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

Thermal Decomposition and Isomerization of Furfural and 2-Pyrone: A Theoretical Kinetic Study

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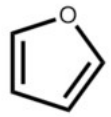
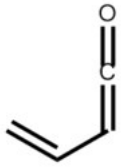
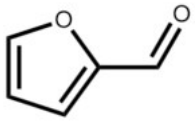
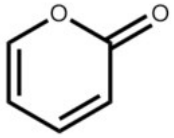
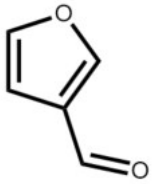
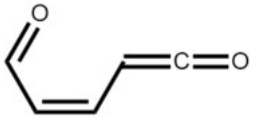
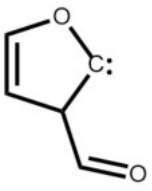
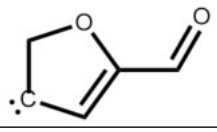
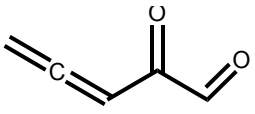
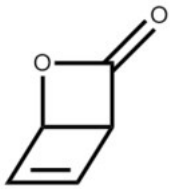
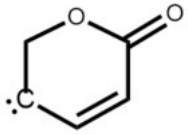
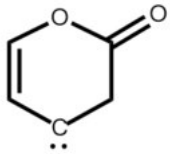
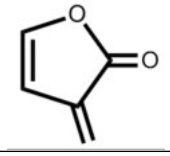
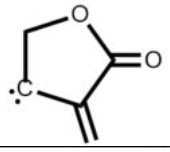
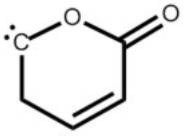
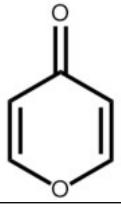
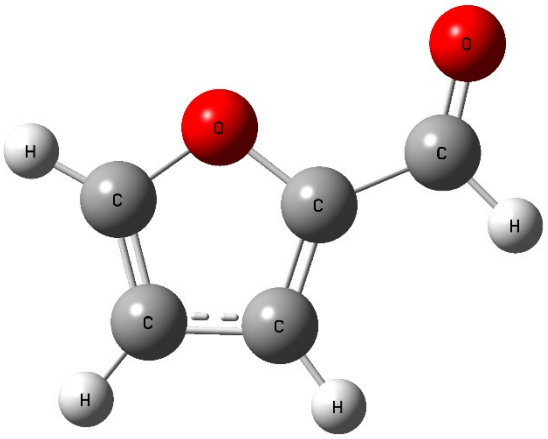
Contents

1. **Chemical structures, names and symbols of the molecules included in the pyrolysis process.**

Symbols	Naming	Chemical Structure
-	Furan	
VK	Vinylketene	
M1	Furfural	
M2	2-Pyrone	
M3	3-Furfural	
M4	Formylvinylketene	
M5	2-Carbene-3-furfural	
M6	Furfural-4-carbene	
M7	2-Keto-3,4-pentadienal	

M8	2-Oxabicyclo[2.2.0]hex-5-en-3-one	
M9	2-Pyrone-5-carbene	
M11	2-Pyrone-4-carbene	
M12	3-Methylene-2(3H)-furanone	
M13	3-Methylene-2(3H)-furanone-4-carbene	
M14	2-Pyrone-6-carbene	
M16	4-pyrone	
CBD	1,3-Cyclobutadiene	
C_4H_4	Butatriene	

2. Optimized structures of furfural and 2-pyrone pyrolysis intermediates and products.



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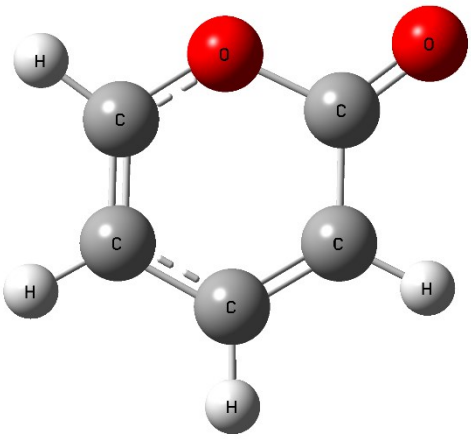

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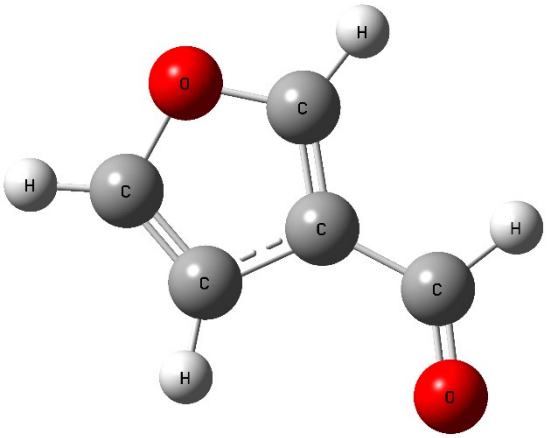

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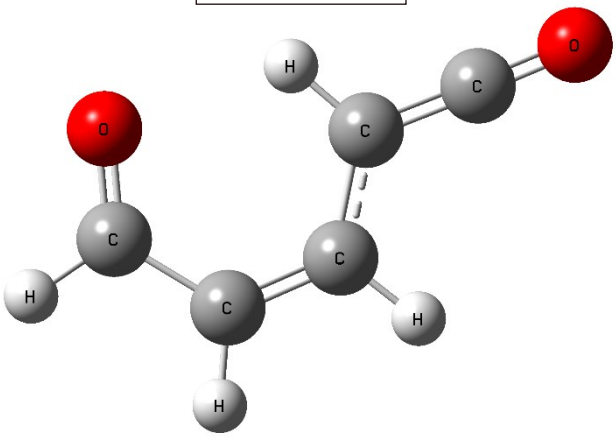

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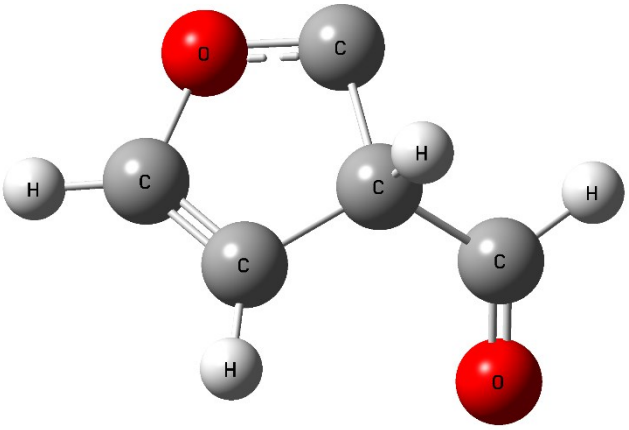

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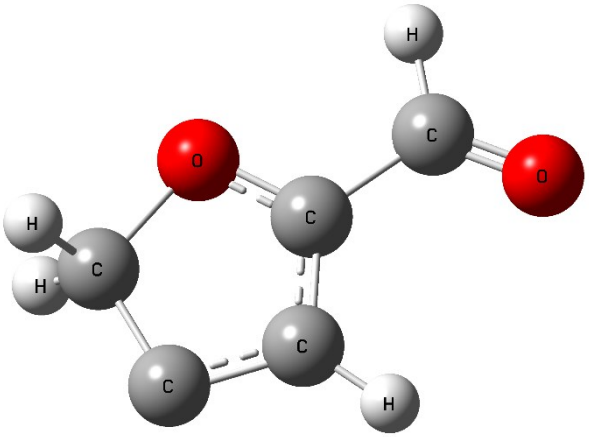

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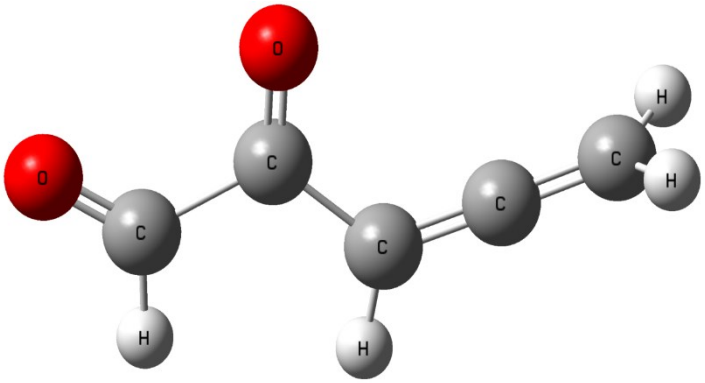

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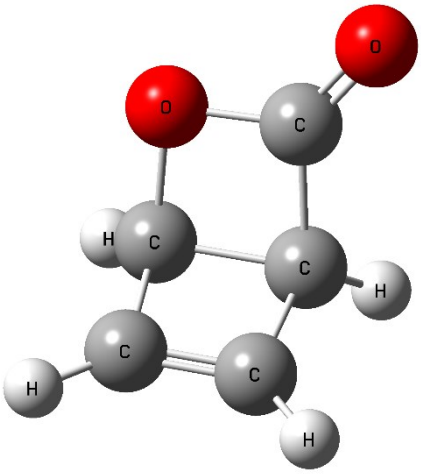

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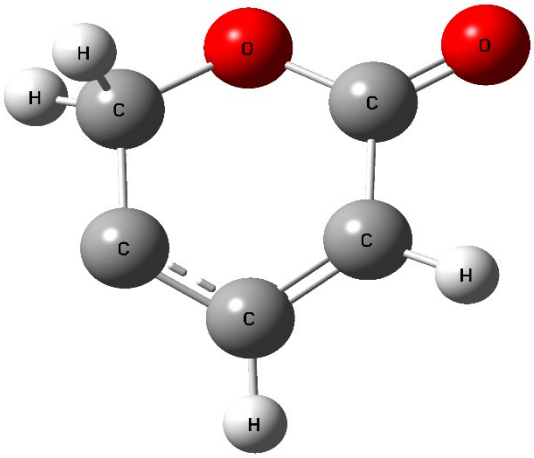

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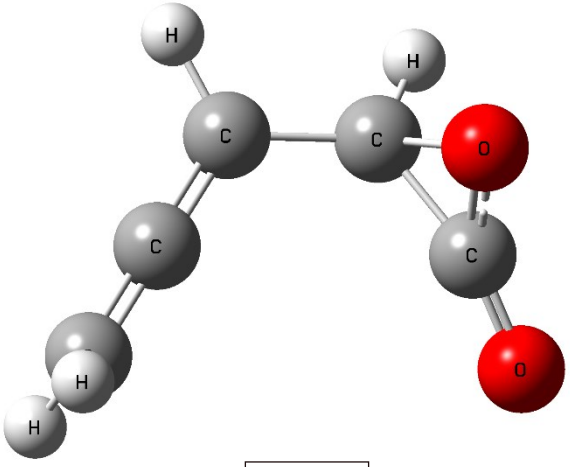

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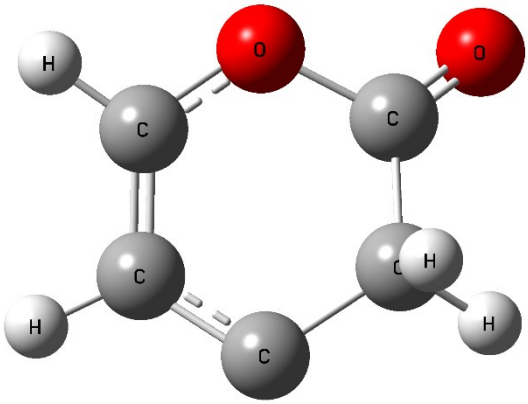

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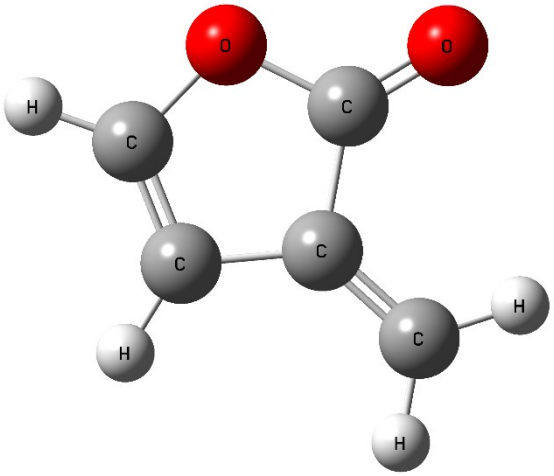

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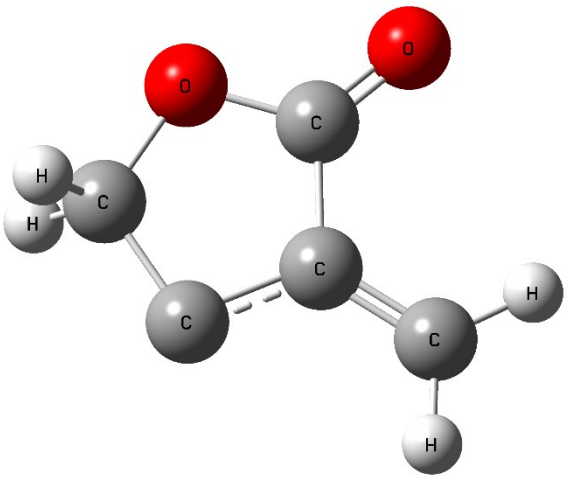

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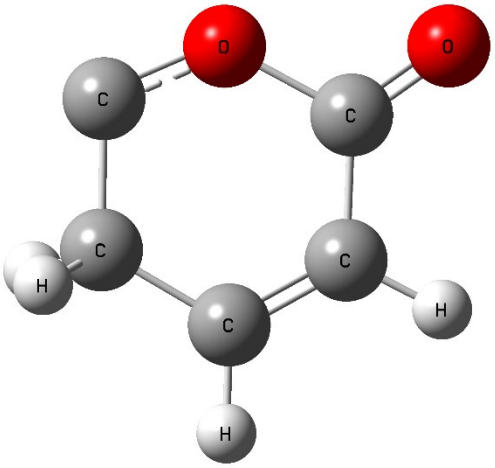

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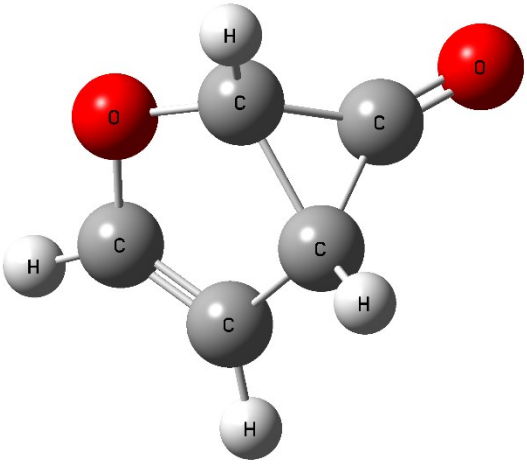

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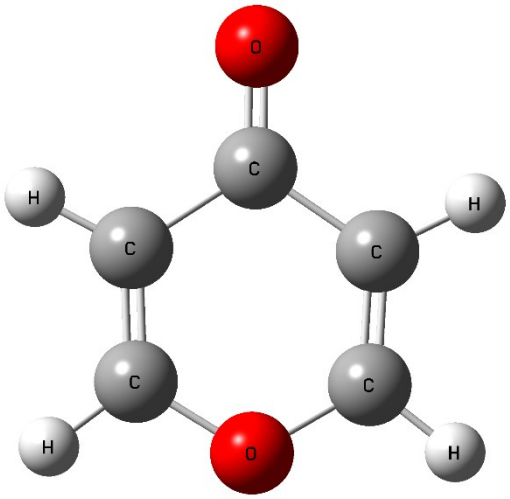

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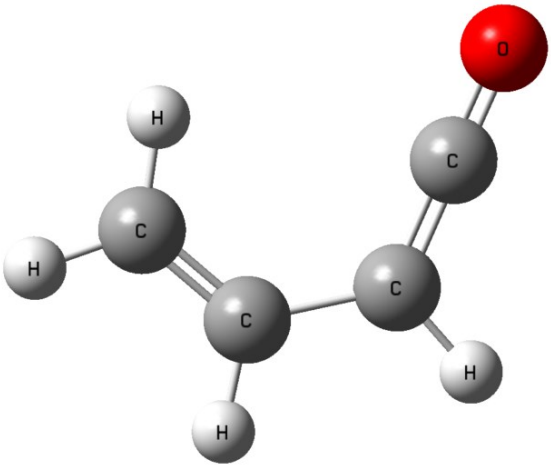

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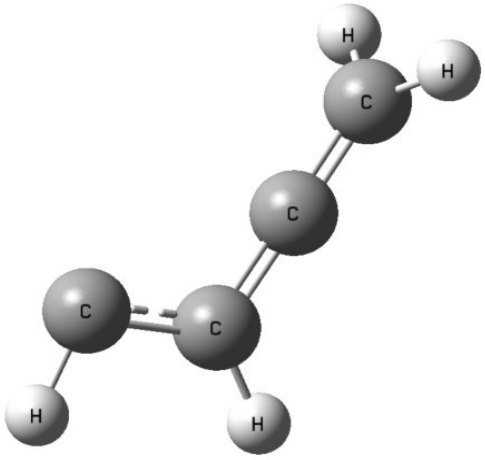

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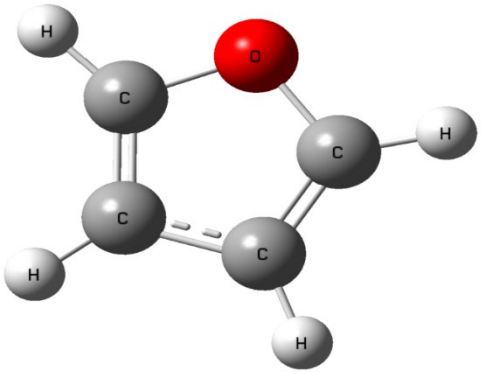

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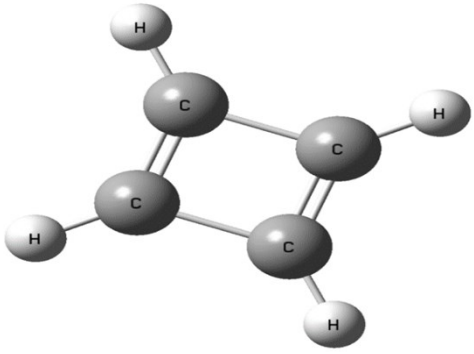

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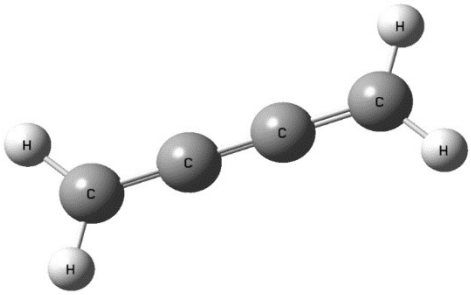

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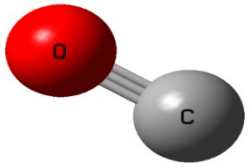

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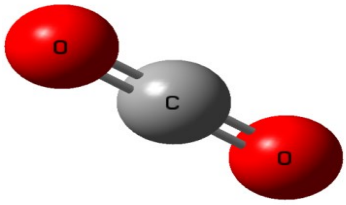
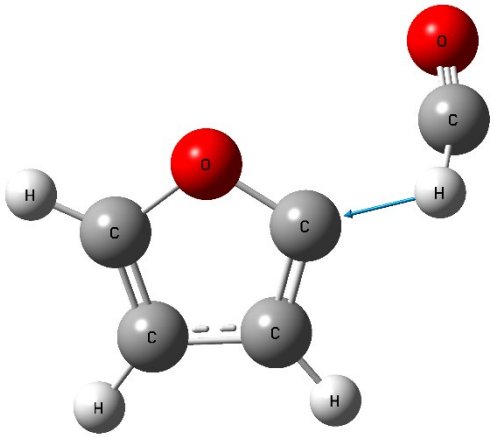


CO_2

3. Optimized structures for transition-state of furfural and 2-pyrone pyrolysis.



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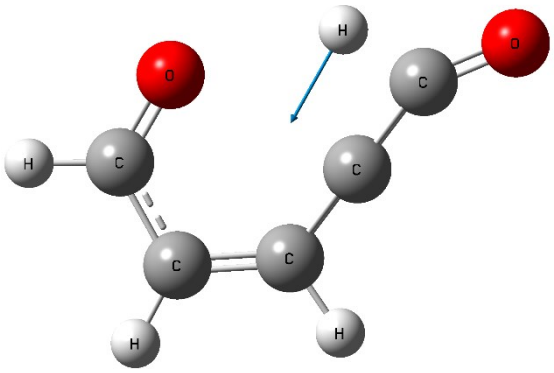

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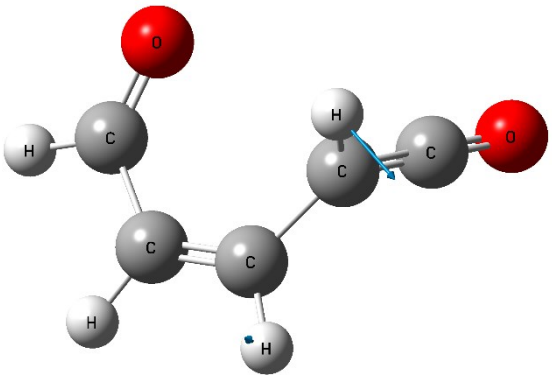

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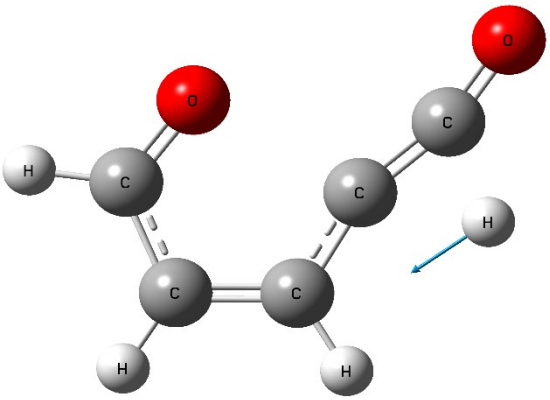

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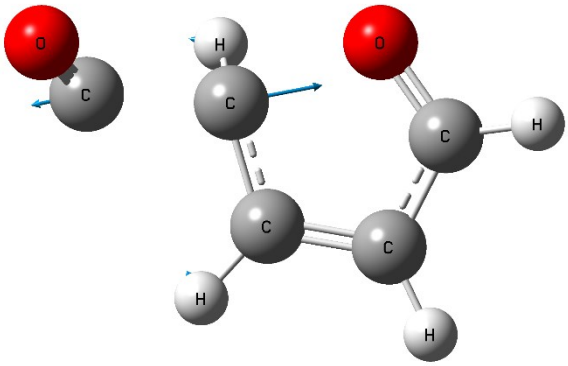

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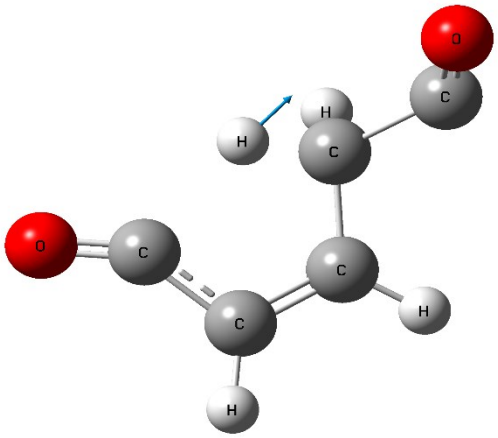

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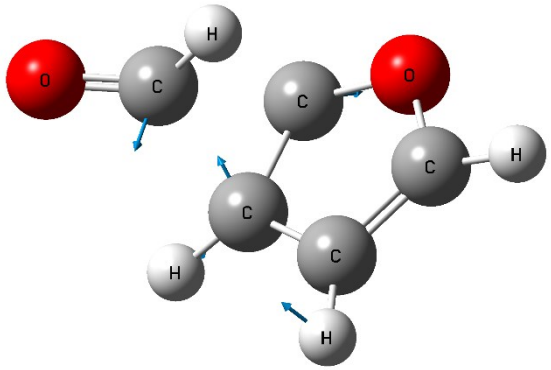

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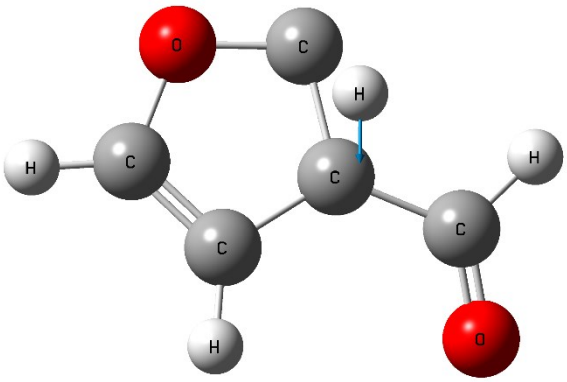

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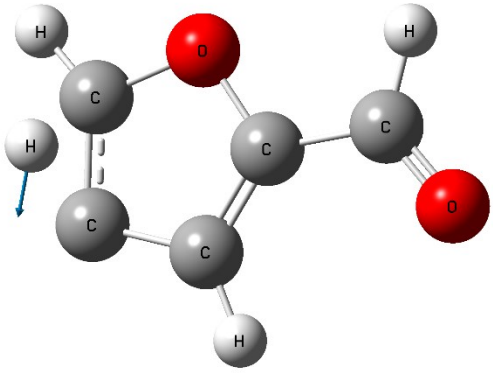

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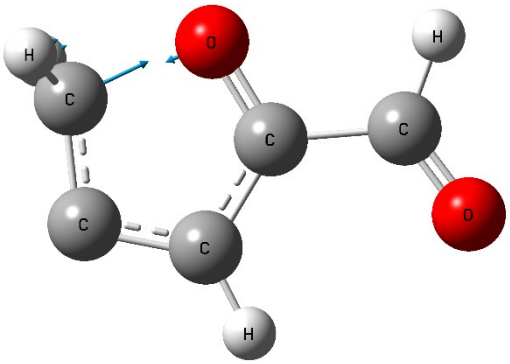

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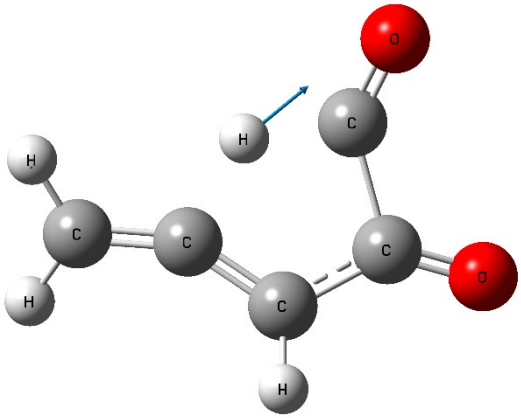

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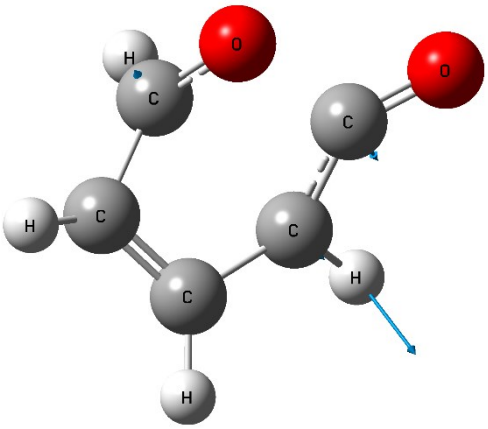

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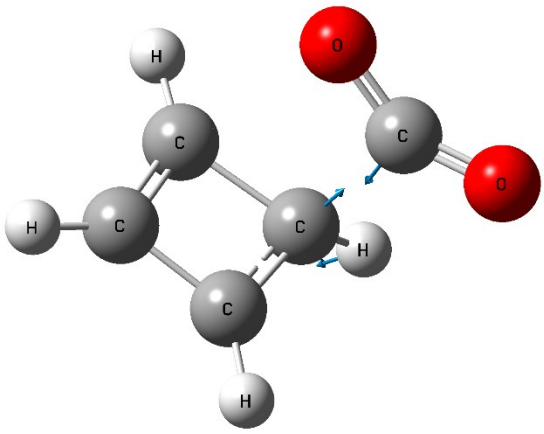

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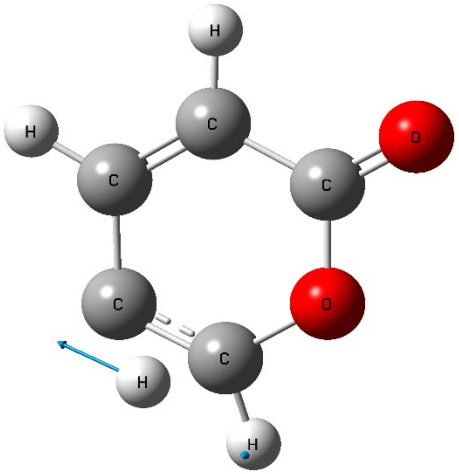

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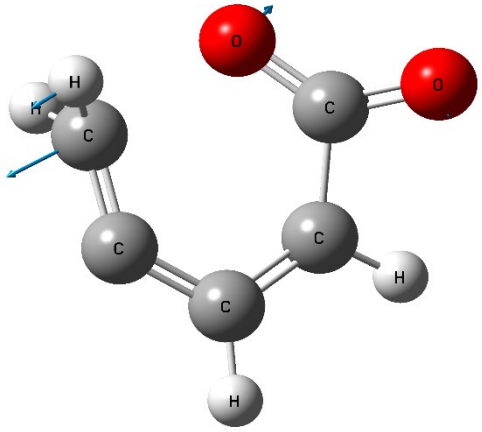

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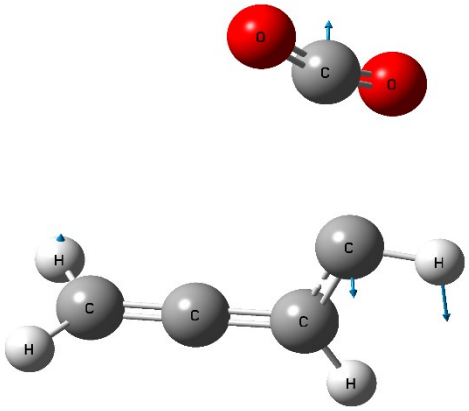

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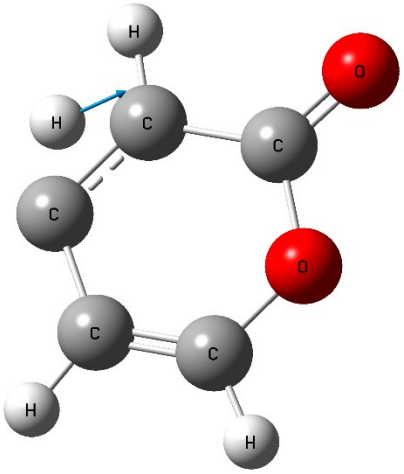

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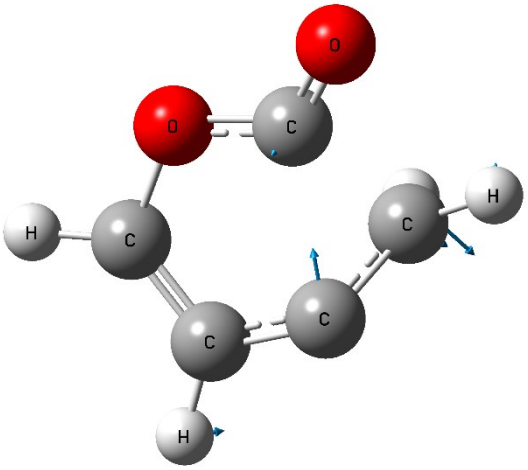

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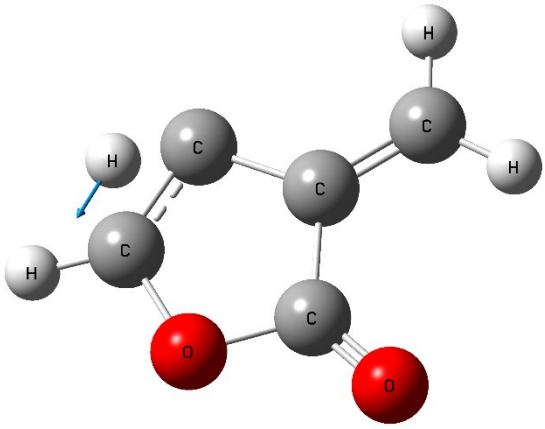
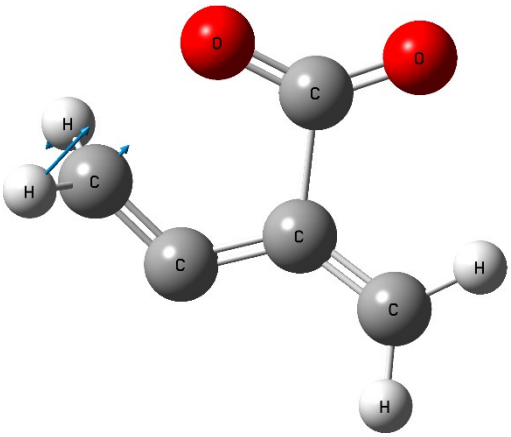
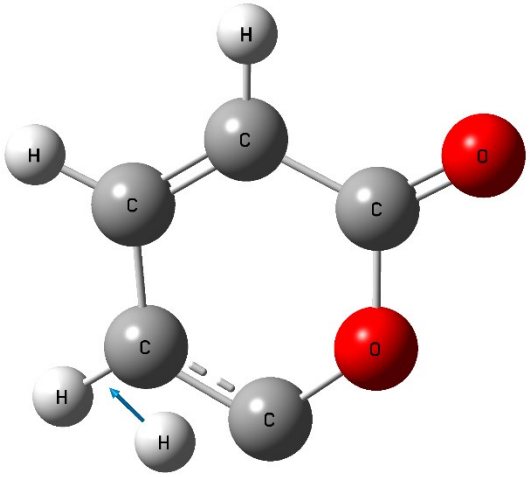


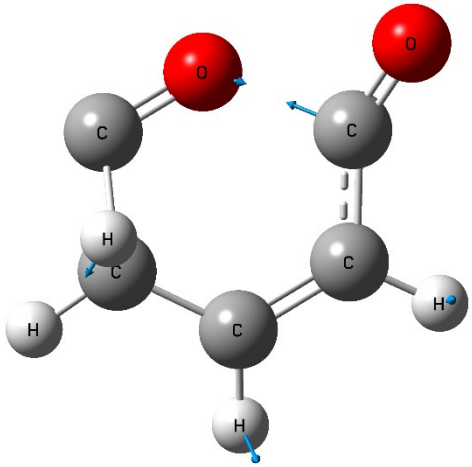
TS19



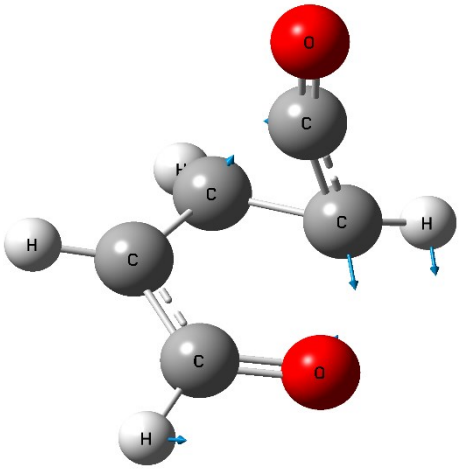
TS20



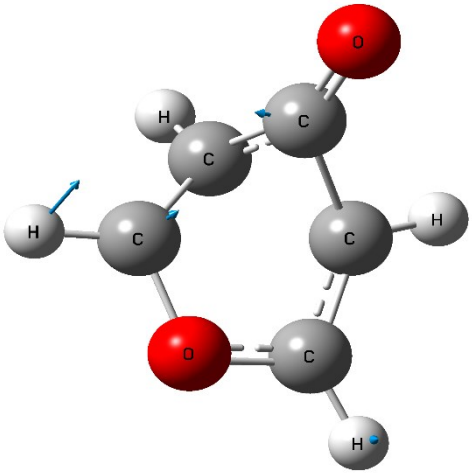
TS21



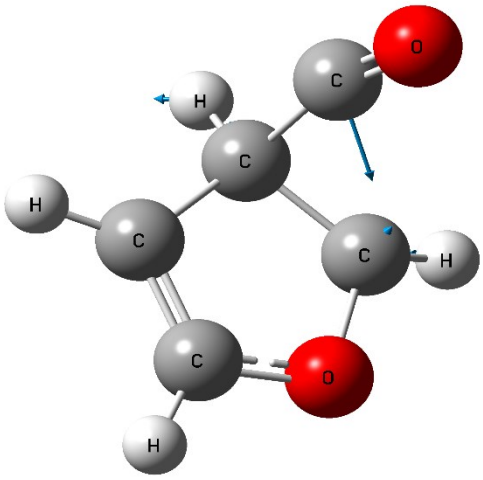
TS22



TS23



TS24



TS25

4. **Structural parameters for furfural and 2-pyrone pyrolysis intermediates and products, calculated at G4 level of energy.**

Furfural			
C	0.95465	-2.71996	-4.56879
C	2.29815	-2.71891	-4.48869
C	2.71772	-1.27691	-4.36167
C	1.58678	-0.54744	-4.37739
O	0.40463	-1.39497	-4.32248
H	2.94234	-3.57264	-4.5213
H	3.71838	-0.90553	-4.28637
H	1.56002	0.5211	-4.42646
C	0.10619	-3.96577	-4.88452
H	0.58281	-4.90833	-5.05569
O	-1.14767	-3.87524	-4.94121

2-Pyrone

O	0.32412	0.06367	-0.16579
C	0.17252	0.02314	1.16721
C	1.21103	-0.01915	2.02767
C	2.53195	-0.0203	1.47826
C	2.72021	0.02001	0.13602
C	1.60386	0.06543	-0.78796
H	3.38734	-0.05379	2.14433
H	1.03436	-0.05075	3.09322
H	-0.87109	0.02872	1.45609
O	1.63321	0.10334	-1.98526
H	3.70329	0.02049	-0.31492

M3

C	0.00748	0.	-0.00554
O	-0.01475	0.	1.34298
C	1.29267	0.	1.76508
C	2.13291	0.	0.70612
C	1.29601	0.	-0.46532
C	1.71891	0.	-1.8655
H	3.2103	0.	0.71877
H	1.43273	0.	2.83231
H	-0.95068	0.	-0.49903
O	2.87396	0.	-2.22873
H	0.88825	0.	-2.60335

M4

C	0.03244	0.	-0.04076
C	0.006	0.	1.28336
C	1.1929	0.	2.09342
C	1.21326	0.	3.45048
C	0.03013	0.	4.30499
O	-1.13013	0.	3.92428
O	0.03101	0.	-1.19648
H	-0.96745	0.	1.76549
H	2.14468	0.	1.56999
H	2.17278	0.	3.95547
H	0.24873	0.	5.39291

M5

C	-2.0948	0.39755	0.
C	-2.07524	0.35404	1.49803
C	-0.8061	0.23264	1.8497
O	0.03699	0.21226	0.69155
C	-0.63167	0.33205	-0.4347
H	-2.92736	0.42031	2.15447
C	-2.85732	1.5352	-0.67326
H	-0.28365	0.15692	2.78931
H	-2.52002	-0.52508	-0.43751
O	-3.54272	2.32272	-0.08107
H	-2.73029	1.56926	-1.77198

M6

C	-0.76453	-0.68807	0.
O	-0.83556	-0.68939	1.30023
C	0.67712	-0.69426	1.70716
C	1.47648	-0.69515	0.50148
C	0.52523	-0.69117	-0.53457
C	-2.07489	-0.68344	-0.73353
O	-2.13594	-0.68186	-1.93469
H	0.71631	-0.69047	-1.59888
H	0.77986	-1.58943	2.32493
H	-2.97143	-0.68161	-0.08561
H	0.78506	0.19881	2.32707

M7

C	-0.22838	0.6953	0.26237
C	0.4268	-0.48114	-0.48484
O	-0.28338	-1.42591	-0.91685
C	-2.91111	0.73098	0.64697
C	-1.56974	0.71314	0.45467
C	1.95108	-0.50141	-0.70336
O	2.48646	-1.46274	-1.31394
H	0.37548	1.49862	0.62971
H	-3.36634	1.54841	1.16608
H	2.55494	0.3019	-0.33602
H	-3.51497	-0.07237	0.27969

M8			
C	0.2392	-0.0463	0.
C	1.2662	-0.68686	-0.90807
C	0.81907	-1.91997	-0.66281
C	-0.2858	-1.46925	0.28199
O	-1.00198	0.29647	-0.68258
H	2.01299	-0.27046	-1.56946
H	1.07594	-2.90452	-1.0305
C	-1.52518	-0.94537	-0.451
O	-2.59806	-1.3444	-0.74958
H	-0.41362	-1.91342	1.26527
H	0.49955	0.67955	0.76553

M9			
O	0.34231	-1.1669	0.03466
C	-1.0849	-1.13703	-0.00491
C	-1.88874	0.02505	-0.16176
C	-1.11088	1.24856	0.02244
C	0.23768	1.24523	0.00304
C	1.03661	-0.00109	-0.00648
H	-1.64529	2.19537	0.08569
H	-1.50407	-1.13232	1.06168
H	-1.41367	-2.09935	-0.40907
O	2.23925	-0.01785	-0.02091
H	0.83691	2.1525	0.02023

M10

O	1.86766	-1.24397	-0.57055
C	-2.5124	-1.09215	0.23539
C	-1.85277	0.00448	0.06092
C	-1.15333	1.12355	-0.12115
C	0.1672	1.00451	-0.66545
C	1.63131	-0.25933	0.02873
H	-1.63336	2.07589	0.13086
H	-2.45628	-1.63558	1.17557
H	-3.12797	-1.50807	-0.55894
O	1.75337	0.53283	0.92199
H	0.62424	1.99803	-0.80465

M11

O	0.02286	-1.21756	0.16226
C	-1.34012	-0.87486	0.14788
C	-1.66656	0.38096	-0.18294
C	-0.58463	1.24526	-0.58349
C	0.4257	1.29264	0.44374
C	0.91535	-0.23257	0.00537
H	0.17979	1.17407	1.51706
H	-2.7018	0.66657	-0.34407
H	-1.96725	-1.74914	0.22292
O	2.06119	-0.40438	-0.25115
H	1.29841	1.92794	0.26191

M12

O	-0.00714	-1.22256	0.17226
C	-1.36012	-0.89986	0.13788
C	-1.63656	0.36096	-0.19294
C	-0.41963	1.08026	-0.53849
C	0.3957	1.44764	0.52374
C	0.85035	-0.24257	-0.12964
H	0.09979	1.45907	1.58206
H	-2.6368	0.76657	-0.27907
H	-1.99225	-1.75414	0.32792
O	2.03118	-0.36938	-0.25615
H	1.37841	1.87294	0.30691

M13

O	1.51372	0.24378	0.74192
C	1.75538	-0.78929	-0.31084
C	0.4907	-1.12806	-0.47369
C	-0.74551	-0.54915	-0.0484
C	-2.05365	-0.85687	-0.22347
C	0.02075	0.58428	0.6749
H	-2.32862	-1.72073	-0.79183
H	2.40977	-1.57014	0.01618
H	2.15561	-0.38866	-1.21871
O	-0.50493	1.62547	1.1473
H	-2.81152	-0.23598	0.20667

M14

O	0.36119	-1.20193	0.00012
C	-0.93666	-1.41134	-0.00011
C	-1.77162	-0.14589	-0.00006
C	-1.09901	1.18112	-0.00001
C	0.2348	1.26602	0.00005
C	1.06216	0.06803	0.00003
H	-1.70693	2.0841	0.00001
H	-2.45783	-0.24953	-0.85611
H	-2.45727	-0.24976	0.85642
O	2.2521	0.00989	-0.00009
H	0.77775	2.20391	0.00007

M15

C	-0.26693	0.46298	0.91179
C	0.10692	-0.96314	0.53164
C	1.55804	0.31773	-0.55051
H	0.07299	-1.79784	1.23464
H	2.40038	0.4993	-1.20894
C	-1.34199	0.07649	0.06324
H	-0.39244	0.86811	1.94087
O	-2.26328	-0.09407	-0.6957
O	1.30435	-0.96237	-0.28294
C	0.74949	1.2115	0.03796
H	0.78232	2.28617	-0.04719

M16

C	-1.29467	0.93763	0.1292
C	0.01756	0.98156	-0.39339
C	0.32641	-0.63799	-0.88284
C	-0.68011	-1.16604	0.07372
O	-1.58202	-0.2913	0.4756
H	-2.08744	1.66909	0.17046
H	0.37291	1.8249	-0.97604
H	-0.92755	-2.2008	0.23946
C	1.14358	0.07787	0.03992
O	2.20279	0.11625	0.59689
H	0.57935	-1.1434	-1.82848

VK

C	-1.74276	-0.61439	0.88896
C	-1.14643	-1.36254	-0.04558
C	0.27873	-1.48331	-0.3381
C	1.24331	-0.73091	0.15725
H	-1.7665	-1.97154	-0.69869
H	-1.18614	-0.00326	1.59255
H	-2.8215	-0.60331	0.98557
O	2.10834	-0.08145	0.57967
H	0.62094	-2.23197	-1.04398

Furan			
C	-1.74312	-0.24465	0.
O	-1.7819	-0.24465	1.36198
C	-0.4894	-0.24465	1.79321
C	0.36377	-0.24465	0.73707
C	-0.45825	-0.24465	-0.43868
H	-0.13116	-0.24465	-1.46612
H	1.44106	-0.24465	0.78265
H	-0.3516	-0.24465	2.86098
H	-2.69867	-0.24465	-0.49604

CBD			
C	1.21665	0.70443	0.53857
C	1.86904	0.07817	-0.4737
C	1.05615	-1.10218	-0.2731
C	0.26345	-0.52445	0.72229
H	2.61828	0.36468	-1.19394
H	1.04684	-2.0871	-0.72916
H	-0.09034	-0.99839	1.63034
H	1.32327	1.63709	1.07423

C_4H_4			
C	1.76603	-0.85288	-0.00028
C	1.87012	0.52172	-0.00016
C	0.85848	1.2458	-0.00072
C	-0.50592	1.42323	0.00072
H	-0.98264	1.79451	-0.90487
H	1.918	-1.41628	-0.9165
H	1.9186	-1.41705	0.91534
H	-0.98054	1.79351	0.90786

5. Structural parameters for furfural and 2-pyrone pyrolysis transition-state geometries, calculated at G4 level of energy.

TS1

C	-0.69602	-0.38094	-1.13446
C	-0.75064	0.96971	-1.18015
C	-2.15753	1.29282	-1.18197
C	-2.85822	0.10104	-1.18485
O	-1.94614	-0.92807	-1.04451
H	0.16421	-1.02812	-1.12034
H	0.0794	1.65251	-1.19815
H	-2.59842	2.27728	-1.20152
C	-4.59542	0.45783	-0.79296
H	-3.53781	0.95403	-0.15505
O	-5.54529	0.02255	-1.35427

TS2

C	-0.31677	0.51665	0.00014
C	0.74585	1.30827	-0.00005
C	1.95011	0.55154	-0.00018
C	1.56185	-0.74959	-0.00004
O	0.26912	-0.96868	-0.00004
H	0.63706	2.37948	0.00015
H	2.9612	0.91732	-0.00001
H	2.10964	-1.6753	-0.00023
C	-1.76014	0.71787	-0.00009
H	-1.21006	-0.5543	0.00046
O	-2.72346	1.43604	-0.02977

TS3			
C	-0.25994	1.16208	0.
C	-0.16149	1.11947	1.30634
O	-0.06162	1.08308	2.46354
C	-0.60447	2.39839	-0.74968
C	-1.83772	2.83039	-1.04644
C	-3.1227	2.17123	-0.69738
O	-3.25131	1.08928	-0.17539
H	-0.11307	0.22651	-0.52946
H	0.23354	2.99596	-1.10734
H	-1.93675	3.75515	-1.60987
H	-4.01666	2.77003	-0.9767

TS4			
C	-1.28537	-1.26374	0.00264
C	-0.90117	0.15061	0.00083
C	0.51142	0.46661	-0.00079
C	1.24655	-0.69134	-0.00027
O	-0.27973	-2.10573	0.00259
H	-2.30623	-1.58429	0.00391
H	-1.64049	0.92411	0.00071
H	0.92073	1.45523	-0.00218
C	2.69541	-1.21327	-0.00106
H	3.2176	-0.74627	0.80772
O	3.33767	-2.02438	-0.71742

TS5

C	0.0359	-0.05368	0.06242
C	0.27879	-0.01882	1.42433
C	1.6092	0.2982	1.81127
O	2.22517	0.52472	0.11116
C	1.23404	0.20032	-0.61671
C	1.93716	-0.46589	3.31828
O	2.75633	-1.19921	3.66361
H	-0.44665	-0.35326	2.15215
H	-0.88655	-0.37402	-0.39826
H	1.38924	0.06119	-1.68811
H	2.01509	1.26861	2.06949

TS6

C	0.21802	0.6686	0.
C	0.37275	0.21955	1.47073
C	1.76649	0.21904	1.9618
C	1.945	0.62046	3.24719
C	0.71378	0.92729	3.90111
O	0.22814	1.01279	4.97026
O	-0.4103	1.52689	-0.48784
H	-0.12614	-0.7538	1.48149
H	2.59219	-0.0589	1.31978
H	2.90733	0.79616	3.72205
H	-0.1426	0.87931	2.30793

TS7

C	-0.98521	-0.4417	0.20925
C	-1.00778	-0.30104	1.5449
C	0.39733	-0.13821	1.92008
C	1.20228	-0.07007	0.71789
C	1.15848	-1.70542	1.8955
O	0.30988	-0.34484	-0.27502
O	1.90949	-2.01399	2.75652
H	0.73872	0.2756	2.85942
H	-1.87106	-0.33871	2.18969
H	-1.75181	-0.60222	-0.53227
H	0.66092	-2.37913	1.17471

TS8

C	-0.03058	0.30581	0.
C	0.06251	0.58646	1.42368
C	1.43114	0.3875	1.87233
C	2.07885	-0.03663	0.77484
O	1.23438	-0.1402	-0.30324
C	-1.01902	1.31009	2.15635
O	-0.83713	1.86489	3.20918
H	1.82481	0.55761	2.86037
H	3.10704	-0.30875	0.59249
H	-0.51664	-0.46891	1.01631
H	-1.99784	1.31582	1.64037

TS9

C	-0.24465	0.79511	0.
O	-0.27569	0.86181	1.35842
C	1.07661	0.89791	1.72428
C	1.97778	0.78252	0.63318
C	1.0301	0.8041	-0.47956
C	-1.55702	0.75697	-0.68396
O	-1.6654	0.68948	-1.883
H	1.28729	0.77631	-1.52777
H	1.68028	1.92535	1.42296
H	1.24046	0.74817	2.78328
H	-2.43327	0.79414	-0.00784

TS10

C	-0.71865	0.77982	0.
C	-0.68483	0.776	1.40753
O	0.47737	0.77497	1.96076
C	1.4487	0.77902	0.6177
C	0.57922	0.78171	-0.5094
C	-1.86997	0.77303	2.3369
O	-3.00202	0.77347	1.93177
H	-1.64563	0.78095	-0.5568
H	2.04402	-0.12208	0.77258
H	-1.61557	0.77043	3.41324
H	2.04324	1.6798	0.77745

TS11

C	-2.73753	0.29052	-0.10489
C	-1.47434	-0.07532	0.04442
C	-0.53196	-1.05564	0.21375
C	0.82944	-0.69383	-0.03005
C	0.75668	0.88213	-0.08676
O	1.47062	1.78065	0.11507
O	1.87745	-1.27537	-0.16004
H	-3.07661	1.30034	0.08967
H	-3.47041	-0.42001	-0.47736
H	-0.7416	-1.97169	0.75226
H	-0.54975	0.96199	-0.22356

TS12

C	2.37718	0.55029	0.0183
C	3.35329	-0.26904	-0.89868
C	2.82077	-1.65003	-0.66103
C	1.6973	-1.29408	0.35419
O	1.11325	0.77456	-0.73809
H	4.16458	0.06186	-1.51287
H	3.12378	-2.59377	-1.06408
C	0.53698	-0.68828	-0.42848
O	-0.57636	-1.19194	-0.7291
H	1.55336	-1.86304	1.24887
H	2.74742	1.3141	0.66977

TS13

C	4.67856	1.26107	0.83249
C	3.97757	2.06759	-0.13176
C	4.7242	3.39647	-0.2166
C	5.59627	3.16855	0.74963
O	6.76451	0.76381	0.17823
H	3.09781	1.79338	-0.67556
H	4.57587	4.24931	-0.84553
C	7.36	1.98991	0.05179
O	8.51311	2.33407	-0.31627
H	5.73149	3.90981	1.50934
H	4.37048	1.19921	1.85532

TS14

C	-0.31751	-1.15792	0.
C	1.02117	-1.1737	0.
C	1.77662	-0.05623	0.
C	1.09825	1.20196	0.
C	-0.25637	1.25206	0.
H	-1.06199	0.04795	0.00001
H	1.67654	2.12086	0.
H	2.40773	-1.23414	-0.07408
O	1.41244	-2.18508	-0.00001
H	-2.25789	-0.04522	-0.00001
C	-0.80731	2.18394	0.

TS15

O	0.49391	-1.27758	0.31864
C	-1.49728	-1.07785	-0.10914
C	-1.76298	0.20893	-0.22115
C	-1.01316	1.35254	-0.03762
C	0.29852	1.12981	0.30319
C	1.05464	-0.17641	0.08801
H	-1.43889	2.34547	-0.08373
H	-1.74548	-1.57118	0.82451
H	-1.43353	-1.70737	-0.99021
O	2.15667	0.07242	-0.38136
H	0.93483	1.95228	0.61132

TS16

O	1.85973	-1.26903	-0.57089
C	-2.49743	-1.09298	0.23583
C	-1.86075	0.0138	0.06156
C	-1.20304	1.15714	-0.11847
C	0.09036	1.07182	-0.7267
C	1.71391	-0.31151	0.0795
H	-1.69605	2.08177	0.19571
H	-2.38755	-1.66471	1.15293
H	-3.14613	-1.49704	-0.53577
O	1.79695	0.51455	0.92213
H	0.51797	2.08615	-0.81299

TS17

O	-0.31751	-1.15792	0.
C	1.02117	-1.1737	0.
C	1.77662	-0.05623	0.
C	1.09825	1.20196	0.
C	-0.25637	1.25206	0.
C	-1.06199	0.04795	0.00001
H	0.4223	2.38427	-0.03385
H	2.85551	-0.12693	0.
H	1.41244	-2.18508	-0.00001
O	-2.25789	-0.04522	-0.00001
H	-0.80731	2.18394	0.

TS18

O	0.34656	-1.15034	-0.79482
C	-1.04513	-1.10808	0.04204
C	-1.76628	0.01784	-0.20836
C	-1.20539	1.3115	-0.09298
C	0.2583	1.27189	0.19694
C	1.10795	0.01622	-0.98267
H	0.29128	1.50821	1.27328
H	-2.82688	-0.11262	-0.38106
H	-1.48807	-2.09392	0.14594
O	2.2524	-0.11965	-1.2462
H	0.80865	2.0893	-0.26806

TS19			
O	-1.23916	-0.81031	0.00007
C	-1.64025	0.50647	-0.00021
C	-0.63081	1.38836	0.00013
C	0.5976	0.61323	0.0001
C	1.88916	0.95986	0.00004
C	0.15576	-0.82087	0.00015
H	2.20848	1.99577	-0.00056
H	-1.14353	1.19044	1.26462
H	-2.71055	0.64888	0.00027
O	0.78158	-1.83733	-0.00017
H	2.65372	0.19099	0.00032

TS20			
O	-0.98806	1.1269	0.00058
C	-1.71932	-0.70128	0.00037
C	-0.54035	-1.52349	-0.00086
C	0.59171	-0.62311	-0.00078
C	1.88016	-1.0137	0.00065
C	0.16245	0.82289	-0.00028
H	2.13014	-2.06942	0.00056
H	-2.35792	-0.85886	-0.88028
H	-2.35752	-0.85935	0.88111
O	0.8402	1.81291	-0.00037
H	2.68574	-0.28339	0.00201

TS21

O	0.32412	0.06367	-0.16579
C	0.17252	0.02314	1.16721
C	1.21103	-0.01915	2.02767
C	2.53195	-0.0203	1.47826
C	2.72021	0.02001	0.13602
C	1.60386	0.06543	-0.78796
H	3.38734	-0.05379	2.14433
H	1.03436	-0.05075	3.09322
H	0.79806	-1.28727	1.59617
O	1.63321	0.10334	-1.98526
H	3.70329	0.02049	-0.31492

TS22

O	0.40881	-1.16514	1.21052
C	-0.88903	-1.37455	1.21029
C	-1.77162	-0.14589	-0.00006
C	-1.09901	1.18112	-0.00001
C	0.2348	1.26602	0.00005
C	1.06216	0.06803	0.00003
H	-1.70693	2.0841	0.00001
H	-2.45783	-0.24953	-0.85611
H	-2.45727	-0.24976	0.85642
O	2.2521	0.00989	-0.00009
H	0.77775	2.20391	0.00007

TS23

C	-0.20627	0.78527	0.7737
C	-0.40529	-0.7513	0.72263
C	1.64284	0.10167	-0.47147
H	-0.66228	-1.47559	1.48905
H	2.53819	0.01763	-1.0704
C	-1.58364	-0.28666	0.01521
H	-0.44722	1.32628	1.68703
O	-2.62935	-0.29631	-0.56554
O	1.41756	-1.1621	-0.20399
C	0.98123	1.18587	-0.06226
H	1.24349	2.20928	-0.28227

TS24

C	-1.32071	0.92343	-0.12533
C	-0.02168	0.97828	0.40837
C	0.31666	-0.5533	0.92207
C	-0.6001	-1.14546	-0.11612
O	-1.61684	-0.30507	-0.45928
H	-2.07341	1.67877	-0.28192
H	0.37543	1.8455	0.91915
H	-0.8301	-2.19271	-0.232
C	1.1515	-0.00426	-0.07453
O	2.22774	0.10508	-0.59496
H	0.48682	-0.92377	1.94189

TS25			
C	0.17168	0.92394	-0.6084
C	0.17761	-0.54656	-0.79175
C	-1.71396	-0.21905	0.3662
H	0.76362	-1.20529	-1.40045
H	-2.38517	-0.65381	1.09569
C	1.2473	0.30017	0.1443
H	1.61389	1.37711	-0.99943
O	2.24313	-0.16134	0.61134
O	-0.85256	-1.15337	-0.0348
C	-1.20532	1.0205	0.36768
H	-1.76107	1.93257	0.24613

6. Master equation parameters, rate coefficients calculations and comparing with the experimental results

Furfural decomposition at P= 1 atm

T (K)	Furfural conversion %	Number of collisions	Number of trials
1400	31.63	6.00E+05	8.00E+05
1500	62.63	2.50E+05	1.00E+06
1600	61.26	8.00E+04	5.00E+06
1700	25.34	1.00E+04	1.00E+07
1800	44.56	1.00E+04	1.00E+07
1900	64.59	1.00E+04	1.00E+07
2000	80.7	1.00E+04	1.00E+07
2100	90.97	1.00E+04	1.00E+07

Furfural decomposition at P= 10 atm

T (K)	Furfural conversion %	Number of collisions	Number of trials
1500	54.65	2.00E+05	1.50E+06
1600	40.35	2.50E+05	1.80E+06
1700	79.38	2.50E+05	1.80E+06
1800	97.98	2.50E+05	1.00E+05
1900	99.95	2.50E+05	1.00E+05
2000	100.00	2.50E+05	1.00E+05
2100	100.00	1.25E+05	5.00E+06

Furfural decomposition at P= 50 atm

T (K)	Furfural conversion %	Number of collisions	Number of trials
1500	73.82	5.24E-01	1.05E+03
1600	44.48	1.00E+06	4.00E+05
1700	64.08	5.00E+05	1.50E+06
1800	76.87	2.50E+05	1.00E+05
1900	96.72	2.50E+05	1.00E+05
2000	99.87	2.50E+05	1.00E+05
2100	99.99	2.50E+05	1.00E+05

Furfural decomposition at P= 100 atm

T (K)	Furfural conversion %	Number of collisions	Number of trials
1500	66.39	7.39E-01	1.05E+03
1600	47.48	2.00E+06	2.00E+05
1700	58.63	7.50E+05	8.00E+05
1800	58.71	2.50E+05	1.00E+05
1900	89.18	2.50E+05	1.00E+05
2000	99.13	2.50E+05	1.00E+05
2100	99.96	2.50E+05	1.00E+05

2-Pyrone decomposition at P= 1 atm

T (K)	2-Pyrone conversion %	Number of collisions	Number of trials
1400	51.54	3.50E+06	1.00E+05
1500	58.16	8.00E+05	3.00E+05
1600	56.57	2.00E+05	5.00E+05
1700	70.41	1.00E+05	1.00E+06
1800	94.04	1.00E+05	1.00E+06
1900	99.62	1.00E+05	1.00E+06
2000	99.99	1.00E+05	1.00E+06
2100	100.00	1.00E+05	1.00E+06

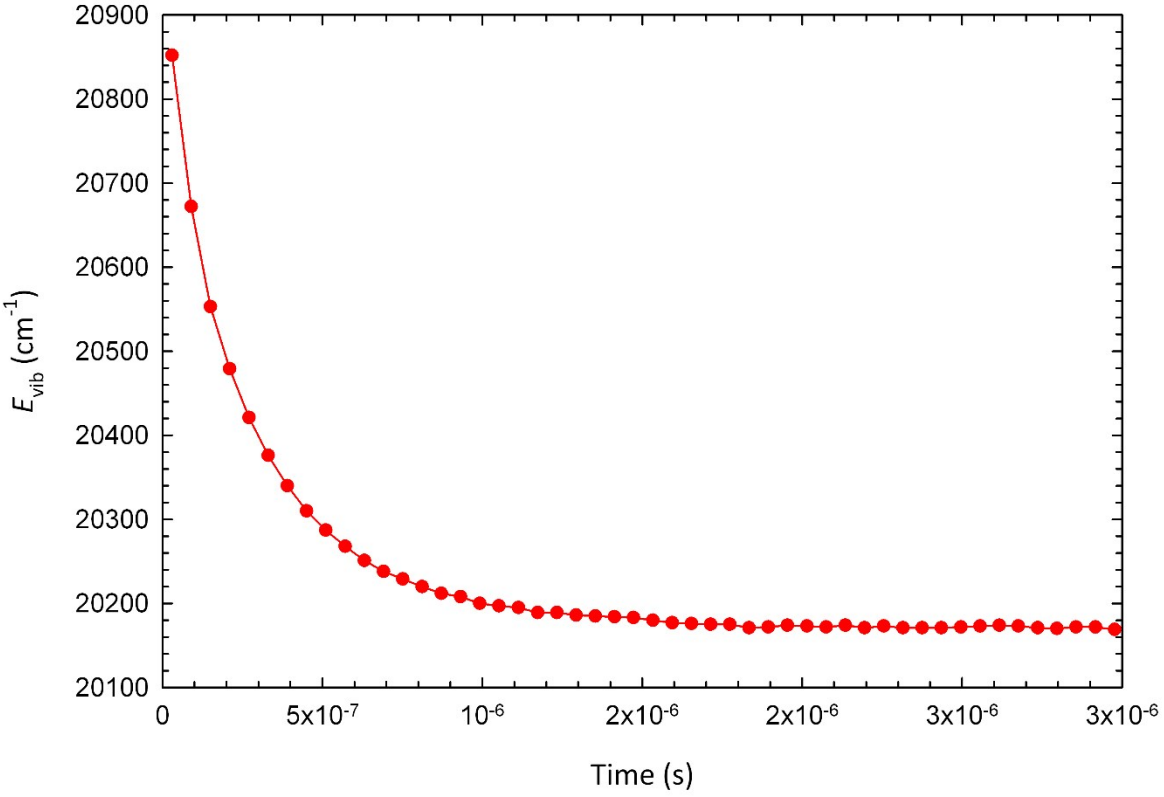


Figure S1: Vibrational energy of furfural dissociation as a function of time at 1800 K and 1 atm.

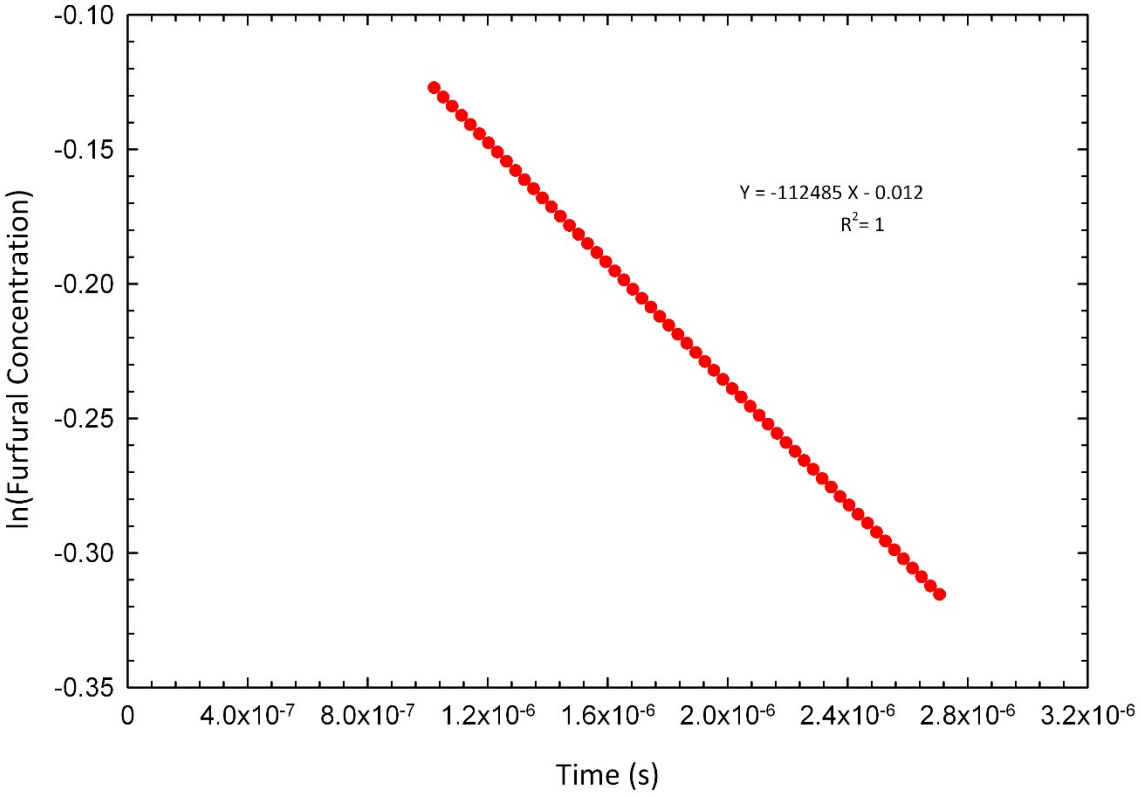


Figure S2: The natural logarithm of furfural concentration versus time for a first-order reaction at 1800 K and 1 atm.

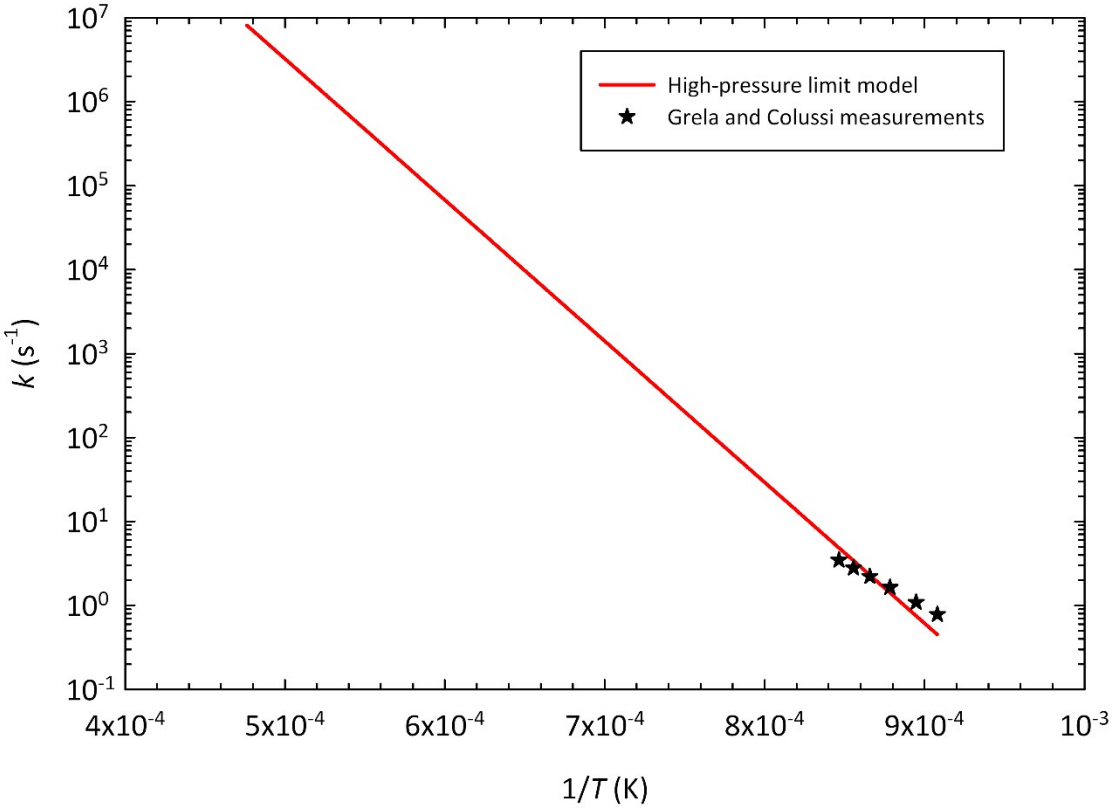


Figure S3: Comparing the high-pressure limit model with Grela and Colussi measurements.

7. Rate coefficients of furfural pyrolysis to its products as a function of temperature and pressure.

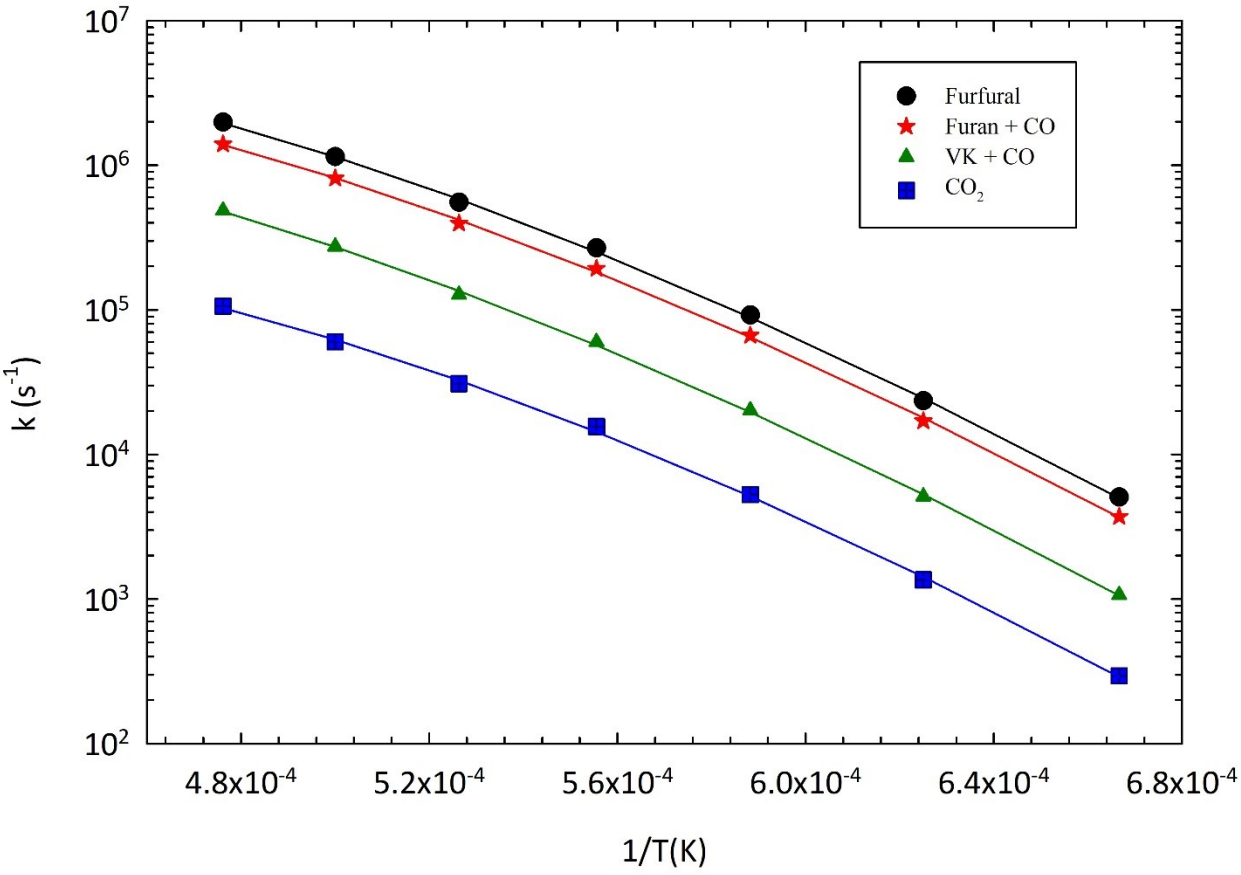


Figure S4: Calculated rate coefficients (dot points) and model fits (solid lines) of furfural pyrolysis to its main products at 10 atm and temperature range 1500 – 2100 K.

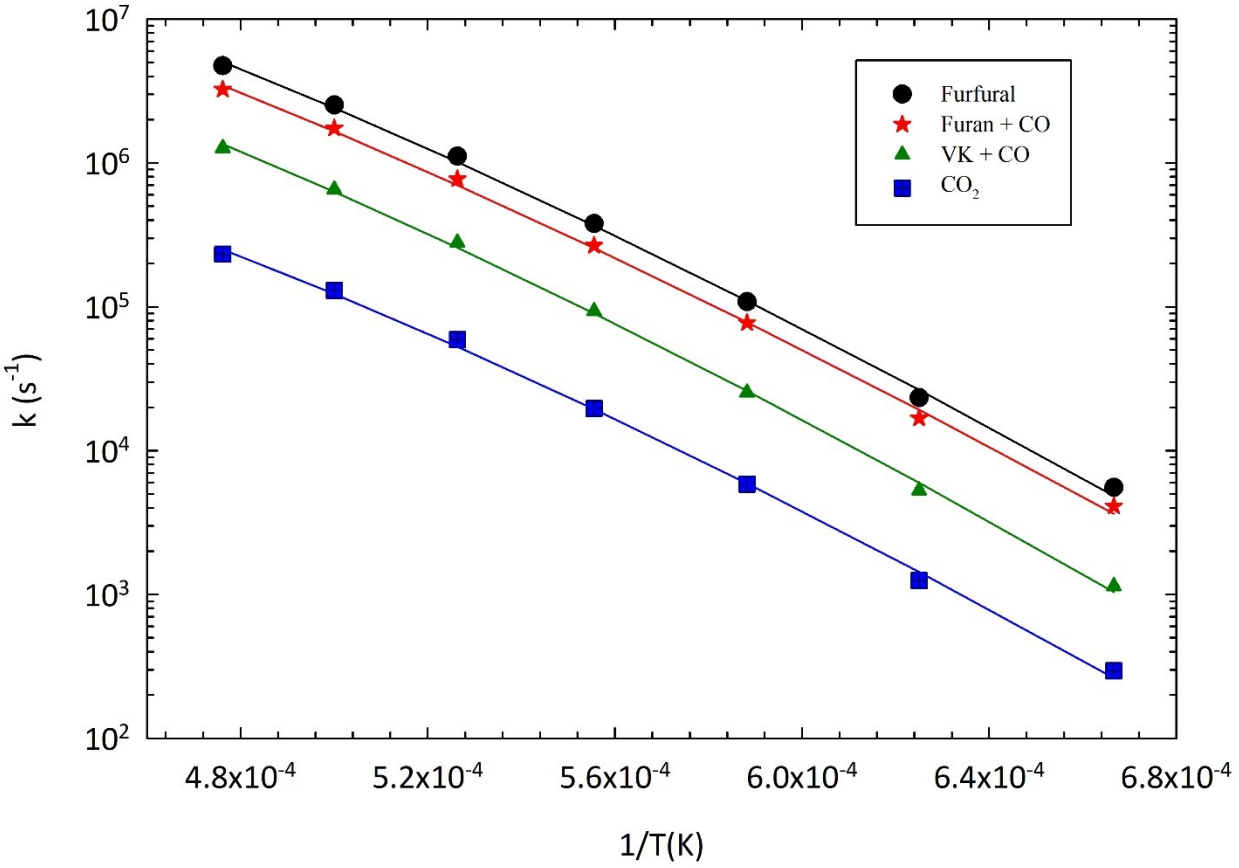


Figure S5: Calculated rate coefficients (dot points) and model fits (solid lines) of furfural pyrolysis to its main products at 50 atm and temperature range 1500 – 2100 K.

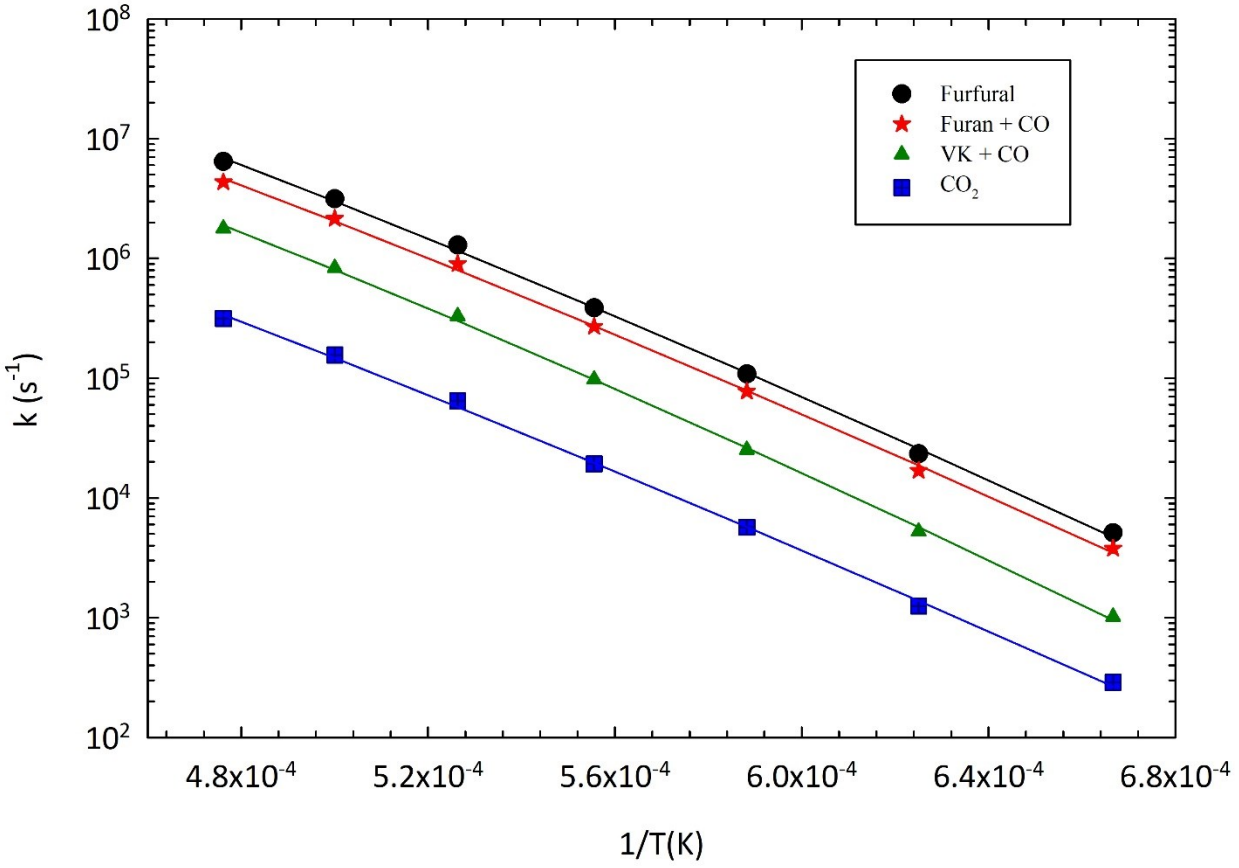


Figure S6: Calculated rate coefficients (dot points) and model fits (solid lines) of furfural pyrolysis to its main products at 100 atm and temperature range 1500 – 2100 K.

8. **Branching Ratio of furfural and 2-pryone pyrolysis products as function of temperature and pressure.**

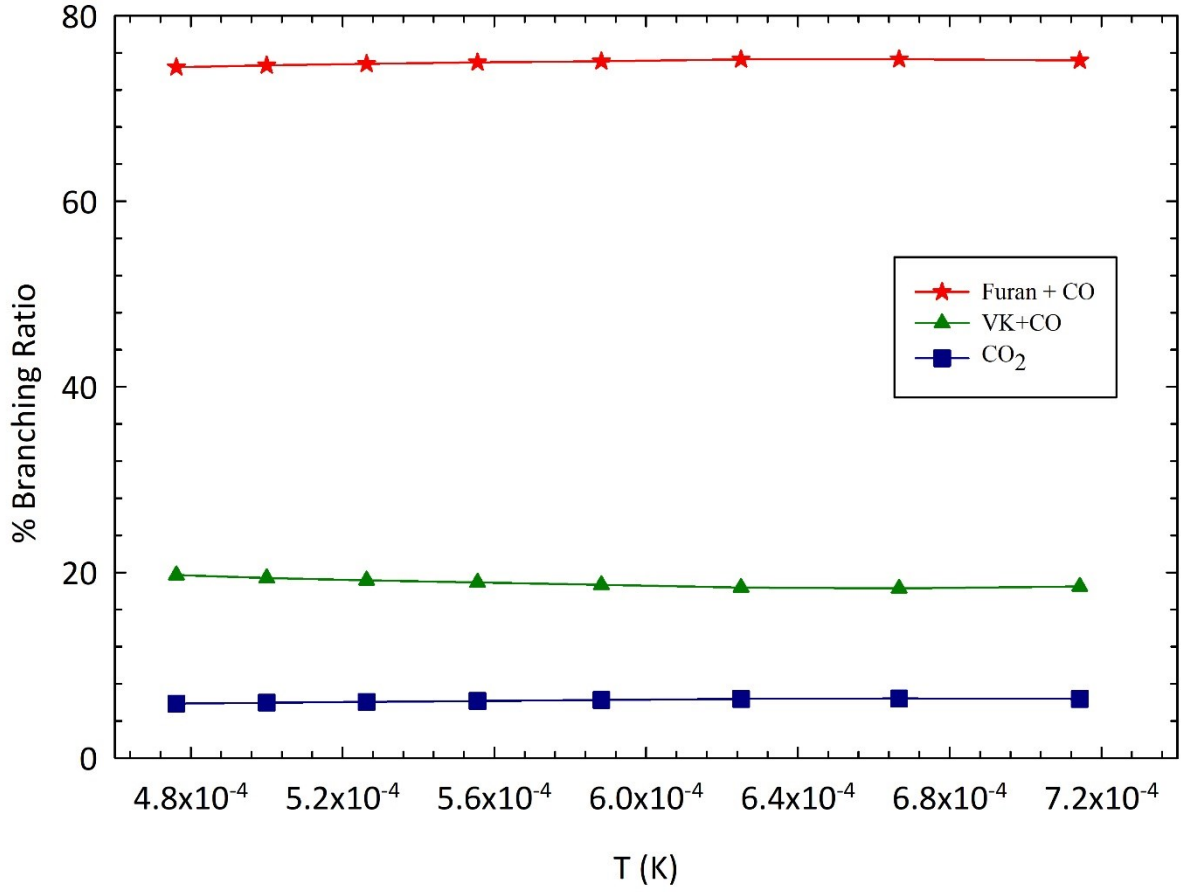


Figure S7: Calculated branching fractions of furfural pyrolysis products as a function of temperature (1400 – 2100 K) and at 1 atm.

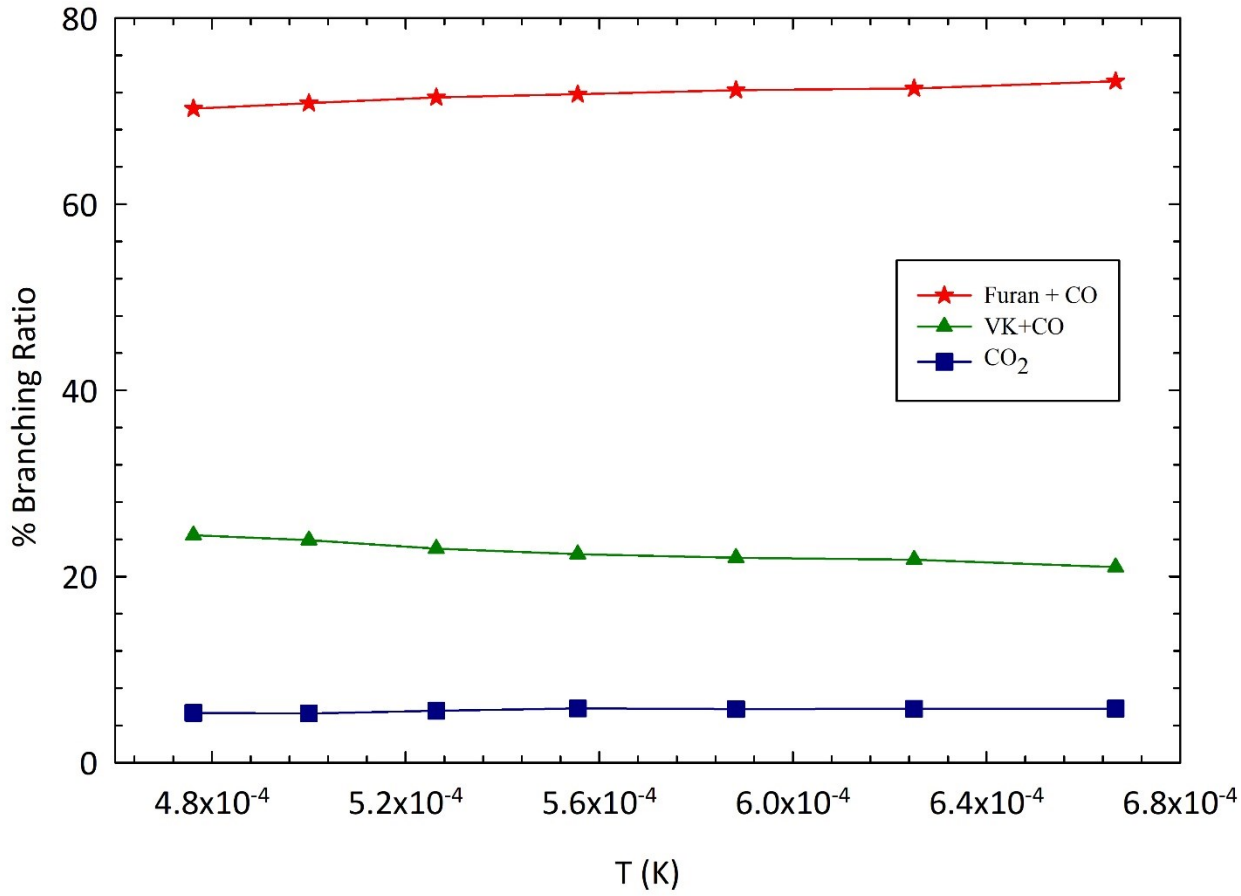


Figure S8: Calculated branching fractions of furfural pyrolysis products as a function of temperature (1500 – 2100 K) and at 10 atm.

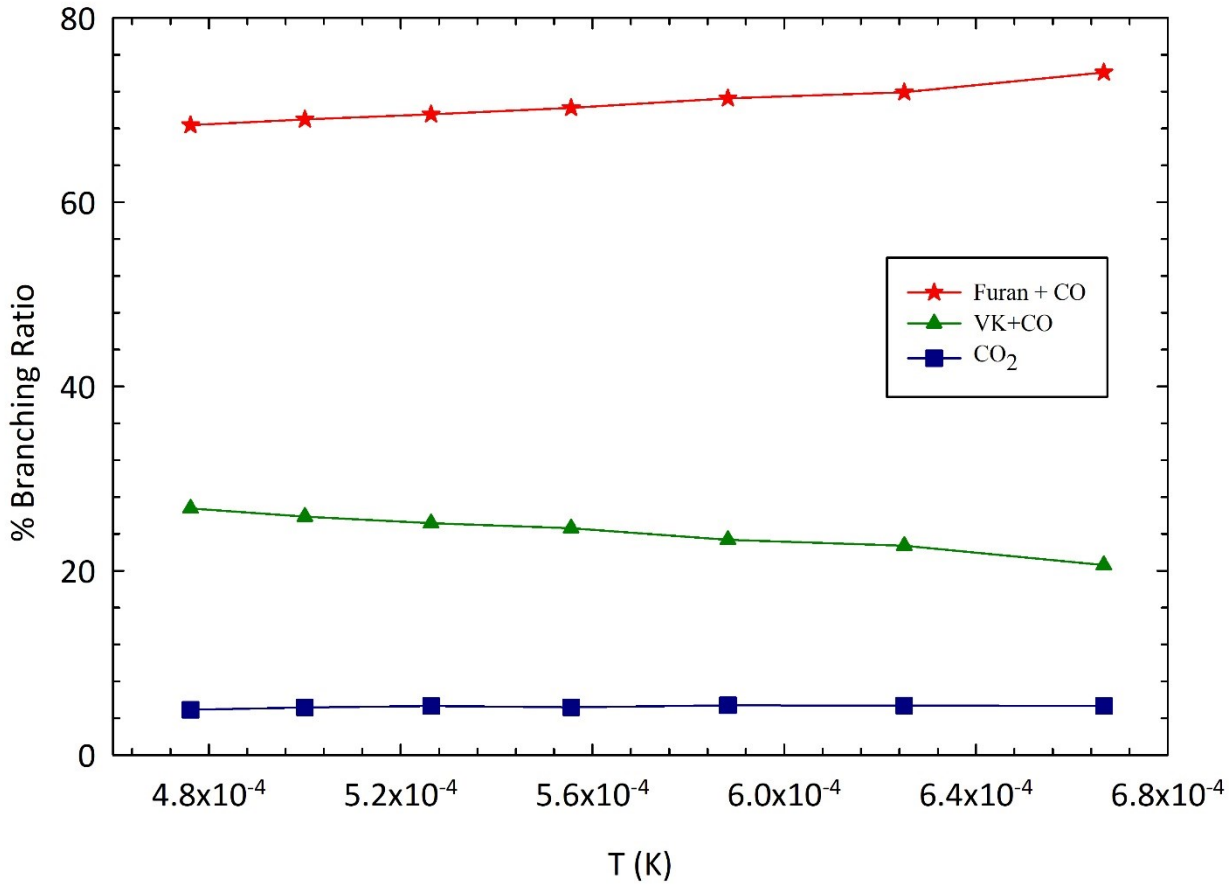


Figure S9: Calculated branching fractions of furfural pyrolysis products as a function of temperature (1500 – 2100 K) and at 50 atm.

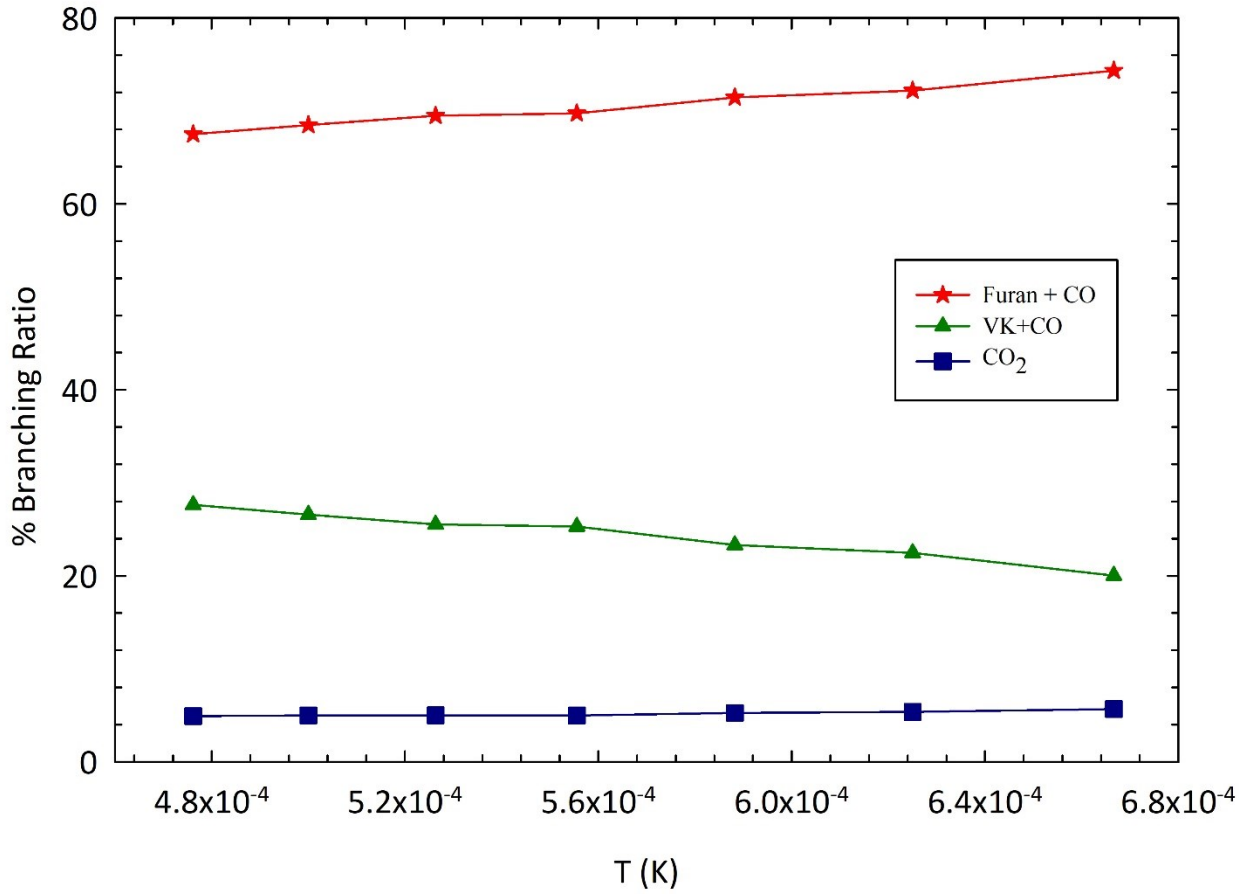


Figure S10: Calculated branching fractions of furfural pyrolysis products as a function of temperature (1500 – 2100 K) and at 100 atm.

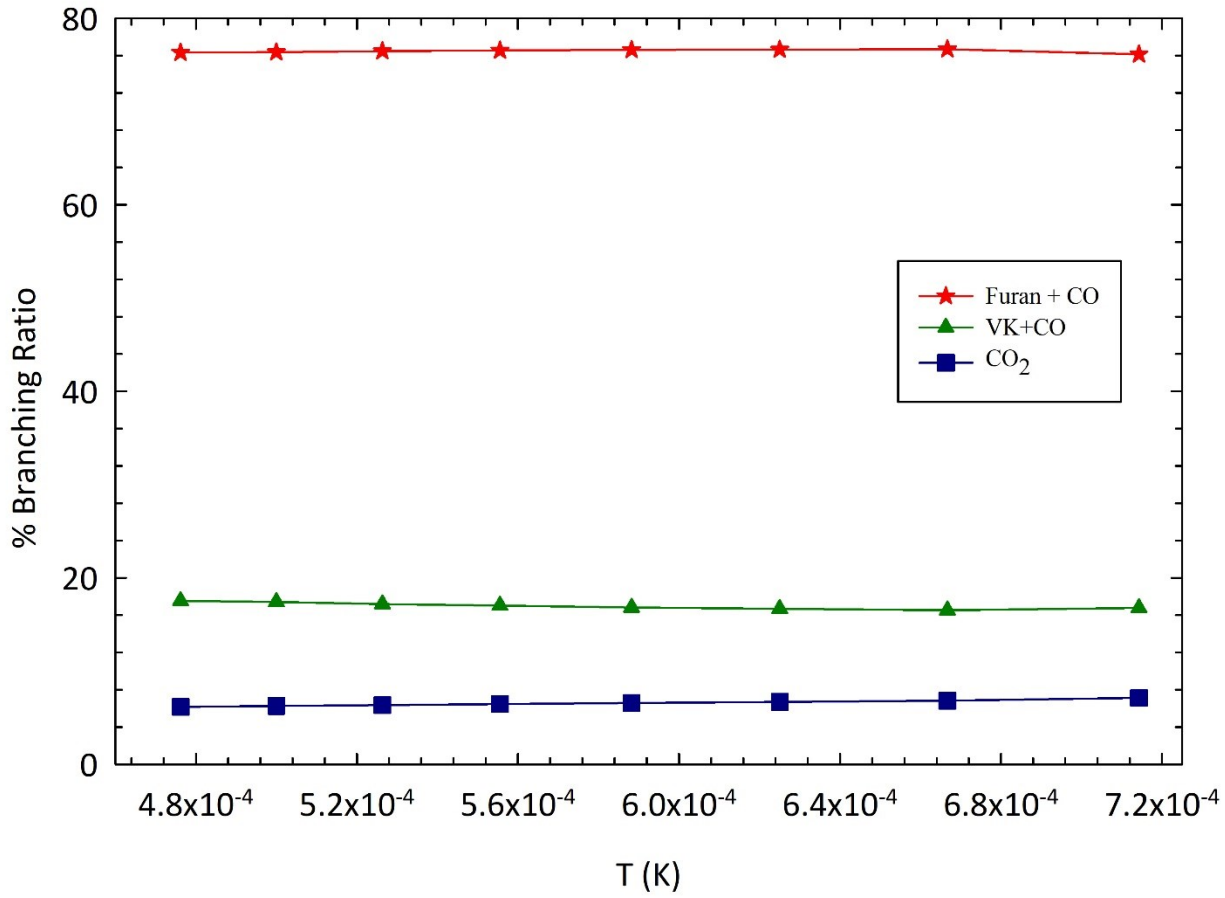


Figure S11: Obtained branching ratio of 2-pyrone dissociation products as a function of temperature and (1400 – 2100 K) at 1 atm.