Supplementary Material (ESI) for PCCP

Electronic Supplementary Information

HCO Formation in the Thermal Unimolecular Decomposition of Glyoxal: Rotational and Weak Collision Effects

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TABLE SI-1: Experimental data. Shock tube experiments with HCO detection (FM spectroscopy) for the investigation of the rate constant of the HCO forming thermal decomposition channel 1d at high total density ($\bar{\rho} = 1.43 \times 10^{-5}$ mol/cm^3, $\bar{p} = 1.60$ bar).

T /K	p /mbar	ρ /(mol/cm^3)	x_0((CHO)$_2$) /%	$k_{\mathrm{II}}{}^a$/s^{-1}	$k_{\mathrm{I}}{}^b$/s^{-1}	$k_{1\mathrm{d}}$/s^{-1}	$(k_{1\mathrm{d}}/k_{\mathrm{total}})^c$/%
1106	1251	1.36×10^{-5}	0.98			4.8×10^{1}	12.5
1268	1477	1.40×10^{-5}	0.98	2.8×10^{3}	1.1×10^{4}	1.3×10^{3}	16.3
1282	1613	1.51×10^{-5}	0.98	4.5×10^{3}	1.8×10^{4}	1.5×10^{3}	15.2
1291	1633	1.52×10^{-5}	0.98	1.1×10^{4}	4.6×10^{4}	2.7×10^{3}	21.9
1304	1550	1.43×10^{-5}	1.13	1.1×10^{4}	4.3×10^{4}	3.0×10^{3}	20.4
1354	1490	1.32×10^{-5}	0.75	2.0×10^{4}	5.9×10^{4}	7.9×10^{3}	24.5
1372	1685	1.48×10^{-5}	0.98	1.8×10^{4}	8.9×10^{4}	7.4×10^{3}	19.1
1410	1499	1.28×10^{-5}	0.98			1.5×10^{4}	22.4
1416	1650	1.40×10^{-5}	0.98			2.2×10^{4}	28.1
1440	1814	1.52×10^{-5}	0.98	4.6×10^{4}	2.1×10^{5}	1.7×10^{4}	18.2
1480	1770	1.44×10^{-5}	1.13	7.2×10^{4}	2.4×10^{5}	3.6×10^{4}	22.5
1258	1636	1.56×10^{-5}	1.68	4.7×10^{3}	1.2×10^{4}	9.4×10^{2}	14.2
1274	1689	1.59×10^{-5}	2.01	6.4×10^{3}	2.4×10^{4}	2.2×10^{3}	23.0
1289	1500	1.40×10^{-5}	2.01	7.0×10^{3}	2.8×10^{4}	2.3×10^{3}	19.8
1329	1589	1.44×10^{-5}	2.01	1.4×10^{4}	5.8×10^{4}	5.0×10^{3}	22.7
1344	1726	1.54×10^{-5}	2.01	1.8×10^{4}	7.7×10^{4}	5.6×10^{3}	20.9
1350	1523	1.36×10^{-5}	2.05	4.1×10^{4}	1.2×10^{5}	1.1×10^{4}	32.3
1394	1387	1.20×10^{-5}	1.68	3.6×10^{4}	1.3×10^{5}	1.3×10^{4}	23.6
1410	1554	1.28×10^{-5}	1.68	3.8×10^{4}	1.5×10^{5}	1.4×10^{4}	21.2
1415	1708	1.45×10^{-5}	1.68	6.5×10^{4}	2.3×10^{5}	1.0×10^{4}	15.3
1423	1867	1.58×10^{-5}	1.68	5.5×10^{4}	2.2×10^{5}	1.6×10^{4}	20.6

[a] k_{II} value based on an evaluation assuming decomposition channels 1b and 1d (scenario II). [b] k_{I} value based on an evaluation assuming decomposition channels 1a and 1d (scenario I). [c] $k_{1\mathrm{a}+1\mathrm{b}+1\mathrm{c}}$ taken from (CHO)$_2$ measurements.

TABLE SI-2: Experimental data. Shock tube experiments with HCO detection (FM spectroscopy) for the investigation of the rate constant of the HCO forming thermal decomposition channel 1d at low total density ($\bar{\rho} = 2.19 \times 10^{-6}$ mol/cm^3, $\bar{p} = 249$ mbar).

T /K	p /mbar	ρ /(mol/cm^3)	x_0((CHO)$_2$) /%	$k_{\mathrm{II}}{}^a$/s^{-1}	$k_{\mathrm{I}}{}^b$/s^{-1}	$k_{1\mathrm{d}}$/s^{-1}	$(k_{1\mathrm{d}}/k_{\mathrm{total}})^c$/%
1333	240	2.17×10^{-6}	1.00	3.3×10^{3}	8.7×10^{3}	1.1×10^{3}	10.2
1360	245	2.17×10^{-6}	1.00	6.5×10^{3}	2.2×10^{4}	1.5×10^{3}	10.3
1377	250	2.18×10^{-6}	1.00	4.4×10^{3}	1.7×10^{4}	1.4×10^{3}	8.2
1185	270	2.74×10^{-6}	2.00			8.2×10^{1}	5.2
1264	262	2.49×10^{-6}	2.00	3.7×10^{3}	1.1×10^{4}	5.0×10^{2}	10.5
1275	261	2.46×10^{-6}	2.00	1.5×10^{3}	4.9×10^{4}	3.2×10^{2}	6.1
1288	239	2.23×10^{-6}	2.00	3.3×10^{3}	1.1×10^{4}	5.6×10^{2}	8.9
1301	258	2.39×10^{-6}	2.00	2.4×10^{3}	7.2×10^{3}	7.3×10^{2}	9.7
1320	236	2.15×10^{-6}	2.00	2.2×10^{3}	8.6×10^{3}	8.6×10^{2}	9.3
1336	251	2.26×10^{-6}	2.00	2.2×10^{3}	6.8×10^{3}	1.1×10^{3}	9.9
1336	249	2.24×10^{-6}	2.00	3.4×10^{3}	9.0×10^{3}	1.1×10^{3}	9.9
1340	250	2.24×10^{-6}	2.00	4.5×10^{3}	1.3×10^{4}	1.1×10^{3}	9.5
1368	234	2.06×10^{-6}	2.00	4.1×10^{9}	1.2×10^{4}	1.2×10^{3}	7.8
1438	267	2.23×10^{-6}	2.00	2.0×10^{4}	6.0×10^{4}	3.1×10^{3}	9.7
1455	261	2.16×10^{-6}	2.00	2.2×10^{4}	6.5×10^{4}	5.4×10^{3}	13.7
1509	249	1.98×10^{-6}	2.00	2.0×10^{4}	7.9×10^{4}	7.9×10^{3}	12.4
1519	249	1.97×10^{-6}	2.00	2.0×10^{4}	7.9×10^{4}	6.9×10^{3}	10.2
1562	240	1.85×10^{-6}	2.00	3.7×10^{4}	1.1×10^{5}	1.1×10^{4}	11.2
1630	232	1.71×10^{-6}	2.00	3.4×10^{4}	1.4×10^{5}	2.2×10^{4}	12.9

[a] k_{II} value based on an evaluation assuming decomposition channels 1b and 1d (scenario II). [b] k_{I} value based on an evaluation assuming decomposition channels 1a and 1d (scenario I). [c] $k_{1\mathrm{a}+1\mathrm{b}+1\mathrm{c}}$ taken from (CHO)$_2$ measurements.

TABLE SI-3: Experimental data. Shock tube experiments with $(CHO)_2$ detection (UV absorption) for the investigation of the rate constant $k_{1a+1b+1c} = (k_I + k_{II})/2$ of the molecular thermal decomposition channels at high total density ($\bar{\rho} = 1.57 \times 10^{-5}$ mol/cm^3, $\bar{p} = 1.70$ bar).

T /K	p /mbar	ρ /(mol/cm^3)	$x_0((CHO)_2)$ /%	$k_{II}{}^a$/s^{-1}	$k_I{}^b$/s^{-1}
1212	1642	1.78×10^{-5}	0.50	1.4×10^3	1.8×10^3
1240	1804	1.75×10^{-5}	0.53	3.5×10^3	5.3×10^3
1265	1755	1.67×10^{-5}	0.53	5.0×10^3	6.7×10^3
1281	1675	1.57×10^{-5}	0.50	4.7×10^3	6.3×10^3
1294	1708	1.59×10^{-5}	0.50	7.2×10^3	8.0×10^3
1359	1727	1.53×10^{-5}	0.53	3.1×10^4	3.5×10^4
1366	1618	1.42×10^{-5}	0.53	2.1×10^4	2.3×10^4
1368	1871	1.65×10^{-5}	0.53	3.3×10^4	4.0×10^4
1448	1640	1.36×10^{-5}	0.53	5.8×10^4	6.1×10^9
1250	1676	1.61×10^{-5}	1.11	4.5×10^3	6.4×10^3
1309	1688	1.55×10^{-5}	1.11	1.4×10^4	1.7×10^4
1316	1824	1.67×10^{-5}	1.11	1.3×10^4	1.7×10^4
1392	1730	1.49×10^{-5}	1.11	5.2×10^4	6.7×10^4
1393	1599	1.38×10^{-5}	1.11	2.8×10^4	3.9×10^4
1461	1584	1.30×10^{-5}	1.11	5.6×10^4	6.5×10^4
1201	1759	1.76×10^{-5}	1.98	2.1×10^3	3.0×10^3
1208	1511	1.50×10^{-5}	2.00	2.0×10^3	2.9×10^3
1215	1795	1.78×10^{-5}	1.98	2.3×10^3	3.0×10^3
1246	1521	1.47×10^{-5}	2.00	2.2×10^3	2.9×10^3
1255	1684	1.61×10^{-5}	2.00	1.0×10^4	1.3×10^4
1285	1731	1.62×10^{-5}	2.01	6.5×10^3	8.1×10^3
1295	1690	1.57×10^{-5}	2.01	1.6×10^4	1.9×10^4
1338	1869	1.68×10^{-5}	2.01	2.2×10^4	2.5×10^4
1350	1746	1.56×10^{-5}	2.01	4.7×10^4	6.2×10^4

[a] k_{II} value based on an evaluation assuming decomposition channels 1b and 1d (scenario II). [b] k_I value based on an evaluation assuming decomposition channels 1a and 1d (scenario I).

TABLE SI-4: Experimental data. Shock tube experiments with $(CHO)_2$ detection (UV absorption) for the investigation of the rate constant $k_{1a+1b+1c} = (k_I + k_{II})/2$ of the molecular thermal decomposition channels at low total density ($\bar{\rho} = 2.57 \times 10^{-6}$ mol/cm^3, $\bar{p} = 281$ mbar).

T /K	p /mbar	ρ /(mol/cm^3)	$x_0((CHO)_2)$ /%	$k_{II}{}^a$/s^{-1}	$k_I{}^b$/s^{-1}
1198	299	3.00×10^{-6}	1.93	1.8×10^3	1.9×10^3
1225	280	2.75×10^{-6}	1.93	2.2×10^3	2.7×10^3
1239	298	2.89×10^{-6}	1.93	4.0×10^3	4.6×10^3
1289	270	2.52×10^{-6}	1.93	3.8×10^3	4.3×10^3
1298	287	2.66×10^{-6}	1.93	9.6×10^3	1.0×10^4
1307	305	2.81×10^{-6}	1.93	9.6×10^3	9.6×10^3
1308	279	2.57×10^{-6}	1.93	5.1×10^3	6.7×10^3
1320	277	2.52×10^{-6}	1.93	1.1×10^4	1.2×10^4
1336	298	2.68×10^{-6}	1.93	7.8×10^3	9.9×10^3
1345	269	2.41×10^{-6}	1.93	1.8×10^4	1.9×10^4
1410	269	2.29×10^{-6}	1.93	2.3×10^4	2.5×10^4
1418	253	2.15×10^{-6}	1.93	1.7×10^4	2.0×10^4
1453	263	2.18×10^{-6}	1.93	3.5×10^4	4.1×10^4

[a] k_{II} value based on an evaluation assuming decomposition channels 1b and 1d (scenario II). [b] k_I value based on an evaluation assuming decomposition channels 1a and 1d (scenario I).

TABLE SI-5: Experimental data. Shock tube experiments with H detection (H-ARAS) for the investigation of the thermal decomposition channels (1a+1b+1c) and 1d at high total density (first 8 points: $\bar{\rho} = 1.73 \times 10^{-5}$ mol/cm^3, $\bar{p} = 1.67$ bar).

T /K	p /mbar	ρ /(mol/cm^3)	$x_0((\mathrm{CHO})_2)$ /ppm	$k_{1a+1b+1c}/\mathrm{s}^{-1}$	k_{1d}/s^{-1}	$\dfrac{(d[\mathrm{H}]/dt)_0}{2\,[(\mathrm{CHO})_2]_0}$	$k_{1d}/k_{\mathrm{total}}$
1032	1616	1.89×10^{-5}	12.2		7.6×10^{0}	6.8×10^{0}	
1085	1655	1.83×10^{-5}	12.2	2.9×10^{2}	2.4×10^{1}	2.2×10^{1}	0.076
1108	1685	1.83×10^{-5}	12.2	7.3×10^{2}	6.0×10^{1}	5.5×10^{1}	0.076
1136	1763	1.84×10^{-5}	12.2	1.2×10^{3}	1.2×10^{2}	1.0×10^{2}	0.091
1206	1688	1.68×10^{-5}	12.2	3.5×10^{3}	4.4×10^{2}	3.7×10^{2}	0.111
1230	1625	1.59×10^{-5}	12.2	5.4×10^{3}	6.5×10^{2}	5.6×10^{2}	0.107
1262	1687	1.61×10^{-5}	12.2	1.1×10^{4}	1.3×10^{3}	7.9×10^{2}	0.105
1298	1654	1.53×10^{-5}	7.4	1.5×10^{4}	2.6×10^{3}	1.5×10^{3}	0.147
1389	1736	1.44×10^{-5}	7.4				0.111
1459	1576	1.30×10^{-5}	7.4				0.191
1488	1607	1.30×10^{-5}	7.4				0.181
1657	1565	1.14×10^{-5}	7.4				0.215
1838	1524	9.97×10^{-6}	7.4				0.285
1890	1505	9.58×10^{-6}	7.4				0.306
2054	1411	8.27×10^{-6}	7.4				0.311
2210	1371	7.46×10^{-6}	7.4				0.365
2320	1341	6.95×10^{-6}	7.4				0.402

TABLE SI-6: Experimental data. Shock tube experiments with H detection (H-ARAS) for the investigation of the thermal decomposition channels (1a+1b+1c) and 1d at low total density (first 8 points: $\bar{\rho} = 4.15 \times 10^{-6}$ mol/cm^3, $\bar{p} = 413$ mbar).

T /K	p /mbar	ρ /(mol/cm^3)	$x_0((\mathrm{CHO})_2)$ /ppm	$k_{1a+1b+1c}/\mathrm{s}^{-1}$	k_{1d}/s^{-1}	$\dfrac{(d[\mathrm{H}]/dt)_0}{2\,[(\mathrm{CHO})_2]_0}$	$k_{1d}/k_{\mathrm{total}}$
1059	433	4.92×10^{-6}	39.9		3.0×10^{0}	2.5×10^{0}	
1101	430	4.70×10^{-6}	39.9		1.1×10^{1}	9.9×10^{0}	
1131	408	4.34×10^{-6}	39.9	1.0×10^{3}	2.5×10^{1}	2.2×10^{1}	0.024
1201	419	4.20×10^{-6}	39.9	2.2×10^{3}	9.7×10^{1}	8.4×10^{1}	0.042
1208	407	4.05×10^{-6}	39.9	2.3×10^{3}	1.1×10^{2}	8.1×10^{1}	0.048
1290	426	3.97×10^{-6}	39.9	7.1×10^{3}	3.9×10^{2}	2.9×10^{2}	0.055
1305	392	3.62×10^{-6}	39.9	9.8×10^{3}	5.1×10^{2}	3.4×10^{2}	0.052
1370	387	3.40×10^{-6}	39.9	1.6×10^{4}	1.0×10^{3}	6.5×10^{2}	0.062
1439	391	3.27×10^{-6}	39.9				0.086
1490	393	3.17×10^{-6}	39.9				0.086
1495	418	3.36×10^{-6}	12.2				0.078
1580	377	2.87×10^{-6}	39.9				0.095
1667	371	2.68×10^{-6}	39.9				0.109
1772	369	2.51×10^{-6}	39.9				0.147
1941	375	2.35×10^{-6}	39.9				0.168
2106	374	2.14×10^{-6}	39.9				0.250

TABLE SI-7: RRKM parameters for glyoxal decomposition channels with *tight* transition state. Molecular structures and vibrational frequencies (0.9496 scaling factor[1]) are based on MP2/6-311G(*d*,*p*) and the critical energy on G3 calculations.[2,3].

	trans-$(CHO)_2$	transition state		
		1a	1b	1d
		CH_2O	TW	HCOH
G3 critical energy, $E_0(J=0)$ / cm^{-1}	0	19376	21370	21232
scaled critical energy $E_0(J=0)$ / cm^{-1}	0	19376	20500	20500
vibrations, $\tilde{\nu}$/ cm^{-1}	$(141)^a$	115	130	173
	316	439	198	226
	535^b	605	212	602
	794	842	596	733
	1025	974	704	770
	1043	$1006i$	918	$1217i$
	1283	1073	1272	1235
	1328	1289	1346	1282
	1657	1437	$1510i$	1453
	1670	1586	1680	1770
	2855	1990	1894	1951
	2860	2892	1909	2874
rotational constants / cm^{-1}	1.865	1.564	1.666	1.270
	0.158	0.157	0.119	0.141
	0.146	0.146	0.114	0.127
symmetry number, enantiomers	2, 1	1, 2	2, 2	1, 1

[a] treated as hindered internal rotor, see text; [b] reaction coordinate.

TABLE SI-8: Correlation scheme and molecular parameters for simplified SACM model of HCO forming thermal decomposition channel of glyoxal, $(CHO)_2 + M \rightarrow 2\,HCO + M$ (1d). Molecular structures and vibrational frequencies (0.9496 scaling factor[1]) are based on MP2/6-311G(*d*,*p*) and the critical energy on G3 calculations.

	$\tilde{\nu}((CHO)_2)$	correlation	assignment
$A((CHO)_2)$ (K rotor)	1.865	→ 1.400	C(HCO)
vibrations /cm^{-1}	141	→ 1.400	C(HCO)
	316	→ 1.494	B(HCO)
	535	reaction coordinate	
	794	→ 1.494	B(HCO)
	1025	→ 22.36	A(HCO)
	1043	→ 22.36	A(HCO)
	1283	1076	$\tilde{\nu}$(HCO)
	1328	1076	$\tilde{\nu}$(HCO)
	1657	1857	$\tilde{\nu}$(HCO)
	1670	1857	$\tilde{\nu}$(HCO)
	2855	2588	$\tilde{\nu}$(HCO)
	2860	2588	$\tilde{\nu}$(HCO)
G3 critical energy [3] / cm^{-1}	$\Delta H_{0K} = 24301$	$E_0(J=0) = 24319$	
critical energy from [4] / cm^{-1}	$\Delta H_{0K} = 24654$		
scaled critical energy / cm^{-1}	$\Delta H_{0K} = 24240$	$E_0(J=0) = 24258$	
Morse parameter, anisotropy ratio	$\beta = 1.51$	$\alpha/\beta = 0.50$	
$(CHO)_2$ rotational constants / cm^{-1}		1.865, 0.158, 0.146	$\sigma = 2$, prolate
HCO rotational constants / cm^{-1}		22.36, 1.494, 1.400	$\sigma = 1$, approx. as spherical top
$(CHO)_2$ structure	quasi-diatomic, $m = 29.0$ (HCO,a) and 29.0 (HCO, b), $r_{ab} = 2.5$ Å		
Lennard-Jones parameters (Ar, $(CHO)_2)^a$		σ/Å= 3.47, 4.76	ϵ/K = 114, 373

[a] estimated from critical constants of $(CHO)_2$.

TABLE SI-9: Energy levels (cm^{-1}) of the hindered internal rotator[a] for energies up to 90000 cm^{-1} (reduced rotational constant $B_{\mathrm{red}} = 1.862\ \mathrm{cm}^{-1}$).

52.06	155.45	257.49	358.37	458.26	557.28	655.52	753.04	849.87
946.00	1041.41	1136.06	1229.88	1322.79	1414.68	1431.27	1505.45	1513.11
1593.40	1594.95	1672.29	1683.01	1749.84	1769.46	1826.05	1854.06	1900.84
1936.54	1974.06	2016.58	2045.47	2093.73	2114.71	2167.38	2181.28	2236.53
2244.27	2299.24	2301.95	2352.89	2353.34	2404.87	2406.03	2466.41	2467.02
2535.98	2536.18	2611.77	2611.82	2693.04	2693.05	2779.37	2779.37	2870.49
2870.49	2966.21	2966.21	3066.37	3066.37	3170.88	3170.88	3279.62	3279.62
3392.55	3392.55	3509.58	3509.58	3630.69	3630.69	3755.83	3755.83	3884.96
3884.96	4018.05	4018.05	4155.09	4155.09	4296.04	4296.04	4440.89	4440.89
4589.62	4589.62	4742.22	4742.22	4898.67	4898.67	5058.96	5058.96	5223.09
5223.09	5391.05	5391.05	5562.81	5562.81	5738.39	5738.39	5917.77	5917.77
6100.94	6100.94	6287.90	6287.90	6478.65	6478.65	6673.18	6673.18	6871.49
6871.49	7073.57	7073.57	7279.42	7279.42	7489.03	7489.03	7702.41	7702.41
7919.56	7919.56	8140.46	8140.46	8365.11	8365.11	8593.53	8593.53	8825.69
8825.69	9061.61	9061.61	9301.27	9301.27	9544.69	9544.69	9791.85	9791.85
10042.76	10042.76	10297.41	10297.41	10555.80	10555.80	10817.94	10817.94	11083.81
11083.81	11353.43	11353.43	11626.79	11626.79	11903.88	11903.88	12184.72	12184.72
12469.29	12469.29	12757.59	12757.59	13049.64	13049.64	13345.42	13345.42	13644.93
13644.93	13948.18	13948.18	14255.16	14255.16	14565.87	14565.87	14880.32	14880.32
15198.50	15198.50	15520.41	15520.41	15846.06	15846.06	16175.43	16175.43	16508.54
16508.54	16845.38	16845.38	17185.95	17185.95	17530.25	17530.25	17878.28	17878.28
18230.04	18230.04	18585.53	18585.53	18944.74	18944.74	19307.69	19307.69	19674.37
19674.37	20044.77	20044.77	20418.91	20418.91	20796.77	20796.77	21178.36	21178.36
21563.68	21563.68	21952.72	21952.72	22345.50	22345.50	22742.00	22742.00	23142.23
23142.23	23546.19	23546.19	23953.87	23953.87	24365.28	24365.28	24780.42	24780.42
25199.29	25199.29	25621.88	25621.88	26048.20	26048.20	26478.25	26478.25	26912.02
26912.02	27349.52	27349.52	27790.75	27790.75	28235.70	28235.70	28684.38	28684.38
29136.79	29136.79	29592.92	29592.92	30052.78	30052.78	30516.36	30516.36	30983.67
30983.67	31454.71	31454.71	31929.47	31929.47	32407.96	32407.96	32890.17	32890.17
33376.11	33376.11	33865.77	33865.77	34359.16	34359.16	34856.28	34856.28	35357.12
35357.12	35861.69	35861.69	36369.98	36369.98	36882.00	36882.00	37397.75	37397.75
37917.21	37917.21	38440.41	38440.41	38967.33	38967.33	39497.97	39497.97	40032.35
40032.35	40570.44	40570.44	41112.26	41112.26	41657.81	41657.81	42207.08	42207.08
42760.08	42760.08	43316.80	43316.80	43877.24	43877.24	44441.42	44441.42	45009.31
45009.31	45580.94	45580.94	46156.28	46156.28	46735.35	46735.35	47318.15	47318.15
47904.67	47904.67	48494.92	48494.92	49088.89	49088.89	49686.59	49686.59	50288.01
50288.01	50893.16	50893.16	51502.03	51502.03	52114.62	52114.62	52730.94	52730.94
53350.99	53350.99	53974.76	53974.76	54602.25	54602.25	55233.47	55233.47	55868.42
55868.42	56507.09	56507.09	57149.48	57149.48	57795.60	57795.60	58445.44	58445.44
59099.01	59099.01	59756.30	59756.30	60417.32	60417.32	61082.06	61082.06	61750.53
61750.53	62422.72	62422.72	63098.64	63098.64	63778.28	63778.28	64461.64	64461.64
65148.73	65148.73	65839.55	65839.55	66534.08	66534.08	67232.35	67232.35	67934.34
67934.34	68640.05	68640.05	69349.49	69349.49	70062.65	70062.65	70779.53	70779.53
71500.14	71500.14	72224.48	72224.48	72952.54	72952.54	73684.32	73684.32	74419.83
74419.83	75159.06	75159.06	75902.02	75902.02	76648.70	76648.70	77399.11	77399.11
78153.24	78153.24	78911.10	78911.10	79672.68	79672.68	80437.98	80437.98	81207.01
81207.01	81979.76	81979.76	82756.24	82756.24	83536.44	83536.44	84320.37	84320.37
85108.02	85108.02	85899.40	85899.40	86694.50	86694.50	87493.32	87493.32	88295.87
88295.87	89102.14	89102.14	89912.14	89912.14				

[a] Fourier expansion of the torsional potential of glyoxal (MP2/6-311G(*d*,*p*), where $\phi = 0$ corresponds to the *trans*-glyoxal isomer: $V(\phi)/\mathrm{cm}^{-1} = \sum_{n=0}^{6} b_n \cos(n\,\phi)$ with $b_0 = 1416.22$, $b_1 = -727.20$, $b_2 = -778.60$, $b_3 = 38.72$, $b_4 = 68.19$, $b_5 = -6.50$, $b_6 = -10.83$).

TABLE SI-10: Pressure dependence of reactions 1a–1d: Chemkin[5] input format for Chebyshev polynomials.[‡]

```
C2H2O2 (+M) <=> CH2O + CO (+M)      1.0 0.0 0.0
TCHEB/ 800. 2500. / PCHEB/ 9.87E-4 98.7 /
CHEB/  4 4  /
CHEB/  2.448     1.014     -1.823E-1   1.643E-2/
CHEB/  3.971     6.341E-1   1.820E-2  -6.206E-3/
CHEB/ -3.926E-1  4.486E-2   2.783E-2   7.470E-3/
CHEB/ -9.117E-2 -2.928E-2   9.074E-4   3.457E-3/

C2H2O2 (+M) <=> H2 + 2 CO (+M)      1.0 0.0 0.0
TCHEB/ 800. 2500. / PCHEB/ 9.87E-4 98.7 /
CHEB/  4 4  /
CHEB/  1.934     1.564     -3.222E-1   4.544E-2/
CHEB/  4.196     6.773E-1   5.283E-2  -4.904E-3/
CHEB/ -4.010E-1  1.327E-2   3.032E-2   9.066E-3/
CHEB/ -8.817E-2 -3.386E-2   5.520E-4   2.635E-3/

C2H2O2 (+M) <=> HCOH + CO (+M)      1.0 0.0 0.0
TCHEB/ 800. 2500. / PCHEB/ 9.87E-4 98.7 /
CHEB/ 4 4  /
CHEB/  1.358     1.456     -3.101E-1   4.624E-2/
CHEB/  4.123     6.779E-1   3.840E-2  -4.933E-3/
CHEB/ -4.105E-1  2.746E-2   2.811E-2   9.274E-3/
CHEB/ -8.727E-2 -3.268E-2   8.627E-4   2.765E-3/

C2H2O2 (+M) <=> 2 HCO (+M)          1.0 0.0 0.0
TCHEB/ 800. 2500. / PCHEB/ 9.87E-4 98.7 /
CHEB/  4 4  /
CHEB/  4.903E-1  3.936    -1.080      1.412E-1/
CHEB/  4.818     4.349E-1  1.747E-1  -1.119E-2/
CHEB/ -3.698E-1 -7.146E-2  4.338E-2   4.738E-3/
CHEB/ -6.307E-2 -5.084E-2  7.064E-3   1.716E-3/
```

The used temperature mapping according to $\tilde{T} = (2T^{-1} - T_{\min}^{-1} - T_{\max}^{-1})/(T_{\max}^{-1} - T_{\min}^{-1})$ is consistent with the data input requirements of Chemkin versions 4.0 and 4.1. For an alternative temperature mapping according to $\tilde{T} = (2T^{-1} - T_{\min}^{-1} - T_{\max}^{-1})/(T_{\min}^{-1} - T_{\max}^{-1})$, the signs of the parameters a_{2m} and a_{4m} have to be changed.

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