA2 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.23133588E+01 2.80184801E-02-1.09451726E-05 1.95844831E-09-1.31760417E-13 2
8.89644693E+03-3.83243476E+01 1.24423624E+00 4.42064645E-02 4.15421950E-06 3
-3.52595594E-08 1.68122366E-11 1.27346870E+04 2.25474617E+01 4
CA3 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.27535134E+01 2.75926049E-02-1.07755774E-05 1.92766128E-09-1.29666561E-13 2
1.13998405E+04-4.12733622E+01-1.08306245E-01 5.40661393E-02-1.68761742E-05 3
-1.63749091E-08 1.06054010E-11 1.54680604E+04 2.75440298E+01 4
CA4 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.28834121E+01 2.74572273E-02-1.07191821E-05 1.91712376E-09-1.28935791E-13 2

1.07163787E+04-4.22845144E+01-5.70616201E-01 5.74137942E-02-2.40114660E-05 3
-1.00222579E-08 8.54387788E-12 1.48543585E+04 2.91312370E+01 4
M8 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.30940321E+01 2.70668478E-02-1.06381992E-05 1.91121139E-09-1.28938139E-13 2
-9.66634020E+03-3.90615283E+01 4.50668767E+00 3.70419329E-02 6.44721856E-06 3
-3.02434093E-08 1.34931046E-11-6.46658909E+03 9.02966777E+00 4
M9 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.24882547E+01 2.72876138E-02-1.06282017E-05 1.89722017E-09-1.27402263E-13 2
-3.80531390E+03-3.45384663E+01 4.97218317E+00 3.66390872E-02 2.27566706E-06 3
-2.40782839E-08 1.10525259E-11-1.02608202E+03 7.41961634E+00 4
M10 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.28232691E+01 2.69286711E-02-1.04786729E-05 1.86950311E-09-1.25498608E-13 2
2.43543735E+03-3.78896146E+01 3.16622256E+00 4.53189015E-02-1.20463104E-05 3
-1.36966975E-08 8.21981588E-12 5.62489099E+03 1.42939047E+01 4
M11 H 8C 6O 1 0g 300.00 5000.00 1000.00 1
1.16869998E+01 2.85998756E-02-1.11700254E-05 1.99842771E-09-1.34438836E-13 2
-1.86127851E+04-3.69189335E+01 1.14318272E+00 4.25878992E-02 7.01478405E-06 3
-3.68831247E-08 1.70604054E-11-1.48629576E+04 2.14728446E+01 4
M2-R1 H 7C 6O 1 0g 300.00 5000.00 1000.00 1
1.30090495E+01 2.48947836E-02-9.70014700E-06 1.73295559E-09-1.16472648E-13 2
-3.35111230E+03-4.31839441E+01-2.69237141E+00 6.70957584E-02-4.69210672E-05 3
1.02196595E-08 2.06604905E-12 1.08153055E+03 3.82920737E+01 4
M2-R2 H 7C 6O 1 0g 300.00 5000.00 1000.00 1
1.30398982E+01 2.48568566E-02-9.68256240E-06 1.72942599E-09-1.16215349E-13 2
-1.37430577E+03-4.38451493E+01-2.28783752E+00 6.58741864E-02-4.56091112E-05 3
9.71124081E-09 2.08683992E-12 2.96724364E+03 3.57492988E+01 4
C6H6-l2 H 6C 6 0 0g 300.00 5000.00 1000.00 1
1.17706113E+01 2.11906643E-02-8.43097565E-06 1.52510194E-09-1.03312403E-13 2
4.39076061E+04-3.53687917E+01-4.43262542E-01 5.80795781E-02-5.19869371E-05 3
2.52558507E-08-5.00425477E-12 4.72281909E+04 2.71877035E+01 4
C5H8-23 H 8C 5 0 0g 300.00 5000.00 1000.00 1
8.44234973E+00 2.56818914E-02-9.93780670E-06 1.76575984E-09-1.18174566E-13 2
1.15651827E+04-1.81226866E+01 3.65389040E+00 2.44799076E-02 2.03843373E-05 3
-3.82363172E-08 1.55042186E-11 1.37075297E+04 1.04053327E+01 4
CH3CH3CHCCH H 8C 5 0 0g 300.00 5000.00 1000.00 1
9.99582553E+00 2.38590599E-02-9.13194455E-06 1.61003258E-09-1.07148556E-13 2
1.16521359E+04-2.69761721E+01-1.70019175E-01 5.51860509E-02-4.68546903E-05 3
2.23696197E-08-4.35068583E-12 1.43745270E+04 2.49068018E+01 4
C5H8-2 H 8C 5 0 0g 300.00 5000.00 1000.00 1
8.42290060E+00 2.56714782E-02-9.92432837E-06 1.76201975E-09-1.17853297E-13 2
1.11526191E+04-1.70327524E+01 2.59065423E+00 3.18378369E-02 3.53243783E-06 3
-2.22443618E-08 1.00485663E-11 1.33694642E+04 1.58032032E+01 4
C5H7-2s H 7C 5 0 0g 300.00 5000.00 1000.00 1
8.44671959E+00 2.29551946E-02-8.90207783E-06 1.58412956E-09-1.06133533E-13 2
2.93668575E+04-1.50768524E+01 3.18158136E+00 2.73126385E-02 6.78819210E-06 3
-2.36021784E-08 1.02525556E-11 3.14342405E+04 1.48804602E+01 4
R5CHO t 5/03C 1 H 1 O 1 0 g 200.000 6000.00 1000.00 1
3.92001542e+00 2.52279324e-03-6.71004164e-07 1.05615948e-10-7.43798261e-15 2
3.65342928e+03 3.58077056e+00 4.23754610e+00-3.32075257e-03 1.40030264e-05 3
-1.34239995e-08 4.37416208e-12 3.87241185e+03 3.30834869e+00 5.08749163e+03 4
R1C6H7O H 7C 6O 1 0g 300.00 5000.00 1000.00 1
1.31102927E+01 2.47948072E-02-9.65974341E-06 1.72554291E-09-1.15964578E-13 2
-4.87490895E+03-4.38217815E+01-2.28163642E+00 6.56313207E-02-4.44613399E-05 3
8.22249915E-09 2.69246635E-12-5.03625687E+02 3.61780235E+01 4
R4CH3 iu0702C 1 H 3 0 0 g 200.000 6000.00 1000.00 1
0.29781206e+01 0.57978520e-02-0.19755800e-05 0.30729790e-09-0.17917416e-13 2
0.16509513e+05 0.47224799e+01 0.36571797e+01 0.21265979e-02 0.54583883e-05 3
-0.66181003e-08 0.24657074e-11 0.16422716e+05 0.16735354e+01 0.17643935e+05 4
M5F-2yl H 5C 5O 1 0g 300.00 5000.00 1000.00 1
1.03070859E+01 1.91794860E-02-7.52851023E-06 1.35195389E-09-9.12029925E-14 2

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 1.92715511E+04-2.87359352E+01-5.22268588E-01 4.23154373E-02-1.47179134E-05    3
-1.23095218E-08 8.41272608E-12 2.26298547E+04 2.89402452E+01                   4
nC4H5                C   4H   5O   0     G  0300.00   5000.00  1000.00      1
 0.87693729E+01 0.12676305E-01-0.35977159E-05 0.50347698E-09-0.28290782E-13    2
 0.38532445E+05-0.19949425E+02-0.11109806E+01 0.46597324E-01-0.45865116E-04    3
 0.23767367E-07-0.50623750E-11 0.40732270E+05 0.29018211E+02                   4
M6-RY                H   7C   6O   1    0g    300.00   5000.00 1000.00      1
 1.49481203E+01 2.30376767E-02-8.84552512E-06 1.56432152E-09-1.04384729E-13    2
 1.45064529E+04-5.04446617E+01-1.59090232E+00 7.69197742E-02-7.70967331E-05    3
 4.10522697E-08-8.73094312E-12 1.86941651E+04 3.30235400E+01                   4
R2OH             iu3/03O   1 H  1    0    0g   200.000  6000.00  1000.00      1
 2.83853033e+00 1.10741289e-03-2.94000209e-07 4.20698729e-11-2.42289890e-15    2
 3.69780808e+03 5.84494652e+00 3.99198424e+00-2.40106655e-03 4.61664033e-06    3
-3.87916306e-09 1.36319502e-12 3.36889836e+03-1.03998477e-01 4.48613328e+03    4
C4H4                 0C   4H   4         G  0300.00   5000.00  1000.00      1
 0.63549404E+01 0.15122039E-01-0.57226539E-05 0.98267505E-09-0.63638168E-13    2
 0.33896547E+05-0.74671631E+01 0.15192467E+01 0.29964752E-01-0.19455949E-04    3
 0.39837320E-08 0.64256348E-12 0.34997141E+05 0.16783657E+02                   4
END

REACTIONS
!
!
!*****************************************************!
!* unimolecular initiation from CBS-QB3 calculations !
!*****************************************************!
!  initial C-H bond fission
!
!R1C6H7O+R1H=M1          6.55E13     0.070     -51.5 ! Harding et al.
M1=>R1C6H7O+R1H         2.37E+15     0.070      85698.2 ! reverse from combination
!M5F-2yl+R4CH3=M1        1.38E+13     0.000        45.7 ! C6H5#+CH3 NIST (Lin)
M1=>M5F-2yl+R4CH3       2.60E+16     0.000    110532.08 ! reverse from combination
!
!  H transfer
!
M1=CA2                    4.93E+11     0.659     68712.0 !CBS-QB3 500-2000K k inf!
CA2=M4                      5.73E+12     0.755       756.0 !CBS-QB3 500-2000K k inf!
CA2=M2                    7.36E+10     0.561     25093.0 !CBS-QB3 500-2000K k inf!
!
!
!  CH3 transfer scheme
!
M1=CA1                    1.31E+11     0.815     81420.0 !CBS-QB3 500-2000K k inf!
CA1=>CH3CHCO+pC3H4              8.52E+13     0.321     31670.0 !CBS-QB3 500-2000K k inf!
CA1=M2                    1.02E+12     0.272     7795.0  !CBS-QB3 500-2000K k inf!
CA1=B1                    4.69E+13     0.015     30862.0 !CBS-QB3 500-2000K k inf!
B1=>CH3CHCO+pC3H4               1.67E+13     0.115     10853.0 !CBS-QB3 500-2000K k inf!
B1=>B3+B2CO                   3.61E+13     0.155     10537.0 !CBS-QB3 500-2000K k inf!
B3=C5H8                   7.30E+05     1.803     7927.0  !5 member ring TS ; CBS-QB3 500-2000K k inf!
duplicate
B3=C5H8                         1.45E+07     1.643     7530.0  !3 member ring TS ; CBS-QB3 300-2000K k inf!
duplicate
B3=C5H8-12                  1.50E+05     2.001     22542.0 !CBS-QB3 500-2000K k inf!
!
! DMF ring opening scheme
!
M1=B2                     7.88E+13     0.489     82727.0 !CBS-QB3 500-2000K k inf!
B2=M3                     2.82E+12     0.049     1610.0  !CBS-QB3 500-2000K k inf!
B2=M5                     3.20E+09     1.006     9294.0  !CBS-QB3 500-2000K k inf!
B2=M6                     1.35E+09     0.892     1230.0  !CBS-QB3 500-2000K k inf!
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```
M6=>C6H6-l2+H2O              2.41E+08    1.523    75786.0 !CBS-QB3 500-2000K k inf!
!M6-RY+R1H=M6                2.00E+13    0.000        0.0 ! literature review
M6=>C6H6-l2+R2OH+R1H         3.61E+14    0.000    81632.2 !from reverse reaction
M3=M2                     9.60E+08    1.157    41665.0 !CBS-QB3 500-2000K k inf!
M5=M7                     4.55E+11   -0.135    20545.0 !CBS-QB3 500-2000K k inf!
!R14CH3CO+nC4H5=M5           2.00E+13    0.000        0.0 ! Litterature review
M5=>R14CH3CO+nC4H5           7.44E+16    0.000    86909.9 !from reverse reaction
!
!****************************!
! M4 decomposition submech  !
!****************************!
!
! initial bond fission
!
!R14CH3CO+C4H5-1s=M4      2.000E+13    0.000     0.00 ! Litterature review
M4=>R14CH3CO+C4H4+R1H     5.88E+16     0.000      70357.7 !reverse fitted
!
! Pericyclic reactions
!
M4=>CH2COZ+C4H6-12            9.25E+08  1.218   77070.0 !CBS-QB3 500-2000K - kinf!
M4=>C5H8-23+B2CO              3.05E+10  0.785   89076.0 !CBS-QB3 500-2000K - kinf!
M4=>CH3CH3CHCCH+B2CO          6.63E+09  0.762   77547.0 !CBS-QB3 500-2000K - kinf!
M4=>CH2COZ+C4H6-1             5.42E+07  1.772   65550.0 !CBS-QB3 500-2000K - kinf!
!
!****************************!
! M2 decomposition submech  !
!****************************!
!
M2=CA4                    7.89E+10  0.794   82894.0 !CBS-QB3 500-2000K - kinf!
CA4=>CH3CHCO+pC3H4            1.87E+14  0.156   32181.0 !CBS-QB3 500-2000K - kinf!
CA4=M11                    1.04E+12  0.254    7553.0 !CBS-QB3 500-2000K - kinf!
M2=CA3                    3.82E+11  0.613   69588.0 !CBS-QB3 500-2000K - kinf!
CA3=M9                    7.69E+12  0.014     323.0 !CBS-QB3 500-2000K - kinf!
M9=>C5H8-2+B2CO              4.44E+08  1.229   37544.0 !CBS-QB3 500-2000K - kinf!
!C5H7-2s+R5CHO=M9             2.00E+13  0.000       0.0 !Litterature review
M9=>C5H7-2s+R5CHO             6.19E+16  0.000   68633.4 !reverse fitted
!M2-R1+R1H=M2                6.55E+13  0.070     -51.5 !Harding et al.
M2=>M2-R1+R1H                2.41E+15  0.070   86098.7 !reverse from combination
!M2-R2+R1H=M2                6.55E+13  0.070     -51.5 !Harding et al.
M2=>M2-R2+R1H                1.49E+15  0.070   90063.3 !reverse from combination
M2=M10                    9.74E+13  0.304   82685.0 !Analogy with M1=M3, from AEQS on B2 (see
manuscript)
M2=M8                     1.10e+11  1.261   90368.8 !Analogy with M1=M5, from AEQS on B2 (see
manuscript)
M10=M11                    9.60E+08  1.157   41665.0 ! from M3=M2
EnD
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