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Modeling of n-Heptane and Iso-Octane Oxidation in Air

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A simplified kinetic mechanism is presented for 1006 reactions involving 134 chemical species of that 23 include nitrogen atoms that describes the combustion of n-heptane, iso-octane, and their mixtures in air. The submechanism for the C_5–C_8 species is directly derived from the earlier presented mechanisms for the combustion of methane, ethane, propane, and butane in air. The following experimental data taken from the literature and obtained by means of shock-tube experiments have been chosen to validate the mechanism: the pyrolysis of i-C_8H_{18} and the ignition delay times of mixtures of n-C_7H_{16} and i-C_8H_{18} with air, respectively. The comparisons have yielded good agreement for the initial temperature T_0 varying between 650 and 1200 K, the initial pressure P_0 ranging from 0.65 to 4.5 MPa, and the fuel-to-oxygen ratio ϕ ranging from 0.5 to 2.

Introduction

TYPICALLY, combustion problems in rocket, diesel, or jet engines are solved numerically by applying detailed hydrodynamic models with only global kinetics and thermodynamics. However, there are certain problems that can be solved only by using detailed chemical kinetic models, which imply a description of elementary reactions. Generally, these models reflect the full complexity of the chemistry of combustion. They enable the prediction of the characteristics of the autoignition of typical fuels such as gasoline, kerosene, or diesel, to quantify the formation and emission of toxic byproducts (carbon monoxides, aldehydes, butadiene, aromatic rings, soot, etc.) and additional pollutants (sulfur oxides, nitrogen oxides, unburned hydrocarbons, and oxygenates), which are the precursors of carcinogens or cause the formation of acid rain and ozone in the lower atmosphere.

In general, n-dodecane and isomers of cetane, n-decane and n-propylcyclohexane,are chosen as reference species for jet, diesel, and aviation fuels. The reaction mechanisms for these hydrocarbons are based on those for n-heptane and iso-octane,[1–4] which are the primary reference fuels in spark ignition engines.

In the course of the development of detailed chemical kinetic models for the oxidation of long hydrocarbons, the very large number of possible reactions and components has been one of the major problems. Parallel to the increase in number of carbon atoms of the fuel, the reaction schemes for detailed and accurate predictions become increasingly larger and more complex because the number of isomers of the same homologous class of molecules and their radicals, as well as the number of reactions, grows drastically. A scheme of 519 reactions and 72 species has been provided by Chakir et al.[5] only for the oxidation of n-heptane in air at atmospheric pressure, with the initial temperature T_0 varying between 950 and 1200 K and fuel oxidizer ratio ϕ varying between 0.2 and 2.0. Nevertheless, results predicted by this model may deviate from experimental data by 50% and in some cases by even 300%. Curran et al.[6] have elaborated a mechanism for the prediction of ignition delays of n-heptane/air mixtures that contains 2450 reactions and 550 different species. This mechanism conforms much better to the experimental data because its deviations generally do not exceed 30% for the initial parameters $P_0 = 0.1$–4.2 MPa, $T_0 = 550$–1700 K, and $\phi = 0.3$–1.5. Fournet et al.[7] have even presented a mechanism for the combustion of n-heptane with 2916 reactions and 571 species. The model of Ranzi et al.[8] for the oxidation of iso-octane involves 1303 reactions and 324 species. This mechanism is able to predict the ignition delay times for $P_0 = 0.1$–4.0 MPa, $T_0 = 550$–1500 K, and $\phi = 0.5$–2.0 with an accuracy better than 40%. Another scheme for this iso-octane oxidation process has been proposed by Fournet et al.[7] that contains 2579 reactions with 477 species. Chevalier et al.[1] have discussed a mechanism of 1200 species with more than 7000 reactions for cetane combustion.

These large systems of equations have led to various methods for the automatic generation of reaction mechanisms for the pyrolysis, combustion, and oxidation of alkanes[1,3,4,7,9,10] by which the elaboration of all of the detailed chemical kinetics of all possible components and reactions can be avoided. In parallel, the development of computer-based methods of mechanism construction stimulated the investigation of details of chemical processes and the definition of the generation of mechanism assembly algorithms. Unfortunately, these automatic reaction generation methods tend to produce mechanisms of an enormous size, which are very difficult to handle, and there are still no widely used codes for mechanism generation. In addition, there are also no universal methods for kinetic mechanism reduction. This is due to both the complexity of the mathematics involved and the lack of knowledge about of the dominating physical and chemical processes.

Typical computational fluid dynamics (CFD) codes can handle chemical mechanisms with ~20 components without significant complications. The lumping of species and reactions, the reduction of the mechanism, depends on the goal of the model, that is, the description of ignition delay times, the behavior of NO_x components, or the formation of soot. Based on information about the details of the constructed mechanism and a good understanding of the underlying chemical processes (the classification of components and reactions into main groups, their interactions and grouped behavior, dominant reactions and their rate expressions, etc.) a problem–oriented kinetic mechanism that is sufficiently detailed and reduced in size can be constructed manually.

The purpose of our work was to elaborate a reasonably chemical kinetic model for the combustion of n-heptane/air, iso-octane/air, and n-heptane and iso-octane/air mixtures. This model can be used to describe the ignition delays of mixtures, can be included as a

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Table 1 Reaction submechanism for n-C_7H_{16} and i-C_8H_{18} combustion. Rate constants $k^{\pm} = AT^n \exp(-E_a/T)$ in cm, mole, s, K

		k^{+a}			k^{-a}			
Number	Reaction	A	n	E_a	A	n	E_a	Ref.
1	$iC_8H_{18} = tC_4H_9 + iC_4H_9$	6.00E+16	0	3.90E+04	1.00E+12	0	0	19,*
2	$iC_8H_{18} = iC_5H_{11} + iC_3H_7$	5.00E+16	0	3.90E+04	1.00E+12	0	0	19,*
3	$iC_8H_{18} = iC_7H_{15} + CH_3$	1.20E+15	0	4.30E+04				20
4	$iC_8H_{18} = 3C_8H_{17} + H$	5.00E+16	0	3.90E+04	1.00E+12	0	0	Here
5	$iC_8H_{18} = 4C_8H_{17} + H$	5.00E+16	0	3.90E+04	1.00E+12	0	0	Here
6	$iC_8H_{18} + H = 1C_8H_{17} + H_2$	1.00E+08	2	3.85E+03				19
7	$iC_8H_{18} + H = 2C_8H_{17} + H_2$	1.00E+07	2	2.50E+03				19
8	$iC_8H_{18} + H = 3C_8H_{17} + H_2$	1.00E+13	0	3.60E+03				19
9	$iC_8H_{18} + H = 4C_8H_{17} + H_2$	1.00E+08	2	3.85E+03				19
10	$iC_8H_{18} + O = 1C_8H_{17} + OH$	1.00E+14	0	3.92E+03	1.00E+12	0	1.50E+04	19
11	$iC_8H_{18} + O = 2C_8H_{17} + OH$	1.00E+13	0	2.60E+03	1.00E+12	0	1.50E+04	19
12	$iC_8H_{18} + O = 3C_8H_{17} + OH$	1.00E+13	0	1.64E+03	1.00E+12	0	1.50E+04	19
13	$iC_8H_{18} + O = 4C_8H_{17} + OH$	1.00E+14	0	3.92E+03	1.00E+12	0	1.50E+04	19
14	$iC_8H_{18} + OH = 1C_8H_{17} + H_2O$	3.00E+08	1.05	9.20E+02	1.00E+12	0	1.50E+04	19,*
15	$iC_8H_{18} + OH = 4C_8H_{17} + H_2O$	3.00E+08	1.05	9.20E+02	1.00E+12	0	1.50E+04	19,*
16	$iC_8H_{18} + OH = 2C_8H_{17} + H_2O$	3.00E+07	1.25	3.50E+02	1.00E+12	0	1.50E+04	19,*
17	$iC_8H_{18} + OH = 3C_8H_{17} + H_2O$	1.00E+11	0	2.20E+02	1.00E+12	0	1.50E+04	19,*
18	$iC_8H_{18} + O_2 = 1C_8H_{17} + HO_2$	1.00E+13	0	2.45E+04	1.00E+12	0	1.50E+04	19,*
19	$iC_8H_{18} + O_2 = 2C_8H_{17} + HO_2$	1.00E+12	0	2.40E+04	1.00E+13	0	1.50E+04	19,*
20	$iC_8H_{18} + O_2 = 3C_8H_{17} + HO_2$	1.00E+11	0	2.30E+04	1.00E+12	0	1.50E+04	19,*
21	$iC_8H_{18} + O_2 = 4C_8H_{17} + HO_2$	1.00E+12	0	2.44E+04	1.00E+12	0	1.50E+04	19,*
22	$iC_8H_{18} + HO_2 = 1C_8H_{17} + H_2O_2$	1.00E+13	0	9.70E+03	1.00E+12	0	1.50E+04	19
23	$iC_8H_{18} + HO_2 = 2C_8H_{17} + H_2O_2$	1.00E+12	0	8.50E+03	1.00E+12	0	1.50E+04	19
24	$iC_8H_{18} + HO_2 = 3C_8H_{17} + H_2O_2$	1.00E+13	0	7.10E+03	1.00E+12	0	1.50E+04	19
25	$iC_8H_{18} + HO_2 = 4C_8H_{17} + H_2O_2$	1.00E+13	0	9.70E+03	1.00E+12	0	1.50E+04	19
26	$iC_8H_{18} + CH_3 = 1C_8H_{17} + CH_4$	4.00E+13	0	5.80E+03	1.00E+12	0	1.50E+04	19,*
27	$iC_8H_{18} + CH_3 = 2C_8H_{17} + CH_4$	4.00E+12	0	4.70E+03	1.00E+12	0	1.50E+04	19,*
28	$iC_8H_{18} + CH_3 = 3C_8H_{17} + CH_4$	4.00E+11	0	3.80E+03	1.00E+12	0	1.50E+04	19,*
29	$iC_8H_{18} + CH_3 = 4C_8H_{17} + CH_4$	4.00E+13	0	5.80E+03	1.00E+12	0	1.50E+04	19,*
30	$iC_8H_{18} + CH_3O = 1C_8H_{17} + CH_3OH$	5.30E+10	0	3.50E+03				6
31	$iC_8H_{18} + CH_3O = 2C_8H_{17} + CH_3OH$	5.50E+11	0	2.50E+03				6
32	$iC_8H_{18} + CH_3O = 3C_8H_{17} + CH_3OH$	1.90E+10	0	1.40E+03				6
33	$iC_8H_{18} + CH_3O = 4C_8H_{17} + CH_3OH$	1.90E+10	0	1.40E+03				6
34	$iC_8H_{18} + C_2H_5 = 1C_8H_{17} + C_2H_6$	1.00E+10	0	8.50E+03				6
35	$iC_8H_{18} + C_2H_5 = 2C_8H_{17} + C_2H_6$	1.00E+10	0	8.50E+03				6
36	$iC_8H_{18} + C_2H_5 = 3C_8H_{17} + C_2H_6$	1.00E+10	0	8.50E+03				6
37	$iC_8H_{18} + C_2H_5 = 4C_8H_{17} + C_2H_6$	1.00E+10	0	8.50E+03				6
38	$1C_8H_{17} = 1C_7H_{14} + CH_3$	1.00E+10	0	1.30E+04	1.00E+10	0	3.50E+03	19
39	$1C_8H_{17} = iC_4H_8 + iC_4H_9$	1.00E+13	0	1.50E+04	1.00E+11	0	4.00E+03	19
40	$2C_8H_{17} = 3C_7H_{14} + CH_3$	1.00E+12	0	1.30E+04	1.00E+11	0	3.50E+03	19,*
41	$3C_8H_{17} = iC_4H_8 + tC_4H_9$	2.00E+13	0	1.45E+04	1.00E+11	0	3.50E+03	19
42	$4C_8H_{17} = 1C_7H_{14} + CH_3$	1.00E+12	0	1.64E+04	1.00E+10	0	3.50E+03	19
43	$4C_8H_{17} = C_3H_6 + iC_5H_{11}$	6.00E+13	0	1.45E+04	1.00E+10	0	3.50E+03	19,*
44	$1C_8H_{17} = C_3H_6 + iC_5H_{11}$	6.00E+13	0	1.45E+04	1.00E+10	0	3.50E+03	19
45	$2C_8H_{17} = C_3H_6 + iC_5H_{11}$	6.00E+13	0	1.45E+04	1.00E+10	0	3.50E+03	19
46	$3C_8H_{17} = C_3H_6 + iC_5H_{11}$	6.00E+13	0	1.45E+04	1.00E+10	0	3.50E+03	19
47	$1C_8H_{17} = 1C_6H_{12} + C_2H_5$	2.00E+12	0	1.10E+04				20,*
48	$2C_8H_{17} = 1C_6H_{12} + C_2H_5$	2.00E+12	0	1.10E+04				20,*
49	$3C_8H_{17} = 1C_6H_{12} + C_2H_5$	2.00E+12	0	1.10E+04				20,*
50	$4C_8H_{17} = 1C_6H_{12} + C_2H_5$	2.00E+12	0	1.10E+04				20,*
51	$1C_8H_{17} = iC_6H_{13} + C_2H_4$	1.00E+12	0	1.10E+04				20,*
52	$2C_8H_{17} = iC_6H_{13} + C_2H_4$	1.00E+12	0	1.10E+04				20,*
53	$3C_8H_{17} = iC_6H_{13} + C_2H_4$	1.00E+12	0	1.10E+04				20,*
54	$4C_8H_{17} = iC_6H_{13} + C_2H_4$	1.00E+12	0	1.10E+04				20,*
55	$1C_8H_{17} = C_5H_{10} + iC_3H_7$	1.00E+13	0	1.38E+04				20
56	$2C_8H_{17} = C_5H_{10} + iC_3H_7$	1.00E+13	0	1.38E+04				20
57	$3C_8H_{17} = C_5H_{10} + iC_3H_7$	1.00E+13	0	1.38E+04				20
58	$4C_8H_{17} = C_5H_{10} + iC_3H_7$	1.00E+13	0	1.38E+04				20
59	$1C_8H_{17} + M = 3C_8H_{17} + M$	2.11E+15	0	8.10E+03	2.20E+16	0	1.05E+04	19
60	$1C_8H_{17} + M = 4C_8H_{17} + M$	2.02E+16	0	7.10E+03	2.20E+16	0	7.10E+03	19
61	$3C_8H_{17} = iC_8H_{16} + H$	2.00E+13	0	1.90E+04	1.00E+10	0	7.50E+02	19
62	$4C_8H_{17} = iC_8H_{16} + H$	2.00E+13	0	1.80E+04	1.00E+09	0	6.00E+02	19
63	$1C_8H_{17} + O_2 = iC_8H_{16} + HO_2$	1.00E+10	0	5.00E+03	1.00E+11	0	1.00E+04	19
64	$2C_8H_{17} + O_2 = iC_8H_{16} + HO_2$	1.00E+10	0	5.00E+03	1.00E+11	0	1.00E+04	19
65	$3C_8H_{17} + O_2 = iC_8H_{16} + HO_2$	1.00E+10	0	5.00E+03	1.00E+11	0	1.00E+04	19
66	$4C_8H_{17} + O_2 = iC_8H_{16} + HO_2$	1.00E+10	0	5.00E+03	1.00E+11	0	1.00E+04	19
67	$1C_8H_{17} + O_2 = 1C_8H_{17}O_2$	2.30E+11	0	0	2.00E+15	0	1.40E+04	8,*
68	$1C_8H_{17}O_2 + M = aC_8H_{16}OOH + M$	5.90E+15	0	1.49E+04				8
69	$1C_8H_{17}O_2 + M = bC_8H_{16}OOH + M$	8.00E+14	0	9.01E+03				8
70	$1C_8H_{17}O_2 + M = cC_8H_{16}OOH + M$	8.00E+14	0	9.01E+03	2.30E+14	0	7.01E+03	8
71	$aC_8H_{16}OOH = 1C_7H_{14} + CH_2O + OH$	1.00E+13	0	1.13E+04	0	0	0	8
72	$cC_8H_{16}OOH = 1C_7H_{14} + CH_2O + OH$	1.00E+13	0	1.13E+04	0	0	0	8
73	$aC_8H_{16}OOH + O_2 = 1OOC_8H_{17}OO$	2.30E+13	0	0				8

(Continued)

Table 1 Reaction submechanism for n-C_7H_{16} and i-C_8H_{18} combustion. Rate constants $k^{\pm} = AT^n \exp(-E_a/T)$ in cm, mole, s, K (continued)

Number	Reaction	k^{+a}			k^{-a}			Ref.
		A	n	E_a	A	n	E_a	
74	$bC_8H_{16}OOH = 3C_7H_{14}+CH_2O+OH$	2.00E+13	0	1.13E+04	0	0	0	8
75	$bC_8H_{16}OOH+O_2 = 2OOC_8H_{17}OO$	2.30E+13	0	0				8
76	$cC_8H_{16}OOH+O_2 = 3OOC_8H_{17}OO$	2.30E+13	0	0				8
77	$1OOC_8H_{17}OO=CH_2O+OH+1C_7H_{14}OO$	2.00E+11	0	1.05E+04	0	0	0	8
78	$1C_7H_{14}OO = C_4H_8O + C_3H_6O$	2.00E+13	0	1.05E+04				8
79	$2OOC_8H_{17}OO=CH_2O+OH+2C_7H_{14}OO$	2.00E+11	0	1.05E+04	0	0	0	8
80	$2C_7H_{14}OO = C_4H_8O + C_3H_6O$	2.00E+13	0	1.05E+04				8
81	$3OOC_8H_{17}OO=CH_2O+OH+3C_7H_{14}OO$	2.00E+11	0	1.05E+04	0	0	0	8
82	$3C_7H_{14}OO = C_4H_8O + C_3H_6O$	2.00E+13	0	1.05E+04				8
83	$C_4H_8O = CH_2O + C_3H_6$	4.40E+15	0	3.00E+04	1.04E+33	−6.80	3.10E+04	21
84	$C_4H_8O + M = iC_3H_7 + HCO + M$	1.00E+13	0	7.50E+03				21
85	$2C_8H_{17} + O_2 = 2C_8H_{17}O_2$	2.30E+11	0	0	2.00E+15	0	1.40E+04	8,*
86	$2C_8H_{17}O_2 + M = aC_8H_{16}OOH + M$	8.00E+14	0	9.01E+03				8
87	$2C_8H_{17}O_2 + M = bC_8H_{16}OOH + M$	5.90E+15	0	1.11E+04	2.30E+14	0	7.01E+03	8
88	$2C_8H_{17}O_2 + M = cC_8H_{16}OOH + M$	8.00E+14	0	9.01E+03	2.00E+15	0	1.40E+04	8
89	$3C_8H_{17} + O_2 = 3C_8H_{17}O_2$	2.30E+11	0	0				22,*
90	$3C_8H_{17}O_2 + M = aC_8H_{16}OOH + M$	8.00E+14	0	9.01E+03				8
91	$3C_8H_{17}O_2 + M = bC_8H_{16}OOH + M$	4.00E+14	0	1.06E+04	2.30E+14	0	7.01E+03	8
92	$3C_8H_{17}O_2 + M = cC_8H_{16}OOH + M$	8.00E+14	0	9.01E+03	2.00E+15	0	1.40E+04	8
93	$4C_8H_{17} + O_2 = 4C_8H_{17}O_2$	2.30E+11	0	0				22
94	$4C_8H_{17}O_2 + M = aC_8H_{16}OOH + M$	8.00E+14	0	9.01E+03				8
95	$4C_8H_{17}O_2 + M = bC_8H_{16}OOH + M$	8.00E+14	0	9.01E+03				8
96	$4C_8H_{17}O_2 + M = cC_8H_{16}OOH + M$	3.00E+13	0	1.20E+04				8
97	$iC_8H_{16} = tC_4H_9 + iC_4H_7$	1.00E+16	0	3.55E+04	1.00E+13	0	0	19,*
98	$iC_8H_{16} = C_6H_{11} + CH_3$	1.00E+16	0	3.55E+04	1.00E+13	0	0	19,*
99	$iC_8H_{16} + H = C_8H_{15} + H_2$	1.00E+12	0	1.85E+03				here
100	$iC_8H_{16} + O = iC_4H_8 + iC_4H_7 + OH$	2.00E+13	0	2.50E+03				19
101	$iC_8H_{16} + O = iC_7H_{15} + HCO$	1.00E+11	0	0	1.00E+10	0	1.50E+04	19
102	$iC_8H_{16} + O\ C_8H_{15} + OH$	1.00E+12	0	2.00E+03				here
103	$iC_8H_{16} + OH = iC_4H_8 + iC_4H_7 + H_2O$	1.00E+09	1.25	3.00E+02				19
104	$iC_8H_{16} + OH = iC_7H_{15} + CH_2O$	1.00E+11	0	0	1.00E+12	0	0	19
105	$iC_8H_{16} + O_2 = C_8H_{15} + HO_2$	4.00E+12	0	2.01E+04				here
106	$iC_8H_{16} + HO_2 = C_8H_{15} + H_2O_2$	2.00E+11	0	8.55E+03				here
107	$iC_8H_{16} + CH_3 = C_8H_{15} + CH_4$	2.00E+11	0	3.65E+03				here
108	$iC_8H_{16} + C_2H_5 = C_8H_{15} + C_2H_6$	1.00E+11	0	4.00E+03				here
109	$C_8H_{15} = iC_4H_7 + iC_4H_8$	1.00E+13	0	1.51E+04				here
110	$C_8H_{15} = C4H_6 + tC_4H_9$	2.52E+13	0	1.51E+04				here
111	$C_7H_{16} = nC_3H_7 + iC_4H_9$	2.30E+17	0	4.10E+04				5
112	$C_7H_{16} = iC_5H_{11} + C_2H_5$	6.50E+16	0	4.10E+04				5
113	$C_7H_{16} = iC_6H_{13} + CH_3$	4.20E+16	0	4.30E+04				5
114	$C_7H_{16} = iC_7H_{15} + H$	2.00E+18	0	5.00E+04				5
115	$C_7H_{16} + H = iC_7H_{15} + H_2$	9.60E+06	2	2.50E+03				5
116	$C_7H_{16} + O = iC_7H_{15} + OH$	2.30E+06	2.4	7.85E+02				23
117	$C_7H_{16} + OH = iC_7H_{15} + H_2O$	5.30E+09	0.97	8.00E+02				23
118	$C_7H_{16} + O_2 = iC_7H_{15} + HO_2$	2.50E+13	0	2.50E+04				23
119	$C_7H_{16} + CH_3 = iC_7H_{15} + CH_4$	1.60E+12	0	5.00E+03				23
120	$C_7H_{16} + HO_2 = iC_7H_{15} + H_2O_2$	1.30E+12	0	9.00E+03				23
121	$C_7H_{16} + C_2H_5 = iC_7H_{15} + C_2H_6$	1.00E+11	0	6.70E+03				23
122	$C_7H_{16} + C_2H_3 = iC_7H_{15} + C_2H_4$	2.00E+11	0	8.00E+03				23
123	$C_7H_{16} + C_3H_5 = iC_7H_{15} + C_3H_6$	4.00E+11	0	9.80E+03				5
124	$C_7H_{16} + iC_4H_7 = iC_7H_{15} + iC_4H_8$	1.00E+12	0	1.40E+04				5
125	$C_7H_{16} + CH_3O = iC_7H_{15} + CH_3OH$	3.20E+11	0	3.60E+03				23
126	$C_7H_{16} = iC_3H_7 + tC_4H_9$	1.30E+17	0	4.10E+04				23
127	$iC_7H_{15} = iC_5H_{11} + C_2H_4$	2.50E+13	0	1.44E+04	1.00E+10	0	3.30E+03	19
128	$iC_7H_{15} = C_5H_{10} + C_2H_5$	1.00E+13	0	1.40E+04				23
129	$iC_7H_{15} + O_2 = 1C_7H_{14} + HO_2$	1.00E+12	0	1.10E+03				23
130	$iC_7H_{15} + O_2 = 3C_7H_{14} + HO_2$	3.00E+12	0	1.10E+03				23
131	$iC_7H_{15} = iC_4H_8 + iC_3H_7$	1.00E+13	0	1.40E+04	1.00E+11	0	3.45E+03	19,*
132	$iC_7H_{15} = 1C_7H_{14} + H$	1.00E+14	0	2.00E+04	1.00E+13	0	6.00E+02	19,*
133	$iC_7H_{15} = tC_4H_9 + C_3H_6$	1.00E+13	0	1.40E+04	1.00E+11	0	4.00E+03	19,*
134	$iC_7H_{15} = 3C_7H_{14} + H$	1.00E+14	0	2.00E+04	1.00E+13	0	6.00E+02	19
135	$iC_7H_{15} = 1C_6H_{12} + CH_3$	5.00E+13	0	1.55E+04				5
136	$iC_7H_{15} + O_2 = C_7H_{15}O_2$	2.30E+11	0	0				12,*
137	$C_7H_{15}O_2 + M = C_7H_{14}OOH + M$	8.90E+14	0	9.00E+03				12,*
138	$C_7H_{14}OOH = 1C_6H_{12} + CH_2O + OH$	1.00E+12	0	1.13E+04	0	0	0	12,*
139	$C_7H_{14}OOH = 1C_7H_{14} + HO_2$	1.00E+12	0	1.13E+04				12,*
140	$C_7H_{14}OOH = 3C_7H_{14} + HO_2$	1.00E+12	0	1.13E+04				12,*
141	$C_7H_{14}OOH = C_5H_{10} + CH_3CHO + OH$	1.00E+12	0	1.13E+04	0	0	0	12,*
142	$C_7H_{14}OOH = C_4H_8O + C_3H_6 + OH$	1.00E+12	0	1.13E+04	0	0	0	12,*
143	$C_7H_{14}OOH = C_3H_6O + C_4H_8 + OH$	1.00E+12	0	1.13E+04	0	0	0	12,*
144	$C_7H_{14}OOH = C_3H_5O_2H + tC_4H_9$	1.50E+12	0	1.43E+04				7
145	$C_7H_{14}OOH = C_3H_5O_2H + iC_4H_9$	2.50E+12	0	1.43E+04				7
146	$C_7H_{14}OOH = C_3H_5O_2H + nC_4H_9$	2.50E+12	0	1.43E+04				7

(Continued)

Table 1 Reaction submechanism for n-C_7H_{16} and i-C_8H_{18} combustion. Rate constants $k^{\pm} = AT^n \exp(-E_a/T)$ in cm, mole, s, K (continued)

Number	Reaction	k^{+a}			k^{-a}			Ref.
		A	n	E_a	A	n	E_a	
147	$C_7H_{14}OOH = C_3H_5O_2H + sC_4H_9$	2.50E+12	0	1.43E+04				7
148	$C_7H_{14}OOH = nC_3H_7O_2 + iC_4H_8$	4.80E+11	0	1.33E+04				7
149	$C_7H_{14}OOH = nC_3H_7O_2 + C_4H_8$	4.80E+11	0	1.33E+04				7
150	$C_7H_{14}OOH = nC_4H_9O_2 + C_3H_6$	4.80E+12	0	1.43E+04				7
151	$C_7H_{14}OOH + O_2 = C_7H_{15}O_4$	8.30E+13	0	0				12,*
152	$C_7H_{15}O_4 = CH_2O + OH + C_6H_{12}OO$	6.00E+13	0	1.05E+04	0	0	0	12,*
153	$C_7H_{15}O_4 = 2C_7H_{14}OO + HO_2$	6.10E+12	0	1.42E+04				7
154	$C_7H_{15}O_4 = 3C_7H_{14}OO + HO_2$	6.10E+12	0	1.42E+04				7
155	$C_7H_{15}O_4 = 1C_7H_{14}OO + HO_2$	6.10E+12	0	1.42E+04				7
156	$C_6H_{12}OO = C_3H_6O + C_3H_6O$	6.00E+13	0	1.05E+04				here
157	$IC_7H_{15} + C_7H_{15}O_2 = C_7H_{15}O + C_7H_{15}O$	1.90E+12	0	−6.00E+02				here
158	$C_7H_{15}O = CH_3CHO + iC_5H_{11}$	3.00E+12	0	7.50E+03				here
159	$C_7H_{16}+C_7H_{15}O_2=C_7H_{15}O+iC_7H_{15}+OH$	3.90E+12	0	5.60E+03	0			6
160	$1C_7H_{14} = C_3H_5 + tC_4H_9$	3.50E+16	0	3.55E+04	1.00E+13	0	0	19
161	$3C_7H_{14} = C_6H_{11} + CH_3$	6.00E+16	0	3.55E+04	1.00E+13	0	0	19
162	$1C_7H_{14} = iC_4H_7 + iC_3H_7$	2.00E+17	0	3.55E+04	1.00E+13	0	0	19,*
163	$1C_7H_{14} = C_2H_5 + C_5H_9$	3.60E+15	0	3.55E+04				5
164	$3C_7H_{14} = C_2H_5 + C_5H_9$	3.60E+15	0	3.55E+04				5
165	$1C_7H_{14} + H = iC_7H_{13} + H_2$	1.00E+13	0	2.00E+03	1.00E+12	0	7.00E+03	19,*
166	$3C_7H_{14} + H = iC_7H_{13} + H_2$	1.00E+14	0	2.00E+03	1.00E+12	0	7.00E+03	19,*
167	$1C_7H_{14} + O = iC_7H_{13} + OH$	1.00E+06	2.56	−5.00E+02	1.00E+12	0	1.50E+04	19,*
168	$3C_7H_{14} + O = iC_7H_{13} + OH$	1.00E+06	2.56	−5.00E+02	1.00E+12	0	1.50E+04	19,*
169	$1C_7H_{14} + O = iC_6H_{13} + HCO$	1.00E+11	0	0	1.00E+12	0	1.50E+04	19,*
170	$3C_7H_{14} + O = iC_5H_{11} + CH_3CO$	1.00E+11	0	0	1.00E+12	0	1.50E+04	19
171	$1C_7H_{14} + O = C_5H_9 + C_2H_4 + OH$	1.00E+14	0	3.92E+03				5
172	$1C_7H_{14} + O = iC_4H_7 + C_3H_6 + OH$	1.00E+13	0	2.60E+03				5
173	$1C_7H_{14} + O = iC_4H_8 + C_3H_5 + OH$	1.80E+13	0	2.60E+03				5
174	$1C_7H_{14} + O = C_5H_{10} + C_2H_3 + OH$	1.80E+13	0	2.60E+03				5
175	$3C_7H_{14} + O = C_5H_9 + C_2H_4 + OH$	1.00E+14	0	3.92E+03				5
176	$3C_7H_{14} + O = C_4H_7 + C_3H_6 + OH$	2.00E+13	0	2.60E+03				5
177	$3C_7H_{14} + O = C_4H_8 + C_3H_5 + OH$	2.80E+13	0	2.60E+03				5
178	$3C_7H_{14} + O = C_5H_{10} + C_2H_3 + OH$	1.00E+13	0	2.60E+03				5
179	$1C_7H_{14} + OH = iC_6H_{13} + CH_2O$	1.00E+11	0	0	1.00E+13	0	1.35E+04	19
180	$3C_7H_{14} + OH = iC_5H_{11} + CH_3CHO$	1.00E+11	0	0	1.00E+12	0	1.35E+04	19
181	$1C_7H_{14} + OH = iC_7H_{13} + H_2O$	1.00E+14	0	1.65E+03	1.00E+13	0	1.35E+04	19
182	$3C_7H_{14} + OH = iC7H_{13} + H_2O$	1.00E+14	0	1.65E+03	1.00E+13	0	1.35E+04	19
183	$1C_7H_{14} + OH = C_5H_9 + C_2H_4 + H_2O$	1.00E+10	1.05	9.00E+02				8
184	$1C_7H_{14} + OH = iC_4H_7 + C_3H_6 + H_2O$	1.00E+09	1.25	3.50E+02				5
185	$1C_7H_{14} + OH = iC_4H_8 + C_3H_5 + H_2O$	1.00E+09	1.25	3.50E+02				5
186	$1C_7H_{14} + OH = C_5H_{10} + C_2H_3 + H_2O$	1.00E+09	1.25	3.50E+02				5
187	$3C_7H_{14} + OH = C_5H_9 + C_2H_4 + H_2O$	1.00E+10	1.05	9.00E+02				5
188	$3C_7H_{14} + OH = C_4H_7 + C_3H_6 + H_2O$	1.00E+09	1.25	3.50E+02				5
189	$3C_7H_{14} + OH = C_4H_8 + C_3H_5 + H_2O$	1.00E+09	1.25	3.50E+02				5
190	$3C_7H_{14} + OH = C_5H_{10} + C_2H_3 + H_2O$	1.00E+09	1.25	3.50E+02				5
191	$1C_7H_{14} + O_2 = iC_7H_{13} + HO_2$	4.00E+12	0	2.01E+04				5
192	$3C_7H_{14} + O_2 = iC_7H_{13} + HO_2$	4.00E+12	0	2.01E+04				5
193	$1C_7H_{14} + CH_3 = iC_7H_{13} + CH4$	2.00E+11	0	3.40E+03				5
194	$3C_7H_{14} + CH_3 = iC_7H_{13} + CH_4$	2.00E+11	0	3.40E+03				5
195	$1C_7H_{14} + HO_2 = iC_7H_{13} + H_2O_2$	1.00E+11	0	8.50E+03				here
196	$3C_7H_{14} + HO_2 = iC_7H_{13} + H_2O_2$	1.00E+11	0	8.50E+03				here
197	$1C_7H_{14} + C_2H_5 = iC_7H_{13} + C_2H_6$	1.70E+11	0	4.00E+03				5
198	$3C_7H_{14} + C_2H_5 = iC_7H_{13} + C_2H_6$	1.70E+11	0	4.00E+03				5
199	$iC_7H_{13} = C_3H_4 + tC_4H_9$	2.52E+13	0	1.51E+04				19
200	$iC_7H_{13} = C_6H_{10} + CH_3$	2.00E+14	0	1.60E+04	1.00E+12	0	4.50E+03	19
201	$iC_7H_{13} = C_2H_4 + C_5H_9$	2.00E+14	0	1.50E+04	0	0	8.50E+03	19
202	$nC_6H_{14} = iC_5H_{11} + CH_3$	3.00E+17	0	4.25E+04	1.00E+13	0	0	24
203	$nC_6H_{14} = C_2H_5 + tC_4H_9$	2.30E+16	0	4.10E+04	1.00E+13	0	0	here
204	$nC_6H_{14} = iC_6H_{13} + H$	2.00E+18	0	5.00E+04	1.00E+14	0	0	here
205	$nC_6H_{14} + H = iC_6H_{13} + H_2$	5.10E+14	0	4.40E+03				25
206	$nC_6H_{14} + O = iC_6H_{13} + OH$	1.30E+14	0	2.20E+03				25
207	$nC_6H_{14} + OH = iC_6H_{13} + H_2O$	1.50E+13	0	5.00E+02				25
208	$nC_6H_{14} + O_2 = iC_6H_{13} + HO_2$	2.50E+13	0	2.50E+04				6
209	$nC_6H_{14} + CH_3 = iC_6H_{13} + CH_4$	2.20E+11	0	5.50E+03				6
210	$nC_6H_{14} + HO_2 = iC_6H_{13} + H_2O_2$	1.30E+12	0	9.00E+03				6
211	$nC_6H_{14} + C_2H_5 = iC_6H_{13} + C_2H_6$	1.70E+10	0	6.70E+03				6
212	$nC_6H_{14} + C_2H_3 = iC_6H_{13} + C_2H_4$	2.00E+11	0	8.00E+03				6
213	$nC_6H_{14} + C_3H_5 = iC_6H_{13} + C_3H_6$	4.00E+11	0	9.80E+03				6
214	$nC_6H_{14} + iC_4H_7 = iC_6H_{13} + iC_4H_8$	1.00E+11	0	1.40E+04				6
215	$nC_6H_{14} + CH_3O = iC_6H_{13} + CH_3OH$	3.20E+10	0	3.60E+03				6
216	$iC_6H_{13} = 1C_6H_{12} + H$	2.00E+13	0	2.00E+04	1.00E+13	0	6.00E+02	19
217	$iC_6H_{13} = C_5H_{10} + CH_3$	1.00E+10	0	1.30E+04				5
218	$iC_6H_{13} = C_3H_6 + iC_3H_7$	1.00E+13	0	1.40E+04	1.00E+11	0	3.45E+03	19,*
219	$iC_6H_{13} = tC_4H_9 + C_2H_4$	2.50E+13	0	1.50E+04	1.00E+11	0	3.45E+03	19

(Continued)

Table 1 Reaction submechanism for n-C_7H_{16} and i-C_8H_{18} combustion. Rate constants $k^{\pm} = AT^n \exp(-E_a/T)$ in cm, mole, s, K (continued)

Number	Reaction	k^{+a} A	k^{+a} n	k^{+a} E_a	k^{-a} A	k^{-a} n	k^{-a} E_a	Ref.
220	$iC_6H_{13} = iC_4H_8 + C_2H_5$	2.00E+12	0	1.10E+04				5
221	$iC_6H_{13} + O_2 = 1C_6H_{12} + HO_2$	2.00E+12	0	1.00E+03				5
222	$1C_6H_{12} = C_3H_6 + C_3H_6$	5.00E+13	0	2.84E+04				5
223	$1C_6H_{12} = iC_3H_7 + C_3H_5$	7.00E+15	0	3.55E+04				19,*
224	$1C_6H_{12} + H = C_6H_{11} + H_2$	1.00E+13	0	2.00E+03	1.00E+12	0	7.00E+03	19,*
225	$1C_6H_{12} + H = iC_4H_7 + C_2H_4 + H_2$	1.00E+07	2	3.85E+03				19,*
226	$1C_6H_{12} + H = C_3H_5 + C_3H_6 + H_2$	1.00E+07	2	2.50E+03				19
227	$1C_6H_{12} + H = iC_4H_8 + C_2H_3 + H_2$	1.00E+07	2	2.50E+03				19
228	$1C_6H_{12} + O = C_6H_{11} + OH$	1.00E+12	0	2.00E+03				5
229	$1C_6H_{12} + O = iC_4H_7 + C_2H_4 + OH$	1.00E+13	0	3.92E+03				19,*
230	$1C_6H_{12} + O = C_3H_5 + C_3H_6 + OH$	1.80E+13	0	2.60E+03				19,*
231	$1C_6H_{12} + O = iC_4H_8 + C_2H_3 + OH$	1.80E+12	0	2.60E+03				19,*
232	$1C_6H_{12} + O = iC_5H_{11} + HCO$	1.00E+11	0	0	1.00E+10	0	1.50E+04	19
233	$1C_6H_{12} + O = tC_4H_9 + CH_3CO$	1.00E+11	0	0	1.00E+10	0	1.50E+04	19
234	$1C_6H_{12} + OH = iC_4H_7 + C_2H_4 + H_2O$	2.00E+10	1.05	9.00E+02				19,*
235	$1C_6H_{12} + OH = C_6H_{11} + H_2O$	1.00E+12	0	6.50E+02				5,*
236	$1C_6H_{12} + OH = C_3H_5 + C_3H_6 + H_2O$	6.50E+09	1.25	3.50E+02				19
237	$1C_6H_{12} + OH = iC_4H_8 + C_2H_3 + H_2O$	6.50E+09	1.25	3.50E+02				19
238	$1C_6H_{12} + OH = iC_5H_{11} + CH_2O$	1.00E+11	0	0	1.00E+10	0	1.50E+04	19
239	$1C_6H_{12} + OH = iC_4H_9 + CH_3CHO$	1.00E+11	0	0	1.00E+10	0	1.50E+04	19
240	$1C_6H_{12} + O_2 = C_6H_{11} + HO_2$	3.00E+12	0	2.01E+04				here
241	$1C_6H_{12} + CH_3 = C_6H_{11} + CH_4$	5.00E+11	0	3.40E+03				5
242	$1C_6H_{12} + HO_2 = C_6H_{11} + H_2O_2$	1.00E+14	0	8.54E+03				here
243	$1C_6H_{12} + C_2H_5 = C_6H_{11} + C_2H_6$	1.70E+11	0	4.00E+03				here
244	$C_6H_{11} = C_3H_5 + C_3H_6$	1.00E+13	0	1.50E+04	0	0	8.50E+03	19
245	$C_6H_{11} = C_6H_{10} + H$	2.00E+14	0	2.40E+04	1.00E+13	0	6.00E+02	19
246	$C_6H_{11} = C_2H_5 + C_4H_6$	5.00E+12	0	1.50E+04				5
247	$C_6H_{11} + H = C_6H_{10} + H_2$	3.16E+12	0	0				5
248	$C_6H_{11} + O_2 = C_6H_{10} + HO_2$	1.00E+11	0	0	1.00E+11	0	8.50E+03	19
249	$C_6H_{11} + CH_3 = C_6H_{10} + CH_4$	1.00E+13	0	0				here
250	$C_6H_{11} + C_2H_3 = C_6H_{10} + C_2H_4$	4.00E+12	0	0				here
251	$C_6H_{11} + C_3H_5 = C_6H_{10} + C_3H_6$	1.00E+13	0	0				here
252	$C_6H_{10} = C_3H_5 + C_3H_5$	2.00E+14	0	2.80E+03	1.00E+13	0	0	19
253	$nC_5H_{12} = CH_3 + tC_4H_9$	6.31E+16	0	4.30E+04	1.90E+13	0	0	24
254	$nC_5H_{12} = iC_5H_{11} + H$	1.00E+15	0	5.04E+04	1.00E+14	0	0	24
255	$nC_5H_{12} = C_2H_5 + iC_3H_7$	6.31E+16	0	4.13E+04	7.94E+12	0	0	24
256	$nC_5H_{12} + H = iC_5H_{11} + H_2$	5.62E+07	2	3.88E+03	3.24E+12	0	7.91E+03	24
257	$nC_5H_{12} + O = iC_5H_{11} + OH$	1.00E+07	2.4	2.25E+03	1.00E+13	0	6.10E+03	24
258	$nC_5H_{12} + OH = iC_5H_{11} + H_2O$	1.00E+07	1.6	2.00E+01	1.00E+10	1.25	1.11E+04	24
259	$nC_5H_{12} + O_2 = iC_5H_{11} + HO_2$	9.00E+14	0	2.40E+04	1.00E+12	0	0	24
260	$nC_5H_{12} + CH_3 = iC_5H_{11} + CH_4$	1.20E+12	0	5.80E+03				21
261	$nC_5H_{12} + HO_2 = iC_5H_{11} + H_2O_2$	1.00E+13	0	8.50E+03	1.00E+12	0	3.60E+03	24
262	$nC_5H_{12} + C_3H_5 = iC_5H_{11} + C_3H_6$	1.00E+12	0	8.80E+03				21
263	$nC_5H_{12} + CH_3O = iC_5H_{11} + CH_3OH$	3.00E+11	0	2.50E+03	1.00E+10	1.25	3.60E+03	24
264	$nC_5H_{12} + iC_4H_7 = iC_5H_{11} + iC_4H_8$	1.00E+12	0	1.01E+04	1.00E+11	0	4.18E+03	24
265	$nC_5H_{12} + C_4H_7 = iC_5H_{11} + C_4H_8$	1.00E+12	0	1.01E+04	1.00E+11	0	4.18E+03	24
266	$nC_5H_{12} + iC_3H_7 = iC_5H_{11} + C_3H_8$	3.26E+11	0	6.20E+03	3.26E+11	0	6.20E+03	24
267	$nC_5H_{12} + iC_4H_9 = iC_5H_{11} + C_4H_{10}$	3.26E+11	0	6.20E+03	3.26E+11	0	6.20E+03	24
268	$nC_5H_{12} + tC_4H_9 = iC_5H_{11} + C_4H_{10}$	1.00E+11	0	6.50E+03	1.00E+11	0	5.24E+03	24
269	$iC_5H_{11} = iC_3H_7 + C_2H_4$	3.20E+13	0	1.43E+04				20
270	$iC_5H_{11} = iC_4H_8 + CH_3$	4.00E+12	0	1.60E+04				20
271	$iC_5H_{11} = C_5H_{10} + H$	1.90E+13	0	2.04E+04	7.94E+12	0	1.46E+03	24
272	$iC_5H_{11} = C_3H_6 + C_2H_5$	1.01E+12	0	1.48E+04	3.98E+10	0	3.78E+03	24
273	$iC_5H_{11} + O_2 = C_5H_{10} + HO_2$	1.00E+12	0	2.10E+03	1.00E+12	0	9.10E+03	24
274	$C_5H_{10} + H = C_5H_9 + H_2$	2.80E+13	0	2.01E+03				23
275	$C_5H_{10} = CH_3 + C_4H_7$	1.00E+19	-1	4.59E+04	1.00E+13	0	0	26
276	$C_5H_{10} = C_3H_6 + C_2H_4$	3.12E+15	0	2.89E+04				23
277	$C_5H_{10} + O = C_3H_6 + CH_3CHO$	1.00E+13	0	0	1.00E+12	0	4.40E+04	26
278	$C_5H_{10} + O = iC_4H_8 + CH_2O$	1.00E+13	0	0	1.00E+12	0	4.25E+04	26
279	$C_5H_{10} + O = C_5H_9 + OH$	2.80E+14	0	4.30E+02				23
280	$C_5H_{10} + O = nC_3H_7 + CH_3CO$	1.00E+12	0	0	1.00E+12	0	2.50E+04	26
281	$C_5H_{10} + O = C_4H_8 + CH_2O$	1.11E+13	0	0	1.00E+12	0	4.25E+04	26
282	$C_5H_{10} + O = C_3H_5 + C_2H_4 + OH$	2.00E+13	0	3.52E+03				23
283	$C_5H_{10} + O = C_3H_6 + C_2H_3 + OH$	1.00E+13	0	3.52E+03				23
284	$C_5H_{10} + OH = iC_3H_7 + CH_3CHO$	1.00E+12	0	0	1.00E+11	0	2.50E+04	26
285	$C_5H_{10} + OH = iC_4H_9 + CH_2O$	1.00E+12	0	0	1.00E+12	0	2.50E+04	26
286	$C_5H_{10} + OH = C_3H_5 + C_2H_4 + H_2O$	2.00E+09	1.2	6.21E+01				23
287	$C_5H_{10} + OH = C_3H_6 + C_2H_3 + H_2O$	1.00E+09	1.2	5.21E+01				23
288	$C_5H_{10} + OH = nC_4H_9 + CH_2O$	1.00E+12	0	0	1.00E+12	0	2.50E+04	26
289	$C_5H_{10} + OH = nC_3H_7 + CH_3CHO$	1.00E+12	0	0	1.00E+11	0	2.50E+04	26
290	$C_5H_{10} + OH = C_5H_9 + H_2O$	6.80E+13	0	1.54E+03				23
291	$C_5H_{10} + O_2 = C_5H_9 + HO_2$	4.00E+12	0	2.01E+04				23
292	$C_5H_{10} + CH_3 = C_5H_9 + CH_4$	2.00E+11	0	3.40E+03				23

(Continued)

Table 1 Reaction submechanism for n-C_7H_{16} and i-C_8H_{18} combustion. Rate constants $k^{\pm} = AT^n \exp(-E_a/T)$ in cm, mole, s, K (continued)

Number	Reaction	k^{+a} A	n	E_a	k^{-a} A	n	E_a	Ref.
293	$C_5H_{10} + HO_2 = C_5H_9 + H_2O_2$	1.00E+11	0	8.54E+03				23
294	$C_5H_{10} + C_2H_5 = C_5H_9 + C_2H_6$	1.70E+11	0	4.00E+03				23
295	$C_5H_9 = C_3H_5 + C_2H_4$	2.50E+13	0	1.51E+04				23
296	$C_5H_9 = C_4H_6 + CH_3$	2.00E+13	0	1.61E+04				23
297	$C_5H_9 = C_5H_8 + H$	6.31E+12	0	1.71E+04				21
298	$C_5H_9 + O_2 = C_5H_8 + HO_2$	2.10E+10	0	0				21
299	$C_5H_9 + C_2H_3 = C_5H_8 + C_2H_4$	4.00E+13	0	0				21
300	$C_5H_9 + C_3H_5 = C_5H_8 + C_3H_6$	4.00E+12	0	0				21
301	$C_5H_9 + C_4H_7 = C_5H_8 + C_4H_8$	1.16E+12	0	0				21
302	$C_5H_9 + iC_4H_7 = C_5H_8 + iC_4H_8$	1.16E+12	0	0				21
303	$C_5H_8 = C_2H_3 + C_3H_5$	5.00E+15	0	3.64E+04				21
304	$C_5H_8 + O = CH_3CHO + C_3H_4$	1.00E+12	0	0				21
305	$C_5H_8 + O = CH_2O + C_4H_6$	1.00E+12	0	0				21
306	$C_5H_8 + OH = CH_3CHO + C_3H_5$	2.00E+12	0	0				21
307	$C_5H_8 + OH = CH_2O + C_4H_7$	2.00E+12	0	0				21
308	$iC_4H_{10} = iC_3H_7 + CH_3$	1.00E+17	0	4.10E+04	1.00E+13	0	0.00E+00	19
309	$iC_4H_{10} = tC_4H_9 + H$	1.00E+15	0	4.10E+04	1.00E+11	0	0.00E+00	19
310	$iC_4H_{10} + H = tC_4H_9 + H_2$	1.00E+14	0	3.60E+03	1.00E+12	0	8.00E+03	19
311	$iC_4H_{10} + H = iC_4H_9 + H_2$	1.00E+14	0	4.10E+03	1.00E+13	0	7.54E+03	19
312	$iC_4H_{10} + O = tC_4H_9 + OH$	1.00E+13	0	1.60E+03	1.00E+12	0	4.80E+03	19
313	$iC_4H_{10} + O = iC_4H_9 + OH$	1.00E+14	0	2.80E+03	1.00E+12	0	4.80E+03	19
314	$iC_4H_{10} + OH = tC_4H_9 + H_2O$	1.00E+12	0	2.00E+02	1.00E+13	0	1.10E+04	19
315	$iC_4H_{10} + OH = iC_4H_9 + H_2O$	1.00E+04	3.02	−3.00E+02	1.00E+04	3.02	1.04E+04	19
316	$iC_4H_{10} + O_2 = iC_4H_9 + HO_2$	1.00E+12	0	2.30E+04	1.00E+12	0	1.00E+03	19
317	$iC_4H_{10} + O_2 = tC_4H_9 + HO_2$	1.00E+14	0	2.40E+04	1.00E+12	0	1.00E+03	19
318	$iC_4H_{10} + CH_3 = iC_4H_9 + CH_4$	1.00E+11	0	3.70E+03	1.00E+11	0	1.05E+04	19
319	$iC_4H_{10} + CH_3 = tC_4H_9 + CH_4$	1.00E+12	0	5.10E+03	1.00E+11	0	7.50E+03	19
320	$iC_4H_{10} + HO_2 = tC_4H_9 + H_2O_2$	1.00E+13	0	7.20E+03	1.00E+13	0	3.70E+03	19
321	$iC_4H_{10} + HO_2 = iC_4H_9 + H_2O_2$	1.00E+13	0	9.20E+03	1.00E+13	0	3.70E+03	19
322	$iC_4H_{10} + C_2H_5 = iC_4H_9 + C_2H_6$	1.00E+11	0	3.90E+03	1.00E+11	0	1.05E+04	19
323	$iC_4H_{10} + C_2H_5 = tC_4H_9 + C_2H_6$	1.00E+12	0	5.20E+03	1.00E+12	0	6.30E+03	19
324	$iC_4H_{10} + C_2H_3 = tC_4H_9 + C_2H_4$	1.00E+12	0	9.00E+03	1.00E+12	0	1.25E+04	19
325	$iC_4H_{10} + C_2H_3 = iC_4H_9 + C_2H_4$	1.00E+12	0	9.00E+03	1.00E+12	0	1.25E+04	19
326	$iC_4H_{10} + CH_3O = tC_4H_9 + CH_3OH$	3.00E+11	0	3.50E+03				6
327	$iC_4H_{10} + CH_3O = iC_4H_9 + CH_3OH$	6.00E+11	0	3.50E+03				6
328	$C_4H_{10} + C_2H_3 = nC_4H_9 + C_2H_4$	1.00E+12	0	9.00E+03	1.00E+12	0	1.25E+04	19
329	$C_4H_{10} + C_2H_5 = nC_4H_9 + C_2H_6$	1.00E+11	0	6.70E+03	1.00E+11	0	6.50E+03	19
330	$C_4H_{10} + C_2H_5 = sC_4H_9 + C_2H_6$	1.00E+11	0	5.20E+03	1.00E+11	0	4.85E+03	19
331	$C_4H_{10} + C_3H_5 = nC_4H_9 + C_3H_6$	1.00E+12	0	1.02E+04	1.00E+11	0	4.85E+03	19
332	$C_4H_{10} + C_3H_5 = sC_4H_9 + C_3H_6$	1.00E+12	0	8.20E+03	1.00E+11	0	4.85E+03	19
333	$iC_4H_9 = C_3H_6 + CH_3$	1.00E+14	0	1.60E+04	1.00E+12	0	4.55E+03	19
334	$tC_4H_9 = C_2H_4 + C_2H_5$	4.50E+13	0	1.50E+04				29
335	$iC_4H_9 = iC_4H_8 + H$	1.00E+15	0	1.70E+04	1.00E+13	0	6.00E+02	19
336	$tC_4H_9 + O_2 = iC_4H_8 + HO_2$	1.00E+12	0	2.40E+03	1.00E+11	0	8.55E+03	19
337	$tC_4H_9 + C_2H_2 = C_6H11$	7.23E+10	0	4.32E+03				29
338	$tC_4H_9 + tC_4H_9 = iC_4H_{10} + iC_4H_8$	7.23E+16	−1.73	0.00E+00				29
339	$iC_4H_9 + O_2 = iC_4H_8 + HO_2$	1.00E+12	0	2.50E+03	1.00E+11	0	8.55E+03	19
340	$iC_4H_9 + H_2 = iC_4H_{10} + H$	1.90E−02	4.24	4.51E+03				29
341	$iC_4H_9 + C_2H_2 = C_6H11$	7.23E+10	0	4.32E+03				29
342	$nC_4H_9 + sC_4H_9 = C_4H_{10} + C_4H_8$	7.23E+16	−1.73	0.00E+00				29
343	$sC_4H_9 = C_4H_8 + H$	1.00E+13	0	1.96E+04	1.00E+13	0	7.56E+02	19
344	$iC_4H_8 = C_2H_3 + C_2H_5$	2.00E+18	−1	4.80E+04				22
345	$iC_4H_8 + M = C_3H_5 + CH_3 + M$	4.00E+18	0	3.70E+04				22
346	$iC_4H_8 + M = iC_4H_7 + H + M$	2.00E+17	0	4.30E+04	1.00E+13	0	0.00E+00	19
347	$iC_4H_8 + H = iC_4H_7 + H_2$	2.00E+13	0	1.90E+03	1.00E+13	0	1.25E+04	19
348	$iC_4H_8 + O = iC_4H_7 + OH$	1.00E+05	2.56	−5.50E+02	1.00E+12	0	1.46E+04	19
349	$iC_4H_8 + O = iC_3H_7 + HCO$	1.00E+06	2.34	−5.50E+02	1.00E+05	2.34	4.03E+04	19
350	$iC_4H_8 + O = C_3H_6 + CH_2O$	2.00E+12	0	0.00E+00				22
351	$iC_4H_8 + O = C_2H_5 + CH_3 + CO$	2.60E+13	0	4.00E+01				22
352	$iC_4H_8 + O = CH_3CHO + C_2H_4$	1.00E+12	0	0.00E+00	1.00E+12	0	4.25E+04	19
353	$iC_4H_8 + OH = CH_3CHO + C_2H_5$	1.00E+11	0	0.00E+00	1.00E+11	0	1.00E+04	19
354	$iC_4H_8 + OH = iC_3H_7 + CH_2O$	1.00E+12	0	0.00E+00	1.00E+13	0	6.60E+03	19
355	$iC_4H_8 + OH = iC_4H_7 + H_2O$	1.00E+12	0	6.50E+02	1.00E+13	0	1.36E+04	19
356	$iC_4H_8 + OH = C_2H_6 + CH_3 + CO$	2.00E+10	0	0.00E+00				22
357	$iC_4H_8 + O_2 = iC_4H_7 + HO_2$	4.00E+12	0	2.00E+04				22
358	$iC_4H_8 + CH_3 = iC_4H_7 + CH_4$	1.00E+12	0	4.40E+03	1.00E+12	0	1.46E+04	19
359	$iC_4H_8 + HO_2 = iC_4H_7 + H_2O_2$	2.00E+11	0	8.50E+03				22
360	$iC_4H_8 + C_2H_5 = C_4H_7 + C_2H_6$	2.00E+11	0	4.03E+03				22
361	$C_4H_8 = C_4H_7 + H$	1.00E+19	−1	4.85E+04	1.00E+14	0	0.00E+00	19
362	$C_4H_8 + M = CH_3 + C_3H_5 + M$	4.00E+18	0	3.70E+04				22
363	$C_4H_8 + H = C_4H_7 + H_2$	1.00E+14	0	1.90E+03	1.00E+12	0	7.00E+03	19
364	$C_4H_8 + O = CH_3CHO + C_2H_4$	1.00E+12	0	0.00E+00	1.00E+12	0	4.25E+04	19
365	$C_4H_8 + O = iC_3H_7 + HCO$	1.00E+13	0	0.00E+00	1.00E+11	0	1.25E+04	19

(Continued)

Table 1 Reaction submechanism for n-C_7H_{16} and i-C_8H_{18} combustion. Rate constants $k^{\pm} = AT^n \exp(-E_a/T)$ in cm, mole, s, K (continued)

Number	Reaction	k^{+a} A	n	E_a	k^{-a} A	n	E_a	Ref.
366	$C_4H_8 + O = C_2H_5 + CH_3 + CO$	1.60E+13	0	4.00E+01				22
367	$C_4H_8 + OH = CH_3CHO + C_2H_5$	1.00E+11	0	0.00E+00	1.00E+11	0	1.00E+04	19
368	$C_4H_8 + OH = C_4H_7 + H_2O$	1.00E+13	0	6.00E+02	1.00E+13	0	1.40E+04	19
369	$C_4H_8 + OH = C_2H_6 + CH_3 + CO$	1.00E+10	0	0.00E+00				22
370	$C_4H_8 + O_2 = C_4H_7 + HO_2$	2.00E+12	0	2.00E+04				22
371	$C_4H_8 + CH_3 = C_4H_7 + CH_4$	2.00E+11	0	3.67E+03	1.00E+12	0	8.00E+03	19
372	$C_4H_8 + HO_2 = C_4H_7 + H_2O_2$	1.00E+11	0	8.50E+03				22
373	$C_4H_8 + C_2H_5 = C_4H_7 + C_2H_6$	2.00E+11	0	4.03E+03				22
374	$C_4H_8 + C_3H_5 = C_4H_7 + C_3H_6$	8.00E+10	0	6.52E+03				22
375	$iC_4H_7 + M = C_3H_4 + CH_3 + M$	2.00E+13	0	1.63E+04	1.00E+11	0	3.75E+03	19
376	$iC_4H_7 + M = C_4H_6 + H + M$	1.20E+14	0	2.48E+04	3.98E+13	0	6.55E+02	19
377	$iC_4H_7 + M = C_2H_4 + C_2H_3 + M$	1.00E+11	0	1.86E+04	1.00E+11	0	3.50E+02	19
378	$iC_4H_7 + H = C_4H_6 + H_2$	3.16E+13	0	0.00E+00	1.15E+13	0	2.86E+04	19
379	$iC_4H_7 + O_2 = C_4H_6 + HO_2$	1.00E+11	0	0.00E+00	1.00E+11	0	8.50E+03	19
380	$iC_4H_7 + CH_3 = C_4H_6 + CH_4$	1.00E+13	0	0.00E+00				22
381	$iC_4H_7 + C_2H_3 = C_4H_6 + C_2H_4$	3.98E+12	0	0.00E+00	1.15E+13	0	2.91E+04	19
382	$iC_4H_7 + C_2H_5 = C_4H_6 + C_2H_6$	3.98E+12	0	0.00E+00	3.24E+12	0	2.51E+04	19
383	$iC_4H_7 + C_2H_5 = iC_4H_8 + C_2H_4$	5.01E+11	0	0.00E+00	8.51E+11	0	2.84E+04	19
384	$iC_4H_7 + C_3H_5 = C_4H_6 + C_3H_6$	1.40E+12	0	0.00E+00				22
385	$iC_4H_7 + iC_4H_7 = C_4H_6 + iC_4H_8$	3.16E+12	0	0.00E+00				22
386	$C_4H_7 + M = C_4H_6 + H + M$	1.20E+14	0	2.48E+04	3.98E+13	0	6.55E+02	25
387	$C_4H_7 + M = C_2H_4 + C_2H_3 + M$	1.00E+11	0	1.86E+04	9.10E+04	1	−1.73E+03	25
388	$C_4H_7 + M = C_3H_4 + CH_3 + M$	1.00E+13	0	1.63E+04	1.00E+11	0	3.75E+03	25
389	$C_4H_7 + H = C_4H_6 + H_2$	3.16E+13	0	0.00E+00	1.15E+13	0	2.86E+04	25
390	$C_4H_7 + O_2 = C_4H_6 + HO_2$	1.00E+11	0	0.00E+00	1.13E+10	0	−4.54E+02	25
391	$C_4H_7 + CH_3 = C_4H_6 + CH_4$	1.00E+13	0	0.00E+00				22
392	$C_4H_7 + C_3H_5 = C_4H_6 + C_3H_6$	1.40E+12	0	0.00E+00				22
393	$C_4H_7 + C_4H_7 = C_4H_6 + C_4H_8$	3.16E+12	0	0.00E+00				22
394	$C_4H_7 + C_2H_3 = C_4H_6 + C_2H_4$	3.98E+12	0	0.00E+00	1.15E+13	0	2.91E+04	25
395	$C_4H_7 + C_2H_5 = C_4H_6 + C_2H_6$	3.98E+12	0	0.00E+00	3.24E+12	0	2.51E+04	25
396	$C_4H_7 + C_2H_5 = C_4H_8 + C_2H_4$	5.01E+11	0	0.00E+00	8.51E+11	0	2.84E+04	25
397	$C_4H_6 = C_2H_3 + C_2H_3$	4.00E+19	−1	4.90E+04				25
398	$C_4H_6 + H = C_3H_4 + CH_3$	5.00E+12	0	1.04E+03				22
399	$C_4H_6 + H = C_4H_5 + H_2$	3.00E+07	2	3.00E+03				30
400	$C_4H_6 + O = C_2H_4 + CH_2CO$	1.00E+12	0	0.00E+00	6.31E+11	0	4.75E+04	19
401	$C_4H_6 + OH = C_2H_5 + CH_2CO$	1.00E+12	0	0.00E+00	3.72E+12	0	1.51E+04	19
402	$C_4H_6 + C_3H_3 = C_4H_5 + C_3H_4$	1.00E+13	0	1.13E+04				30
403	$C_4H_5 = C_4H_4 + H$	1.00E+14	0	1.51E+04				31
404	$C_4H_5 = C_2H_3 + C_2H_2$	2.00E+15	0	2.31E+04				31
405	$C_4H_5 + H = C_4H_4 + H_2$	1.00E+14	0	0.00E+00				31
406	$C_4H_5 + OH = C_4H_4 + H_2O$	2.00E+07	2	5.03E+02				31
407	$C_4H_5 + O_2 = C_4H_4 + HO_2$	1.20E+11	0	0.00E+00				31
408	$C_4H_4 = C_4H_3 + H$	8.63E+12	0	2.97E+04				31
409	$C_4H_4 + H = C_4H_3 + H_2$	3.00E+07	2	2.53E+03				31
410	$C_4H_4 + OH = C_4H_3 + H_2O$	7.50E+06	2	2.53E+03				31
411	$C_4H_4 + C_2H_3 = C_2H_4 + C_4H_3$	5.00E+11	0	8.15E+03				31
412	$C_4H_4 + C_2H = C_4H_2 + C_2H_3$	1.00E+13	0	0.00E+00				31
413	$C_4H_4 + C_2H = C_4H_3 + C_2H_2$	4.00E+13	0	0.00E+00				31
414	$C_4H_3 + M = C_4H_2 + H + M$	2.00E+15	0	2.40E+04				31
415	$C_4H_3 + H = C_4H_2 + H_2$	5.00E+13	0	0.00E+00				31
416	$C_4H_3 + O = CH_2CO + C_2H$	2.00E+15	0	0.00E+00				31
417	$C_4H_3 + H_2 = C_2H_2 + C_2H_3$	5.01E+10	0	1.00E+04				30
418	$C_4H_3 + OH = C_4H_2 + H_2O$	3.00E+13	0	0.00E+00				31
419	$C_4H_3 + CH_2 = C_3H_4 + C_2H$	2.00E+13	0	0.00E+00				30
420	$C_4H_3 + O_2 = CH_2CO + C_2HO$	1.90E+12	0	0.00E+00				31
421	$C_4H_2 + O = CO + cC_3H_2$	2.80E+13	0	8.70E+02				31
422	$C_4H_2 + M = C_4H + H + M$	3.50E+17	0	4.10E+04	2.00E+12	1	−8.2E+03	19
423	$C_4H_2 + C_2H = C_4H + C_2H_2$	2.00E+13	0	0.00E+00				30
424	$C_3H_8 + CH_2 = CH_3 + iC_3H_7$	2.19E+12	0	3.20E+03				31
425	$C_3H_8 + CH_2 = CH_3 + nC_3H_7$	1.79E+12	0	3.20E+03				31
426	$iC_3H_7 + C_3H_8 = nC_3H_7 + C_3H_8$	1.00E+10	0	6.45E+03	1.00E+10		6.45E+03	19
427	$C_3H_6 + CH_2 = C_3H_5 + CH_3$	7.00E+11	0	3.10E+03				31
428	$C_3H_6 + C_2H = C_3H_5 + C_2H_2$	1.20E+13	0	0.00E+00				31
429	$C_3H_5 + C_2H_3 = C_3H_6 + C_2H_2$	4.80E+12	0	0.00E+00				31
430	$C_3H_5 + C_2H_3 = C_3H_4 + C_2H_4$	2.41E+12	0	0.00E+00				29
431	$C_3H_5 + C_2H_5 = C_3H_4 + C_2H_6$	9.64E+11	0	−6.62E-02				29
432	$C_3H_5 + C_3H_4 = C_3H_3 + C_3H_6$	2.00E+12	0	3.88E+03				29
433	$C_3H_5 + C_3H_5 = C_3H_4 + C_3H_6$	8.43E+10	0	−1.32E+02				29
434	$C_3H_4 + H = C_3H_5$	4.00E+12	0	1.36E+03				29
435	$C_3H_4 + H = C_3H_3 + H_2$	2.00E+14	0	7.56E+03				29
436	$C_3H_4 + H = CH_3 + C_2H_2$	2.00E+13	0	1.20E+03				29
437	$C_3H_4 + OH = CH_2O + C_2H_3$	3.12E+12	0	−2.00E+02				29
438	$C_3H_4 + OH = C_3H_3 + H_2O$	1.45E+13	0	2.10E+03				29

(Continued)

Table 1 Reaction submechanism for n-C_7H_{16} and i-C_8H_{18} combustion. Rate constants $k^{\pm} = AT^n \exp(-E_a/T)$ in cm, mole, s, K (continued)

		k^{+a}			k^{-a}			
Number	Reaction	A	n	E_a	A	n	E_a	Ref.
439	$C_3H_4 + O_2 = C_3H_3 + HO_2$	4.00E+13	0	3.10E+04				29
440	$C_3H_4 + CH_3 = C_3H_3 + CH_4$	2.00E+12	0	3.88E+03				29
441	$C_3H_4 + C_2H = C_3H_3 + C_2H_2$	1.00E+13	0	0.00E+00				29
442	$C_3H_4 + M = C_3H_3 + H + M$	2.00E+18	0	4.03E+04				29
443	$C_3H_3 + M = cC_3H_2 + H + M$	2.00E+48	−8.5	4.93E+04				29
444	$C_3H_3 + H = cC_3H_2 + H_2$	5.00E+12	0	0.00E+00				29
445	$C_3H_3 + O_2 = CH_2CO + HCO$	3.00E+10	0	1.44E+03				29
446	$C_3H_3 + CH = C_4H_3 + H$	7.00E+13	0	0.00E+00				29
447	$cC_3H_2 + M = C_3H + H + M$	1.00E+15	0	5.11E+04				29
448	$cC_3H_2 + O = C_2H_2 + CO$	7.00E+13	0	0.00E+00				29
449	$cC_3H_2 + OH = C_2H_2 + CO + H$	5.00E+13	0	0.00E+00				29
450	$cC_3H_2 + O_2 = C_2H_2 + CO_2$	2.00E+12	0	0.00E+00				29
451	$cC_3H_2 + CH_2 = C_4H_3 + H$	3.00E+13	0	0.00E+00				29
452	$cC_3H_2 + cC_3H_2 = C_4H_2 + C_2H_2$	2.00E+13	0	4.25E+04				29
453	$C_2H_6 + CH_2 = CH_3 + C_2H_5$	6.50E+12	0	3.86E+03				29
454	$C_2H_5 + O = C_2H_4 + OH$	3.05E+13	0	0.00E+00				30
455	$C_2H_5 + CH_2 = C_3H_6 + H$	9.00E+12	0	0.00E+00				30
456	$C_2H_4 + CH_2 = C_3H_6$	0.00E+00	0	5.00E+03				30
457	$C_2H_3 + C_2H = C_4H_4$	9.22E+27	−4.3	5.51E+03				31
458	$C_2H_3 + O = CH_3 + CO$	3.00E+13	0	0.00E+00				31
459	$C_2H_3 + O_2 = CH_2O + HCO$	1.00E+12	0	1.25E+02				31
460	$C_2H_2 + O_2 = C_2HO + OH$	2.00E+08	0	1.50E+04				31
461	$C_2H_2 + CH_2 = C_3H_3 + H$	1.20E+13	0	3.31E+03				31
462	$C_2H_2 + CH_2 = C_3H_4$	1.20E+13	0	3.31E+03				31
463	$C_2H_2 + C_2H = C_4H_3$	4.17E+36	−7.3	4.39E+03				31
464	$C_2H_2 + CH = C_3H + H_2$	1.00E+14	0	5.01E+03				31
465	$C_2H_2 + CH_3 = C_3H_4 + H$	2.70E+15	−1.96	1.04E+04				31
466	$CH_3CHO + H = H_2 + CH_3CO$	1.09E+14	0	2.21E+03	1.00E+13	0	1.15E+04	19
467	$CH_3CHO + HO_2 = H_2O_2 + CH_3CO$	3.01E+12	0	5.00E+03	1.00E+12	0	7.50E+04	19
468	$CH_3CHO + CH_3 = CH_4 + CH_3CO$	1.01E+12	0	4.24E+03	1.00E+13	0	1.40E+04	19
469	$C_2HO + OH = HCO + CO + H$	1.00E+13	0	0.00E+00				31
470	$C_2HO + O = CO + CO + H$	1.93E+14	0	2.94E+02				31
471	$C_2HO + O_2 = CO + CO + OH$	1.46E+12	0	1.25E+03				31
472	$C_2HO + CH_2 = C_2H + CH_2O$	1.00E+13	0	1.00E+03				31
473	$C_2HO + CH_2 = C_2H_3 + CO$	3.00E+13	0	0.00E+00				31
474	$CH_2CO + O_2 = CH_2O + CO_2$	1.00E+08	0	0.00E+00				31
475	$CH_3O + C_2H_4 = CH_2O + C_2H_5$	1.20E+11	0	3.50E+03				31
476	$CH_2OH + H = CH_2O + H_2$	3.00E+13	0	0.00E+00				31
477	$CH_4 + CH = C_2H_4 + H$	2.00E+12	0	0.00E+00				31
478	$C_3H + O = C_2H + CO$	6.80E+13	0	0.00E+00				29
479	$CH_3 + H = CH_2 + H_2$	7.00E+13	0	7.50E+03				29
480	$CH_3 + CH = C_2H_3 + H$	2.00E+13	0	0.00E+00				29
481	$C_3H + OH = C_2H_2 + CO$	6.80E+13	0	0.00E+00				29
482	$C_3H + O_2 = C_2HO + CO$	2.00E+12	0	0.00E+00				29
483	$CH_3 + OH = CH_2OH + H$	2.64E+19	0	4.04E+03				31
484	$CH_3 + OH = CH_3O + H$	5.70E+12	0	6.90E+03				31
485	$CH_3 + CH_3 = C_2H_5, + H$	3.00E+13	0	6.75E+03				31
486	$CH_2 + O_2 = CH_2O + O$	1.00E+14	0	2.25E+03				31
487	$CH_2 + CO_2 = CH_2O + CO$	1.00E+11	0	5.00E+02				31
488	$CH_2 + CH_2 = C_2H_2 + H_2$	3.20E+13	0	0.00E+00				31
489	$CH_2 + CH_3 = C_2H_4 + H$	4.00E+13	0	0.00E+00				31
490	$CH_2 + CH = C_2H_2 + H$	4.00E+13	0	0.00E+00				31
491	$CH_2 + OH = CH_2O + H$	2.50E+13	0	0.00E+00				31
492	$HCO + HO_2 = CO_2 + OH + H$	3.00E+13	0	0.00E+00				31
493	$CH + OH = HCO + H$	3.00E+13	0	0.00E+00				31
494	$CH + O = CO + H$	3.00E+14	0	0.00E+00				31
495	$HCO + O_2 = HO_2 + CO$	3.00E+12	0	0.00E+00				29
496	$HCO + HO_2 = CO_2 + OH + H$	3.00E+13	0	0.00E+00				31
497	$CH + OH = HCO + H$	3.00E+13	0	0.00E+00				31
498	$CH + O = CO + H$	3.00E+14	0	0.00E+00				31

subset of mechanisms for the combustion of higher of hydrocarbon fuels up to kerosene, and can be developed for investigations into the formation of soot precursors, other pollution species, or the influence of ions on combustion.

Reaction Mechanism

The construction of the detailed kinetic model for n-C_7H_{16}/air and i-C_8H_{18}/air combustion is based on the principles established for comprehensive reaction mechanisms.[1−15] The mechanisms for the more complex fuels are sequentially built upon the resolved submechanisms that have been developed for the simpler fuel molecules. The baseline mechanism for the system consists of 562 elementary reversible reactions and 83 species for H_2/O_2 and C_1-C_4/air mixtures (including N/O/H species) that have been described in Refs. 16 and 17. To prepare the mechanism for polycyclic aromatic hydrocarbons (PAH) formation capabilities, reactions related to CH, C_2, C_2H, C_3H_5, and other species have been included, as well as same reactions for C_4 (mainly reactions of C_4H_5, C_4H_4, C_4H_3, C_4H_2, and C_4H), components that were not presented in Refs. 16 and 17.

The submechanisms for C_5–C_8 were constructed for both the low- and high-temperature oxidation of n-C_7H_{16} and i-C_8H_{18}. The following principles have been applied.

1) The system includes iso- and normal noncyclic hydrocarbons only.

2) The primary reactants are the initial alkane molecules, oxygen, and C_0–C_1–C_2 free radicals resulting from the base reaction.

3) For each new species, an appropriate set of reactions is generated.

4) Each new species is analyzed to determine if a redefinition, an analysis of the atomic groups in the molecules, or an evaluation of possible isomers are necessary.

5) Isomeric molecules having the same molecular formula and the same functional groups are considered as one single species only if this reduction is of negligible influence on the entire process.

6) Each free radical is systematically submitted to all propagation reactions.

7) Free radicals disappear in reactions of combination and disproportionation (dismutation) and produce smaller and more stable radicals and primary molecules.

8) All reactions are reversible.

The scheme for the description of the general features of alkane oxidation has already been described.[18] Hence, here the type of reactions taking place in our system is mentioned only briefly. The alkyl radicals with n atoms of carbon have been denoted as R_n and the appropriate olefin structures as Q_n. All of the other terms are defined according to common terminology.[11]

For both the low- and high-temperature oxidation, the initiation reactions are those of decomposition and oxidation:

$$R_nH = R_m^\bullet + R_{n-m}^\bullet, \qquad R_nH + O_2 = R_n^\bullet + HO_2^\bullet$$

For the high-temperature mechanism, the reactions of propagation are as follows.

1) The metathesis reactions lead to the production of alkyl radicals:

$$R_nH + r^\bullet = R_n^\bullet + rH$$

where $r^\bullet$ stands for $H^\bullet$, $O^\bullet$, $OH^\bullet$, $CH_3^\bullet$, $C_2H_5^\bullet$, $HO_2^\bullet$, or $CH_2OH^\bullet$, the main free radicals resulting from the C_0–C_1–C_2 base reaction.

2) The β scission of alkyl radicals with production of alkenes is

$$R_n^\bullet = R_mH_{2m} + R_{n-m}^\bullet$$

3) The oxidation of alkyl radicals is

$$R_n^\bullet + O_2 = Q_n + HO_2^\bullet$$

4) The reactions of olefins with free radicals $r^\bullet$ lead to the production of the smaller radicals, formyl, formaldehydes, and acetaldehydes.

5) The β scission of alkene radicals.

For the low-temperature mechanism, the reactions of propagation are as follows.

1) Oxygen addition to alkyl radicals to form peroxy radicals is

$$R_n^\bullet + O_2 = R_nOO^\bullet$$

2) Isomerization (internal rearrangement) of peroxy radicals to form hydro–peroxy–alkyl radicals is

$$R_nOO^\bullet = Q_nOOH^\bullet$$

3) Oxygen addition to hydro–peroxy–alkyl radicals to form hydro–peroxy–alkyl–peroxy radicals is

$$Q_nOOH^\bullet + O_2 = OOQ_nOOH^\bullet$$

4) The hydro–peroxy–alkyl and hydro–peroxy–alkyl–peroxy radicals decompose to olefins, alkenyl–hydro–peroxides, carbonyl, hydroxy radicals.

For both the low- and high-temperature oxidation the termination reactions are reactions of pairs of free radicals, for example,

$$R_n^\bullet + r^\bullet = \text{product}, \qquad R_n^\bullet + R_n^\bullet = Q_{2n}$$

$$R_nOO^\bullet + HO_2^\bullet = R_nOOH + O_2$$

The low-temperature mechanism for both alkanes was reduced by means of the reduction technique and the sensitivity analyses described in Refs. 4, 8, and 12–14 and Refs. 1 and 4, respectively. Some components and reactions were already eliminated during mechanism construction, and redundant components and reactions were identified and combined using standard lumping procedures. The codes used to find the redundant species and unimportant reactions were developed in-house and are based on sensitivity analysis and chemical flow analysis.[14] Figures 1 and 2 show the schemes for the final lumped low-temperature submechanisms for n-C_7H_{16} and i-C_8H_{18} oxidation, respectively.

The complete mechanism involves 1006 reactions with 134 chemical species for the combined n-C_7H_{16} + i-C_8H_{18}/air oxidation (928 reactions of 120 species in the case of n-C_7H_{16}/air combustion and 987 reactions of 128 species in the case of i-C_8H_{18}/air combustion).

Table 1 shows the reactions of the presented mechanism and the corresponding rate constants together with the appropriate literature sources. The modified rate constants are indicated with an asterisk together with the number of the reference from which the reaction rates have been taken for evaluation.

Kinetic and Thermodynamic Data

The rate constants for all reactions were evaluated on the basis of a set of independent kinetic parameters deduced from the literature.[5–8,19–31] In case the relevant kinetic parameters could not be found in the literature, these parameters were estimated on the basis of the similarity and analogy rules.[1,3,4,7,13] The rate constants for reactions with reactants entering as one single species

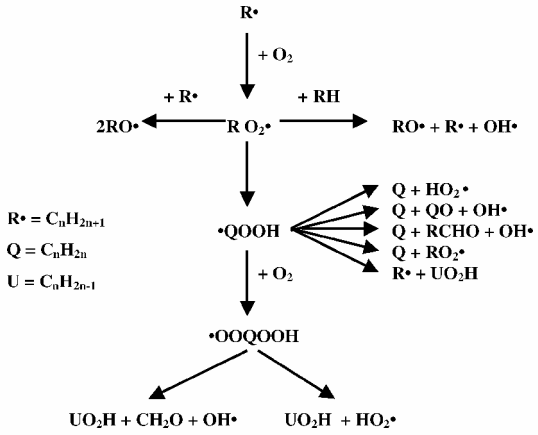


Fig. 1 Lumped scheme of the n-heptane low-temperature oxidation.

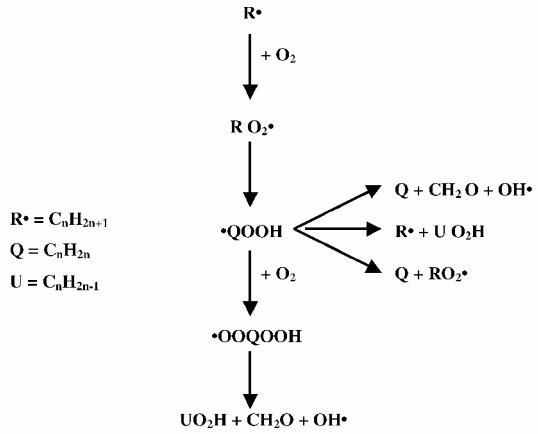


Fig. 2 Lumped scheme of the iso-octane low-temperature oxidation.

```
1C8H17O2            Hf(298)=-0.16596000E+03 kJ/mol

1C8H17O2     GAdd/01C  8H      17O  2      0G      300.000     3000.000                1
 0.35927546E+02  0.10651612E-01  0.62788259E-05 -0.33287101E-08  0.41810310E-12  2
-0.35588806E+05 -0.17235695E+03 -0.28629033E+01  0.94492927E-01 -0.42862104E-04  3
-0.81880397E-08  0.93697790E-11 -0.22914206E+05  0.35708994E+02 -0.19961511E+05  4

2C8H17O2            Hf(298)=-0.18419000E+03 kJ/mol

2C8H17O2     GAdd/01C  8H      17O  2      0G      300.000     3000.000                1
 0.35495405E+02  0.11163092E-01  0.65966198E-05 -0.34954194E-08  0.43903438E-12  2
-0.37430833E+05 -0.16884056E+03 -0.33554596E+01  0.97766003E-01 -0.44838003E-04  3
-0.11313704E-07  0.11944444E-10 -0.25083061E+05  0.38375850E+02 -0.22154198E+05  4

3C8H17O2            Hf(298)=-0.19389000E+03kJ/mol

3C8H17O2     GAdd/01C  8H      17O  2      0G      300.000     3000.000                1
 0.34881233E+02  0.11670939E-01  0.69147864E-05 -0.36620536E-08  0.45995501E-12  2
-0.38203905E+05 -0.17770602E+03 -0.47514146E+01  0.11117176E+00 -0.82500685E-04  3
 0.31263313E-07 -0.49152941E-11 -0.26172803E+05  0.30975542E+02 -0.23320904E+05  4

4C8H17O2            Hf(298)=-0.16596000E+03 kJ/mol

4C8H17O2     GAdd/01C  8H       17  2      0G      300.000     3000.000                1
 0.35927546E+02  0.10651612E-01  0.62788259E-05 -0.33287101E-08  0.41810310E-12  2
-0.35588806E+05 -0.17235695E+03 -0.28629033E+01  0.94492927E-01 -0.42862104E-04  3
-0.81880397E-08  0.93697790E-11 -0.22914206E+05  0.35708994E+02 -0.19961511E+05  4

aC8H16OOH           Hf(298)=-0.14793000E+03 kJ/mol

aC8H16OOH    GAdd/01C  8H       17  2      0G      300.000     3000.000                1
 0.47040538E+02  0.12364541E-01  0.72524182E-05 -0.38487823E-08  0.48344532E-12  2
-0.37631935E+05 -0.19431570E+03 -0.17903476E-01  0.11657747E+00 -0.56617000E-04  3
-0.94871175E-08  0.12839197E-10 -0.22451718E+05  0.57264788E+02 -0.17792879E+05  4

bC8H16OOH           Hf(298)=-0.14887000E+03 kJ/mol

bC8H16OOH    GAdd/01C  8H       17  2      0G      300.000     3000.000                1
 0.41204268E+02  0.11307784E-01  0.66443089E-05 -0.35247846E-08  0.44274194E-12  2
-0.34901728E+05 -0.18548024E+03 -0.28977250E+01  0.12953167E+00 -0.11580540E-03  3
 0.58892110E-07 -0.13643729E-10 -0.21882038E+05  0.44882484E+02 -0.17905942E+05  4

cC8H16OOH           Hf(298)=-0.15746000E+03 kJ/mol

cC8H16OOH    GAdd/01C  8H       17  2      0G      300.000     3000.000                1
 0.41612864E+02  0.10870645E-01  0.63745716E-05 -0.33830933E-08  0.42495097E-12  2
-0.36252942E+05 -0.18758553E+03 -0.19318739E+01  0.12021125E+00 -0.92998875E-04  3
 0.36198638E-07 -0.55751045E-11 -0.22949445E+05  0.41863085E+02 -0.18939139E+05  4

1OOC8H16OO          Hf(298)=-0.24458000E+03 kJ/mol

1OOC8H16OO   GAdd/01C  8H       16  4      0G      300.000     3000.000                1
 0.42693880E+02  0.90887730E-02  0.52865524E-05 -0.28103732E-08  0.35303395E-12  2
-0.47627137E+05 -0.20231954E+03 -0.47841749E+01  0.13295379E+00 -0.13077756E-03  3
```

Fig. 3 Thermochemical data for some peroxides calculated applying the group additivity method[34] (continued).

and representing a group of isomers were evaluated as sums of the isomer reactions (taking all possible isomers into account). The rate constants of the reactions of the lumped low-temperature sub-mechanism (reactions 67–96 and 136–159) were estimated on the basis of the detailed reaction scheme for the low-temperature submechanism.[6,8] Rate constants for the reverse reactions for which the necessary information had not been found in the literature were computed using equilibrium constants. Generally, all of the rate constants obtained as described were continuously adjusted during the improvement of the kinetic mechanism.

Thermodynamic data were taken from literature sources[32,33] whenever possible.[‡] For some of the species, thermochemical data were calculated by applying the group additivity method[34] [also Slavinskaya, N. A., "Thermo-chemical Properties of Large Hydrocarbons Peroxy Radicals" (in preparation)]. As already mentioned, isomers containing 4-8 carbon atoms are conveniently lumped or

[‡]Data also available online at "Burcat's Ideal Gas Thermo–chemical Database," http://garfield.elte.chem/Burcat/burcat. html>;data.

```
 0.81765291E-07  -0.24542818E-10  -0.32891633E+05   0.47846354E+02  -0.29417849E+05  4
2OOC8H16OO        Hf(298)=-0.29074000E+03 kJ/mol

2OOC8H16OO      GAdd/01C  8H      16  4        0G      300.000     3000.000             1
 0.41210445E+02  0.10631106E-01   0.62309197E-05  -0.33072026E-08   0.41541998E-12  2
-0.52082408E+05 -0.20585716E+03  -0.72525760E+01   0.15357145E+00  -0.17416514E-03  3
 0.12005586E-06 -0.37023662E-10  -0.38310490E+05   0.44409966E+02  -0.34969930E+05  4

3OOC8H16OO        Hf(298)=-0.29074000E+03 kJ/mol

3OOC8H16OO      GAdd/01C  8H      16  4        0G      300.000     3000.000             1
 0.41210445E+02  0.10631106E-01   0.62309197E-05  -0.33072026E-08   0.41541998E-12  2
-0.52082408E+05 -0.20585716E+03  -0.72525760E+01   0.15357145E+00  -0.17416514E-03  3
 0.12005586E-06 -0.37023662E-10  -0.38310490E+05   0.44409966E+02  -0.34969930E+05  4

C7H15O2           Hf(298)=-0.14590000E+03 kJ/mol

C7H15O2         GAdd/01C  7H      15  2        0G      300.000     3000.000             1
 0.29860546E+02  0.10173402E-01   0.60321514E-05  -0.31941129E-08   0.40117921E-12  2
-0.30441079E+05 -0.14867747E+03  -0.14386142E+01   0.80638960E-01  -0.43967077E-04  3
 0.57941207E-08  0.22503244E-11  -0.20325176E+05   0.18605161E+02  -0.17548713E+05  4

C7H14OOH          Hf(298)=-0.23269990E+02 kJ/mol

C7H14OOH        GAdd/01C  7H      15  2        0G      300.000     3000.000             1
 0.32410877E+02  0.19483320E-01  -0.31821278E-05  -0.14290526E-09   0.55444024E-13  2
-0.16969801E+05 -0.13250487E+03   0.20114346E+01   0.86469414E-01  -0.44056103E-04  3
-0.97672994E-08  0.14074429E-10  -0.68364462E+04   0.30641313E+02  -0.27988928E+04  4

OOC7H14OOH        Hf(298)=-0.24275000E+03 kJ/mol

OOC7H14OOH      GAdd/01C  7H      15  4        0G      300.000     3000.000             1
 0.36189811E+02  0.91334468E-02   0.53483837E-05  -0.28392959E-08   0.35664836E-12  2
-0.44319453E+05 -0.17682870E+03  -0.40188462E+01   0.12364137E+00  -0.13723807E-03  3
 0.96367428E-07 -0.30556087E-10  -0.32455073E+05   0.32367450E+02  -0.29197739E+05  4

C4H9OO            Hf(298)=-0.67160000E+02 kJ/mol

C4H9OO          GAdd/01C  4H       9  2        0G      300.000     3000.000             1
 0.17468905E+02  0.52590049E-02   0.31020192E-05  -0.16443154E-08   0.20653346E-12  2
-0.15813674E+05 -0.86917442E+02  -0.18260766E+01   0.52532552E-01  -0.48053307E-04  3
 0.33631801E-07 -0.11891319E-10  -0.95031500E+04   0.15937441E+02  -0.80779408E+04  4

C2H5OO            Hf(298)=-0.26820000E+02 kJ/mol

C2H5OO          GAdd/01C  2H       5  2        0G      300.000     3000.000             1
 0.89203293E+01  0.23223080E-02   0.13616167E-05  -0.72265384E-09   0.90772781E-13  2
-0.72903181E+04 -0.44557706E+02  -0.24185616E+01   0.36018344E-01  -0.52196498E-04  3
 0.50209817E-07 -0.19639703E-10  -0.37337632E+04   0.14806727E+02  -0.32258841E+04  4

C2H5OO            HF(298)=-4. kcal        REF=NIST, 1994, estimate [33]

C2H5OO PEROXYETH  T08/00C  2H       5 O  2        0G      200.000     6000.000 C  61.06050  1
 8.05957692E+00  1.52921019E-02  -5.54442603E-06   9.00496195E-10  -5.41302799E-14  2
-7.31028500E+03 -1.59992904E+01   5.21694144E+00   1.24160003E-04   6.15529492E-05  3
-7.94505636E-08  3.12101317E-11  -5.41455775E+03   4.22381533E+00  -3.45206633E+03  4
```

Fig. 3 Thermochemical data for some peroxides calculated applying the group additivity method[34] (finished).

grouped into a single equivalent component. In those cases, the thermodynamic properties were calculated for the components presented in Table 1. The results of thermodynamic property calculations for some particularly problematic species such as $C_2H_5OO^{\bullet}$ are presented in Fig. 3 in CHEMKIN format. For this • radical, we show the calculated polynomials following[33] as an example of the accuracy of the applied thermochemical property estimation method.

Comparison Between Experimental and Modeling Results

In the development of a kinetic mechanism, it is difficult to separate the direct chemical problem (the modeling of chemical processes based on known reaction schemes and rate coefficients) and the inverse chemical problem (the estimation of rate parameters of elementary reactions based on known production rates of species, ignition delay times, etc.). We have used the available experimental

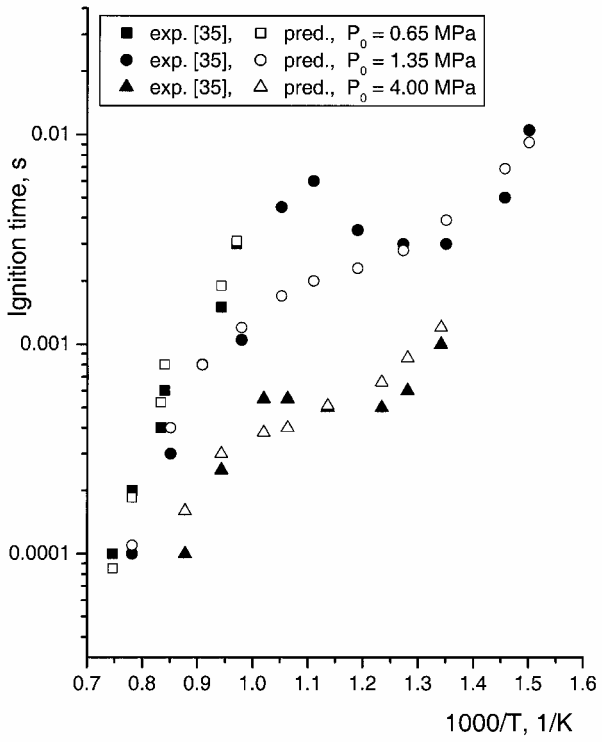


Fig. 4 Oxidation of stoichiometric n-heptane/air mixtures in a shock tube; comparison between predicted (open symbols) and experimental (filled symbols)[35] ignition times vs initial temperatures for the initial pressures $P_0 = 0.65$, 1.35, and 4.0 MPa.

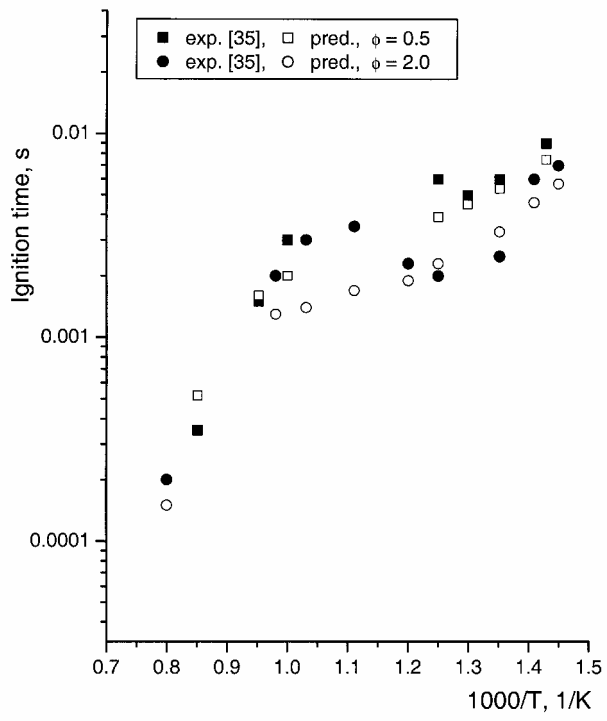


Fig. 5 Oxidation of n-heptane/air mixtures in a shock tube at 1.35 MPa; comparison between predicted (open symbols) and experimental (filled symbols)[35] ignition times vs initial temperatures for mixture ratios $\phi = 0.5$ and 2.

data both for validating our reaction mechanism and for estimating the rate coefficients, especially for lumped reactions.

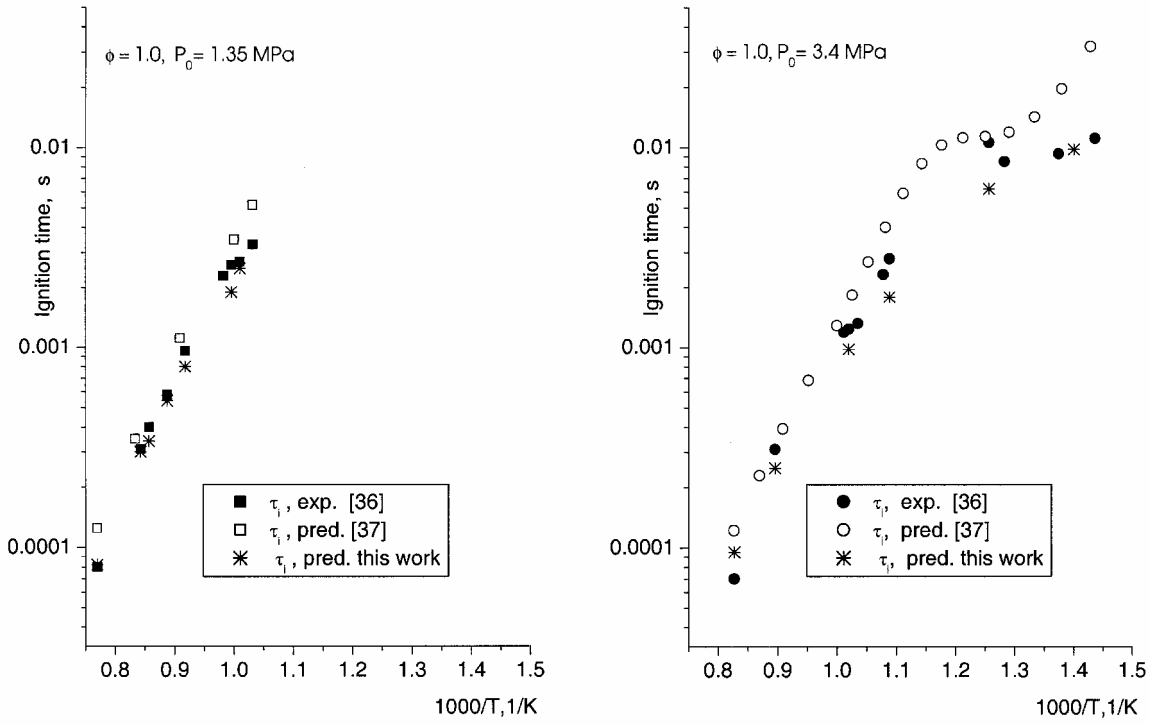
For our modeling purposes, it is sufficient to reproduce the ignition delay times and distribution of components by pyrolysis. Therefore, we chose the following three experimental investigations for the mechanism validation and reaction rate expression correction. The first set of experiments refers to the pyrolysis of pure iso-octane in a shock tube provided by Doolan and Mackie.[20] The second and third set of data, obtained by Ciezki and Adomeit[35] and Fieweger et al.,[36] relate to the ignition time of n-heptane/air and iso-octane/air mixtures and their oxidation in a shock tube. These three sets of experimental data provide detailed information on pyrolysis products and show the influence of pressure, temperature, and composition on the ignition time.

The calculations were performed assuming adiabatic homogeneous mixtures in a closed vessel using the code described in Ref. 16 at initial pressures $P_0 = 0.65$–4.5 MPa, initial temperatures $T_0 = 700$–1300 K, and fuel to oxygen ratios $\phi = 0.5$–2. After extensive sensitivity analyses, a few rate constants were modified to be able to predict the experimental data more precisely. The modified reaction rates belong to the class of reactions with C_5–C_8 species only. Mainly the reactions of species representing a group of isomers, reactions with rate expressions evaluated in the literature by the analogy method applied to similar reactions of smaller hydrocarbons or adjusted to the overall decay kinetics, were modified. The uncertainty limits of reaction rate parameters may vary within 200 and 500%, and for low–temperature submechanism reactions, they may even increase to 1000%. We consider our modifications of the rate constants justified because they never exceed these limits. Thus, to reduce the ignition period for iso-octane and n-heptane by high-temperature oxidation, the rate constants of the thermal decomposition reaction (reactions 1, 2, and 111) were increased by a factor of two compared to the value given by Axelsson et al.[19] and Chakir et al.[5] To increase the ignition time for the initial temperature range (700–900 K), the rate constants of the reactions of H abstraction from iso-octane and n-heptane by OH radicals or O_2 (reactions 14–21, 117, and 118) and the constants of the reactions of oxygen addition to alkyl radicals (reactions 67, 85, 89, 93, and 136) were decreased by a factor between 2 and 10, in contrast to the values recommended in Refs. 8 and 12. To further minimize the deviation between the computed and the experimental species concentrations resulting from iso-octane pyrolysis, the rate constants of the reactions 26–29 and 43 were increased by a factor of 4 and those of the reactions 40, 43, 48–54, 97, and 98 were decreased by a factor between 1.25 and 10, in contrast to the values recommended in Refs. 19 and 20.

Comparisons of the computed ignition delay times with the experimental data for n-C_7H_{16}/air mixtures are shown in Figs. 4 and 5 and for iso–octane/air mixtures in Figs. 6a–6c and 7a and 7b for different pressures and mixture ratios ϕ. For comparison, Figs. 6a–6c and 7a and 7b also include numerical results from Curran et al.[37] obtained with a much larger model (3600 reactions and 860 species). The influence of the presence of the second hydrocarbon fuel is shown in Fig. 8 where the ignition delay times of various stoichiometric iso-octane/n-heptane mixtures with air are compared with results from Fieweger et al.[36] Good agreement between computed and experimental ignition times was obtained for all initial parameters of oxidation, for both high- and low-temperature regions. However, the present model underpredicts the ignition times of n-C_7H_{16} in the range of the temperatures $T_0 = 850$–950 K and initial pressures $P_0 < 4.0$ MPa and of i-C_8H_{18} for temperatures $T_0 < 900$ K, initial pressure $P_0 = 4.0$ MPa, and for $\phi = 0.5$ and yields discrepancies that exceed 30%. A comparison of the final composition for iso-octane pyrolysis with experimental data is shown in Fig. 9. Rather good agreement was obtained for all of the major species of the pyrolysis process. For the minor species, a reasonable fit between the computed and the experimental concentrations could be achieved.

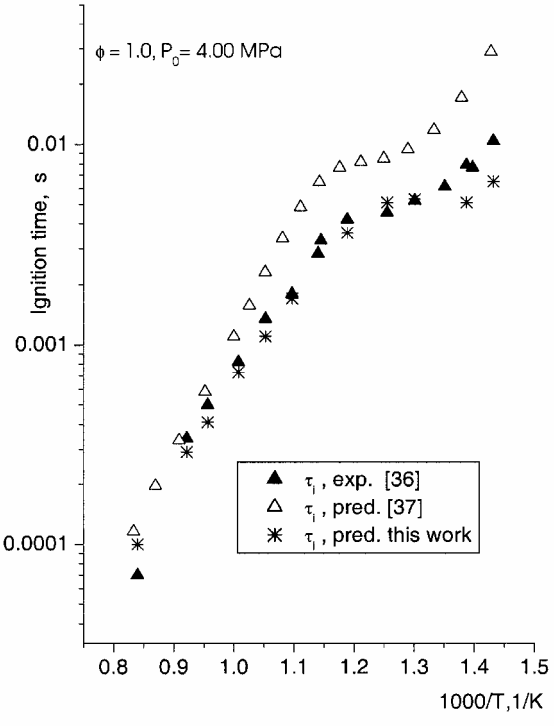
Analysis of the Mechanism

The developed simplified mechanism reflects the main properties (two-stage ignition period, ignition delay time, and distribution of species by pyrolysis) of n-heptane and iso-octane oxidation and enables a deeper analysis of the characteristics of pure n-C_7H_{16} and i-C_8H_{18} oxidation, as well as n-C_7H_{16}/i-C_8H_{18} mixture oxidation in air. Figures 10–12 show the schemes representing the main



a) $P_0 = 1.3$ MPa

b) $P_0 = 3.4$ MPa



c) $P_0 = 4.0$ MPa

Fig. 6 Oxidation of stoichiometric iso-octane/air mixtures in a shock tube; comparison between experimental[36] predicted with model[37] and with present model ignition times vs the initial temperatures for different the initial pressures.

reaction paths of iso-octane and n-heptane oxidation for a pressure of 4.0 MPa, an equivalence ratio of 1, and initial temperatures of 730 and 1200 K, respectively, at the time when 10% of the initial concentration of i-C_8H_{18} and n-C_7H_{16} are converted. The schemes represent all possible contributions of each reaction to the production of individual components and illustrate the importance of specific reactions and components. The concentration Δc of all species i consumed in reaction q throughout the time period τ were calculated according to

$$\Delta c_{iq} = \int_0^{\tau} S_{iq}\, \mathrm{d}t$$

with

$$S_{iq} = \frac{\alpha_{iq}^{-} - \alpha_{iq}^{+}}{N}\left(R_q^{+} - R_q^{-}\right), \qquad R_q^{+(-)} = k_{+(-)q} \prod_{j=1}^{n_q^{+(-)}} N_j^{\alpha_{jq}^{+(-)}}$$

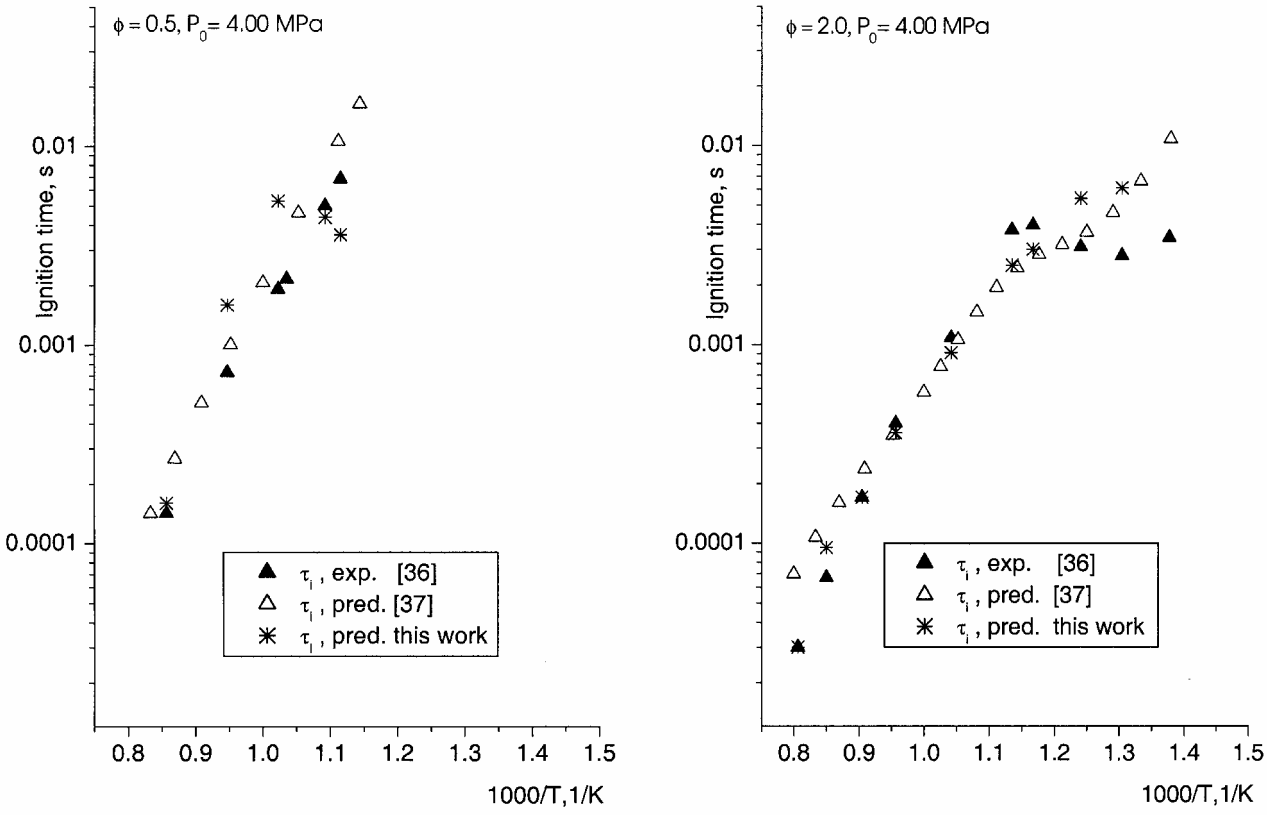


Fig. 7 Oxidation of iso-octane/air mixtures in a shock tube at 4.0 MPa; comparison between experimental,[36] predicted with model,[37] and present model ignition times vs the initial temperatures for different equivalence ratios.

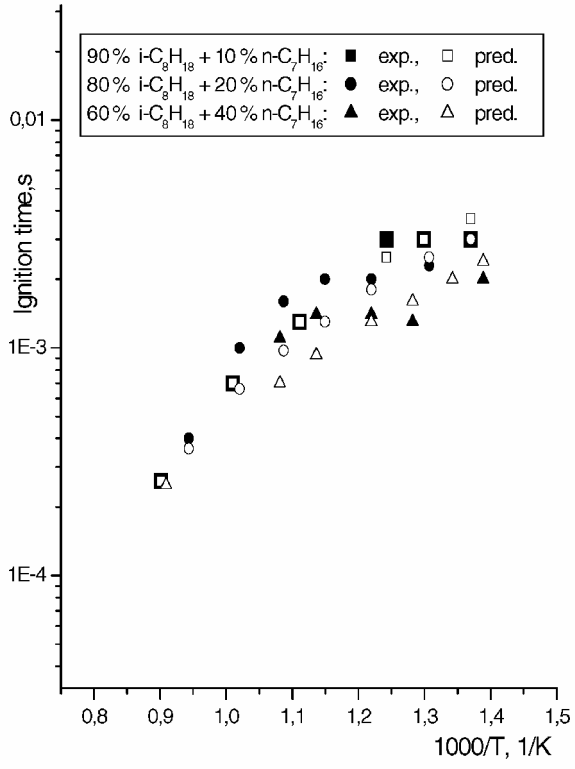


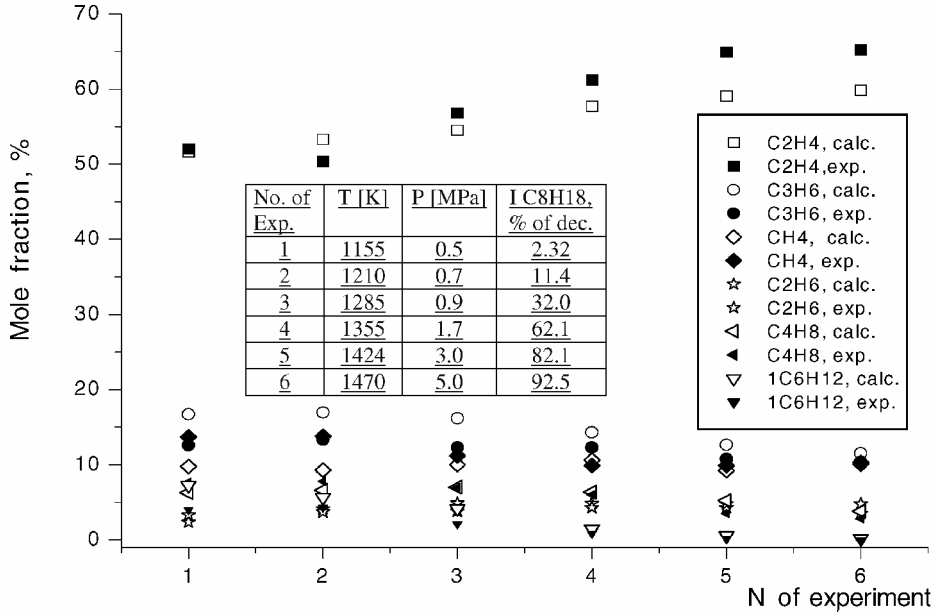
Fig. 8 Oxidation of stoichiometric different mixtures of iso-octane and n-heptane/air mixtures in a shock tube at $P_0 = 4.0$ MPa: comparison between predicted and experimental[36] ignition times vs initial temperature.

where k_{+q} and k_{-q} are the rate constants of direct and reverse reactions q, α_{iq}^{+} and α_{iq}^{-} are the stoichiometric coefficients of components in reaction q,

$$N = \sum_{i=1}^{M_1} N_i$$

where N_i is the number of molecules i, M_1 is the number of species in the mixture, and $n_q^{+(-)}$ is the number of species in direct and reverse reactions. In Figs. 10–12, the thickness of the arrows between the single species indicates the relative importance of the different reaction paths. Figures 10–12 clearly show the difference between the primary mechanisms at low and high temperatures and the main reaction paths. In combination with Table 1, Figs. 10–12 can used as a guideline for either problem-oriented modifications or a further reduction of the mechanism.

At low temperatures and a pressure of 4.0 MPa, about 90% of the iso-octane have gone through the peroxyl radical production by oxygen addition to alkyl radicals (reactions 67, 85, 89, and 93). Iso-octane molecules mainly react with OH radicals that have been produced through decomposition of either hydro–peroxy–alkyl and hydro–peroxy–alkyl–peroxy radicals or ethers in the low-temperature branching mechanism (67–96) yielding alkyl radicals. The further evolution of ignition at low temperatures is determined by the reactions involving the alkenes $1C_7H_{14}$, $3C_7H_{14}$, and $1C_5H_{10}$. These alkenes can form light oxygenated products such as acetaldehyde, formaldehyde, and carbon monoxide or carbon dioxide. Our lumped low-temperature schemes reflect the difference between the reactivity of i-C_8H_{18} and n-C_7H_{16} (Figs. 1, 2, 10, and 11). There are two main reasons for the high reactivity of n-C_7H_{16}: First, the production of less alkenes, which are good branching agents, and second, the production of more peroxides, which yield high conversion rates of n-C_7H_{16}. In the same temperature range, i-C_8H_{18}



No. of Exp.	T [K]	P [MPa]	I C8H18, % of dec.
1	1155	0.5	2.32
2	1210	0.7	11.4
3	1285	0.9	32.0
4	1355	1.7	62.1
5	1424	3.0	82.1
6	1470	5.0	92.5

Fig. 9 Comparison of calculated and experimental data[20] for concentrations of the major components obtained by pyrolysis of i-C_8H_{18} in a shock tube. The table shows pressure and temperature conditions after shock waves and the amount of i-C_8H_{18} decomposition.

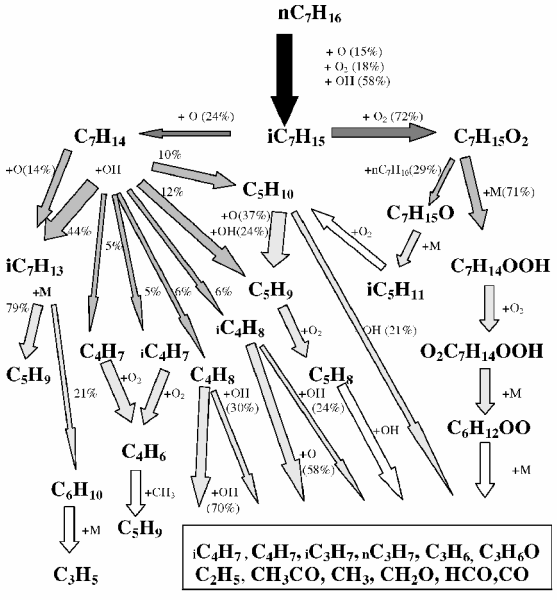


Fig. 10 Main reaction paths for n-heptane at $T_0 = 730$ K, $P_0 = 4.0$ MPa, and $\phi = 1$, when 10% of the initial n-C_7H_{16} is converted.

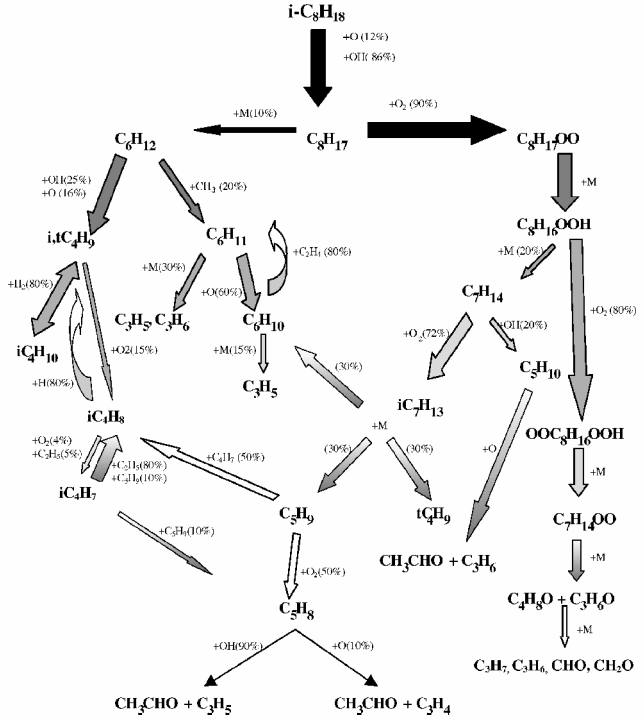


Fig. 11 Main reaction paths for iso-octane at $T_0 = 730$ K, $P_0 = 4.0$ MPa, and $\phi = 1$, when 10% of the initial i-C_8H_{18} is converted.

produces more stable large olefines, such as $1C_7H_{14}$, $3C_7H_{14}$, and $1C_5H_{10}$ and later C_4H_8 and C_3H_6, and less peroxidic spieces.[38]

At high temperatures, the reaction paths for both i-octane and n-heptane are quite similar, and therefore only the scheme for i-octane oxidation is shown. Under these conditions, the effect of oxygen addition on the overall kinetic is negligible, and the major reaction path is the decomposition by β scission yielding olefins and smaller alkyl radicals. The higher alkanes are mainly consumed by H abstraction, mostly with CH_3 radicals, forming alkyl radicals. These alkyl radicals produce smaller alkyl radicals, alkenes, ethylene, and propylene. Furthermore, the quite reactive ethyl and methyl radicals easily undergo further reactions, forming either light oxygenated products or methane and ethane. To compare the temperature profiles of species at low and high temperatures in the case of iso-octane oxidation, Figs. 13a and 13b and 14a and 14b show the time-dependent mole fractions of the smaller branching species and the heavy radicals produced during the combustion of i-C_8H_{18} at a constant pressure of 4.0 MPa, an equivalence ratio $\phi = 1$, and a temperature of 730 and 1200 K, respectively. Evidently, at low temperatures, the total induction time is mainly affected by the accumulation rate of peroxy radicals. The development of the mole fractions of the small branching agents O, H, OH, HO_2, CH_3, and C_2H_5 at low temperatures corresponds to a well-known effect of two-stage ignition of hydrocarbons. The first increase of these branching agents appears in the first low-temperature ignition phase. For high temperatures, the rate of accumulation of both the light and heavy components is almost constant for most of the time and changes drastically at the time of ignition.

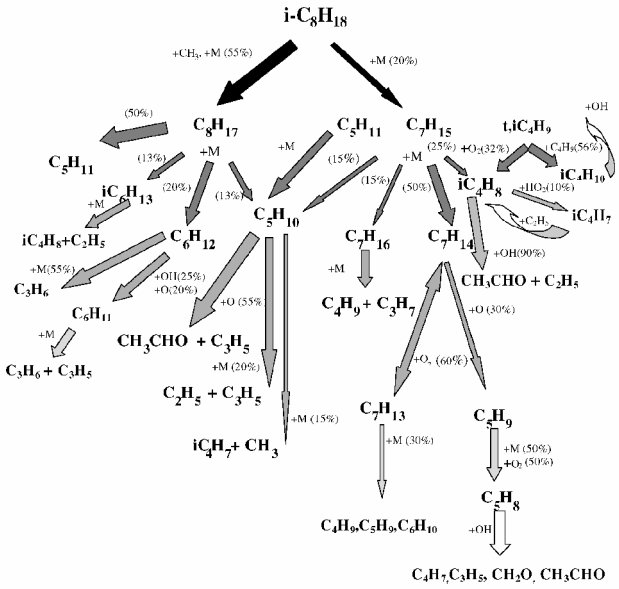


Fig. 12 Main reaction paths for iso-octane at $T_0 = 1200$ K, $P_0 = 4.0$ MPa, and $\phi = 1$, when 10% of the initial i-C_8H_{18} is converted.

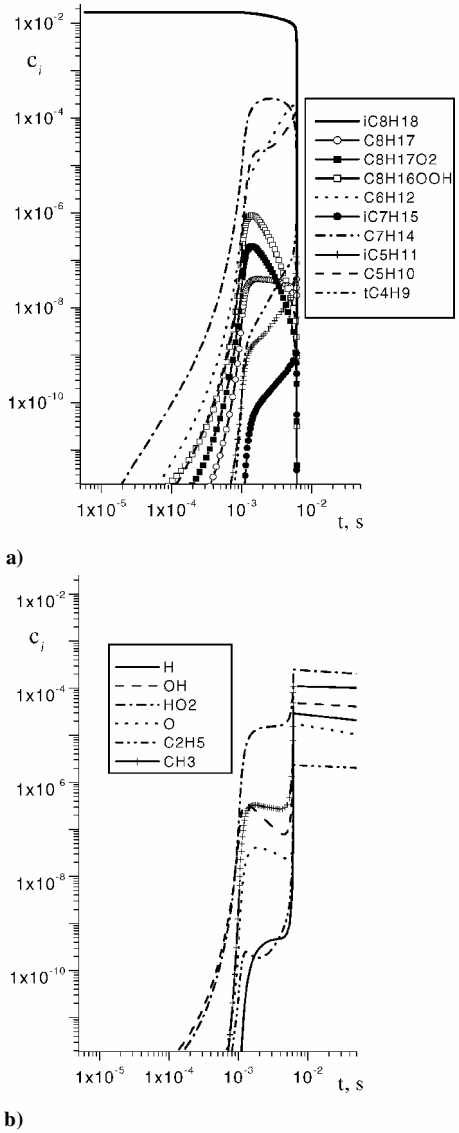


Fig. 13 Mole fractions of a) the small branching radicals and b) the heavy radicals produced during i-C_8H_{18} combustion in air vs time for $T_0 = 730$ K, $P_0 = 4.0$ MPa, and $\phi = 1$.

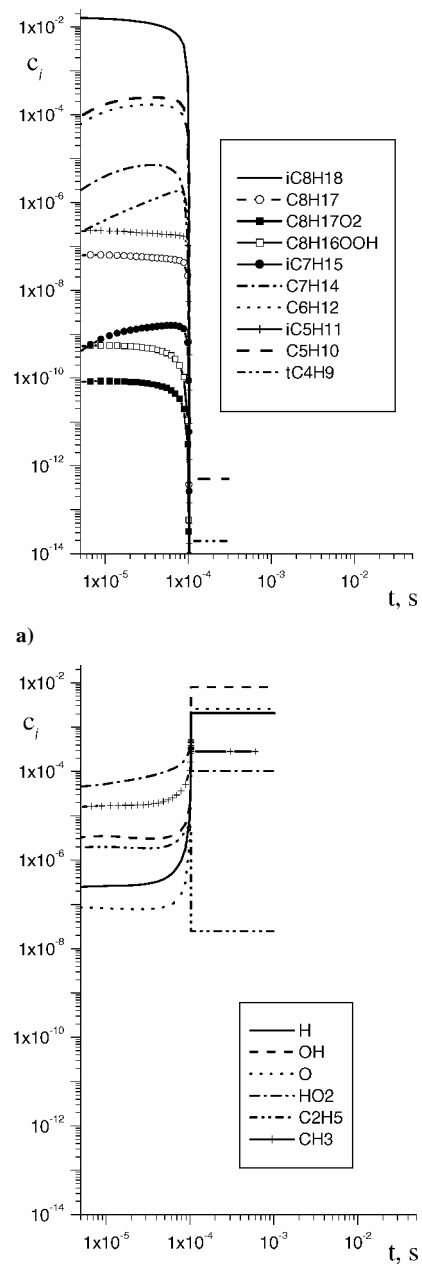


Fig. 14 Mole fractions of a) the small branching radicals and b) the heavy radicals produced during i-C_8H_{18} combustion in air vs time for $T_0 = 1200$ K, $P_0 = 4.0$ MPa, and $\phi = 1$.

Conclusions

Analytic reaction mechanisms for the combustion of n-heptane, iso-octane, and their mixtures in air remarkably smaller than those found in the literature have been presented. The comparison of predicted and experimental ignition delays measured behind shock waves has been performed for initial temperatures $T_0 = 650$–1200 K, initial pressures $P_0 = 0.65$–4.5 MPa, and equivalence ratios $\phi = 0.5$–2. The schemes presented demonstrate rather good accuracy and their applicability to investigations of primary propagation reactions of the alkanes under study. Further comparison of experimental and predicted results has revealed that the same kinetic scheme correctly predicts the concentrations of the major species measured during the pyrolysis of i-C_8H_{18} behind shock waves. Although this mechanism is less accurate when applied to ignition delay time predictions in the initial temperature range of 800–900 K at high pressure (4.0 MPa) it can, nevertheless, be used successfully for reaction path analyses and for the identification of different stages

of n-C_7H_{16} and i-C_8H_{18} oxidation, the main steps leading to the formation and consumption of the intermediate species involved in the reaction process.

The proposed scheme can be easily extended to the combustion of larger n-paraffins, as well as to the prediction of soot and formation of pollutants. Furthermore, the scheme seems to be quite suitable to be applied in cases where the number of reactions has to be drastically reduced to establish an engineering tool with short turnaround times and proven accuracy. This may be achieved by reducing components that contain nitrogen atoms or components, which are important for PAH precursors formation.

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