

Hydroxyl Radical Regeneration in the Photochemical Oxidation of Glyoxal: Kinetics and Mechanism of the HC(O)CO + O₂ Reaction

Supplementary Material

Gabriel da Silva

gdasilva@unimelb.edu.au

Optimized Geometries (B3LYP/6-31G(2df,p), Å)

HC(O)CO

C	0.71342	0.46150	-0.00041
C	-0.63749	0.13222	0.00132
O	-1.74755	-0.19367	-0.00056
O	1.57530	-0.44429	0.00000
H	0.92240	1.54135	-0.00061

HC(O)C(O)O₂

C	-1.46857	0.27704	0.00038
C	0.05033	0.47171	0.00000
O	0.59681	1.52433	-0.00028
O	-2.00726	-0.79155	-0.00027
O	0.70350	-0.78308	-0.00011
O	2.02045	-0.66737	0.00022
H	-1.99851	1.24879	0.00130

OCC(O)OOH

C	-0.97263	-0.36915	0.35435
C	0.03747	0.67976	0.00061
O	-0.19675	1.85277	-0.02827
O	-1.89154	-0.87853	-0.16426
O	1.31986	0.20858	-0.04378
O	1.26006	-1.23156	-0.12011
H	1.67792	-1.47374	0.72154

OCOOH

C	-0.64734	-0.34273	0.02088
O	-1.78286	-0.01206	0.01504
O	0.38960	0.50831	-0.03978
O	1.62501	-0.24608	-0.08395
H	2.03009	0.05493	0.74430

TS1

C	0.46319	1.13531	0.37732
C	1.01833	-0.16880	0.08066
O	1.83767	-0.91353	-0.25085
O	-0.35455	1.64407	-0.37073
O	-0.84977	-1.15741	0.20781
O	-1.83116	-0.48297	-0.10486
H	0.69338	1.47969	1.40120

TS2

C	-0.80261	-0.65054	0.00001
C	0.04764	0.67382	0.00000
O	-0.33917	1.79496	0.00000
O	-1.96698	-0.78927	0.00000
O	1.33845	0.27997	0.00000
O	1.51039	-1.12601	0.00000
H	0.18833	-1.41682	0.00002

TS3

C	-1.40787	-0.24859	0.46269
C	0.42472	0.68312	-0.08854
O	0.56201	1.85479	-0.02243
O	-2.31638	-0.19767	-0.22675
O	1.42213	-0.20633	0.08386
O	0.95689	-1.53877	-0.20224
H	0.90169	-1.90331	0.69563

TS4

C	0.95834	0.41735	-0.19993
C	-0.99638	0.29134	0.38738
O	-1.81834	-0.26076	-0.18741
O	1.69860	-0.45911	0.07197
H	1.18625	1.50680	-0.20120

Vibrational Frequencies (B3LYP/6-31G(2df,p), cm⁻¹)
(bold frequencies removed and treated as free rotors)

HC(O)CO

3007.5	2167.2	1479.6	1352.4	990.9
784.8	680.8	266.8	179.9	

HC(O)C(O)O₂

2965.4	1885.3	1839.0	1380.6	1169.2
1128.1	1013.7	819.8	677.4	535.2
509.0	350.4	207.5	140.6	92.1

OCC(O)OOH

3740.0	1996.6	1817.2	1410.7	1156.6
964.3	721.8	706.3	581.8	463.1
349.0	287.8	247.9	171.2	150.5

OCOOH

3745.3	1877.4	1429.6	1037.7	950.7
600.7	353.0	261.8	162.7	

TS1

2964.8	2097.7	1653.8	1431.0	1369.0
918.2	819.9	642.5	380.9	294.7
234.1	169.0	137.6	103.9	

TS2

1997.9	1941.8	1846.7	1087.6	1002.9
966.8	781.0	652.7	622.3	500.7
470.3	295.1	148.4	63.0	

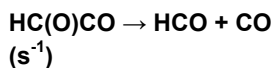
TS3

3736.5	2091.2	1884.1	1429.0	1028.3
955.0	607.0	418.7	372.8	251.0
242.2	173.7	154.1	66.6	

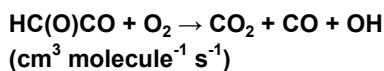
TS4

2830.2	2066.7	1890.0	1163.2	634.9
324.7	264.3	84.4		

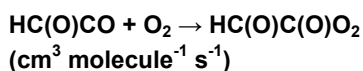
Calculated Rate constants



<i>T</i> (K)	<i>P</i> (atm)		
	0.01	0.1	1
150	9.099E-04	7.693E-03	5.873E-02
200	1.679E+00	1.486E+01	1.237E+02
250	1.339E+02	1.219E+03	1.067E+04
300	2.232E+03	2.073E+04	1.871E+05
350	1.523E+04	1.435E+05	1.323E+06
400	5.955E+04	5.670E+05	5.312E+06



<i>T</i> (K)	<i>P</i> (atm)		
	0.01	0.1	1
150	1.418E-15	2.474E-15	4.315E-16
200	6.488E-15	6.336E-15	3.969E-15
250	1.220E-14	1.204E-14	8.829E-15
300	1.953E-14	1.940E-14	1.585E-14
350	2.842E-14	2.833E-14	2.568E-14
400	3.882E-14	3.882E-14	3.855E-14

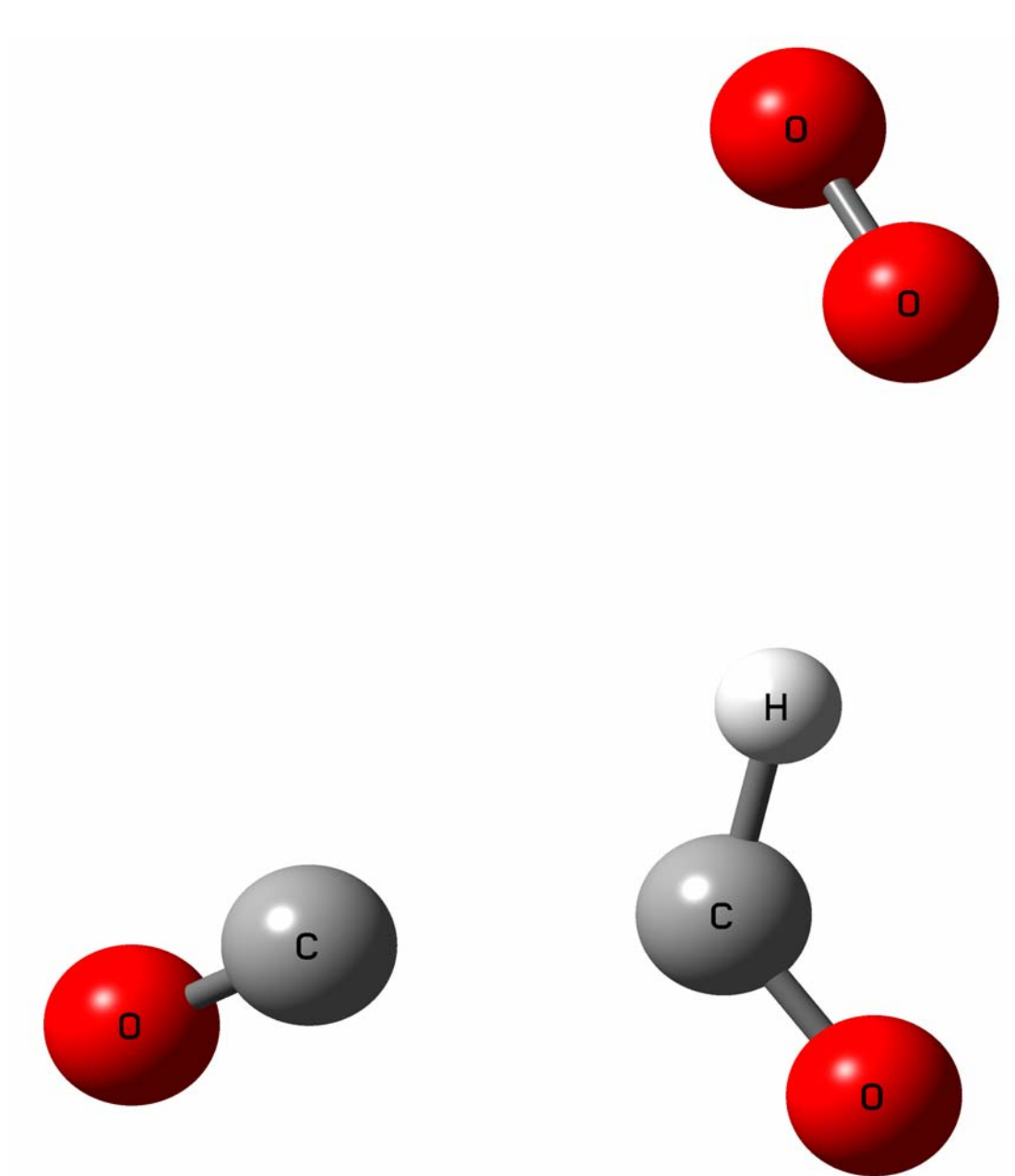


<i>T</i> (K)	<i>P</i> (atm)		
	0.01	0.1	1
150	3.610E-18	1.295E-16	1.342E-15
200	4.334E-18	1.627E-16	2.543E-15
250	4.202E-18	1.595E-16	3.379E-15
300	3.688E-18	1.392E-16	3.694E-15
350	2.731E-18	9.224E-17	2.760E-15
400	8.168E-19	1.228E-17	3.024E-16

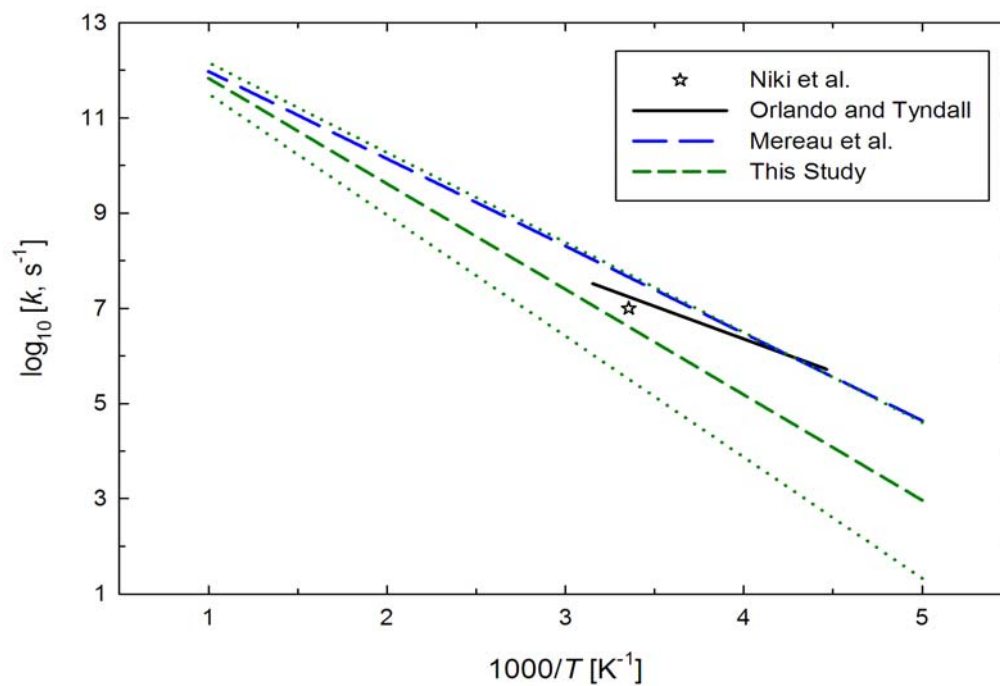
Branching Ratios for HC(O)CO Oxidation

<i>T</i> (K)	<i>P</i> (atm)		
	0.01	0.1	1
150	1.000	1.000	1.000
200	0.997	0.997	0.997
250	0.854	0.865	0.880
300	0.320	0.336	0.360
350	0.077	0.081	0.087
400	0.023	0.025	0.026

Abstraction Transition State



Comparison of Experimental and Theoretical values of k_3



Dotted lines represent uncertainty of $1.5 \text{ kcal mol}^{-1}$ in E_a from this study
Experimental results are at ca. 1 atm, theoretical values are in the high-pressure limit

Effect of Uncertainty in k_3 on Branching to the $\text{HC(O)CO} + \text{O}_2$ Reaction (1 atm)

