

REACTIVITY, CHEMICAL KINETICS,  
AND CATALYSIS

The Mechanisms of Oxidation and Combustion  
of Normal Alkane Hydrocarbons:  
The Transition from C<sub>1</sub>–C<sub>3</sub> to C<sub>4</sub>H<sub>10</sub>

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**Abstract**—The known detailed mechanisms of oxidation of the higher hydrocarbons include hundreds of particles and thousands of reactions. In spite of their merits, the use of such mechanisms for solving applied problems of the gas dynamics of combustion is impeded at present because of great computational expenditures. We suggest a compact kinetic mechanism of the oxidation of *n*-butane including the main processes and intermediate and final reaction products. The mechanism can be classified as a nonempirical detailed mechanism, because all its elementary reactions are kinetically substantiated. The mechanism does not contain reactions of the double addition of oxygen and intermediate species in the form of isomeric compounds and their derivatives. The calculation results are compared with the experimental data on the oxidation, self-ignition, and combustion of *n*-butane.

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INTRODUCTION

Several detailed mechanisms of the oxidation of the higher hydrocarbons were suggested. These mechanisms include diverse intermediate stable molecules and radicals, hundreds of species, and thousands of reactions. For instance, the mechanism of *n*-heptane oxidation with 650 species and 2300 reactions was described in [1], the mechanism of isooctane oxidation with 126 species and 976 reactions, in [2], and the mechanism of *n*-decane oxidation with 715 species and 3872 reactions, in [3]. In spite of several undeniable merits of such detailed mechanisms, their direct application to multidimensional problems of the gas dynamics of combustion is impracticable at present because of unacceptably great computational expenditures. At the same time, simple calculations show that the inclusion of all possible isomers and reactions (e.g., the inclusion of polyaromatic hydrocarbons, soot, fullerenes, reactions of their formation and consumption, etc.) would substantially expand the detailed mechanisms described in [1–3]. It follows that such detailed mechanisms are in a certain sense limited and cannot lay claim to a complete description of oxidation reactions. Note one more important point. Detailed mechanisms include poorly verified data on reaction thermochemistry and rates, which adversely affects their validity and accuracy.

Optimum rather than comprehensive kinetic mechanisms are of interest for practical calculations. They only contain the main processes determining reaction rates and the formation of the most important intermediate and final products [4]. Such mechanisms, even if

they are fairly compact, rank as nonempirical detailed mechanisms, because all of the elementary reactions they include are kinetically substantiated.

The phenomenology of the oxidation of normal alkane hydrocarbons is known to be fairly universal [4–6]. An algorithm for constructing a chemical mechanism of the oxidation and combustion of such hydrocarbons was suggested in [4]. This algorithm was used to suggest a compact mechanism of the oxidation of propane. In this work, it is applied to obtain a compact mechanism of the oxidation of *n*-butane (*n*-C<sub>4</sub>H<sub>10</sub>). The resulting mechanism differs from those suggested earlier (e.g., see [7, 8]) by a substantially smaller number of species and reactions. The algorithm suggested in [4] is based on two key principles: it is assumed that (1) low-temperature branching occurs in reactions with single oxygen addition and (2) the oxidation path through isomeric hydrocarbon forms can be excluded from consideration because it is slower than the oxidation path through normal-structure particles (in other words, no distinction is drawn between normal-structure particles and isomers).

THE MECHANISM OF *n*-BUTANE OXIDATION

A mathematical program was written [4] for the development of compact kinetic mechanisms based on the principles specified above. In this program, the mechanism of oxidation of hydrocarbon C<sub>*n*</sub>H<sub>2*n*+2</sub> is constructed on the basis of the oxidation mechanism of its analogue, a homologue containing *n* – 1 carbon atoms.

**Table 1.** Additional species in the mechanism of *n*-butane oxidation

Component no.	Formula	$\Delta H_f^{\circ}{}_{298}$ , kcal/mol	$S_{298}$ , cal/(mol K)
46	C <sub>4</sub> H <sub>10</sub>	-29.6	64.51
47	C <sub>4</sub> H <sub>9</sub>	18.46	77.34
48	C <sub>4</sub> H <sub>9</sub> O <sub>2</sub>	-10.5	101.38
49	C <sub>4</sub> H <sub>9</sub> O <sub>2</sub> H	-40.6	93.3
50	C <sub>4</sub> H <sub>9</sub> O	-6.5	86.1
51	C <sub>3</sub> H <sub>7</sub> CHO	-50.7	82.2
52	C <sub>3</sub> H <sub>7</sub> CO	-16.0	83.5
53	C <sub>4</sub> H <sub>8</sub>	-2.74	73.52
54	C <sub>4</sub> H <sub>7</sub>	26.36	70.1

Such an analogue of *n*-butane is propane. For this reason, the mechanism of oxidation of *n*-C<sub>4</sub>H<sub>10</sub> was constructed on the basis of the oxidation mechanism of propane [4] including 45 species and 204 reversible reactions. According to [4], this mechanism satisfactorily describes both low- and high-temperature methane, ethane, and propane oxidation and combustion kinetics.

The new mechanism of *n*-C<sub>4</sub>H<sub>10</sub> oxidation includes the whole mechanism of propane oxidation, additional species and reactions similar to those involved in propane oxidation, and new cross reactions between hydrocarbon radicals and molecules characteristic of *n*-C<sub>4</sub>H<sub>10</sub>. For instance, analogues of the C<sub>3</sub>H<sub>7</sub>, C<sub>3</sub>H<sub>7</sub>O, and C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> radicals from the mechanism of propane oxidation are the C<sub>4</sub>H<sub>9</sub>, C<sub>4</sub>H<sub>9</sub>O, and C<sub>4</sub>H<sub>9</sub>O<sub>2</sub> radicals in butane oxidation. The new species in the mechanism of *n*-butane oxidation are listed in Table 1. This table also contains the corresponding enthalpies of formation  $\Delta H_f^{\circ}{}_{298}$  and entropies  $S_{298}$  taken from handbooks or calculated by the additivity scheme.

Analogues of the C<sub>3</sub>H<sub>7</sub> + O<sub>2</sub> = C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>, C<sub>3</sub>H<sub>8</sub> + OH = C<sub>3</sub>H<sub>7</sub> + H<sub>2</sub>O, and C<sub>3</sub>H<sub>8</sub> = C<sub>3</sub>H<sub>7</sub> + H propane oxidation reactions in the new *n*-butane oxidation mechanism were the C<sub>4</sub>H<sub>9</sub> + O<sub>2</sub> = C<sub>4</sub>H<sub>9</sub>O<sub>2</sub>, C<sub>4</sub>H<sub>10</sub> + OH = C<sub>4</sub>H<sub>9</sub> + H<sub>2</sub>O, and C<sub>4</sub>H<sub>10</sub> = C<sub>4</sub>H<sub>9</sub> + H reactions. Instead of the two propane oxidation monomolecular reactions C<sub>3</sub>H<sub>8</sub> = C<sub>3</sub>H<sub>7</sub> + H and C<sub>3</sub>H<sub>8</sub> = C<sub>2</sub>H<sub>5</sub> + CH<sub>3</sub>, the mechanism of *n*-C<sub>4</sub>H<sub>10</sub> oxidation included three monomolecular reactions, C<sub>4</sub>H<sub>10</sub> = C<sub>4</sub>H<sub>9</sub> + H, C<sub>4</sub>H<sub>10</sub> = C<sub>3</sub>H<sub>7</sub> + CH<sub>3</sub>, and C<sub>4</sub>H<sub>10</sub> = C<sub>2</sub>H<sub>5</sub> + C<sub>2</sub>H<sub>5</sub>.

The selection of the Arrhenius parameters of the rate constants for elementary reactions is of the greatest importance for a kinetic mechanisms. Fairly accurate values of these parameters are known for only a limited number of reactions. For this reason, the reaction rate constants in the mechanism of *n*-C<sub>4</sub>H<sub>10</sub> oxidation were obtained using the constants from the mechanism of propane oxidation [4].

The two-parameter rate constant for the *i*th reaction has the form

$$k_i = A_i \exp(-E_i/RT),$$

where  $A_i$  is the preexponential factor,  $E_i$  is the activation energy,  $T$  is the temperature, and  $R$  is the gas constant.

It is well known that the  $A_i$  preexponential factor is proportional to  $\exp(\Delta S_i/R)$ . For reactions of the same type in the mechanisms of oxidation of C<sub>*n*</sub>H<sub>2*n*+2</sub> and propane ( $n = 3$ ), we have

$$A_{i(n)} = A_{i(n=3)} \exp[(\Delta S_{i(n)} - \Delta S_{i(n=3)})/R],$$

where  $\Delta S_{i(n)}$  and  $\Delta S_{i(n=3)}$  are the corresponding entropies of the reactions.

Activation energies  $E_i$  satisfy the approximate equations [9]

$$E_i = 11.5 - 0.25\Delta H_i \text{ for exothermic reactions}$$

and

$$E_i = 11.5 + 0.75\Delta H_i \text{ for endothermic reactions.}$$

Here,  $\Delta H_i$  is the enthalpy of the reaction. It follows that reactions of the same type in the mechanisms of hydrocarbon C<sub>*n*</sub>H<sub>2*n*+2</sub> and propane ( $n = 3$ ) oxidation are characterized by the equations

$$E_{i(n)} = E_{i(n=3)} - 0.25[\Delta H_{i(n)} - \Delta H_{i(n=3)}] \\ \text{for exothermic reactions,}$$

$$E_{i(n)} = E_{i(n=3)} + 0.75[\Delta H_{i(n)} - \Delta H_{i(n=3)}] \\ \text{for endothermic reactions,}$$

where  $\Delta H_{i(n)}$  and  $\Delta H_{i(n=3)}$  are the enthalpies of the reactions. It follows that reaction rates in the mechanism for a hydrocarbon with the number of carbon atoms  $n > 3$  can be estimated using the Arrhenius parameters of reaction rates from the mechanism of propane oxidation. The validity of this approach can be checked using the kinetic data published in the literature.

Compared with the mechanism of propane oxidation, we had to introduce a new species and 84 new elementary reactions into the mechanism of *n*-butane oxidation; these are listed in Table 2. The mechanism of *n*-butane oxidation obtained included a total of 54 species and 288 reversible reactions.

Critical chemical kinetics phenomena (e.g., the appearance of cool or blue flame in multistage ignition [5]) are known to be polyfunctional and exist at a certain ratio between the rates of elementary reactions. For this reason, the construction of models of the observed phenomena requires bringing approximate governing kinetic parameter values into consistency with each other. In other words, we must additionally analyze and select rate constants within the range of theoretically acceptable values, and our analysis should take into account measurement errors in these constants. The new compact mechanism of *n*-butane oxidation required the corresponding corrections to be introduced into eight elementary reactions, including *n*-butane

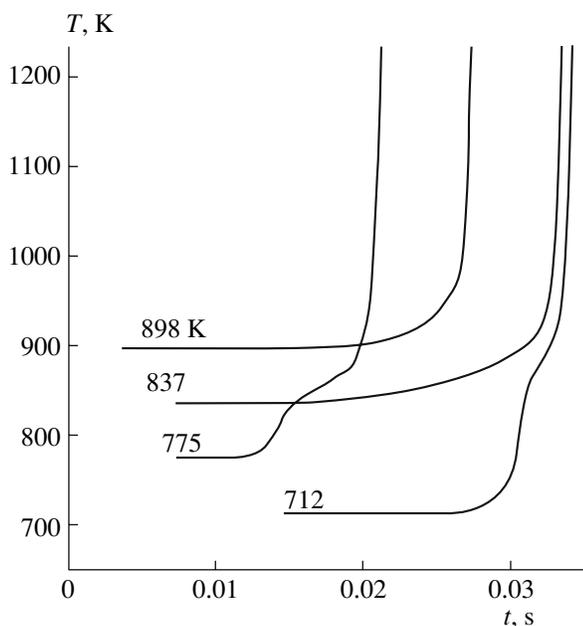
**Table 2.** Mechanism of butane oxidation and combustion

No.	Reaction	A, l, mol, s	E/R, K
1	$C_4H_{10} + O_2 = C_4H_9 + HO_2$	0.259E+10	0.240E+05
2	$C_4H_{10} + OH = C_4H_9 + H_2O$	0.409E+10	0.580E+03
3	$C_4H_{10} + H = C_4H_9 + H_2$	0.603E+11	0.401E+04
4	$C_4H_{10} + O = C_4H_9 + OH$	0.328E+12	0.481E+04
5	$C_4H_{10} + HO_2 = C_4H_9 + H_2O_2$	0.389E+09	0.862E+04
6	$C_4H_8 + H = C_4H_9$	0.141E+10	0.652E+03
7	$C_4H_9 + O_2 = C_4H_8 + HO_2$	0.300E+11	0.700E+04
8	$C_4H_9 + OH = C_4H_8 + H_2O$	0.803E+10	-0.337E+03
9	$C_4H_{10} = H + C_4H_9$	0.233E+14	0.376E+05
10	$C_4H_{10} = CH_3 + C_3H_7$	0.324E+16	0.422E+05
11	$C_4H_{10} = C_2H_5 + C_2H_5$	0.194E+17	0.428E+05
12	$C_4H_9 + H = C_4H_8 + H_2$	0.803E+10	-0.337E+03
13	$C_4H_9 + CH_3 = C_4H_8 + CH_4$	0.470E+09	-0.443E+03
14	$C_4H_9 + C_2H_5 = C_4H_8 + C_2H_6$	0.131E+09	0.128E+03
15	$C_4H_9 + C_3H_7 = C_4H_8 + C_3H_8$	0.184E+09	0.151E+03
16	$C_4H_9 + O = C_4H_8 + OH$	0.268E+12	-0.337E+03
17	$C_4H_9 + O_2 = C_4H_9O_2$	0.684E+09	-0.659E+03
18	$C_4H_{10} + CH_3O_2 = C_4H_9 + CH_3O_2H$	0.890E+10	0.600E+04
19	$C_4H_{10} + C_2H_5O_2 = C_4H_9 + C_2H_5O_2H$	0.890E+10	0.600E+04
20	$C_4H_{10} + C_3H_7O_2 = C_4H_9 + C_3H_7O_2H$	0.890E+10	0.600E+04
21	$C_4H_{10} + C_4H_9O_2 = C_4H_9 + C_4H_9O_2H$	0.890E+10	0.600E+04
22	$C_4H_9O_2H = C_4H_9O + OH$	0.643E+16	0.198E+05
23	$C_4H_9O = H_2CO + C_3H_7$	0.257E+15	0.983E+04
24	$C_4H_9O = CH_3CHO + C_2H_5$	0.627E+15	0.975E+04
25	$C_4H_9O = C_2H_5CHO + CH_3$	0.126E+15	0.991E+04
26	$C_4H_9O = C_4H_8O + H$	0.108E+13	0.834E+04
27	$C_4H_9O_2 + H = C_4H_9O + OH$	0.105E+10	-0.830E+03
28	$C_4H_9O_2 + CH_3 = C_4H_9O + CH_3O$	0.162E+08	0.614E+03
29	$C_4H_9O_2 + C_2H_5 = C_4H_9O + C_2H_5O$	0.369E+08	0.131E+03
30	$C_4H_9O_2 + C_3H_7 = C_4H_9O + C_3H_7O$	0.281E+08	0.780E+03
31	$C_4H_9O_2 + C_4H_9 = C_4H_9O + C_4H_9O$	0.214E+08	0.140E+04
32	$C_4H_9O_2 + H_2CO = C_4H_{10}O_2 + HCO$	0.111E+08	0.353E+04
33	$C_4H_9O_2 + CH_3CHO = C_4H_{10}O_2 + CH_3CO$	0.109E+08	0.364E+04
34	$C_4H_9O_2 + C_2H_5CHO = C_4H_{10}O_2 + C_2H_5CO$	0.109E+08	0.382E+04
35	$C_4H_9O_2 + C_4H_8O = C_4H_{10}O_2 + C_4H_7O$	0.109E+08	0.401E+04
36	$C_4H_9 + HO_2 = C_4H_9O + OH$	0.229E+11	0.622E+03
37	$C_4H_9 + O_2 = C_4H_8O + OH$	0.479E+10	0.893E+04
38	$C_4H_9 + C_2H_5 = C_4H_{10} + C_2H_4$	0.963E+09	0.355E+03
39	$C_4H_9 + C_3H_7 = C_4H_{10} + C_3H_6$	0.293E+10	0.201E+02
40	$C_4H_9 + C_4H_9 = C_4H_{10} + C_4H_8$	0.392E+10	-0.317E+03
41	$C_4H_9 + O_2 = H_2CO + C_3H_7O$	0.400E+09	0.500E+04
42	$C_4H_9 + O_2 = CH_3CHO + C_2H_5O$	0.400E+09	0.500E+04
43	$C_4H_9 + O_2 = C_2H_5CHO + CH_3O$	0.400E+09	0.500E+04
44	$C_4H_9 + OH = CH_3 + C_3H_7O$	0.229E+11	-0.104E+04
45	$C_4H_9 + OH = C_2H_5 + C_2H_5O$	0.179E+12	-0.228E+03

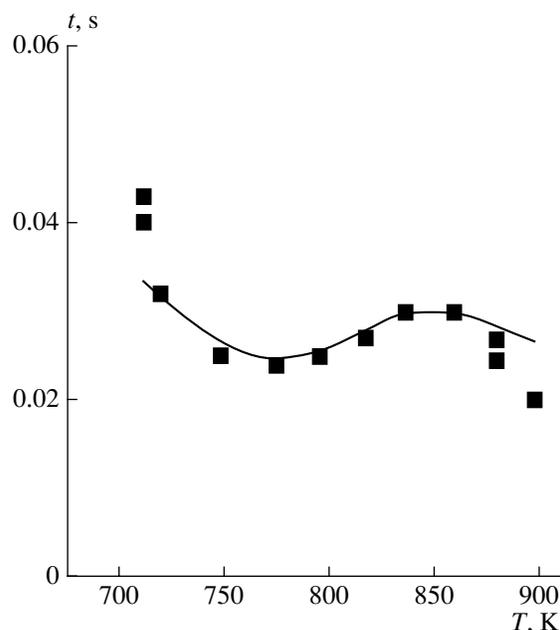
Table 2. (Contd.)

No.	Reaction	A, l, mol, s	E/R, K
46	$C_4H_9 + OH = C_3H_7 + CH_3O$	0.132E+11	0.481E+03
47	$C_4H_9 + H = CH_3 + C_3H_7$	0.480E+11	0.547E+03
48	$C_4H_9 + H = C_2H_5 + C_2H_5$	0.287E+12	0.322E+03
49	$C_4H_9 + H = CH_2 + C_3H_8$	0.845E+10	0.302E+04
50	$C_4H_9 + H = C_2H_4 + C_2H_6$	0.127E+10	-0.143E+04
51	$C_4H_9 + H = C_3H_6 + CH_4$	0.232E+10	-0.111E+04
52	$C_4H_9 + O = H + C_4H_8O$	0.842E+09	0.494E+03
53	$C_4H_9 + O = CH_3 + C_2H_5CHO$	0.979E+11	-0.951E+03
54	$C_4H_9 + O = C_2H_5 + CH_3CHO$	0.487E+12	-0.111E+04
55	$C_4H_9 + O = C_3H_7 + H_2CO$	0.200E+12	-0.252E+01
56	$C_4H_7O + HO_2 = C_4H_8O + O_2$	0.530E+08	0.629E+02
57	$C_4H_8O + OH = C_4H_7O + H_2O$	0.100E+11	-0.629E+02
58	$C_4H_8O + H = C_4H_7O + H_2$	0.140E+11	0.159E+04
59	$C_4H_8O + O = C_4H_7O + OH$	0.568E+10	0.717E+03
60	$C_4H_8O + HO_2 = C_4H_7O + H_2O_2$	0.600E+09	0.494E+04
61	$C_3H_7 + HCO = C_4H_8O$	0.216E+11	-0.679E+02
62	$C_3H_7 + CO = C_4H_7O$	0.181E+09	0.229E+04
63	$C_4H_7O + H = C_3H_7 + HCO$	0.501E+10	0.253E+04
64	$C_4H_7O + O = C_3H_7O + CO$	0.381E+10	0.780E+03
65	$C_4H_8 + OH = C_4H_7 + H_2O$	0.241E+11	0.392E+04
66	$C_4H_7 + H_2 = C_4H_8 + H$	0.319E+12	0.735E+04
67	$C_4H_7 + O_2 = C_2H_5O_2 + C_2H_2$	0.608E+11	0.547E+04
68	$C_4H_8 + HCO = C_4H_7 + H_2CO$	0.161E+11	0.698E+04
69	$C_4H_8 + CH_3 = C_4H_7 + CH_4$	0.286E+08	0.336E+04
70	$C_4H_8 + C_2H_5 = C_4H_7 + C_2H_6$	0.797E+07	-0.105E+04
71	$C_4H_8 + C_3H_7 = C_4H_7 + C_3H_8$	0.112E+08	-0.112E+04
72	$C_2H_5 + C_2H_2 = C_4H_7$	0.330E+09	0.176E+04
73	$C_4H_8 = C_2H_3 + C_2H_5$	0.446E+14	0.369E+05
74	$C_4H_8 = C_3H_5 + CH_3$	0.268E+13	0.429E+05
75	$C_4H_8 + O_2 = C_4H_7 + HO_2$	0.161E+11	0.215E+05
76	$C_4H_8 + O = C_3H_7 + HCO$	0.373E+10	0.565E+03
77	$C_4H_7 + OH = C_3H_7 + HCO$	0.168E+11	-0.339E+03
78	$C_4H_7 + H = C_2H_6 + C_2H_2$	0.278E+11	0.679E+01
79	$C_4H_7 + O = C_3H_7 + CO$	0.168E+11	-0.339E+03
80	$C_4H_7 + O = C_2H_5O + C_2H_2$	0.227E+12	-0.105E+04
81	$CH_3 + C_3H_7 = C_4H_8 + H_2$	0.268E+10	0.188E+03
82	$C_2H_5 + C_2H_5 = C_4H_8 + H_2$	0.449E+09	0.190E+03
83	$C_4H_8 + H + H = CH_3 + C_3H_7$	0.134E+07	-0.467E+03
84*	$C_4H_8 + H + H = C_2H_5 + C_2H_5$	0.802E+07	-0.489E+03

\* Further, the mechanism of C<sub>1</sub>–C<sub>3</sub> oxidation (see [4]).



**Fig. 1.** Calculated time dependences of temperature in self-ignition of an *n*-butane–air mixture at various initial temperatures; mixture composition 3.11% *n*-C<sub>4</sub>H<sub>10</sub> + air, initial pressure  $P_0 = 10.22$  ata.



**Fig. 2.** Self-ignition delay times for a 3.11% *n*-C<sub>4</sub>H<sub>10</sub>–20.25% O<sub>2</sub>–N<sub>2</sub>–Ar mixture at various initial temperatures and pressures  $P_0 = 9.39$ –11.85 ata; the experimental data [12] are shown by squares, and calculation results, by a solid line.

reactions with hydroperoxyl radicals and butyl radical reactions with molecular oxygen.

### MECHANISM VERIFICATION

The predicting ability of the new mechanism was checked by applying it to characterize the oxidation and self-ignition of *n*-butane described in the literature [10].

The oxidation and self-ignition of a homogeneous mixture of *n*-butane and an oxidizer is described by material and heat balance equations at a constant volume as [11]

$$\frac{dn_j}{dt} = \sum_i w_{ij}, \quad (1)$$

$$\rho c_v \frac{dT}{dt} = \sum_{i,j} \Delta H_{ij} w_{ij} + \kappa F(T - T_w)/V, \quad (2)$$

where  $n_j$  is the concentration of the  $j$ th component,  $t$  is the time,  $\rho$  is the density,  $c_v$  is the heat capacity at a constant volume,  $w_{ij}$  and  $\Delta H_{ij}$  are the rate and heat effect of the  $i$ th reaction with the participation of the  $j$ th component,  $\kappa$  is the coefficient of heat transfer to the reactor wall,  $F$  and  $V$  are the surface area and volume of the reaction vessel or combustion chamber, and  $T_w$  is the temperature of the wall. The first term on the right-hand side of (2) corresponds to heat release in the reaction, and the second term, to heat exchange with the wall. The density was determined according to the equation of state of an ideal gas as  $\rho = P/RT$ , where  $P$  is the pres-

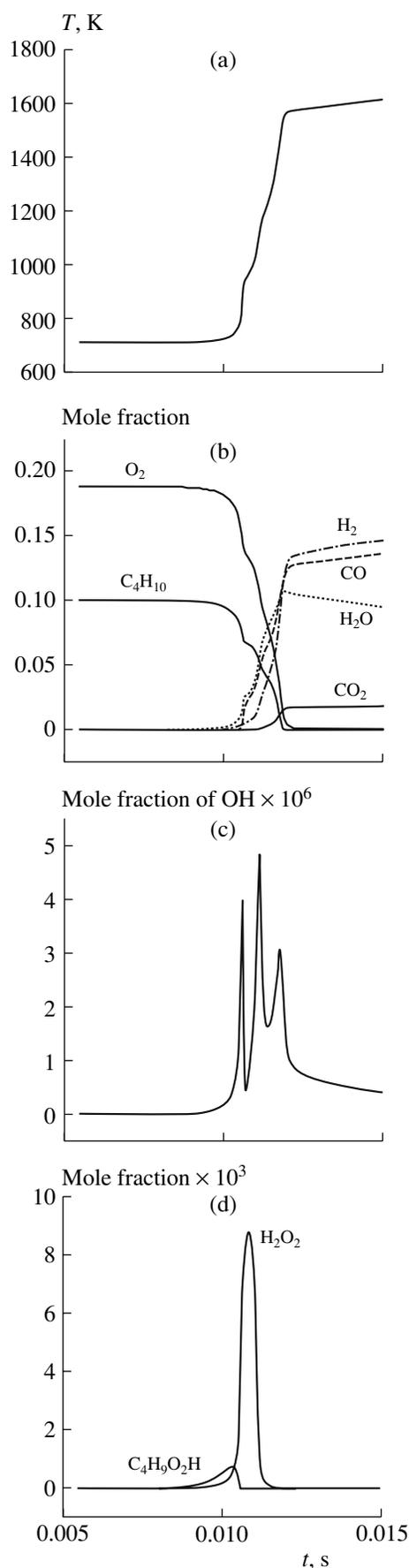
sure. System (1), (2) was augmented by the initial conditions

$$\text{at } t = 0 \quad n = n_{j0}, \quad T = T_0.$$

### Minetti Experiments [12]

Reactions on reactor walls and heat loss to the environment can be ignored at comparatively high pressures and low temperatures [11]. Typical calculated time dependences of the temperature characteristic at the self-ignition of an *n*-butane–air mixture are shown in Fig. 1. We see that mixture self-ignition at low temperatures involves two stages. First, cool flame appears, and then hot explosion occurs. The two-stage character of self-ignition results in a negative reaction rate temperature coefficient in both calculations and experiment [12]. According to these data, self-ignition delay is the larger the higher the initial temperature (Fig. 2).

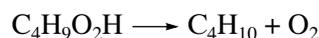
The multistage character of self-ignition characteristic of hydrocarbon oxidation manifests itself under certain conditions [4]. The results obtained in self-ignition calculations for a 10% *n*-C<sub>4</sub>H<sub>10</sub>–air mixture at the initial temperature  $T_0 = 712$  K and initial pressure  $P_0 = 9.4$  ata are shown by way of example in Figs. 3a–3d. The temperature and concentration curves for stable and intermediate (hydroxyl) products contain characteristic “waves” corresponding to multistage self-ignition with the sequential appearance of cool and blue flame and then hot explosion. Cool flames appear in the decay of alkylhydroperoxides such as butylhydroper-



oxide  $C_4H_{10}O_2H$  in the process under consideration. The decay of alkylhydroperoxides is accompanied by chain branching, a sharp increase in the concentration of hydroxyls, and an increase in the rate of  $n$ - $C_4H_{10}$  oxidation. After the consumption of alkylhydroperoxide accumulated, the reaction rate decreases, and hydrogen peroxide  $H_2O_2$  begins to accumulate. Its subsequent decay is a branching, it manifests itself by the second hydroxyl concentration maximum corresponding to the appearance of blue flame. The subsequently increasing rate of branching in the reaction between atomic hydrogen  $H$  and molecular oxygen  $O_2$  results in the appearance of the third hydroxyl concentration maximum and hot explosion.

#### Dechaux Experiments [13]

Reactions on walls and heat loss to the environment through reactor walls should be included at low pressures and temperatures [11]. Reactions on walls involved in oxidation have been studied poorly, and we do not take them into account except effective diffusion reactions of the decay of alkylhydroperoxide,



and hydrogen peroxide,



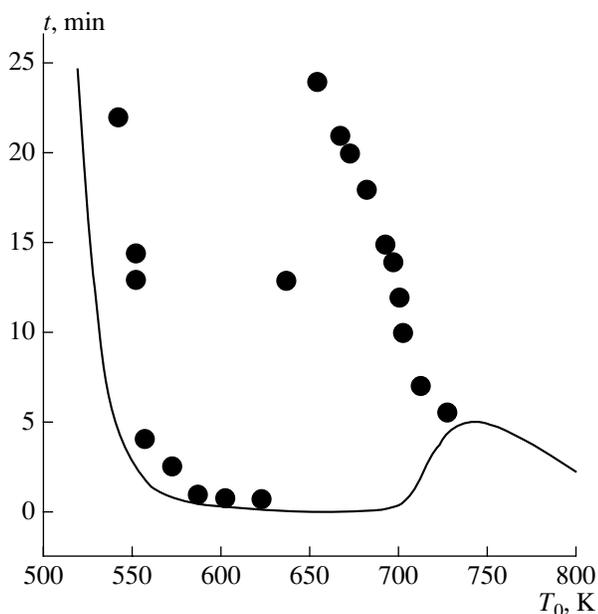
with the formation of stable products. The diffusion rate constant for these reactions [11] is

$$K = 23.2 \frac{D}{d^2},$$

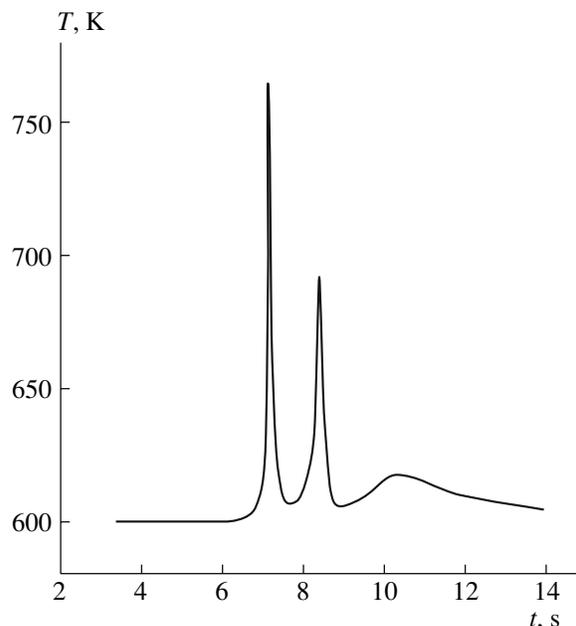
where  $D$  is the diffusion coefficient and  $d$  is the diameter of the reactor. As far as heat transfer to reactor walls is concerned, the heat transfer coefficient changed over the range  $\kappa F/V \approx 13.7$ – $35.2$  cal/(l s) under the conditions used in [13].

The calculated and experimental temperature dependences of the reaction delay time at equal pressures ( $P_0 = 52$  torr) are compared in Fig. 4. Negative temperature coefficient regions are clearly seen in both experimental and calculated dependences, at  $T_0 = 625$ – $660$  and  $700$ – $730$  K, respectively. To the left of the negative temperature coefficient region (at low temperatures), we observe cool flame. To the right of it, oxidation reactions occur at a low rate, and the delay is indistinct. The calculated time dependence of temperature is

←  
**Fig. 3.** Self-ignition calculations for a 10%  $n$ - $C_4H_{10}$ -air mixture at  $T_0 = 712$  K and  $P_0 = 9.4$  ata: (a) temperature, (b) stable product concentrations, (c) hydroxyl concentration, and (d) concentrations of  $C_4H_9O_2H$  and  $H_2O_2$  peroxides.



**Fig. 4.** Self-ignition delay times for a 20%  $n\text{-C}_4\text{H}_{10}$ –80%  $\text{O}_2$  mixture at various initial temperatures and pressure  $P_0 = 52$  torr; the experimental data [13] are shown by solid circles, and calculation results, by a curve.



**Fig. 5.** Calculated time dependence of temperature for a 20%  $n\text{-C}_4\text{H}_{10}$ –80%  $\text{O}_2$  mixture at  $T_0 = 600$  K and  $P_0 = 52$  torr.

shown in Fig. 5 for  $T_0 = 600$  K and  $P_0 = 52$  torr. The dependence contains three sequential temperature peaks corresponding to three cool flames. Cool flames disappear at higher temperatures. Note that the calculation results and experimental data are in satisfactory phenomenological and qualitative agreement but substantially diverge quantitatively. The divergence is likely caused by the exclusion of wall reactions from consideration.

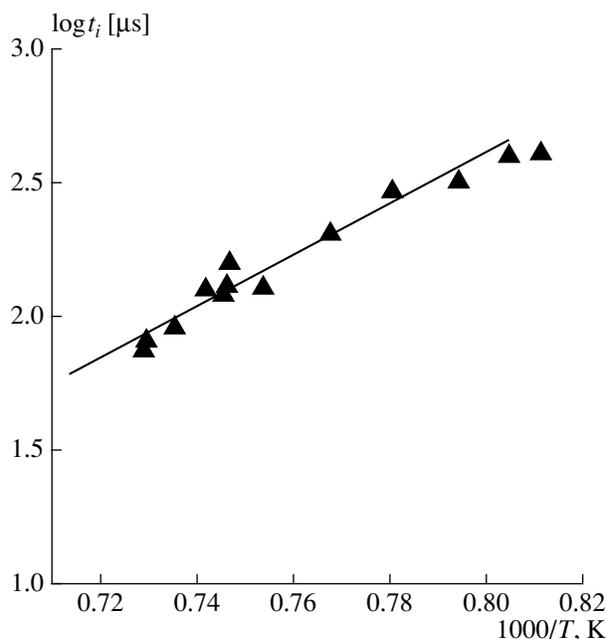
#### *Burcat Experiments [14]*

The calculated and experimental [14] self-ignition delay times for a 2.5%  $n\text{-C}_4\text{H}_{10}$ –20%  $\text{O}_2$ –Ar mixture at high initial temperatures and pressures from 9.19 to 10.58 ata are shown in Fig. 6. Ignition delay times were calculated as times required to reach a  $10^7$  K/s temperature increase rate. Such a definition of the ignition delay time allowed us to obtain results close to those obtained using other generally accepted definitions (based on the intersection of the tangents to the temperature curve etc.). Note that the results closely agree with each other quantitatively and qualitatively.

#### *Flame Propagation Experiments [15–19]*

The new kinetic mechanism was checked by calculating the laminar flame propagation velocity  $u_n$  in an  $n$ -butane–air mixture under normal conditions (atmospheric pressure and initial temperature  $T_0 = 293$  K). The calculations were performed following the proce-

cedure described in [20]. The  $u_n = 34.8$  cm/s value was obtained for a stoichiometric mixture. The laminar flame propagation velocity measured in [15–19] was  $u_n = 33.1$ – $44.5$  cm/s.



**Fig. 6.** Self-ignition delay times for a 2.5%  $n\text{-C}_4\text{H}_{10}$ –20%  $\text{O}_2$ –Ar mixture at various initial temperatures and  $P_0 = 9.39$ – $10.58$  ata; the experimental data [14] are shown by triangles, and calculation results, by a solid line.

## CONCLUSIONS

A new compact mechanism of *n*-butane oxidation containing 54 species and 288 reversible reactions was constructed using the algorithm suggested in [4]. The mechanism was verified by comparing the calculation results with the experimental data over wide ranges of initial temperatures, pressures, and compositions of *n*-butane mixtures with air and oxygen. The conclusion can be drawn that, on the whole, satisfactory qualitative agreement with measurement results was obtained. The principles for constructing compact mechanisms of the oxidation of normal alkane hydrocarbons suggested in [4] and tested for the examples of propane and *n*-butane are likely also applicable to the higher *n*-alkanes.

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