

A model of tetrahydrofuran low-temperature oxidation based on theoretically calculated rate constants

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SUPPLEMENTARY DESCRIPTION

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1/ C-H bond dissociation energies for THF molecule

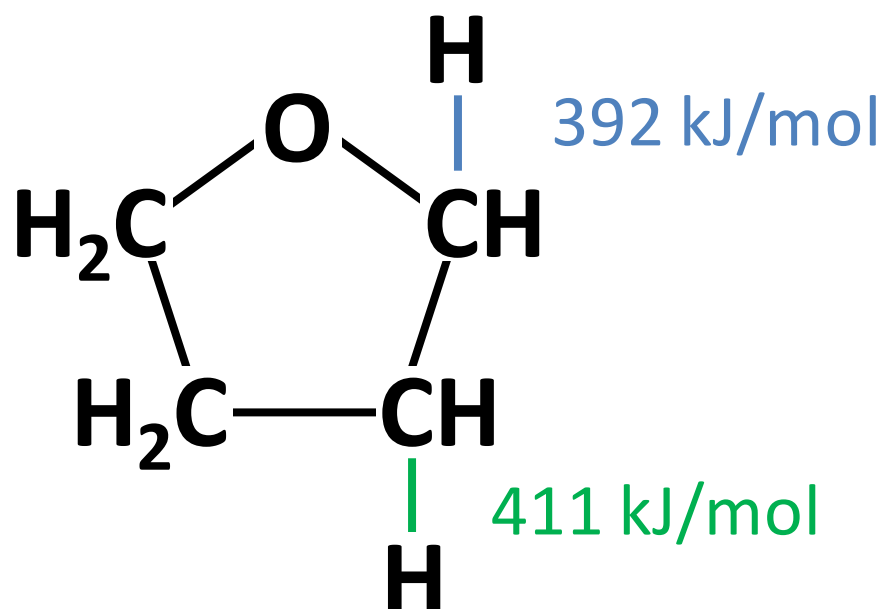


Figure S1: C-H bond dissociation energies for THF molecule obtained at CBS-QB3 level of theory

2/ Optimized geometries used in the present work

Table S1. Optimized geometries (Cartesian coordinates) obtained at CBS-QB3 level of theory for species of figure 1. Small species such as O2, OH and HO2 are ignored.

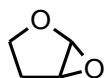
Figure 1a



6	-0.011294	-0.029814	-0.002867
8	-0.005876	-0.069850	1.440010
6	1.292981	0.007074	1.885163
6	2.234517	0.281803	0.755968
6	1.436284	-0.286969	-0.435204
1	1.677725	0.188951	-1.387126
1	1.618802	-1.360302	-0.528955
1	2.420099	1.360164	0.614877
1	3.209213	-0.196267	0.883509
1	1.392648	0.347312	2.907664
1	-0.356560	0.962993	-0.313698
1	-0.722193	-0.776399	-0.359924

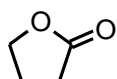


6	-0.012607	-0.019316	-0.012325
8	0.013958	0.202231	1.426136
6	1.330822	0.290474	1.779108
6	2.203990	0.024360	0.811366
6	1.436496	-0.357699	-0.437461
1	1.738483	0.210455	-1.321863
1	1.560717	-1.420443	-0.678405
1	3.278353	0.022418	0.910398
1	1.499387	0.556599	2.813186
1	-0.366879	0.904671	-0.478521
1	-0.730780	-0.814999	-0.210236

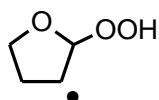


6	-0.000134	0.072004	0.039296
8	-0.001476	-0.023359	1.417982
6	1.381293	0.004832	1.841233

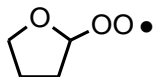
6	2.162108	0.757776	0.737898
6	1.279410	0.549449	-0.472907
8	0.861805	-0.833606	-0.648023
1	1.408508	1.125335	-1.382787
1	2.231296	1.830125	0.946600
1	3.172842	0.362809	0.614820
1	1.742487	-1.020870	1.934331
1	1.414199	0.488928	2.816999
1	-0.986388	0.233849	-0.376522



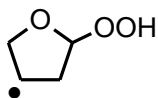
6	-0.021166	0.042569	-0.025297
6	0.006410	-0.113148	1.492543
8	1.239591	0.249915	1.953455
6	2.078377	0.708965	0.872861
6	1.458745	0.125497	-0.405257
8	-0.868457	-0.478292	2.220291
1	1.659140	0.742713	-1.281821
1	2.068285	1.803535	0.870516
1	3.092238	0.364394	1.073110
1	1.858269	-0.874028	-0.593825
1	-0.572437	-0.781128	-0.476644
1	-0.558992	0.968365	-0.255640



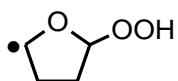
6	-0.041492	0.024245	0.023433
8	-0.028009	0.022096	1.439059
6	1.345631	0.042313	1.869306
6	2.081994	0.894179	0.817855
6	1.223105	0.697458	-0.383668
8	0.002563	-1.301902	-0.500402
8	-1.286065	-1.918575	-0.227119
1	1.465542	0.966949	-1.400596
1	2.110004	1.952176	1.119409
1	3.119973	0.579725	0.667013
1	1.748042	-0.976260	1.893181
1	1.363967	0.458878	2.875849
1	-0.978676	0.487184	-0.296620
1	-1.201351	-2.106427	0.720146



8	0.000937	0.010706	-0.002161
6	0.001378	-0.001077	1.450583
6	1.475718	-0.000820	1.875488
6	2.171414	0.602902	0.644342
6	1.288797	0.079592	-0.477140
8	1.692863	-1.328264	-0.806612
8	2.853207	-1.352115	-1.425792
1	2.121390	1.695515	0.653435
1	1.645663	0.572242	2.787541
1	1.827538	-1.021223	2.039362
1	-0.547553	-0.881920	1.786130
1	-0.528835	0.895643	1.783437
1	1.328764	0.611679	-1.426528
1	3.210207	0.302797	0.514017



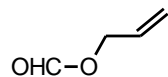
6	-0.004382	-0.004113	-0.039252
8	-0.022048	0.042285	1.373841
6	1.334440	0.056994	1.862738
6	2.153864	0.551716	0.722977
6	1.301812	0.660418	-0.495673
8	0.054293	-1.342220	-0.503158
8	-1.195025	-1.978116	-0.144004
1	1.109361	1.701880	-0.789663
1	1.712275	0.150351	-1.373276
1	3.216624	0.739978	0.766205
1	1.631696	-0.952848	2.189032
1	1.357366	0.705879	2.746705
1	-0.930941	0.454594	-0.386291
1	-1.096836	-2.048654	0.818663



6	0.000079	0.001037	0.001164
6	0.000258	-0.004156	1.528863
8	1.377142	-0.012508	1.914587
6	2.117752	-0.588223	0.897753
6	1.305439	-0.749348	-0.351393
8	-0.637630	-1.192292	1.936008
8	-0.690826	-1.189216	3.381965
1	0.039160	1.035769	-0.344523
1	-0.901138	-0.465526	-0.395060
1	1.798974	-0.333753	-1.235264
1	1.097246	-1.804788	-0.567435
1	3.181348	-0.411855	0.972192
1	-0.460304	0.849899	2.025418
1	0.217727	-1.447998	3.601042

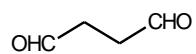


6	0.132641	0.277614	-0.069710
6	0.080440	-0.162975	1.403850
8	1.367716	0.160313	1.928094
6	2.211049	-0.430763	0.901286
6	1.095927	-0.936095	-0.027931
8	0.195587	-1.537505	0.969238
1	0.520323	1.271083	-0.301924
1	-0.780514	0.046014	-0.613709
1	1.335768	-1.572115	-0.876310
1	2.801908	-1.242939	1.328252
1	2.862283	0.326221	0.457160
1	-0.700413	0.044704	2.128883



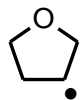
6	0.002464	-0.013653	0.004826
6	0.003229	-0.007440	1.333510
6	1.251328	0.016976	2.160654
8	1.384402	-1.190436	2.970724
6	0.732444	-1.199047	4.142332
8	0.037420	-0.321404	4.575698
1	2.143636	0.026053	1.536307
1	1.257337	0.877212	2.833480

1	-0.930975	-0.000303	1.887411
1	-0.920702	-0.005517	-0.563172
1	0.926571	-0.019551	-0.565557
1	0.939186	-2.150688	4.653083



6	-0.009593	-0.014066	-0.006327
8	-0.029045	-0.135152	1.191678
6	1.249778	0.003210	-0.845536
6	2.523953	0.023028	-0.011356
6	2.833364	1.386304	0.568591
8	2.227817	2.393148	0.304339
1	1.211232	-0.877121	-1.499903
1	1.198145	0.876003	-1.505086
1	2.459862	-0.685896	0.820964
1	3.397123	-0.279167	-0.603738
1	-0.954982	0.077625	-0.583382
1	3.697255	1.409908	1.267373

Figure 1b (species common with Figure 1a are not repeated)

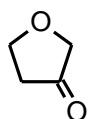


6	0.007893	0.002984	-0.000388
8	0.024489	0.369053	1.382441
6	1.316787	0.046190	1.897029
6	2.299624	0.324689	0.744342
6	1.433851	0.049977	-0.440892
1	1.769058	-0.050075	-1.463535
1	2.638959	1.372296	0.766141
1	3.197040	-0.301757	0.790067
1	1.361264	-1.014216	2.187392
1	1.481894	0.659596	2.783655
1	-0.646369	0.708958	-0.527724
1	-0.432423	-1.003604	-0.129430

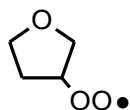


6	0.046764	0.086407	0.067111
6	0.003685	0.006973	1.567486
8	1.362748	0.162920	1.989204

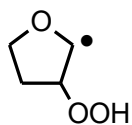
6	2.214680	0.330103	0.850997
6	1.297297	0.269152	-0.338149
1	2.973845	-0.465008	0.835453
1	2.744913	1.290630	0.921982
1	1.639352	0.364060	-1.360639
1	-0.831542	0.002974	-0.559878
1	-0.615967	0.799428	2.011150
1	-0.387666	-0.956331	1.924785



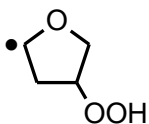
6	0.009159	0.048319	0.013606
6	0.018611	-0.022527	1.543485
8	1.382228	0.002305	1.930464
6	2.104533	0.721526	0.918702
6	1.457700	0.304645	-0.403274
8	-0.952763	-0.063406	-0.698362
1	-0.541621	0.838918	1.941059
1	1.511956	1.039619	-1.206904
1	2.006138	1.804909	1.078728
1	-0.450185	-0.938938	1.906791
1	3.154671	0.448761	1.013791
1	1.876303	-0.639160	-0.768587



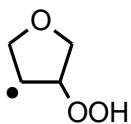
6	-0.031031	0.006335	0.028516
8	0.023712	0.333916	1.418972
6	1.325391	0.020580	1.915247
6	2.259712	0.276182	0.728733
6	1.414699	-0.223201	-0.437027
1	1.643163	0.218439	-1.406357
8	1.707244	-1.660766	-0.566331
1	2.445442	1.346350	0.610199
1	3.216618	-0.244449	0.790267
1	1.379742	-1.028802	2.234755
1	1.518648	0.661690	2.775915
1	-0.494872	0.841957	-0.501630
1	-0.626405	-0.894895	-0.150323
8	0.996501	-2.223349	-1.520430



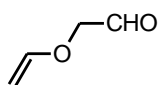
6	0.000088	-0.005951	0.003197
6	0.002579	0.003493	1.533086
6	1.505983	0.006803	1.852290
6	2.055362	0.715591	0.677164
8	1.210845	0.693907	-0.387176
8	2.056464	-1.335151	1.825272
8	1.528307	-2.054541	2.997006
1	1.751364	0.456411	2.819098
1	-0.456377	0.917914	1.918291
1	-0.497512	-0.857935	1.974214
1	0.062054	-1.021514	-0.396013
1	-0.842011	0.514438	-0.451960
1	3.074213	1.005512	0.475437
1	2.350453	-2.198466	3.484274



6	0.001429	0.000232	0.003074
6	0.007165	0.002384	1.539134
6	1.500235	0.007047	1.871201
8	2.175304	-0.582456	0.744898
6	1.294623	-0.685885	-0.304923
8	-0.639569	-1.211301	1.921283
8	-0.662186	-1.234481	3.379628
1	-0.526728	0.845861	1.985086
1	-0.040841	1.038950	-0.362040
1	-0.877988	-0.517783	-0.387945
1	1.761850	-0.772444	-1.276465
1	1.868353	1.030539	2.002493
1	1.723625	-0.570510	2.767539
1	-0.361508	-2.140485	3.530324



6	0.004881	0.013145	0.003550
6	0.007323	0.013970	1.491517
6	1.510567	0.019520	1.787570
8	2.133788	-0.640122	0.685774
6	1.359186	-0.370610	-0.483362
8	-0.644528	-1.209966	1.889476
8	-0.694385	-1.203894	3.353995
1	-0.526220	0.851290	1.953298
1	-0.864839	0.170970	-0.617596
1	1.356429	-1.272136	-1.109771
1	1.821394	0.436313	-1.081183
1	1.866249	1.057239	1.874994
1	1.758956	-0.517916	2.702374
1	-0.279194	-2.057980	3.532465

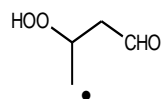


6	-0.003040	-0.025166	0.001751
6	-0.000249	0.008966	1.333644
8	1.070465	0.059866	2.169479
6	2.359334	0.080290	1.581651
6	3.378620	0.137189	2.703639
8	4.563708	0.164886	2.507359
1	2.489287	0.955173	0.930629
1	2.538161	-0.818360	0.976180
1	-0.914627	-0.001355	1.915564
1	-0.951468	-0.064560	-0.515917
1	0.893574	-0.015890	-0.602567
1	2.937197	0.151096	3.722287

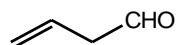


6	-0.021093	-0.011729	0.010742
8	0.005345	-0.017179	1.439851
6	1.357620	0.036240	1.899832
6	2.200222	-0.478445	0.756388
6	1.337066	-0.508436	-0.426313
8	1.725356	-1.724940	0.227864
1	1.694211	-0.366709	-1.441400
1	3.272153	-0.311895	0.720700
1	1.424537	-0.578694	2.800646
1	1.660579	1.065358	2.145974

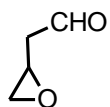
1	-0.187900	1.001030	-0.386681
1	-0.843310	-0.657669	-0.306761



6	-0.059249	-0.076726	-0.037996
6	-0.094572	-0.186526	1.442672
1	0.972374	-0.128220	-0.403076
8	-0.727877	-1.249120	-0.577900
6	-0.741655	1.200458	-0.542160
1	-0.712627	0.463690	2.049766
1	0.392577	-1.030323	1.913040
8	0.066531	-1.812329	-1.648690
1	-0.109745	-1.167492	-2.360043
6	-0.777406	1.422156	-2.031933
1	-1.787042	1.218401	-0.202006
1	-0.276487	2.086864	-0.089794
8	-0.433391	0.636422	-2.884417
1	-1.171489	2.415042	-2.333904



6	-0.001609	-0.001151	0.002767
6	0.000937	-0.005572	1.331101
6	1.238371	0.003857	2.178590
6	1.226323	1.020217	3.304138
8	0.290314	1.717020	3.597180
1	-0.927189	-0.015815	-0.561082
1	0.919464	0.018981	-0.572474
1	-0.940176	-0.008684	1.872945
1	1.389568	-0.973463	2.665588
1	2.142148	0.166544	1.578635
1	2.176699	1.072025	3.881711




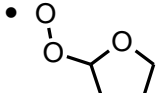
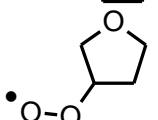
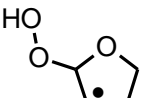
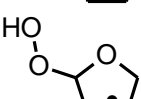
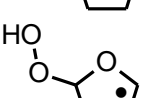

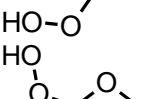
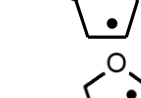




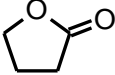
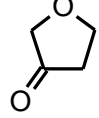
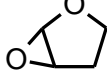

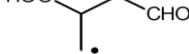
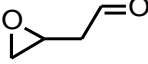
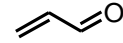
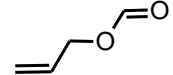
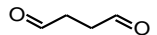
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6	-0.005423	-0.018211	1.473962
6	1.269267	-0.006089	2.279158

6	1.662026	1.361250	2.788999
8	1.026327	2.368176	2.607316
8	-0.245474	-1.206468	0.711157
1	-0.847412	0.434400	-0.523392
1	0.954147	0.066978	-0.518827
1	1.180389	-0.672543	3.148972
1	2.102102	-0.412190	1.691492
1	2.609854	1.384479	3.371116
1	-0.882697	0.372904	1.983394

3/ Theoretically calculated thermochemical data

Table S2. Theoretically calculated thermochemical data for furan, furyl radicals and the species presented in figure 1.

Species name	Structure	$\Delta_f H_{298}^\circ$ (kcal/mol)	S_{298K}° (cal/mol/K)	C_p° (T) (cal/mol/K)						
				300	400	500	600	800	1000	1500
cy(OCCCC)		-42.60	70.97	24.19	29.87	34.91	39.38	46.79	52.50	61.46
cy(OCJCCC)		-0.7	71.58	24.59	29.53	33.92	37.81	44.26	49.23	57.02
cy(OCCJCC)		3.8	72.64	24.93	29.87	34.25	38.13	44.56	49.49	57.21
JOOcy(COCCCC)		-36.5	85.8	32.07	37.51	42.33	46.59	53.63	59.01	67.35
JOOcy(CCOCC)		-29.7	87.24	32.04	37.51	42.36	46.63	53.69	59.08	67.42
HOOcy(COCCCCJ)		-25.6	85.24	39.75	44.17	48.09	51.53	57.22	61.55	68.26
HOOcy(COCCJC)		-26.3	86.75	41.22	45.36	49.03	52.28	57.67	61.83	68.35
HOOcy(COCJCC)		-29.5	84.84	40.93	45.13	48.86	52.15	57.6	61.78	68.33
HOOcy(CCJOCC)		-23.8	87.56	36.67	41.37	45.55	49.25	55.36	60.06	67.41
HOOcy(CCOCCJ)		-16.1	88.63	35.88	40.72	45.01	48.8	55.07	59.88	67.37
HOOcy(CCOCJC)		-21	88.15	35.62	40.49	44.81	48.63	54.95	59.79	67.36
cy(OC*CCC)		-16.8	69.41	23.04	27.49	31.44	34.93	40.73	45.18	52.15

cy(OCC*CC)		-13.9	67.93	22.71	27.26	31.29	34.85	40.73	45.24	52.25
O*cy(COCCC)		-87.4	73.18	25.91	30.84	35.21	39.06	45.4	50.23	57.69
O*cy(CCOCC)		-67.9	74.05	26.41	31.3	35.64	39.45	45.73	50.51	57.87
bicy(O)(CCOCC)		-47.6	72.11	26.79	31.6	35.86	39.62	45.81	50.54	57.84
bicy(O)(CCCOC)		-41.3	71.17	26.52	31.41	35.72	39.53	45.8	50.57	57.91
CJC(OOH)CCHO		-19.5	97.08	41.89	45.55	48.81	51.69	56.49	60.19	66.08
OHCCcy(COC)		-44.3	84.82	27.78	32.15	36.03	39.46	45.15	49.52	56.36
C*CCHO		-16.2	66.56	18.68	21.63	24.23	26.52	30.27	33.09	37.38
C*CCOCHO		-66.2	83.94	27.08	31.57	35.54	39.05	44.87	49.32	56.27
OHCCCCHO		-70.5	83.76	30.45	34.44	37.97	41.09	46.23	50.17	56.3

4/ Model validation against the 10 bar JSR results of Dagaut et al. [6]

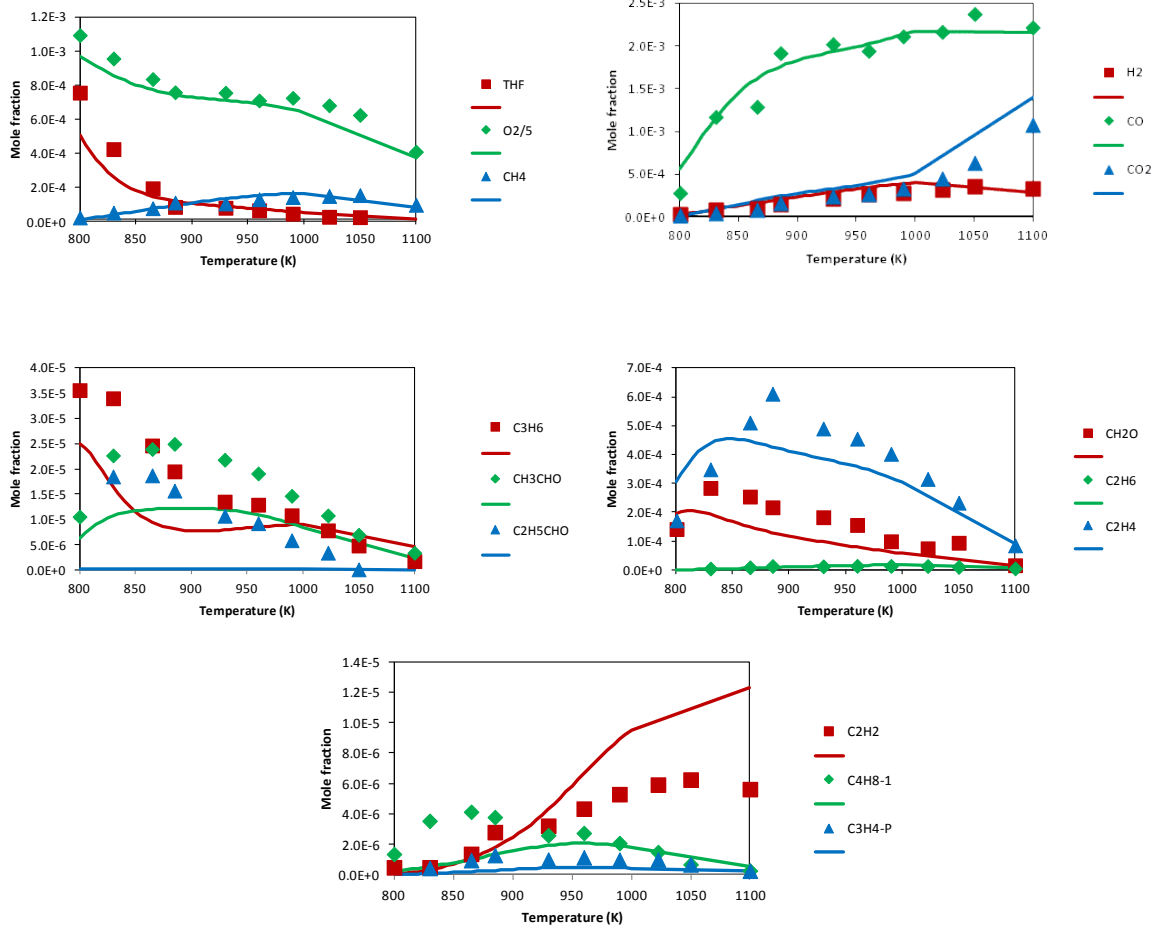


Figure S2: Simulations of the mole fraction profiles of species the THF oxidation in a JSR at $p = 1.023$ MPa, $\tau = 0.1$ s and $\phi = 1$ (Dagaut et al. [6]).

5/ Model validation against the low-pressure laminar premixed THF flame results of Tran et al. [3]

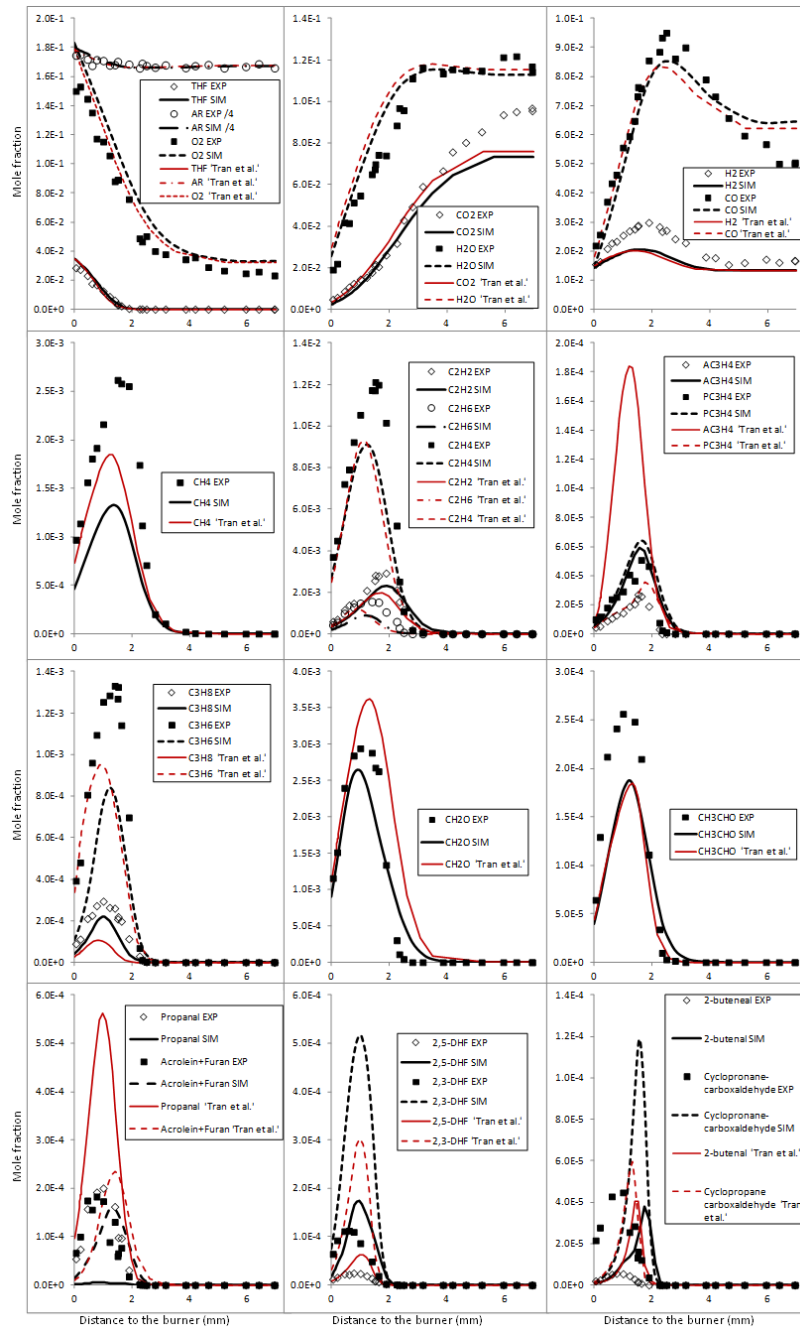


Figure S3: Simulations of the mole fraction profiles of species sampled in flames (laminar premixed low-pressure (6.7 kPa) argon-diluted (78%) stoichiometric THF flames [3]). Black lines: simulations performed with the model developed in this work **with** the low-temperature submechanism of the oxidation of THF. Red lines: simulations with the model developed by Tran et al. [3].

6/ Sensitivity analysis under JSR conditions

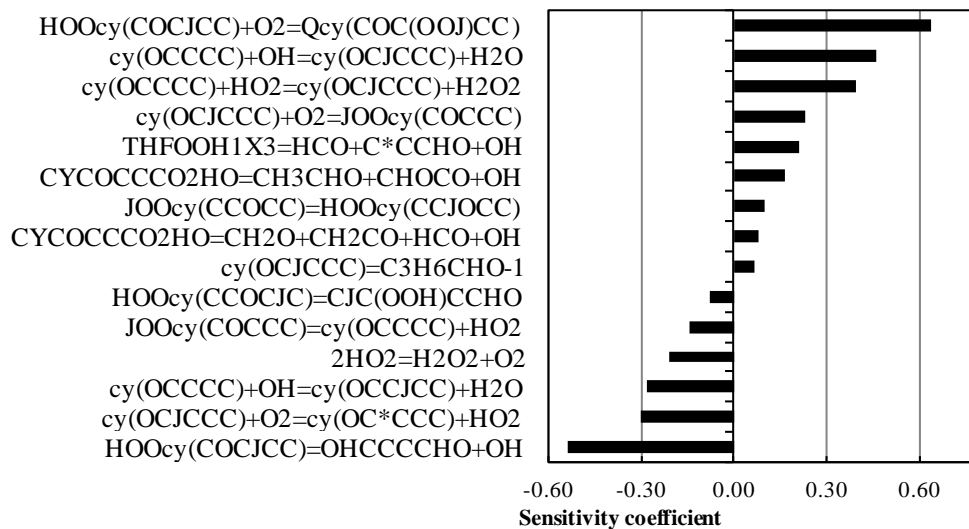


Figure S4: Sensitivity analysis on CO mole fraction under the conditions of figure 3 at 600K and $\phi = 1$.