APPENDIX

APPENDIX A

This appendix describes the cyclohexane and 1-hexene reaction mechanisms and the rate constants of unimolecular reactions at 25, 50, 100, 150 and 200 Torr. If a rate constant is estimated, the method of its estimation is given in its corresponding footnote.

TABLE VIII: REACTION MECHANISM OF CYCLOHEXANE AND 1-HEXENE DISSOCIATION

No.	Reaction	P (Torr)	log(A)	n	Ea	Reference
1	$cC_6H_{12} \rightarrow 1C_6H_{12}$ or $cC_6H_{12} \rightarrow C_3H_7 + C_3H_5$ (for 25 Torr)					
2	$1C_6H_{12} \rightarrow C_3H_7 + C_3H_5$	25	80.035	-19.331	95.177	THIS WORK
		50	68.399	-16.040	86.832	
		100	59.170	-13.261	82.596	
		150	61.386	-13.999	82.637	
		200	59.574	-13.427	82.179	
3	$1C_6H_{12} \rightarrow C_4H_7 + C_2H_5$	25	80.433	-19.331	107.015	THIS WORK Estimated
		50	68.797	-16.040	98.670	
		100	59.568	-13.261	94.434	
		150	61.784	-13.999	94.475	
		200	59.972	-13.427	94.017	

TABLE VIII: REACTION MECHANISM OF CYCLOHEXANE AND 1-HEXENE DISSOCIATION (Continued)

No.	Reaction	P (Torr)	log(A)	n	Ea	Reference
4	$C_3H_7 \rightarrow C_2H_4 + CH_3$	25	19.509	-3.396	17.919	See Text
		50	21.355	-3.807	19.812	
		100	23.211	-4.220	21.780	
		150	24.306	-4.464	22.970	
		200	25.115	-4.646	23.856	
5	$C_3H_7 \rightarrow C_3H_6 + H$	25	27.903	-5.613	29.791	See Text
		50	29.350	-5.909	31.693	
		100	30.503	-6.125	33.369	
		150	31.142	-6.243	34.332	
		200	31.531	-6.309	34.963	
6	$C_3H_5 \rightarrow aC_3H_4 + H$ [a]	25	58.246	-13.715	76.013	[81]
		50	58.403	-13.661	76.765	
		100	58.637	-13.628	77.634	
		150	58.907	-13.645	78.292	
		200	59.172	-13.677	78.833	
7	$1\text{-}C_4H_8 \rightarrow CH_3 + C_3H_5$	25	67.816	-15.605	97.302	See Text
		50	68.784	-15.765	99.264	
		100	69.972	-15.986	101.451	
		150	70.713	-16.129	102.783	
		200	71.220	-16.226	103.719	

TABLE VIII: REACTION MECHANISM OF CYCLOHEXANE AND 1-HEXENE DISSOCIATION (Continued)

No.	Reaction	P (Torr)	log(A)	n	Ea	Reference
8	$C_4H_7 \rightarrow C_2H_3 + C_2H_4$	25	24.365	-4.802	25.054	92
		50	26.131	-5.195	26.785	
		100	27.925	-5.595	28.575	
		150	28.998	-5.836	29.653	
		200	29.771	-6.011	30.433	
9	$C_4H_7 \rightarrow C_4H_6 + H$	25	24.104	-4.752	23.777	92
		50	26.139	-5.221	25.729	
		100	28.243	-5.709	27.764	
		150	29.499	-6.003	28.985	
		200	30.430	-6.222	29.890	
10	$C_2H_6 \rightarrow CH_3 + CH_3$	25	49.018	-10.565	93.135	84
		50	48.820	-10.403	93.697	
		100	48.969	-10.325	94.904	
		150	48.944	-10.245	95.662	
		200	48.667	-10.116	96.023	
11	$C_2H_4 + H \rightarrow C_2H_3 + H_2$		7.705	1.930	12.951	
12	$H + C_2H_3 \rightarrow C_2H_2 + H_2$		13.850			
13	$C_2H_3 + (M) \rightarrow C_2H_2 + H + (M)$		41.019	-7.500	45.500	
14	$C_2H_6 + H \rightarrow C_2H_5 + H_2$		1.500	3.500	5.200	
15	$C_2H_6 + CH_3 \rightarrow C_2H_5 + CH_4$		-0.261	4.000	8.300	

TABLE VIII: REACTION MECHANISM OF CYCLOHEXANE AND 1-HEXENE DISSOCIATION (Continued)

No.	Reaction	P (Torr)	log(A)	n	Ea	Reference
16	$C_2H_5 + (M) \rightarrow C_2H_4 + H + (M)$		17.000		31.000	[84]
17	$C_2H_5 + H \rightarrow C_2H_4 + H_2$		12.258			
18	$CH_3 + CH_3 \rightarrow C_2H_5 + H$		13.479		13.500	
19	$C_2H_4 + (M) \rightarrow C_2H_3 + H + (M)$		17.413	0.000	96.600	
20	$C_2H_4 + (M) \rightarrow C_2H_2 + H_2 + (M)$		16.543	0.000	71.500	
21	$CH_4 + H \rightarrow CH_3 + H_2$		3.610	3.160	8.800	
22	$CH_4 + (M) \rightarrow CH_3 + H + (M)$		47.279	-8.110	117.430	
23	$H + 1C_6H_{12} \rightarrow 1C_6H_{11} + H_2$ [b]		5.813	2.500	6.756	ESTMD from [7]
24	$H + 1C_6H_{12} \rightarrow 3C_6H_{11} + H_2$		6.500	2.500	6.756	ESTMD from [101]
25	$H + 1C_6H_{12} \rightarrow 4C_6H_{11} + H_2$ [c]		6.115	2.400	4.470	
26	$H + 1C_6H_{12} \rightarrow 5C_6H_{11} + H_2$ [c]		6.115	2.400	4.470	
27	$CH_3 + 1C_6H_{12} \rightarrow 1C_6H_{11} + CH_4$ [d]		-0.345	3.650	7.153	ESTMD from [7]
28	$CH_3 + 1C_6H_{12} \rightarrow 3C_6H_{11} + CH_4$		0.450	3.600	7.153	ESTMD from [101]
29	$CH_3 + 1C_6H_{12} \rightarrow 4C_6H_{11} + CH_4$ [e]		0.178	3.460	5.480	
30	$CH_3 + 1C_6H_{12} \rightarrow 5C_6H_{11} + CH_4$ [e]		0.178	3.460	5.480	
31	$1C_6H_{11} \rightarrow C_4H_7 + C_2H_4$		9.041		27.881	(k_∞ from [82])*10^{-4} (See Text)
32	$3C_6H_{11} \rightarrow C_2H_5 + C_4H_6$		9.875		34.937	(k_∞ from [82])*10^{-4} (See Text)
33	$4C_6H_{11} \rightarrow C_5H_8 + CH_3$		9.041		27.881	k(31)
34	$5C_6H_{11} \rightarrow C_3H_6 + C_3H_5$		9.114		24.714	(k_∞ from [82])*10^{-4} (See Text)

TABLE VIII: REACTION MECHANISM OF CYCLOHEXANE AND 1-HEXENE DISSOCIATION (Continued)

No.	Reaction	P (Torr)	log(A)	n	Ea	Reference
35	$C_3H_6 \rightarrow C_3H_5 + H$ [f]	25	84.725	-20.034	132.787	[112]
		50	81.819	-19.122	131.835	
		100	81.746	-18.982	133.148	
		150	78.53	-18.064	130.958	
		200	76.35	-17.435	129.580	
36	$C_3H_6 \rightarrow CH_3 + C_2H_3$ [f]	25	63.112	-13.738	124.846	[112]
		50	63.992	-13.900	126.185	
		100	65.005	-14.092	127.464	
		150	64.238	-13.848	127.279	
		200	63.819	-13.705	127.316	
37	$C_2H_3 + CH_3 \rightarrow C_3H_5 + H$ [f]	25	12.271	0.262	-1.979	[112]
		50	13.115	0.038	-1.018	
		100	14.915	-0.440	1.024	
		150	15.194	-0.513	1.377	
		200	15.484	-0.589	1.739	
38	$C_3H_5 + H \rightarrow C_3H_4 + H_2$ [g]		6.538	2.070	4.955	[113]
39	$C_3H_6 + H \rightarrow CH_3 + C_2H_4$ [h]	76	16.944	-1.050	6.461	[114]
40	$C_3H_6 + H \rightarrow C_3H_5 + H_2$		5.231	2.500	2.483	[115]
41	$C_3H_5 + CH_3 \rightarrow a\text{-}C_3H_4 + CH_4$		12.478	-0.320	-0.130	[102]
42	$a\text{-}C_3H_4 \rightarrow p\text{-}C_3H_4$ [i]	76	62.321	-14.674	87.042	[114]
		300	63.279	-14.714	90.053	

TABLE VIII: REACTION MECHANISM OF CYCLOHEXANE AND 1-HEXENE DISSOCIATION (Continued)

No.	Reaction	P (Torr)	log(A)	n	Ea	Reference
43	$C_3H_6 \rightarrow H_2 + p\text{-}C_3H_4$ [j]	25-200	95.072	-23.570	125.649	ESTMD
44	$CH_3 + C_2H_3 \rightarrow C_2H_2 + CH_4$		11.593			[116]
45	$C_2H_3 + C_2H_3 \rightarrow C_2H_2 + C_2H_4$		11.984			[116]
46	$C_2H_4 + CH_3 \rightarrow C_2H_3 + CH_4$		12.619		11.130	[117]
47	$C_2H_5 + CH_3 \rightarrow C_2H_4 + CH_4$ [k]		4.072	2.450	-2.921	[118]
48	$a\text{-}C_3H_4 \rightarrow C_3H_3 + H$ [L]	170	51.480	-10.955	102.317	ESTMD
49	$p\text{-}C_3H_4 \rightarrow C_3H_3 + H$ [m]	155	45.049	-9.060	100.390	ESTMD
50	$CH_3 + C_3H_6 \rightarrow CH_4 + C_3H_5$		0.345	3.500	5.684	[102]
51	$C_4H_7 + H \rightarrow C_3H_5 + CH_3$	N/A	21.301	-2.000	11.000	[114]
52	$C_2H_2 + CH_3 \rightarrow p\text{-}C_3H_4 + H$ [n]	76	6.653	1.860	11.600	[119]
53	$a\text{-}C_3H_4 + CH_3 \rightarrow C_3H_3 + CH_4$		-3.180	5.000	8.300	[120]
54	$p\text{-}C_3H_4 + CH_3 \rightarrow C_3H_3 + CH_4$		-3.660	5.000	8.300	[120]
55	$a\text{-}C_3H_4 + H \rightarrow C_3H_3 + H_2$		6.700	2.000	6.000	[120]
56	$p\text{-}C_3H_4 + H \rightarrow C_3H_3 + H_2$		14.300		15.000	[120]
57	$C_3H_5 + C_3H_5 \rightarrow C_3H_4 + C_3H_6$		10.926	0.000	-0.263	[102]
58	$C_4H_6 \rightarrow C_2H_2 + C_2H_4$ [o]		13.806		77.100	[121]
59	$C_3H_7 + C_3H_5 \rightarrow C_3H_6 + C_3H6$		12.461		-0.130	[102]
60	$C_2H_3 + C_3H_5 \rightarrow C_2H_4 + C_3H_4$		12.38			[102]
61	$C_2H_3 + C_3H_5 \rightarrow C_2H_2 + C_3H_6$		12.683			[102]

TABLE VIII: REACTION MECHANISM OF CYCLOHEXANE AND 1-HEXENE DISSOCIATION (Continued)

No.	Reaction	P (Torr)	log(A)	n	Ea	Reference
62	$C_2H_3 + C_2H_4 \rightarrow H + C_4H_6$ [p]	90	17.279	-1.320	10.600	[92]
63	$C_2H_2 + CH_3 \rightarrow a\text{-}C_3H_4 + H$ [q]	70	9.380	0.910	20.700	[119]
64	$H + C_4H_6 \rightarrow iC_4H_5 + H_2$		5.823	2.530	9.240	[114]
65	$CH_3 + C_4H_6 \rightarrow iC_4H_5 + CH_4$		14.000	0.000	19.800	[114]
66	$iC_4H_5 \rightarrow C_2H_2 + C_2H_3$	90	47.134	-10.947	63.522	[114]
67	$C_4H_6 \rightarrow iC_4H_5 + H$	90	45.519	-8.950	115.930	[114]
68	$C_2H_3 + C_2H_3 \rightarrow iC_4H_5 + H$	90	28.857	-4.490	14.273	[114]
69	$CH_3 + H \rightarrow {}^3CH_2 + H_2$		13.780		15.100	[117]
70	${}^3CH_2 + C_2H_4 \rightarrow C_3H_6$		10.258			[122]
71	${}^3CH_2 + CH_3 \rightarrow C_2H_4 + H$		13.625			[117]
72	$C_3H_3 + C_3H_3 \rightarrow C_6H_4 + 2H$ [r]		12.301		3.000	[123]
73	$C_4H_8 + H \rightarrow C_4H_7 + H_2$		5.813	2.540	6.756	[114]
74	${}^3CH_2 + C_2H_4 \rightarrow C_2H_3 + CH_3$		12.699			ESTMD
75	$H + cC_6H_{12} \rightarrow cC_6H_{11} + H_2$		10.429	1.385	8.299	THIS WORK (See Text)
76	$CH_3 + cC_6H_{12} \rightarrow cC_6H_{11} + CH_4$ [s]		0.956	3.460	5.480	ESTMD
77	$cC_6H_{11} \rightarrow cC_6H_{10} + H$		9.708		33.850	(k_∞ from [82])*10^{-4} (See Text)
78	$cC_6H_{10} \rightarrow C_2H_4 + C_4H_6$ [t]	101-170	102.260	-25.300	115.500	[120]
79	$cC_6H_{11} \rightarrow 1C_6H_{11}$		9.322		29.653	(k_∞ from [82])*10^{-4} (See Text)

[a] The rate constants for (6) are taken from Fernandes, et al. [81]. Fall-off rate constants are calculated using RRKM parameters given in ref. 81.

[b] The rate constant of (23) is assumed the same as the rate of primary H-atom abstraction from 1-butene to form 1-buten-4-yl radical,

$H + 1\text{-}C_4H_8 \rightarrow C_4H_7 + H_2$. The rate constant of this reference reaction is taken from ref. 7.

[c] Rate constants of (25) and (26) are assumed to be the same as that of secondary H-atom abstraction from propane to form iso-propyl radical, $H + C_3H_8 \rightarrow \text{iso-}C_3H_7 + H_2$. The rate constant for this reference reaction is taken from ref. 101.

[d] The rate constant of (27) is assumed the same as that of primary H-atom abstraction from 1-butene to form 1-buten-4-yl radical, $CH_3 + 1\text{-}C_4H_8 \rightarrow C_4H_7 + CH_4$. The rate constant for this reference reaction is taken from ref. 7.

[e] Rate constants of (29) and (30) are assumed to be the same as that of secondary H-atom abstraction from propane to form iso-propyl radical. $CH_3 + C_3H_8 \rightarrow \text{iso-}C_3H_7 + CH_4$. The rate constant for this reference reaction is taken from ref. 101.

[f] The rates of (35)-(37) are taken from the recent computational work of Stoliarov, et al. [112] Fall-off rate constants at experimental pressures are calculated by linear interpolation.

[g] The rate for (38) is calculated by L. B. Harding and S. J. Klippenstein [113].

[h] The fall-off rate constant at 76 Torr from ref. 114 (See Figure 20 below) was used to simulate the experimental data over the entire pressure range.

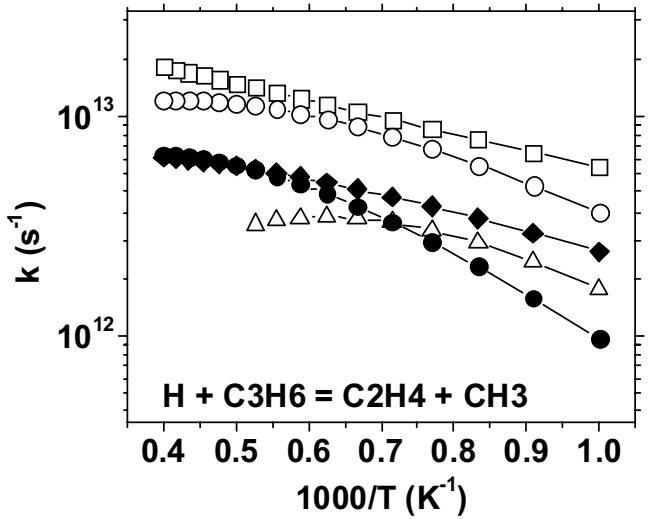

Figure 20: Comparison between the rate constants for the reaction $H + C_3H_6 \rightarrow C_2H_4 + CH_3$ (i) —◆— P=76 Torr, [114]; (ii) —●— P=7600 Torr, [114]; (iii) —□—, [124]; (iv) —△—, [1].

i

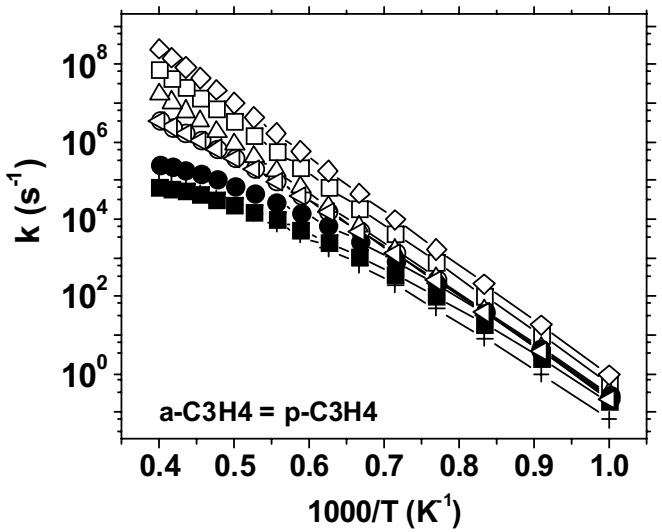

Figure 21: Comparison between the rate constants for the reaction a-C_3H_4 → p-C_3H_4 (i) —■— P=76 Torr, [114] from reverse; (ii) —●— P=300 Torr, [114] from reverse; (iii) — + — P= 30 Torr, [125]; (iv) —△—, [126]; (v) —◇—, [127]; (vi) —□—, [128]; (vii) —○—, [81]; (viii) —◁— P=760 Torr, [125].

The rate constants (i) and (ii) are used in the mechanism at P = 25, 50, 100 Torr and at P = 150, 200 Torr respectively.

j

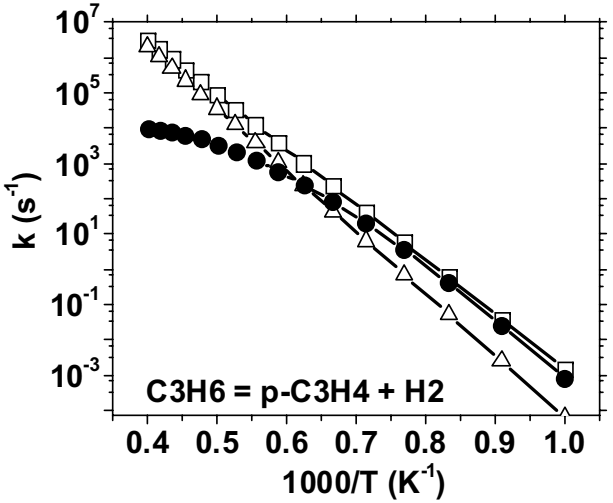

Figure 22: Comparison between the rate constants for the reaction $C_3H_6 \rightarrow H_2 + p\text{-}C_3H_4$ (i) —●—, estimated; (ii) —□—, [129]; (iii) —△—, [124].

The rate constant of (43) is forced to match the k_∞ of ref. 129 at low temperatures and the reduced rate of 10^4 s^{-1} at 2000 K. The value, 10^4 s^{-1} is chosen considering a comparison with other unimolecular reactions. [129, 124]

[k] The rate constant for reaction (47) is taken from a recent theoretical calculation on the C_3H_8 potential energy surface by Zhu, et al. [118]

L

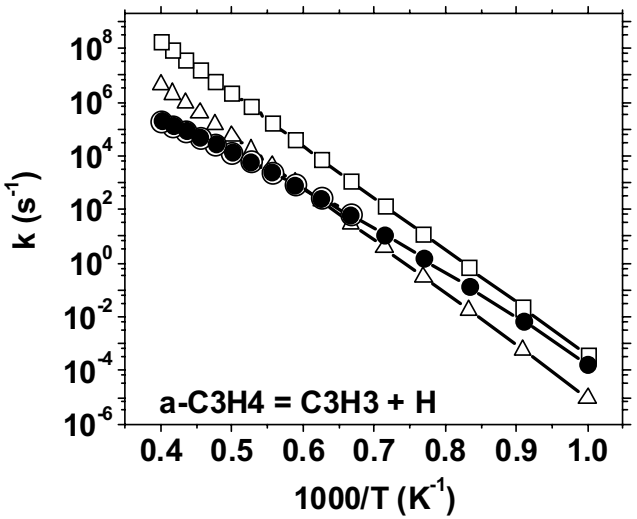

Figure 23: Comparison between the rate constants for the reaction a-$C_3H_4 \rightarrow C_3H_3 + H$ (i) —●— P = 170 Torr, estimated; (ii) —□—, from reverse [130]; (iii) —△—, from reverse [7]; (iv) —○— P = 170 Torr, [120].

The rate constant of (48) is forced to match the k_∞ of ref. 130 at low temperatures and the fall-off rate constant of [120] at high temperatures. This resulting rate constant is used in the mechanism over the entire pressure range.

m

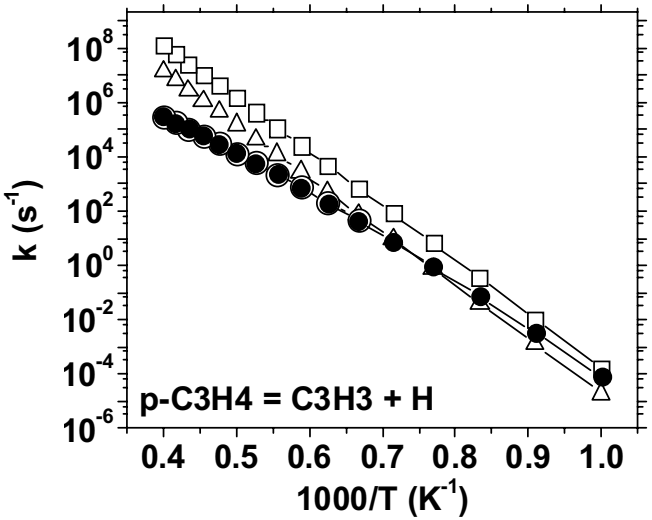

Figure 24: Comparison between the rate constants for the reaction p-$C_3H_4 \rightarrow C_3H_3 + H$ (i) —●— P = 155 Torr, estimated; (ii) —□—, [130] from reverse; (iii) —△—, [114] from reverse; (iv) —○— P = 155 Torr, [120].

The rate constant of (49) is forced to match the k_∞ of ref. 130 at low temperatures and the fall-off rate constant of ref. 120 at high temperatures. This resulting rate constant is used here over the entire pressure range.

n The RRKM rate constant reported in [119] at 76 Torr is used in the mechanism for (52) over the entire pressure range.

o The rate constant for (58) is taken from Arrhenius plot of 1,3 butadiene dissociation in [131]. The rate constant used is fall-off rate at P ~ 100 Torr . This rate is also in agreement with the rate constant reported for (58) in [121].

p

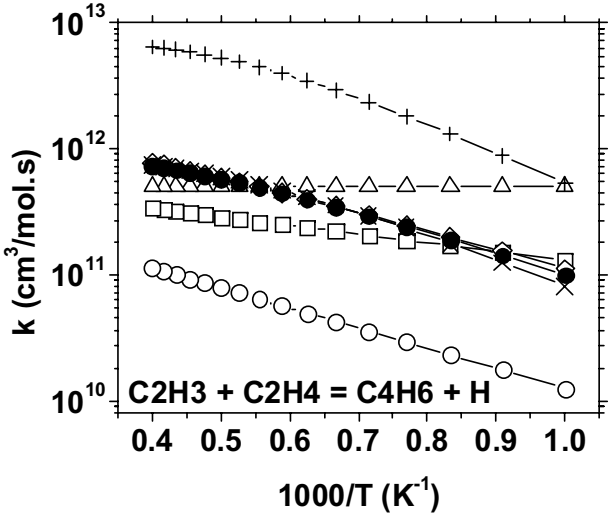

Figure 25: Comparison between the rate constants for the reaction $C_2H_3 + C_2H_4 \rightarrow H + C_4H_6$ (i) —●— P=90 Torr, [92] ; (ii) —◇— P = 20 Torr, [92]; (iii) —×— P =760 Torr, [92]; (iv) — + —, [7]; (v) —○—, [116]; (vi) —□—, [132]; (vii) —△—, [133].

The rate constant for (62) was taken from Wang and Frenklach [92] at P = 90 Torr, i.e., (i) in Figure F and used in the mechanism over the entire pressure range.

[q] RRKM rate constant reported in ref. 119 at 76 Torr is used for reaction (63).

[r] The rate constant used for (72) is for the reaction $C_3H_3 + C_3H_3 \rightarrow C_6H_5 + H$ taken from ref. 123. It is assumed that the subsequent H loss from phenyl radical, forming benzyne, is instantaneous and thus the two steps are combined and written as a one step reaction, (72).

[s] The process of H-atom abstraction from cyclohexane is assumed similar to the secondary H-atom abstraction from propane to form iso-propyl radical. Hence the rate of $CH_3 + C_3H_8 \rightarrow$ iso-$C_3H_7 + CH_4$, taken from the ref. 101, is considered as the reference rate constant. To account for 6 secondary carbon atoms, the rate is further multiplied by 6

[t] The fall-off rate constant at P=101-170 Torr from [120] was used. The same rate constant was used here over the entire experimental pressure range.

APPENDIX B

LIST OF REACTIONS

TABLE IX: THE LIST OF REACTIONS REFERRED TO IN THE TEXT BUT NOT USED IN THE CHOSEN CYCLOHEXANE DISSOCIATION MECHANISM OF TABLE XIII, APPENDIX A.

(Ia)	$cC_6H_{12} \rightarrow \cdot CH_2(CH_2)_4CH_2\cdot$ (n-hex-di-yl diradical)
(Ib)	$\cdot C_6H_{12}\cdot \rightarrow$ 1- C_6H_{12}
(II)	$cC_6H_{12} \rightarrow 3C_2H_4$
(IIa)	$cC_6H_{12} \rightarrow C_2H_4 + \cdot C_4H_8\cdot$
(IIaa)	$\cdot C_6H_{12}\cdot \rightarrow C_2H_4 + \cdot C_4H_8\cdot$
(IIb)	$\cdot C_4H_8\cdot \rightarrow 2C_2H_4$
(III)	$cC_6H_{12} \rightarrow 2C_3H_6$
(IV)	$cC_6H_{12} \rightarrow C_4H_6 + C_2H_4 + H_2$
(V)	$cC_6H_{12} \rightarrow \cdot cC_6H_{11} + H$
(VI)	$cC_6H_{12} \rightarrow cC_6H_{10} + H_2$
(VII)	$\cdot C_6H_{12}\cdot \rightarrow CH_2{=}CHCH_2CH_2CH_2CH_2\cdot + H$
(VIII)	$\cdot C_6H_{12}\cdot \rightarrow C_3H_6$-$cC_3H_6$ (propylcyclopropane)
(IX)	$\cdot C_6H_{12}\cdot \rightarrow 2\ cC_3H_6$ (both cyclopropane)
(X)	1- $C_6H_{12} \rightarrow CH_3CH{=}CH_2 + CH_3CH{=}CH_2$
(XI)	1- $C_6H_{12} \rightarrow \cdot CH_3 + \cdot CH_2CH_2CH_2CH{=}CH_2$
(XII)	1- $C_6H_{12} \rightarrow CH_3CH_2CH_2CH_2\cdot + \cdot CH{=}CH_2$
(XIII)	1- $C_6H_{12} \rightarrow CH_3$-$CH_2$-$CH_2$-$\cdot$CH-$CH{=}CH_2 + H$
(XIV)	$\cdot C_5H_9 \rightarrow C_2H_4 + \cdot C_3H_5$
(XV)	$\cdot C_3H_7 + \cdot C_3H_5 \rightarrow \cdot C_4H_7 + \cdot C_2H_5$
(XVI)	$\cdot C_6H_{12}\cdot \rightarrow 3\ C_2H_4$
(XVII)	1-CH_3-$cC_6H_9 \rightarrow$ Isoprene (2-methylbuta-1,3-diene) + C_2H_4
(XVIII)	$\cdot C_3H_5 + C_7H_8$ (toluene) $\rightarrow C_3H_6 + \cdot C_7H_7$ (benzyl)
(XIX)	t-$C_4H_9OH \rightarrow$ ·t-$C_4H_9 + \cdot OH$
(XX)	t-$C_4H_9OH \rightarrow \cdot CH_3 + (CH_3)_2\cdot COH$
(XXI)	t-$C_4H_9OH \rightarrow$ iso-$C_4H_8 + H_2O$

REFERENCES

1. Silke, E. J.; Pitz, W. J.; Westbrook, C. K.; Ribaucour, M., Detailed chemical kinetic modeling of cyclohexane oxidation. *Journal of Physical Chemistry A* **2007,** 111, (19), 3761-3775.

2. *World Oil Outlook* OPEC Secretariat: Vienna, 2007; pp ISBN 978-3-200-00965-3 http://www.opec.org/library/World%20Oil%20Outlook/pdf/WorldOilOutlook.pdf.

3. Ullmann, F.; Gerhartz, W.; Yamamoto, Y. S.; Campbell, F. T.; Pfefferkorn, R.; Rounsaville, J. F.; Ullmann, F., Ullmann's Encyclopedia of industrial chemistry. In 5th ed.; VCH: Weinheim, Germany, 1985; Vol. A13, pp 490-491.

4. Westbrook, C. K. In *Challenges in Combustion*, Presentation at GCEP Research Symposium, Stanford, CA, 2005; Stanford, CA, 2005.

5. Zhang, H. Z. R.; Huynh, L. K.; Kungwan, N.; Yang, Z. W.; Zhang, S. W., Combustion modeling and kinetic rate calculations for a stoichiometric cyclohexane flame. 1. Major reaction pathways. *Journal of Physical Chemistry A* **2007,** 111, (19), 4102-4115.

6. Cavallotti, C.; Rota, R.; Faravelli, T.; Ranzi, E., Ab initio evaluation of primary cyclohexane oxidation reaction rates. *Proceedings of the Combustion Institute* **2007,** 31, 201-209.

7. Law, M. E.; Westmoreland, P. R.; Cool, T. A.; Wang, J.; Hansen, N.; Taatjes, C. A.; Kasper, T., Benzene precursors and formation routes in a stoichiometric cyclohexane flame. *Proceedings of the Combustion Institute* **2007,** 31, 565-573.

8. Knepp, A. M.; Meloni, G.; Jusinski, L. E.; Taatjes, C. A.; Cavallotti, C.; Klippenstein, S. J., Theory, measurements, and modeling of OH and HO2 formation in the reaction of cyclohexyl radicals with O2. *Physical Chemistry Chemical Physics* **2007,** 9, (31), 4315-4331.

9. Billaud, F.; Duret, M.; Elyahyaoui, K.; Baronnet, F., Survey of Recent Cyclohexane Pyrolysis Literature and Stoichiometric Analysis of Cyclohexane Decomposition. *Industrial & Engineering Chemistry Research* **1991,** 30, (7), 1469-1478.

10. Yahyaoui, M.; Djebaili-Chaumeix, N.; Paillard, C. E.; Touchard, S.; Fournet, R.; Glaude, P. A.; Battin-Leclerc, F., Experimental and modeling study of 1-hexene oxidation behind reflected shock waves. *Proceedings of the Combustion Institute* **2005,** 30, 1137-1145.

11. Yahyaoui, M.; Djebaïli-Chaumeix, N.; Dagaut, P.; Paillard, C. E.; Gail, S., Kinetics of 1-hexene oxidation in a JSR and a shock tube: Experimental and modeling study. *Combustion and Flame* **2006,** 147, (1-2), 67-78.

12. Miller, J. A.; Kee, P. J.; Westbrook, C. K., Chemical Kinetics and Combustion Modeling. *Annual Review of Physical Chemistry* **1990,** 41, 345-387.

13. Gardiner, W. C., *Gas-phase combustion chemistry*. Springer: New York, 2000; p xi, 543 p.

14. Tsang, W., Thermal-Stability of Cyclohexane and 1-Hexene. *International Journal of Chemical Kinetics* **1978,** 10, (11), 1119-1138.

15. Aribike, D. S.; Susu, A. A.; Ogunye, A. F., Mechanistic and Mathematical-Modeling of the Thermal-Decomposition of Cyclohexane. *Thermochimica Acta* **1981,** 51, (2-3), 113-127.

16. Aribike, D. S.; Susu, A. A.; Ogunye, A. F., Kinetics of the Thermal-Decomposition of Cyclohexane. *Thermochimica Acta* **1981,** 47, (1), 1-14.

17. Brown, T. C.; King, K. D.; Nguyen, T. T., Kinetics of primary processes in the pyrolysis of cyclopentanes and cyclohexanes. *Journal of Physical Chemistry* **1986,** 90, (3), 419-24.

18. Voisin, D.; Marchal, A.; Reuillon, M.; Boettner, J. C.; Cathonnet, M., Experimental and kinetic modeling study of cyclohexane oxidation in a JSR at high pressure. *Combustion Science and Technology* **1998,** 138, (1-6), 137-158.

19. El-Bakali, A.; Braun-Unkhoff, M.; Dagaut, P.; Frank, P.; Cathonnet, M., Detailed kinetic reaction mechanism for cyclohexane oxidation at pressure up to ten atmospheres. *Proceedings of the Combustion Institute* **2000,** 28, 1631-1638.

20. Granata, S.; Faravelli, T.; Ranzi, E., A wide range kinetic modeling study of the pyrolysis and combustion of naphthenes. *Combustion and Flame* **2003,** 132, (3), 533-544.

21. Ranzi, E.; Dente, M.; Goldaniga, A.; Bozzano, G.; Faravelli, T., Lumping procedures in detailed kinetic modeling of gasification, pyrolysis, partial oxidation and combustion of hydrocarbon mixtures. *Progress in Energy and Combustion Science* **2001,** 27, (1), 99-139.

22. Bonner, B. H.; Tipper, C. F. H., The cool flame combustion of hydrocarbons I Cyclohexane. *Combustion and Flame* **1965,** 9, (3), 317-327.

23. Zeelenberg, A. P.; De Bruijn, H. W., Kinetics, mechanism and products of the gaseous oxidation of cyclohexane. *Combustion and Flame* **1965,** 9, (3), 281-295.

24. Lemaire, O.; Ribaucour, M.; Carlier, M.; Minetti, R., The production of benzene in the low-temperature oxidation of cyclohexane, cyclohexene, and cyclohexa-1,3-diene. *Combustion and Flame* **2001,** 127, (1-2), 1971-1980.

25. Davis, S. G.; Law, C. K., Determination of and fuel structure effects on laminar flame speeds of C-1 to C-8 hydrocarbons. *Combustion Science and Technology* **1998,** 140, (1-6), 427-449.

26. McEnally, C. S.; Pfefferle, L. D., Experimental study of fuel decomposition and hydrocarbon growth processes for cyclohexane and related compounds in non-premixed flames. *Combustion and Flame* **2004,** 136, (1-2), 155-167.

27. Braun-Unkhoff, M.; Naumann, C.; Frank, P., Study on the initial product channels of cyclohexane pyrolysis. *Abstracts of Papers of the American Chemical Society* **2004,** 227, U1096-U1096.

28. Zhang, H. R.; Eddings, E. G.; Sarofim, A. F., Criteria for selection of components for surrogates of natural gas and transportation fuels. *Proceedings of the Combustion Institute* **2007,** 31, 401-409.

29. Zhang, H. R.; Eddings, E. G.; Sarofim, A. F.; Westbrook, C. K., Mechanism reduction and generation using analysis of major fuel consumption pathways for n-heptane in premixed and diffusion flames. *Energy & Fuels* **2007,** 21, (4), 1967-1976.

30. Sirjean, B.; Buda, F.; Hakka, H.; Glaude, P. A.; Fournet, R.; Warth, V.; Battin-Leclerc, F.; Ruiz-Lopez, M., The autoignition of cyclopentane and cyclohexane in a shock tube. *Proceedings of the Combustion Institute* **2007,** 31, 277-284.

31. Glaude, P. A.; Warth, V.; Fournet, R.; Battin-Leclerc, F.; Scacchi, G.; Come, G. M., Modeling of the oxidation of n-octane and n-decane using an automatic generation of mechanisms. *International Journal of Chemical Kinetics* **1998,** 30, (12), 949-959.

32. Fournet, R.; Battin-Leclerc, F.; Glaude, P. A.; Judenherc, B.; Warth, V.; Come, G. M.; Scacchi, G.; Ristori, A.; Pengloan, G.; Dagaut, P.; Cathonnet, M., The gas-phase oxidation of n-hexadecane. *International Journal of Chemical Kinetics* **2001,** 33, (10), 574-586.

33. Sirjean, B.; Glaude, P. A.; Ruiz-Lopez, M. F.; Fournet, R., Detailed kinetic study of the ring opening of cycloalkanes by CBS-QB3 calculations. *Journal of Physical Chemistry A* **2006,** 110, (46), 12693-12704.

34. King, K. D., Very low-pressure pyrolysis (VLPP) of 1-Hexene - kinetics of the retro-ene decomposition of a mono-olefin. *International Journal of Chemical Kinetics* **1979,** 11, (10), 1071-1080.

35. Greene, E. F.; Toennies, J. P., *Chemical reactions in shock waves*. Academic Press: New York, 1964; p xvi, 352 p.

36. Bradley, J. N., *Shock waves in chemistry and physics*. Wiley: London, New York, 1962; p 369 p.

37. Kiefer, J. H., The Laser-Schlieren Technique in Shock Tube Kinetics In *Shock Waves in Chemistry*, Lifshitz, A., Ed. Marcel Dekker: New York, 1981; pp 219-277.

38. Kiefer, J. H.; Manson, A. C., Refractive index change and curvature in shock waves by angled beam refraction. *Review of Scientific Instruments* **1981,** 52, (9), 1392-1396.

39. Kiefer, J. H.; Hajduk, J. C. In *Rate measurement in shock waves with the laser-schlieren technique*, Proceedings of Twelfth International Symposium on Shock Tubes and Waves, Jerusalem, 1979; Magnes Press: Jerusalem, 1979; pp 97-110.

40. Gardiner, W. C., Jr.; Wakefield, C. B.; Walker, B. F., Mathematical Methods for Modeling Chemical Reactions in Shock Waves. In *Shock Waves in Chemistry*, Lifshitz, A., Ed. Marcel Dekker: New York, 1981; p p 319.

41. Srinivasan, N. K.; Kiefer, J. H.; Tranter, R. S., Dissociation, relaxation, and incubation in the pyrolysis of neopentane: Heat of formation for tert-butyl radical. *Journal of Physical Chemistry A* **2003,** 107, (10), 1532-1539.

42. Saxena, S.; Kiefer, J. H.; Tranter, R. S., Relaxation, incubation, and dissociation in CO2. *Journal of Physical Chemistry A* **2007,** 111, (19), 3884-3890.

43. CRC, *CRC handbook of chemistry and physics*. 57 ed.; CRC Press: Cleveland, Ohio, 1976-1977.

44. Gardiner, W. C.; Hidaka, Y.; Tanzawa, T., Refractivity of Combustion Gases. *Combustion and Flame* **1981,** 40, (2), 213-219.

45. Burcat, A.; Ruscic, B., Ideal Gas Thermochemical Database with updates from Active Thermochemical Tables. In 2008; p ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics.

46. Grange, J.; Albiser, G.; Fousse, H., Experimental study of refractivities. *Cahiers de Physique* **1962,** 137, 35-44.

47. Breiland, W. G.; Coltrin, M. E.; Ho, P., Comparisons between a gas-phase model of silane chemical vapor deposition and laser-diagnostic measurements. *Journal of Applied Physics* **1986,** 59, (9), 3267-3273.

48. Al-Alami, M. Z. A shock tube laser schlieren study of propane pyrolysis at high temperature. University of Illinois at Chicago, Chicago IL, 1982.

49. Kiefer, J. H.; Alalami, M. Z.; Hajduk, J. C., Physical Optics of the Laser-Schlieren Shock-Tube Technique. *Applied Optics* **1981,** 20, (2), 221-230.

50. Boer, P. C. T. D., Curvature of Shock Fronts in Shock Tubes. *Physics of Fluids* **1963,** 6, (7), 962-971.

51. Dove, J. E.; Teitelbaum, H. In Eleventh International Symposium on Shock Tubes and Waves, Seattle, WA, 1978; Seattle, WA, 1978; p 474.

52. Kiefer, J. H.; Lutz, R. W., Vibrational Relaxation of Deuterium by a Quantitative Schlieren Method. *Journal of Chemical Physics* **1966,** 44, (2), 658-667.

53. Conte, S. D.; De Boor, C., *Elementary numerical analysis: An algorithmic approach*. 3rd ed.; McGraw-Hill: New York, 1980; p xii, 432 p.

54. Farrow, L. A.; Edelson, D., Steady-state approximation - fact or fiction. *International Journal of Chemical Kinetics* **1974,** 6, (6), 787-800.

55. Gear, C. W., *Numerical initial value problems in ordinary differential equations*. Prentice-Hall: Englewood Cliffs, N.J., 1971; p xvii, 253 p.

56. Bunker, D. L., *Theory of elementary gas reaction rates*. 1st ed.; Pergamon Press: Oxford, New York, 1966; p xii, 115 p.

57. Steinfeld, J. I.; Francisco, J. S.; Hase, W. L., *Chemical kinetics and dynamics*. Prentice Hall: Englewood Cliffs, N.J., 1989; p xii, 548 p.

58. Holbrook, K. A.; Pilling, M. J.; Robertson, S. H.; Robinson, P. J., *Unimolecular reactions*. 2nd ed.; Wiley: Chichester; New York, 1996; p xv, 417 p.

59. Benson, S. W.; Golden, D. M., Physical chemistry, an advanced treatise. In Eyring, H.; Henderson, D.; Jost, W., Eds. Academic Press: New York, 1975; Vol. 7, p 11 v. in 14.

60. Smith, G. P.; Golden, D. M., Application of RRKM theory to the reactions; a modified Gorin model transition state. *International Journal of Chemical Kinetics* **1978,** 10, (5), 489-501.

61. Gilbert, R. G.; Luther, K.; Troe, J., Theory of Thermal Unimolecular Reactions in the Fall-Off Range .2. Weak Collision Rate Constants. *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics* **1983,** 87, (2), 169-177.

62. Troe, J., Theory of Thermal Unimolecular Reactions in the Fall-Off Range .1. Strong Collision Rate Constants. *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics* **1983,** 87, (2), 161-169.

63. Luther, K.; Troe, J., In *Reactions of Small Transient Species*, Fontijn, A., Ed. Academic Press: London, 1983.

64. Troe, J., Theory of Thermal Unimolecular Reactions at Low-Pressures .1. Solutions of Master Equation. *Journal of Chemical Physics* **1977,** 66, (11), 4745-4757.

65. Troe, J., Predictive possibilities of unimolecular rate theory. *Journal of Physical Chemistry* **1979,** 83, (1), 114-126.

66. Whitten, G. Z.; Rabinovitch, B. S., Accurate and Facile Approximation for Vibrational Energy-Level Sums. *Journal of Chemical Physics* **1963,** 38, (10), 2466-2473.

67. Whitten, G. Z.; Rabinovitch, B. S., Approximation for Rotation---Vibration Energy Level Sums. *Journal of Chemical Physics* **1964,** 41, (6), 1883-1883.

68. Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B.; University of Wisconsin. Theoretical Chemistry Laboratory., *Molecular theory of gases and liquids*. Wiley: New York, 1965; p xxvi, 1249 p.

69. Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K., *The properties of gases and liquids*. 3rd ed.; McGraw-Hill: London, 1977; p 688.

70. Bethe, H. A.; Teller, E. *Aberdeen Proving Ground Ballistic Research laboratory Report X*; 1941.

71. Cottrell, T. L.; McCoubrey, J. C., *Molecular energy transfer in gases*. Butterworths: London, 1961; p 205 p.

72. Kiefer, J. H.; Buzyna, L. L.; Dib, A.; Sundaram, S., Observation and analysis of nonlinear vibrational relaxation of large molecules in shock waves. *Journal of Chemical Physics* **2000,** 113, (1), 48-58.

73. Dib, A. Vibrational relaxation in large molecules. University of Illinois at Chicago, Chicago IL, 1995.

74. Blythe, P. A., *Journal of Fluid Mechanics* **1961,** 10, 33.

75. Tsang, W., Mechanism and rate constants for the decomposition of 1-pentenyl radicals. *Journal of Physical Chemistry A* **2006,** 110, (27), 8501-8509.

76. Tsang, W.; Bedanov, V.; Zachariah, M. R., Master equation analysis of thermal activation reactions: Energy-transfer constraints on falloff behavior in the decomposition of reactive intermediates with low thresholds. *Journal of Physical Chemistry* **1996,** 100, (10), 4011-4018.

77. Just, T., Multichannel reactions in combustion. *proceedings of the Combustion Institute* **1994,** 25, 687-704.

78. Miller, J. A.; Klippenstein, S. J., The H+C2H2 (+M) = C2H3 (+M) and H+C2H4 (+M) = C2H5 (+M) reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. *Physical Chemistry Chemical Physics* **2004,** 6, (6), 1192-1202.

79. Bencsura, A.; Knyazev, V. D.; Xing, S. B.; Slagle, I. R.; Gutman, D., Kinetics of the thermal decomposition of the n-propyl radical. *Proceedings of the Combustion Institute* **1992,** 24, 629-635.

80. Curran, H. J., Rate constant estimation for C-1 to C-4 alkyl and alkoxyl radical decomposition. *International Journal of Chemical Kinetics* **2006,** 38, (4), 250-275.

81. Fernandes, R. X.; Giri, B. R.; Hippler, H.; Kachiani, C.; Striebel, F., Shock wave study on the thermal unimolecular decomposition of allyl radicals. *Journal of Physical Chemistry A* **2005,** 109, (6), 1063-1070.

82. Iwan, I.; McGivern, W. S.; Manion, J. A.; Tsang, W., The decomposition and Isomerization of cyclohexyl and 1-hexenyl radicals. *Proceedings of 5th US Combustion Meeting, San Diego, CA* **2007**, CO2.

83. Kiefer, J. H., Some unusual aspects of unimolecular falloff of importance in combustion modeling. *Proceedings of the Combustion Institute* **1998,** 27, 113-124.

84. Kiefer, J. H.; Santhanam, S.; Srinivasan, N. K.; Tranter, R. S.; Klippenstein, S. J.; Oehlschlaeger, M. A., Dissociation, relaxation and incubation in the high-temperature pyrolysis RRKM of ethane, and a successful modeling. *Proceedings of the Combustion Institute* **2005,** 30, 1129-1135.

85. Gupte, K. S.; Kiefer, J. H.; Tranter, R. S.; Klippenstein, S. J.; Harding, L. B., Decomposition of acetaldehyde: experiment and detailed theory. *Proceedings of the Combustion Institute* **2007,** 31, (Pt. 1), 167-174.

86. Saxena, S.; Kiefer, J. H.; Klippenstein, S. J., A shock tube and theory study of the dissociation of acetone and subsequent recombination of methyl radicals. *Submitted to Proceedings of the Combustion Institute* **2008,** 32.

87. Johnson III, R. D., NIST Computational Chemistry Comparison and Benchmark Database In Sept 2006 ed.; NIST Standard Reference Database Number 101 2006; Vol. Release 14, p http://srdata.nist.gov/cccbdb

88. Dean, A. M., Predictions of Pressure and Temperature Effects Upon Radical-Addition and Recombination Reactions. *Journal of Physical Chemistry* **1985,** 89, (21), 4600-4608.

89. Miller, J. L., Theoretical study of the straight-chain C4H7 radical isomers and their dissociation and isomerization transition states. *Journal of Physical Chemistry A* **2004,** 108, (12), 2268-2277.

90. Fahr, A.; Halpern, J. B.; Tardy, D. C., Calculational and experimental investigations of the pressure effects on radical-radical cross combination reactions: C2H5+C2H3. *Journal of Physical Chemistry A* **2007,** 111, (29), 6600-6609.

91. Matheu, D. M.; Green, W. H.; Grenda, J. M., Capturing pressure-dependence in automated mechanism generation: Reactions through cycloalkyl intermediates. *International Journal of Chemical Kinetics* **2003,** 35, (3), 95-119.

92. Wang, H.; Frenklach, M., A detailed kinetic modeling study of aromatics formation in laminar premixed acetylene and ethylene flames. *Combustion and Flame* **1997,** 110, (1-2), 173-221.

93. Andersson, M. P.; Uvdal, P., New scale factors for harmonic vibrational frequencies using the B3LYP density functional method with the triple-xi basis set 6-311+G(d,p). *Journal of Physical Chemistry A* **2005,** 109, (12), 2937-2941.

94. Santhanam, S.; Kiefer, J. H.; Tranter, R. S.; Srinivasan, N. K., A shock tube, laser-schlieren study of the pyrolysis of isobutene: Relaxation, incubation, and dissociation rates. *International Journal of Chemical Kinetics* **2003,** 35, (8), 381-390.

95. Kiefer, J. H.; Shah, J. N., Unimolecular dissociation of cyclohexene at extremely high-temperatures - behavior of the energy-transfer collision efficiency. *Journal of Physical Chemistry* **1987,** 91, (11), 3024-3030.

96. Harding, L. B.; Georgievskii, Y.; Klippenstein, S. J., Predictive Theory for Hydrogen Atom-Hydrocarbon Radical Association Kinetics. *Journal of Physical Chemistry A* **2005,** 109, (21), 4646-4656.

97. Ventura, E.; Dallos, M.; Lischka, H., Revisiting the stationary points on the potential energy surface of tetramethylene at the MR-AQCC level using analytic gradients. *Journal of Chemical Physics* **2003,** 118, (24), 10963-10972.

98. Szalay, P. G.; Bartlett, R. J., Approximately Extensive Modifications of the Multireference Configuration-Interaction Method - a Theoretical and Practical Analysis. *Journal of Chemical Physics* **1995,** 103, (9), 3600-3612.

99. Doubleday, C., Tetramethylene. *Journal of the American Chemical Society* **1993,** 115, (25), 11968-11983.

100. Scherzer, K.; Loeser, U.; Stiller, W., Bsbl Calculations for Hydrogen Abstraction Reactions by Alkenyl Radicals - Vinyl Radicals. *Zeitschrift Fur Chemie* **1987,** 27, (8), 300-301.

101. Tsang, W., Chemical Kinetic Data-Base for Combustion Chemistry .3. Propane. *Journal of Physical and Chemical Reference Data* **1988,** 17, (2), 887-952.

102. Tsang, W., Chemical Kinetic Data Base for Combustion Chemistry Part V. Propene. **1991,** 20, (2), 221-273.

103. Loeser, U.; Scherzer, K.; Weber, K., Kinetic-Data Estimation for Hydrogen-Transfer Reactions, Using the Bond-Strength-Bond-Length (Bsbl) Method. *Zeitschrift Fur Physikalische Chemie-Leipzig* **1989,** 270, (2), 237-245.

104. Forst, W., *Unimolecular reactions : a concise introduction*. Cambridge University Press: Cambridge, U.K. ; New York, 2003; p xi, 319 p.

105. Oref, I.; Tardy, D. C., Energy transfer in highly excited large polyatomic molecules. *Chemical Reviews* **1990,** 90, (8), 1407-1445.

106. Tranter, R. S.; Brezinsky, K.; Fulle, D., Design of a high-pressure single pulse shock tube for chemical kinetic investigations. *Review of Scientific Instruments* **2001,** 72, (7), 3046-3054.

107. Throssell, J. J., Rates of reaction of allyl radicals. Reassessment. *International Journal of Chemical Kinetics* **1972,** 4, (3), 273-276.

108. Tsang, W., Thermal-Decomposition of Cyclopentane and Related Compounds. *International Journal of Chemical Kinetics* **1978,** 10, (6), 599-617.

109. Kalra, B. L.; Feinstein, S. A.; Lewis, D. K., Pyrolysis of Cyclopentane Behind Reflected Shock-Waves. *Canadian Journal of Chemistry* **1979,** 57, (11), 1324-1328.

110. Skinner, G. B.; Rogers, D.; Patel, K. B., Consistency of Theory and Experiment in the Ethane-Methyl Radical System. *International Journal of Chemical Kinetics* **1981,** 13, (5), 481-495.

111. Braun-Unkhoff, M., Private Communications, 2008. In.

112. Stoliarov, S. I.; Knyazev, V. D.; Slagle, I. R., Computational study of the mechanism and product yields in the reaction systems C2H3+CH3 reversible arrow C3H6 reversible arrow H+C3H5 and C2H3+CH3 -> CH4+C2H2. *Journal of Physical Chemistry A* **2002,** 106, (30), 6952-6966.

113. Harding, L. B.; Klippenstein, S. J., C3H5 + H = C3H4 + H2. *Poster in 31st International Symposium on Combustion* **2006**.

114. Wang, H.; You, X.; V., J. A.; Davis, S. G.; Laskin, A.; Egolfopoulos, F.; Law, C. K., USC Mech Version II. High-Temperature Combustion Reaction Model of H2/CO/C1-C4 Compounds. In May 2007 ed.; 2007; p http://ignis.usc.edu/USC_Mech_II.htm.

115. Tsang, W., Chemical Kinetic Data-Base for Hydrocarbon Pyrolysis. *Industrial & Engineering Chemistry Research* **1992,** 31, (1), 3-8.

116. Tsang, W.; Hampson, R. F., Chemical kinetic data base for combustion chemistry. Part I. methane and related compounds. *Journal of Physical and Chemical Reference Data* **1986,** 15, (3), 1087-1279.

117. Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J., Evaluated Kinetic Data for Combustion Modeling. *Journal of Physical and Chemical Reference Data* **1992,** 21, (3), 411-734.

118. Zhu, R. S.; Xu, Z. F.; Lin, M. C., Ab initio studies of alkyl radical reactions: Combination and disproportionation reactions of CH3 with C2H5, and the decomposition of chemically activated C3H8. *Journal of Chemical Physics* **2004,** 120, (14), 6566-6573.

119. Davis, S. G.; Law, C. K.; Wang, H., Propyne pyrolysis in a flow reactor: An experimental, RRKM, and detailed kinetic modeling study. *Journal of Physical Chemistry A* **1999,** 103, (30), 5889-5899.

120. Kiefer, J. H.; Mudipalli, P. S.; Sidhu, S. S.; Kern, R. D.; Jursic, B. S.; Xie, K.; Chen, H., Unimolecular dissociation in allene and propyne: The effect of isomerization on the low-pressure rate. *Journal of Physical Chemistry A* **1997,** 101, (22), 4057-4071.

121. Hidaka, Y.; Higashihara, T.; Ninomiya, N.; Masaoka, H.; Nakamura, T.; Kawano, H., Shock tube and modeling study of 1,3-butadiene pyrolysis. *International Journal of Chemical Kinetics* **1996,** 28, (2), 137-151.

122. Laufer, A. H.; Bass, A. M., Mechanism and Rate Constant of Reaction between Methylene and Methyl Radicals. *Journal of Physical Chemistry* **1975,** 79, (16), 1635-1638.

123. Burcat, A.; Dvinyaninov, M., Detailed kinetics of cyclopentadiene decomposition studied in a shock tube. *International Journal of Chemical Kinetics* **1997,** 29, (7), 505-514.

124. Hidaka, Y.; Nakamura, T.; Tanaka, H.; Jinno, A.; Kawano, H.; Higashihara, T., Shock-Tube and Modeling Study of Propene Pyrolysis. *International Journal of Chemical Kinetics* **1992,** 24, (9), 761-780.

125. Miller, J. A.; Klippenstein, S. J., From the multiple-well master equation to phenomenological rate coefficients: Reactions on a C3H4 potential energy surface. *Journal of Physical Chemistry A* **2003,** 107, (15), 2680-2692.

126. Hidaka, Y.; Nakamura, T.; Miyauchi, A.; Shiraishi, T.; Kawano, H., Thermal decomposition of propyne and allene in shock waves. *International Journal of Chemical Kinetics* **1989,** 21, (8), 643-666.

127. Kiefer, J. H.; Kumaran, S. S.; Mudipalli, P. S., The Mutual Isomerization of Allene and Propyne. *Chemical Physics Letters* **1994,** 224, (1-2), 51-55.

128. Wu, C. H.; Kern, R. D., Shock-tube study of allene pyrolysis. *Journal of Physical Chemistry* **1987,** 91, 6291-6296.

129. Barbe, P.; Martin, R.; Perrin, D.; Scacchi, G., Kinetics and modeling of the thermal reaction of propene at 800 K. Part I. Pure propene. *International Journal of Chemical Kinetics* **1996,** 28, (11), 829-847.

130. Harding, L. B.; Klippenstein, S. J.; Georgievskii, Y., On the combination reactions of hydrogen atoms with resonance-stabilized hydrocarbon radicals. *Journal of Physical Chemistry A* **2007,** 111, (19), 3789-3801.

131. Kiefer, J. H.; Mitchell, K. I.; Wei, H. C., The High-Temperature Pyrolysis of 1,3-Butadiene-II - Pulsed Laser Flash Absorption Rate Constants, and Consideration of Possible Molecular Dissociation Pathways. *International Journal of Chemical Kinetics* **1988,** 20, (10), 787-809.

132. Fahr, A.; Stein, S. E., Reactions of vinyl and phenyl radicals with ethyne, ethene and benzene. *Proceedings of the Combustion Institute* **1989,** 22nd, 1023-1029.

133. Benson, S. W.; Haugen, G. R., Mechanisms for some high-temperature gas-phase reactions of ethylene, acetylene, and butadiene. *Journal of Physical Chemistry* **1967,** 71, (6), 1735-1746.