Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

High Temperature Pyrolysis of 2-Methyl Furan

R. S. Tranter,[a, †] P. T. Lynch[a,b] J. B. Randazzo[a], J. P. A. Lockhart[a,c], X. Chen[d] and C. F. Goldsmith[a,e]

[a] Chemical Sciences and Engineering Division, Argonne National Laboratory Argonne, IL 60439.

[b] Current Address: Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago IL 60607

[c] Current Address: Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973

[d] Current Address: Department of Chemistry, Brown University, Providence, RI 02912

[e] Current Address: Department of Chemical and Biochemical Engineering, Brown University, Providence, RI 02912

† Corresponding author, tranter@anl.gov.

Table S1. Full reaction mechanism used to model 2-methyl furan chemistry. $k=AT^n\exp(-R/T)$. Units: mol, s, cm^3, cal, K.

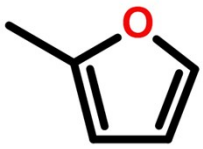
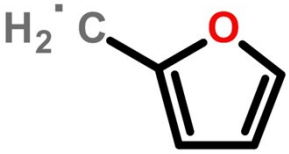
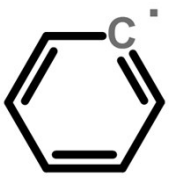
#	Rxn	A		n	Ea/R	$\Delta H_{r,\,298\,K}$	Ref.
R1	2MF = MF22 + H	**60 Torr**	**100.96**	**-24.42**	**71079**	85203	p.w.
		120 Torr	**106.17**	**-25.72**	**74758**		
		240 Torr	**141.07**	**-35.23**	**90552**		
		60 Torr	80.90	-18.98	61600		
		120 Torr	86.50	-20.49	65418		
		240 Torr	89.89	-21.28	68086		
R2	2MF = $pC_3H_4 + C_2H_2O$	60 Torr	78.78	-18.70	61399	51052	p.w.
		120Torr	85.60	-20.50	65721		
		240 Torr	90.33	-21.55	68790		
R3	2MF = $1\text{-}C_4H_6 + CO$	60 Torr	74.10	-17.36	55964	31327	p.w.
		120 Torr	75.12	-17.54	57417		
		240 Torr	74.25	-17.20	58021		
R4	2MF = $C_3H_3 + CH_3 + CO$	**60 Torr**	**23.64**	**-3.65**	**31725**	110839	p.w.
		120 Torr	**46.14**	**-9.78**	**41261**		
		240 Torr	**196.81**	**-50.00**	**121271**		
		60 Torr	57.56	-12.58	51434		
		120 Torr	81.82	-19.10	63456		
		240Torr	111.91	-27.20	78401		
R5a	2MF = $C_4H_4 + H + HCO$	60 Torr	83.39	-19.91	65979	149273	p.w.
		120 Torr	90.83	-21.79	74068		
		240 Torr	94.97	-22.77	71927		
R5b	2MF = $C_2H_2 + C_2H_3 + HCO$	60 Torr	83.09	-19.91	65979	153795	p.w.
		120 Torr	90.54	-21.79	70149		
		240 Torr	94.67	-22.77	72917		
R7	HCO + M = H + CO + M		17.681	-1.20	8923	15576	2
R8	H + 2MF = MF22 + H_2		5.908	2.38	2370	-19003	1
R9	MF22 = CO + $N13C_4H_5$		12.977	0.27	20584	45597	1
R10	$N13C_4H_5 = C_2H_3 + C_2H_2$		40.660	-8.96	24117	38571	1
R11	$N13C_4H_5 = C_4H_4 + H$		48.628	-11.18	25694	34049	1
R12	$C_2H_6 + M = H + C_2H_5 + M$		42.519	-8.07	55561	100751	3
R13	$C_2H_6 + H = C_2H_5 + H_2$		2.740	3.50	2600	-3455	3
R14	$C_2H_6 + CH_3 = C_2H_5 + CH_4$		-0.261	4.00	4170	-4216	3
R15	$CH_3 + CH_3 = C_2H_5 + H$		13.732	0.00	8080	10744	3
R16	$H + C_2H_4 = C_2H_5$		40.870	-8.81	5838	-36042	3
R17	$H + C_2H_4 = H_2 + C_2H_3$		7.703	1.93	6543	6233	3
R18	$C_2H_4 + M = H_2 + C_2H_2 + M$		17.310	0.00	39392	41993	3
R19	$C_2H_4 + M = H + C_2H_3 + M$		17.413	0.00	48606	110439	3
R20	$C_2H_5 + H = H_2 + C_2H_4$		12.300	0.00	0	-68164	3
R21	$H + C_2H_2 = C_2H_3$		30.248	-5.98	3020	-35760	3
R22	$H + C_2H_3 = H_2 + C_2H_2$		13.600	0.00	0	-68446	3
R23	$H + CH_4 = CH_3 + H_2$		5.778	2.50	4882	761	3
R24	$CH_3 + CH_2(T) = H + C_2H_4$		15.070	-0.34	77	-63832	3
R25	$CH_4 + CH_2(T) = CH_3 + CH_3$		6.390	2.00	4162	-5651	3
R26	$H_2 + CH_2(S) = CH_3 + H$		13.800	0.00	0	-15393	3
R27	$CH_3 + M = H + CH_2(T) + M$		16.000	0.00	45602	110618	3

R28	$CH_3 + C_2H_5 = CH_4 + C_2H_4$	11.950	0.00	0	-68925	3
R29	$H + H + M = H_2 + M$	18.000	-1.00	0	-104206	
R30	$CH_4 + CH_2(S) = CH_3 + CH_3$	13.204	0.00	-287	-14632	3
R31	$CH_3 + CH_2(S) = H + C_2H_4$	13.079	0.00	-287	-72813	3
R32	$CH_2(S) + M = CH_2(T) + M$	12.950	0.00	302	-8981	3
R33	$C_2H_6 + CH_2(S) = CH_3 + C_2H_5$	13.600	0.00	-277	-18848	3
R34	$CH_2(T) + CH_2(T) = C_2H_2 + H_2$	13.500	0.00	0	-132457	3
R35	$H_2 + CH_2(T) = CH_3 + H$	5.700	2.00	3624	-6412	3
R36	$C_3H_3 + C_3H_3 = C_6H_{6,other}$[a]	67.507	-15.93	15775	-87574	4
R37	$C_3H_3 + C_3H_3 =$ Benzene	77.336	-18.68	22404	-148138	4–6
R38	$C_3H_3 + C_3H_3 = C_6H_5 + H$	61.173	-13.59	21173	-35305	4–6
R39	$C_6H_5 = oC_6H_4 + H$	74.300	-17.20	58178	81697	7
R40	$C_6H_5 + H =$ Benzene	49.495	-10.20	11410	-112833	7
R41	$C_6H_5 + H = oC_6H_4 + H_2$	-5.928	6.18	4540	-22509	8
R42	$oC_6H_4 = C_2H_2 + C_4H_2$	63.070	-14.27	52693	53871	9
R43	$C_2H_6 + M = CH_3 + CH_3 + M$	18.200	0.00	35229	90007	3
R44	$C_3H_3 + M = C_3H_2(T) + H + M$	12.884	0.00	39439	148601	10
R45	$CH_4 + M = CH_3 + H + M$	47.219	-8.00	61132	104967	3
R46	$H + C_3H_3 = pC_3H_4$	53.029	-11.91	8668	-91923	11
R47	$H + C_3H_3 = H_2 + C_3H_2(T)$	5.330	2.52	3751	44395	11
R48	$pC_3H_4 + H = C_2H_2 + CH_3$	5.114	2.50	503	-6770	12
R49	$C_4H_4 = C_2H_2 + C_2H_2$	15.060	0.00	43647	40282	13
R50	$1\text{-}C_4H_6 = C_3H_3 + CH_3$	86.912	-20.97	55887	79512	4

a) For reactions 1 and 4 the numbers in bold type are from the LS experiments and are recommended for $1600 < T < 2200$ K. The non-bold numbers are from the current RRKM/ME analysis ($1400 < T < 2200$ K) and are provided for comparison.

b) $C_6H_{6,other}$ refers to the stable C_6H_6 isomers other than benzene that are formed by recombination of propargyl radicals. See Lockhart et al.[14] for details.

Table S2. Species identifiers for select species found in Table S1.

Identifier	Name	Structure	InChI
2MF	2-methyl furan		InChI=1S/C5H6O/c1-5-3-2-4-6-5/h2-4H,1H3
MF22	2-furanylmethyl		InChI=1S/C5H5O/c1-5-3-2-4-6-5/h2-4H,1H2
pC_3H_4	propyne		InChI=1S/C3H4/c1-3-2/h1H,2H3
$1\text{-}C_4H_6$	1-butyne		InChI=1S/C4H6/c1-3-4-2/h1H,4H2,2H3
C_4H_4	1-butene-3-yne		InChI=1S/C4H4/c1-3-4-2/h1,4H,2H2
$N13C_4H_5$	n-1,3-butadienyl		InChI=1S/C4H5/c1-3-4-2/h1,3-4H,2H2
$CH_2(S)$	methylene (singlet)		InChI=1S/CH2/h1H2
$CH_2(T)$	methylene (triplet)		InChI=1S/CH2/h1H2
C_6H_5	phenyl radical		InChI=1S/C6H5/c1-2-4-6-5-3-1/h1-5H

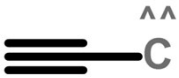
oC_6H_4	ortho-benzyne		InChI=1S/C6H4/c1-2-4-6-5-3-1/h1-4H
$C_3H_2(T)$	propargylene (triplet)		InChI=1S/C3H2/c1-3-2/h1-2H

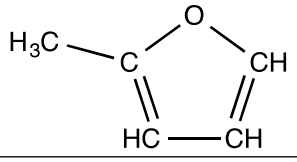
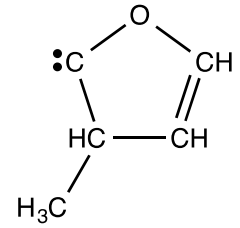
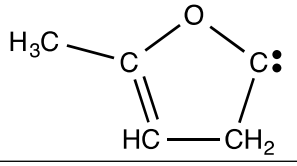
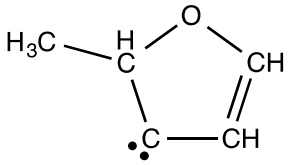
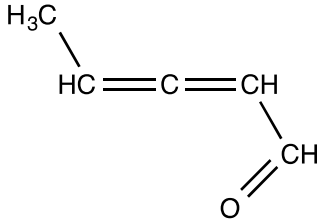
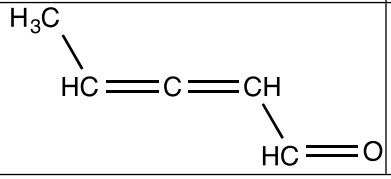
Table S3. List of all experimental conditions and select reaction rates extracted from this study.

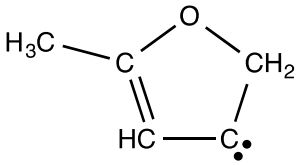
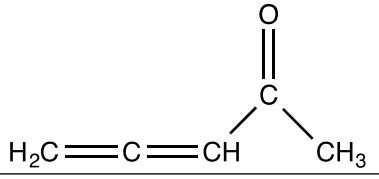
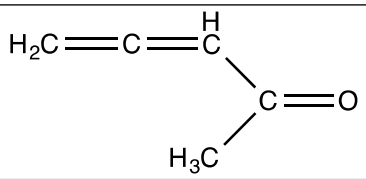
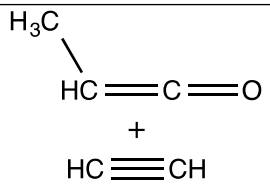
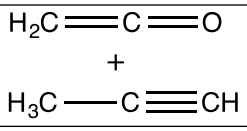
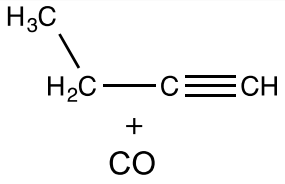
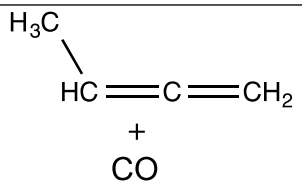
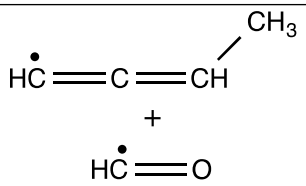
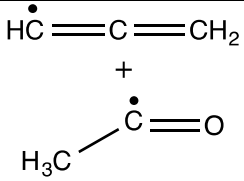
1% 2-methyl furan; 120 Torr						
P_1 / Torr	**T_1 / °C**	**P_2 / Torr**	**T_2 / K**	**k_1 / s^{-1}**	**k_4 / s^{-1}**	**k_{tot} / s^{-1}**
5.30	21.9	121	1805	2.59E+04	1.68E+04	6.08E+04
5.15	22.0	121	1847	3.68E+04	2.42E+04	8.60E+04
5.05	26.3	119	1867	4.52E+04	3.49E+04	1.09E+05
5.00	21.9	120	1878	4.70E+04	3.10E+04	1.09E+05
5.41	22.0	131	1887	4.48E+04	3.32E+04	1.11E+05
4.85	22.0	119	1908	5.87E+04	3.89E+04	1.36E+05
4.90	26.3	119	1921	6.75E+04	5.27E+04	1.62E+05
4.72	21.8	118	1938	6.46E+04	4.84E+04	1.60E+05
4.65	21.8	116	1942	6.64E+04	4.98E+04	1.64E+05
4.71	22.0	118	1952	7.97E+04	5.33E+04	1.84E+05
4.80	26.3	120	1961	8.86E+04	6.98E+04	2.13E+05
4.55	22.0	118	2002	1.10E+05	7.41E+04	2.53E+05
4.75	26.3	122	2009	1.20E+05	8.68E+04	2.79E+05
4.80	26.3	124	2019	1.27E+05	1.01E+05	3.05E+05
4.65	26.3	121	2035	1.40E+05	1.02E+05	3.24E+05
4.50	21.8	120	2053	1.31E+05	1.01E+05	3.24E+05
4.55	26.3	122	2094	1.92E+05	1.42E+05	4.47E+05
4.30	26.3	118	2132	1.97E+05	1.54E+05	4.86E+05
4.55	26.3	127	2161	2.26E+05	1.77E+05	5.56E+05
4.05	26.3	118	2246	3.22E+05	2.58E+05	7.95E+05
4.15	26.3	121	2248	3.25E+05	2.60E+05	8.01E+05
1% 2-methyl furan; 240 Torr						
P_1 / Torr	**T_1 / °C**	**P_2 / Torr**	**T_2 / K**	**k_1 / s^{-1}**	**k_4 / s^{-1}**	**k_{tot} / s^{-1}**
11.9	21.5	240	1622	5.79E+03	7.82E+03	1.77E+04
11.3	21.5	236	1672	9.50E+03	1.45E+04	3.12E+04
11.6	20.6	250	1706	1.24E+04	1.70E+04	3.97E+04
10.6	20.6	231	1726	1.94E+04	2.11E+04	5.30E+04
10.8	20.6	246	1787	3.56E+04	5.46E+04	1.12E+05
10.5	20.6	241	1801	4.55E+04	7.82E+04	1.49E+05
10.2	20.6	243	1857	5.24E+04	1.13E+05	2.05E+05
9.9	20.6	240	1886	6.63E+04	1.41E+05	2.57E+05
9.6	21.5	238	1921	8.65E+04	1.83E+05	3.33E+05
9.4	21.5	239	1966	9.45E+04	1.97E+05	3.78E+05
9.2	21.5	237	1984	1.07E+05	2.21E+05	4.24E+05
9	21.5	241	2052	2.04E+05	3.27E+05	6.76E+05

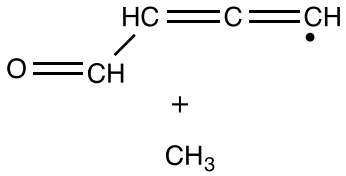
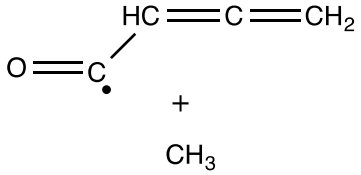
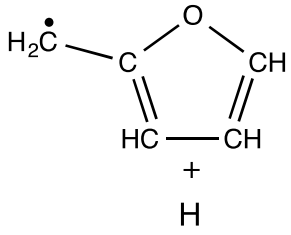
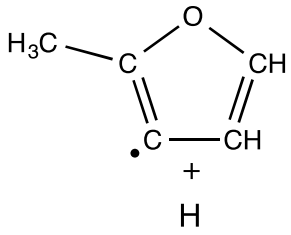
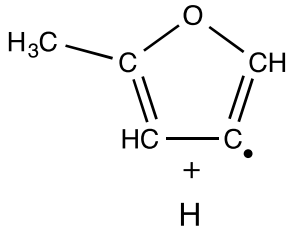
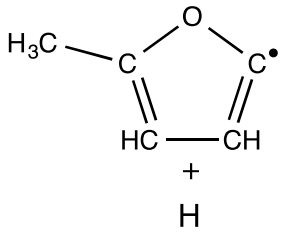
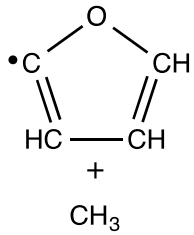
2% 2-methyl furan; 60 Torr						
P_1 / Torr	T_1 / °C	P_2 / Torr	T_2 / K	k_1 / s^{-1}	k_4 / s^{-1}	k_{tot} / s^{-1}
2.7	26.3	62	1709	7.82E+03	6.58E+03	2.10E+04
2.5	23.6	59	1718	1.08E+04	6.43E+03	2.43E+04
2.51	23.6	60	1746	1.41E+04	8.47E+03	3.16E+04
2.62	26.3	62	1756	1.51E+04	9.33E+03	3.43E+04
2.54	26.3	62	1787	1.99E+04	1.24E+04	4.51E+04
2.5	23	63	1807	2.41E+04	1.33E+04	5.23E+04
2.45	26.3	61	1826	2.76E+04	1.75E+04	6.23E+04
2.25	23	58	1854	3.13E+04	1.97E+04	7.22E+04
2.38	26.2	61	1864	3.71E+04	2.14E+04	8.12E+04
2.2	23.1	58	1881	3.84E+04	2.18E+04	8.57E+04
2.15	23	58	1918	4.99E+04	3.25E+04	1.15E+05
2.15	23.1	58	1934	5.56E+04	3.26E+04	1.24E+05
2.31	26.3	62	1938	6.26E+04	3.76E+04	1.37E+05
2.15	23	59	1945	5.98E+04	3.96E+04	1.38E+05
2.15	23.1	59	1950	6.17E+04	3.65E+04	1.38E+05
2.31	26.3	64	1972	7.10E+04	4.26E+04	1.58E+05
2.24	26.3	62	1992	8.02E+04	4.87E+04	1.79E+05
2.1	23.1	59	1992	8.02E+04	5.47E+04	1.85E+05
2.2	26.3	61	1995	8.16E+04	4.97E+04	1.82E+05
2.05	23	59	2031	1.00E+05	6.27E+04	2.25E+05
2.15	26.1	62	2051	1.12E+05	7.09E+04	2.52E+05
2.15	26.3	62	2054	1.14E+05	7.22E+04	2.56E+05
2	23	60	2094	1.40E+05	9.14E+04	3.16E+05
2% 2-methyl furan; 120 Torr						
P_1 / Torr	T_1 / °C	P_2 / Torr	T_2 / K	k_1 / s^{-1}	k_4 / s^{-1}	k_{tot} / s^{-1}
6.13	26.6	127	1571	2.11E+03	2.59E+03	6.42E+03
5.85	26.6	122	1577	2.87E+03	2.81E+03	7.54E+03
5.6	26.6	126	1682	8.12E+03	1.01E+04	2.42E+04
5.1	26.6	116	1694	9.25E+03	1.15E+04	2.75E+04
5.48	26.6	125	1699	8.90E+03	1.22E+04	2.81E+04
5.62	26.6	130	1720	1.21E+04	1.52E+04	3.59E+04
5.25	26.6	122	1724	1.15E+04	1.58E+04	3.63E+04
5.5	26.6	129	1732	1.37E+04	1.72E+04	4.05E+04
5.25	21.7	125	1733	1.38E+04	1.05E+04	3.40E+04
5.1	26.6	120	1740	1.48E+04	1.86E+04	4.38E+04
5.05	26.6	120	1754	1.51E+04	1.51E+04	4.20E+04
4.8	26.6	116	1783	1.98E+04	2.82E+04	6.31E+04

4.95	26.6	120	1785	1.64E+04	2.87E+04	6.04E+04
4.4	26.6	108	1806	2.73E+04	2.09E+04	6.64E+04
5.11	21.5	128	1807	2.76E+04	2.21E+04	6.80E+04
4.81	21.5	122	1823	3.16E+04	2.54E+04	7.78E+04
4.5	26.6	114	1848	3.46E+04	3.14E+04	9.12E+04
4.7	26.6	122	1877	4.35E+04	3.96E+04	1.14E+05
4.61	21.6	122	1883	5.11E+04	3.70E+04	1.21E+05
4.55	26.3	119	1893	6.93E+04	4.48E+04	1.49E+05
4.5	21.6	121	1904	5.97E+04	3.87E+04	1.36E+05
4.5	26.4	120	1922	1.24E+05	6.38E+04	2.30E+05
4.4	26.4	118	1926	8.02E+04	6.27E+04	1.87E+05
4.5	21.6	124	1947	8.07E+04	5.91E+04	1.90E+05
4.4	21.6	122	1958	8.69E+04	6.38E+04	2.04E+05
4.5	21.6	126	1975	9.70E+04	6.37E+04	2.20E+05
4.45	26.3	123	1984	1.29E+05	9.54E+04	2.87E+05
4.35	26.4	122	2001	1.12E+05	9.06E+04	2.71E+05
4.25	26.4	122	2037	1.38E+05	1.13E+05	3.35E+05
4.3	21.7	126	2052	1.54E+05	1.02E+05	3.47E+05
4.15	26.4	123	2097	1.91E+05	1.58E+05	4.63E+05

Table S4: Zero-point corrected electronic energies in kcal/mol for the C_5H_6O PES. The reference method is the third column, which is UCCSD(T)-F12a/cc-pVTZ-f12//M06-2X/MG3S and all values are relative to 2MF. In the remaining columns the values are the changes in energy relative to the reference method. For the columns F12//M062X and F12/B2PLYPD3, the numbers in parenthesis are the E0 for the pure DFT method without the F12a energy..

Name	Structure	Relative energy F12// M062X	ΔE_0, relative to F12//M062X			
			F12// B2PLYPD3	CBS-QB3	CBS-APNO	G3
2MF		0.0 (0.0)	0.0 (0.0)	0.0	0.0	0.0
M2		59.8 (2.5)	-0.1 (2.7)	1.3	1.5	0.6
M3		53.8 (1.9)	0.0 (2.2)	1.2	1.3	0.4
M4		60.7 (2.3)	Not found		1.1	0.2
M5		30.8 (0.5)	-0.1 (-2.1)	0.2	0.9	-0.9
M6		28.0 (0.4)	-0.1 (-2.2)	0.2	0.8	-1.0

M7		55.9 (1.5)	0.0 (-0.2)	1.1	1.0	0.2
M8		25.4 (0.2)	-0.1 (-1.8)	0.3	0.6	-0.9
M9		23.3 (0.1)	-0.1 (-1.8)	0.3	0.7	-1.0
P1		57.1 (0.2)	-0.3 (-3.0)	0.2	0.9	-1.3
P2		50.3 (-1.0)	-0.4 (-3.8)	0.2	0.3	-1.4
P3		30.2 (2.9)	-0.3 (0.6)	1.0	1.3	-0.3
P4		29.0 (1.9)	-0.2 (-0.2)	0.9	1.1	-0.5
P5		103.2 (1.8)	-0.2 (-4.1)	0.4	-0.1	-0.9
P6		98.3 (1.4)	0.0 (-3.9)	0.4	0.0	-1.1

P7		105.3 (1.1)	-0.1 (-3.5)	-0.3	-0.2	-1.9
P8		107.8 (0.8)	-0.2 (-4.7)	0.9	0.9	
P9		86.2 (-0.4)	0.2 (-1.3)			
P10		118.7 (-1.7)	-0.1 (-1.0)			
P11		118.6 (-1.7)	-0.1 (-1.0)			
P12		118.7 (-1.9)	-0.2 (-1.0)			
P13		111.7 (-0.7)	-0.4 (-1.4)			
TS1: 2MF to M2		82.0 (-0.2)	-0.3 (1.0)	0.7	0.5	0.7
TS2:		64.4	-0.1	1.2	0.4	0.8

2MF to M3		(0.0)	(1.2)			
TS3: M2 to P1		89.3 (6.5)	-0.3 (-3.1)	-0.7	-0.4	-0.7
TS4: M3 to P2		86.1 (5.4)	-0.3 (-3.8)	-0.8	-0.7	-0.9
TS5: 2MF to M4		69.7 (0.7)	-0.1 (1.3)	0.9	0.5	0.4
TS6: M4 to M5		60.6 (3.8)	Not found		0.6	-0.3
TS7: M5 to M6		35.9 (0.8)	-0.2 (-1.2)	0.2	0.9	-0.9
TS8: M6 to P3		73.2 (3.4)	-1.1 (-4.3)	-1.1	-1.3	
TS9: M6 to P4		107.6 (2.0)	0.0 (-4.4)			-19.1
TS10: 2MF to M7		68.1 (0.1)	0.0 (1.1)	1.0	0.5	0.5
TS11: M7 to M8		56.6 (3.7)	0.3 (-1.1)	1.3	0.5	-0.4
TS12: M8 to M9		29.6 (0.4)	-0.1 (-1.2)	0.2	0.9	-1.0
TS13: M9 to P2		92.1 (-0.7)	-0.6 (-6.3)	0.2	-3.5	-1.1

Figure S1: Potential Energy Surface for the unimolecular dissociation of 2-methyl furan. Labels correspond to Table S4.

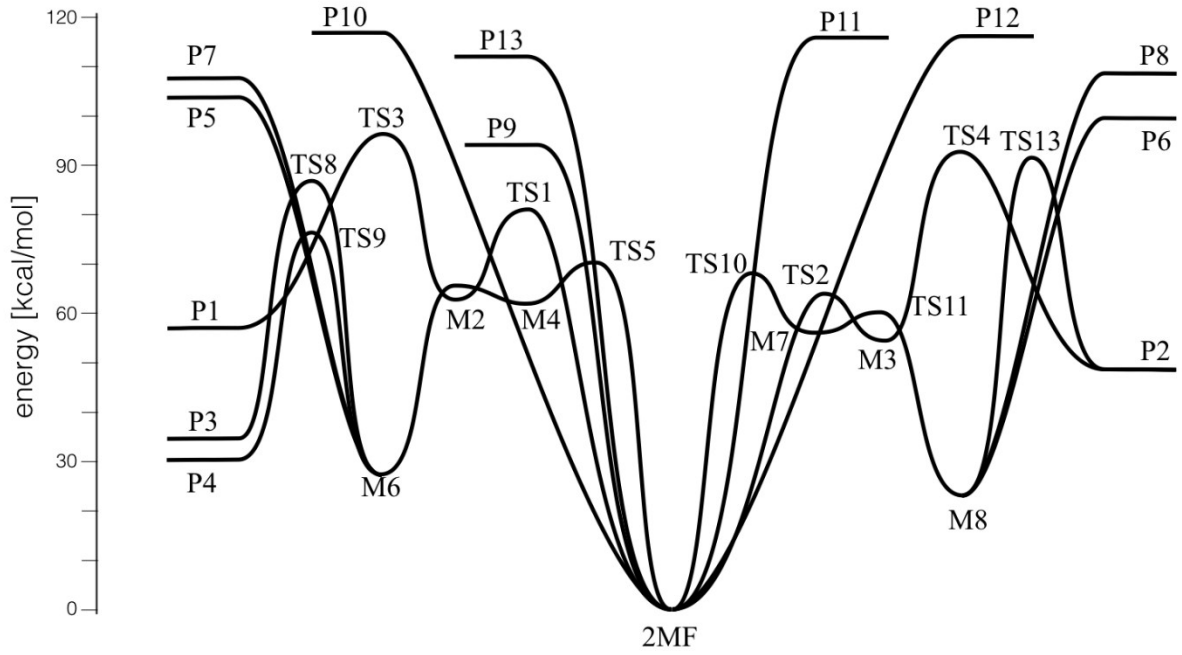
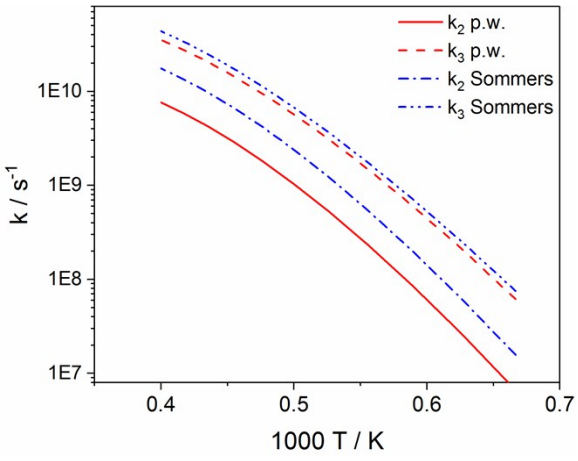


Figure S2: Comparison of theoretical predictions of k_2 (2MF = pC_3H_4 + CH_2CO) and k_3 (2MF = 1-butyne + CO) from this work and Somers et al.[1]



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