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Detailed Kinetic Mechanism of the Combustion of Homogeneous Gaseous Mixtures with Participation of Oxygen-containing Oxidants

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The kinetic mechanisms of the oxidation and combustion of hydrogen, methane, methyl alcohol, acetylene, ethylene, ethane, and methylamine, using oxygen as well as hydrogen peroxide and nitric acid as oxidants, are discussed. The calculated and experimental data obtained under static conditions, in a flow, during flame propagation, and in shock tubes are compared. The bibliography includes 184 references.

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I. INTRODUCTION

The aim of the present review is a joint examination of the available kinetic schemes for the oxidation of hydrogen, hydrocarbons, and their derivatives, which permit the construction of fairly general detailed kinetic mechanisms (DKM) of oxidation and combustion processes. It has been found that, despite the individual differences between the initial molecules of the fuel and the oxidant, the atomic composition of such molecules is important for the course of the reaction. Depending on this composition, the same or different intermediate species are formed which determine the character of the interaction. Even when all the reaction channels are not know accurately and despite extremely approximate values of the rate constants being frequently employed, it is possible to achieve by computation a fairly satisfactory description of the kinetics of experimental processes.

We may note that, although the questions analysed below are of intrinsic importance, they constitute a small part of the general kinetic theory whose foundations have been laid in a number of fundamental monographs and textbooks (see, for example, Refs.1–10).

The number of fuels and oxidants used in practice and important for the theory of combustion processes is very large. Fuels having a complex multicomponent composition are usually employed. However, at the present time one may hope to be able to construct detailed kinetic mechanisms only for an extremely limited number of simplest fuel–oxidant pairs, which are the subject of the exposition below. Complex compositions can be modelled by simpler ones but even the latter have frequently a direct practical application.

II. HYDROGEN AND HYDROGEN PEROXIDE

The principal characteristics of the DKM of combustion can be illustrated in relation to the oxidation of hydrogen. The mechanism of the oxidation of hydrogen has become one of the first DKM in the study of which many fundamental postulates of chemical kinetics were developed and tested, including the theory of branched processes.[1,2,6,7,11–19]

Extensive experimental data referring to the oxidation of hydrogen, mainly in the region of the ignition peninsula, and all the known fundamental elementary stages of the process were described, i.e. in essence a DKM had been constructed, already in a monograph of Nalbandyan and Voevodskii[8] and then in the studies of Semenov[1] and Kondrat'ev[7] [Table 1, reactions† (1), (–4), (–6), (7), (–8), (–11), (–14a), and (–83)].

In these studies it is possible to find all the fundamental features of simple and branched chain hydrogen oxidation reactions (as well as the oxidation reactions of hydrocarbons and other combustible substances), including those accompanied by a rise of temperature, and the relevant communications give compilations of numerous experimental and calculated data and comparisons which provide a quantitative justification of the theory. A general solution of many ignition problems can be found with the aid of the following approximate system of equations:[2,7,16]

$$\frac{dn_j}{dt} = \sum_l w_{lj} \,, \qquad (I)$$

$$\rho C \frac{dT}{dt} = \sum_{il} h_{il} w_{il} + \frac{\varkappa S}{V}(T - T_c) \,, \qquad (II)$$

where n_j is the concentration of species j, t the time, T the temperature, ρ the density, C the heat capacity, and ω_{ij} and h_{ij} are respectively the rate and heat of reaction in the i^{th} elementary step with participation of the j^{th} component, κ is the coefficient of heat evolution in the wall of the reaction vessel, S and V are respectively the surface and volume of the reaction vessel, and T_c is the temperature of the vessel wall. The usual initial conditions apply: $t = 0$, $n_j = n_{j0}$, and $T = T_0$.

Later communications contain a series of revisions which specify in greater detail the mechanism of the combustion of hydrogen. Thus a mechanism has been proposed[17] for the oxidation of hydrogen under conditions remote from the ignition peninsula, namely under detonation conditions characterised by high temperatures and pressures. For this reason, a number of bi- and tri-molecular processes involving the recombination of active centres, which in this case play a significant role owing to the high concentration of atoms and radicals, have been included in the mechanism [Table 1, reactions (11)–(13), (19), and (83)].

It has been established[18,19] that the mechanism of the ignition reaction of hydrogen–oxygen mixtures, proposed by Nalbandyan and Voevodskii[8] and supplemented by recombination processes of the kind described above is very suitable for the description of the propagation of a laminar flame. This follows from a comparison of the calculated and experimental data for the rate of heat evolution Σhw in the reaction zone at low pressures P (Fig. 1). A theoretical basis for such calculations is provided by the system of equations describing the stationary one-dimensional propagation of the flame:[2,7,16]

$$\frac{d}{dx} D_j \rho \frac{d(n_j/\rho)}{dx} - \rho_0 u_n \frac{d(n_j/\rho)}{dx} + \sum_l w_{lj} = 0 \,, \qquad (III)$$

$$\frac{d}{dx} \lambda \frac{dT}{dx} - \rho_0 u_n \frac{dCT}{dx} + \sum_{ij} h_{il} w_{il} = 0 \,, \qquad (IV)$$

where x is the coordinate of the propagation of the flame, λ the thermal conductivity, u_n the laminar rate of propagation of the flame, ρ_0 and ρ are respectively the initial and current densities, and D_j is the diffusion coefficient of the jth component of the chemical reactions. The boundary conditions at $x = 0$ and $x = 1$ (end of the reaction zone) are as follows:

$$\left(T - \frac{\lambda}{\rho_0 u_n C}\frac{dT}{dx}\right)\Big|_{x=0} = T_0; \quad \left(n_j - \frac{\rho D_j}{u_n \rho_0}\frac{dn_j}{dx}\right)\Big|_{x=0} = n_{j0};$$
$$\frac{dT}{dx}\Big|_{x=l} = 0; \quad \frac{dn_j}{dx}\Big|_{x=l} = 0 \,.$$

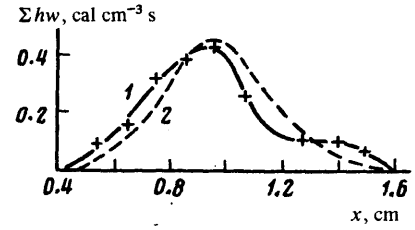


Figure 1. Dependence of the rate of heat evolution on the coordinates in the reaction zone;[19] $[H_2]_0 = 7.2\%$, $[O_2]_0 = 92.8\%$, $T = 295$ K, $P = 0.068$ atm, rate of propagation of the flame $u_n = 19.6$ cm s^{-1}: *1*) experiment; *2*) calculation (here and henceforth volume percentages are quoted).

The rate of heat evolution profile was calculated from the material balance equations (III) in which the terms describing the appearance and consumption of each substance were set up on the basis of the kinetic scheme [Table 1, reactions (1), (–4), (–6), (7), (11), (12), (17), and (28)]. Readings of the non-inertial resistance thermometer on a spherical bomb with central ignition were used to determine $T(x)$.[18]

Here it is necessary to make certain general remarks concerning the rate constants. For certain reactions, these quantities have been frequently measured by different workers and fairly similar results have been obtained. However, frequently there is a large scatter in the experimental values. In such cases (and these are in the majority) it is sometimes difficult to find arguments for the justification of the *a priori* selection of the value of the rate constant and the problem is solved by comparing the calculated data with the results of experiments carried out under different initial conditions. Special attention has been devoted in the present review to such comparisons. Furthermore, we may note that processes corresponding to the exothermic direction of the reaction are regarded as forward processes, while those involving the endothermic direction of the reaction are regarded as reverse processes. Strictly speaking, it is necessary to take into account all the forward and reverse processes. However, in each specific calculation one needs to consider only those which contribute appreciably to the development of the process.

†Here and henceforth M is any third species removing or supplying energy; the minus sign refers to the reverse reaction.

Table 1. Combustion mechanisms.

No. of reaction	Reaction	h, kcal mol^{-1}	Forward reaction			Reverse reaction		
			A, mol litre^{-1}s^{-1}	E, kcal mol^{-1}	Refs.	A, mol litre^{-1}s^{-1}	E, kcal mol^{-1}	Refs.
1	$OH+H_2 \rightleftarrows H+H_2O$	15	$2.4\cdot10^{10}$	5.2	[20]	$1.14\cdot10^{11}$	20.4	—
4	$OH+O \rightleftarrows H+O_2$	17	$4.16\cdot10^{9}$	−0.78	—	$7.8\cdot10^{10}$	15.9	[21]
6	$OH+H \rightleftarrows O+H_2$	2	$6.9\cdot10^{9}$	7.04	—	$1.5\cdot10^{10}$	8.9	[22]
9	$OH+OH \rightleftarrows O+H_2O$	17	$1.44\cdot10^{10}$	0	[23]	$1.51\cdot10^{11}$	17	—
11	$H+H+M \rightleftarrows H_2+M$	103	$3.6\cdot10^{9}$	0	[24]	$1.74\cdot10^{13}$	105	—
12	$O+O+M \rightleftarrows O_2+M$	118	$1.8\cdot10^{9}$	0	[25]	$7.4\cdot10^{13}$	120	—
13	$OH+H+M \rightleftarrows H_2O+M$	118	$3.6\cdot10^{10}$	0	[24]	$8.3\cdot10^{14}$	120	—
19	$O+H+M \rightleftarrows OH+M$	101	$1.44\cdot10^{10}$	0	[17]	$3.1\cdot10^{13}$	104	—
83	$OH+OH \rightleftarrows H_2+O_2$	19	$6\cdot10^{7}$	20.4	—	$2.5\cdot10^{9}$	39	[26]
17a	$H+HO_2 \rightleftarrows H_2+O_2$	56	$6\cdot10^{9}$	0	[27]	$1.1\cdot10^{10}$	56	—
7	$H+O_2+M \rightleftarrows HO_2+M$	47	$4.14\cdot10^{9}$	0	[28]	$5.7\cdot10^{12}$	48.8	—
17	$H+HO_2 \rightleftarrows OH+OH$	37	$2\cdot10^{10}$	0	[29]	$1.62\cdot10^{9}$	37.6	—
26	$O+HO_2 \rightleftarrows O_2+OH$	54	$6\cdot10^{10}$	0	[28]	$9.43\cdot10^{10}$	54	—
27	$OH+HO_2 \rightleftarrows O_2+H_2O$	71	$6\cdot10^{9}$	0	[30]	$9.9\cdot10^{10}$	71.2	—
17d	$H+HO_2 \rightleftarrows H_2O+O$	54	$6\cdot10^{9}$	0	[29]	$5.28\cdot10^{8}$	54.4	—
8	$OH+H_2O_2 \rightleftarrows HO_2+H_2O$	31	$7.8\cdot10^{9}$	1.6	[31]	$8.45\cdot10^{9}$	32.6	—
14	$H+H_2O_2 \rightleftarrows H_2O+OH$	66	$7.05\cdot10^{9}$	4.2	[32]	$6.4\cdot10^{8}$	72.6	—
28	$OH+OH+M \rightleftarrows H_2O_2+M$	50	$1.61\cdot10^{8}$	−9.6	—	$4.07\cdot10^{13}$	42	[33]
30	$O+H_2O_2 \rightleftarrows O_2+H_2O$	42,5	$2.8\cdot10^{10}$	6.4	[32]	$4.77\cdot10^{10}$	91.4	—
14a	$H+H_2O_2 \rightleftarrows H_2+HO_2$	16	$7\cdot10^{9}$	4.2	[32]	$1.6\cdot10^{9}$	20	—
29a	$HO_2+HO_2 \rightleftarrows H_2O_2+O_2$	40	$2.4\cdot10^{10}$	1.5	[32]	$3.67\cdot10^{11}$	41.8	—
32	$O+H_2O_2 \rightleftarrows HO_2+OH$	14	$2.8\cdot10^{10}$	6.4	[32]	$2.89\cdot10^{9}$	20.4	—
21	$CO+OH \rightleftarrows CO_2+H$	26	$2.9\cdot10^{9}$	5.7	[34]	$1.12\cdot10^{13}$	30.4	—
24	$CO+HO_2 \rightleftarrows CO_2+OH$	62	$1.33\cdot10^{11}$	23	[35]	$4.26\cdot10^{12}$	85	—
43	$H_2CO+OH \rightleftarrows HCO+H_2O$	45	$3.6\cdot10^{11}$	1.5	[36]	$1\cdot10^{11}$	46.4	—
44	$H_2CO+H \rightleftarrows HCO+H_2$	30	$6\cdot10^{10}$	1.5	[37]	$3.7\cdot10^{9}$	31	—
45	$H_2CO+O \rightleftarrows HCO+OH$	28	$8.4\cdot10^{11}$	5.5	[38]	$2.3\cdot10^{10}$	33.4	—
47	$HCO+HO_2 \rightleftarrows H_2CO+O_2$	26	$5.35\cdot10^{6}$	5.6	—	$3\cdot10^{9}$	32	[1]
66	$H+CO+M \rightleftarrows HCO+M$	30	$1\cdot10^{8}$	−17	—	$1.6\cdot10^{11}$	14.7	[39]
48	$H_2CO+HO_2 \rightleftarrows H_2O_2+HCO$	14	$6\cdot10^{6}$	8	[1]	$1.6\cdot10^{6}$	22	—
70	$HCO+O_2 \rightleftarrows HO_2+CO$	17	$6\cdot10^{10}$	7.25	[37]	$5.5\cdot10^{10}$	24.4	—
86	$HCO+O \rightleftarrows CO_2+H$	96	$1.2\cdot10^{9}$	0	[40]	$6.8\cdot10^{11}$	96	—
46a	$HCO+H+M \rightleftarrows H_2CO+M$	73	$6.3\cdot10^{8}$	−3.2	—	$5\cdot10^{13}$	72	[39]
68	$HCO+OH \rightleftarrows CO+H_2O$	88	$6\cdot10^{10}$	0	[37]	$8.9\cdot10^{11}$	88	—
69	$HCO+H \rightleftarrows CO+H_2$	73	$6.\cdot10^{10}$	5	[37]	$1.9\cdot10^{11}$	78	—
70a	$HCO+O \rightleftarrows CO+OH$	71	$6\cdot10^{9}$	0	[41]	$8.5\cdot10^{9}$	71.6	—
31	$CH_4+OH \rightleftarrows CH_3+H_2O$	17	$6\cdot10^{10}$	8.5	[42]	$6.9\cdot10^{9}$	24.8	—
33	$CH_4+H \rightleftarrows CH_3+H_2$	2	$2\cdot10^{11}$	11.6	[43]	$4.8\cdot10^{9}$	12.5	—
35	$CH_4+O \rightleftarrows CH_3+OH$	0	$2.05\cdot10^{10}$	7.8	[44]	$2.2\cdot10^{6}$	7.0	—
39	$CH_4+O \rightleftarrows CH_3+H_2O$	34	$2\cdot10^{10}$	7.8	[44]	$8.3\cdot10^{9}$	41.4	—
40	$CH_3+HO_2 \rightleftarrows CH_4+O_2$	54	$4.3\cdot10^{6}$	−0.4	—	$6\cdot10^{10}$	55	[1]
55	$CH_3+H+M \rightleftarrows CH_4+M$	101	$1\cdot10^{9}$	−15.8	—	$2\cdot10^{14}$	88	[45]
38	$CH_3+H_2O_2 \rightleftarrows CH_4+HO_2$	14	$6.5\cdot10^{7}$	4.3	—	$6.06\cdot10^{6}$	19	[46]
42	$CH_3+CH_3 \rightleftarrows CH_4+CH_2$	17	$6\cdot10^{7}$	9.24	[30]	$1.9\cdot10^{9}$	27.4	—
50	$CH_3+H_2CO \rightleftarrows CH_4+HCO$	28	$6\cdot10^{10}$	4.5	[37]	$1.5\cdot10^{11}$	33.2	—
72	$CH_3+HCO \rightleftarrows CH_4+CO$	71	$6\cdot10^{10}$	0	[37]	$7.8\cdot10^{12}$	72.2	—
53	$CH_3+H_2CO \rightleftarrows CH_4+CO$	82	$6\cdot10^{10}$	0	[37]	$6\cdot10^{11}$	82.6	—
54	$CH_3+OH \rightleftarrows CH_2+H_2O$	34	$6\cdot10^{9}$	2.76	[30]	$2.2\cdot10^{10}$	37.2	—
59	$CH_2+O \rightleftarrows HCO+H$	79	$6\cdot10^{9}$	0	[30]	$9.5\cdot10^{9}$	78.6	—
65	$CH_2+H_2O \rightleftarrows H_2CO+H_2$	30	$6\cdot10^{9}$	2.5	[30]	$7.4\cdot10^{10}$	38.2	—
57	$CH_2+O_2 \rightleftarrows H_2CO+OH$	51	$3\cdot10^{10}$	10	[47]	$3.3\cdot10^{10}$	61.6	—
56	$CH_2+O \rightleftarrows H_2CO+H$	68	$1.86\cdot10^{10}$	0	[48]	$3.8\cdot10^{11}$	68.2	—
74	$CHO+H_2CO \rightleftarrows CH_3+CO_2$	28	$6\cdot10^{9}$	4.5	[30]	$1.7\cdot10^{11}$	32.2	—
5d	$CH_2+O_2 \rightleftarrows CO+OH+H$	32	$6\cdot10^{9}$	3.5	[49]	$3.3\cdot10^{5}$	33.8	—
4d	$CH_2+O_2 \rightleftarrows CO_2+H+H$	57	$1.8\cdot10^{8}$	0	[49]	$4\cdot10^{6}$	54.8	—
87**	$CH_3+O_2+M \rightleftarrows CH_3O_2+M$	22	$3.6\cdot10^{8}$	2	—	$2.73\cdot10^{15}/T$	30.6	—
88**	$CH_3O_2 \rightleftarrows H_2CO+OH$	29	$1\cdot10^{12}$	25	—	$6\cdot10^{9}$	56	—
89**	$CH_3O_2+CH_4 \rightleftarrows CH_3O_2H+CH_3$	13	$6\cdot10^{9}$	10	—	$6\cdot10^{9}$	23	—
90**	$CH_2O+OH \rightleftarrows CH_3O_2H$	43	$6\cdot10^{7}$	0	—	$1\cdot10^{9}$	43	—
91**	$CH_3+HO_2 \rightleftarrows H_2CO+H_2O$	122	$1.2\cdot10^{9}$	0	—	$1.2\cdot10^{9}$	122	—
95	$CH+H_2O \rightleftarrows CH_2+OH$	8	$3.1\cdot10^{8}$	8.9	—	$6\cdot10^{9}$	18.3	[50]
96	$CH+H_2 \rightleftarrows CH_2+H$	23	$6.6\cdot10^{8}$	5.1	—	$6\cdot10^{9}$	29.5	[50]
97	$CH+OH \rightleftarrows CH_2+O$	25	$3\cdot10^{9}$	4.6	—	$6\cdot10^{9}$	31	[50]
98	$CH+OH \rightleftarrows CO+H_2$	177	$6\cdot10^{9}$	0	[50]	$6.2\cdot10^{11}$	179	—
99	$CH+O \rightleftarrows CO+H$	175	$6\cdot10^{9}$	0	[50]	$2.8\cdot10^{11}$	177	—
1a	$CH_3OH+O \rightleftarrows CH_2OH+OH$	0	$4.3\cdot10^{9}$	2	[51]	$3.2\cdot10^{8}$	1	—
2a	$CH_3OH+OH \rightleftarrows CH_2OH+H_2O$	17	$6\cdot10^{9}$	7.25	[51]	$4.7\cdot10^{9}$	23.2	—
3a	$CH_3OH+H \rightleftarrows CH_2OH+H_2$	2	$1.3\cdot10^{9}$	8.5	[52]	$2.05\cdot10^{8}$	9.3	—
4a	$CH_3O+HO_2 \rightleftarrows CH_2OH+O_2$	54	$2.64\cdot10^{8}$	52	[51]	$6\cdot10^{9}$	52	—
5a	$CH_3+OH+M \rightleftarrows CH_2OH+M$	92	$3.6\cdot10^{9}$	0	—	$2\cdot10^{14}$	69	[53]
6a	$CH_3O+O \rightleftarrows H_2CO+OH$	79	$6\cdot10^{9}$	0	[51]	$7.9\cdot10^{8}$	79	—
7a	$CH_3O+OH \rightleftarrows H_2CO+H_2O$	96	$6\cdot10^{9}$	0	[51]	$8.3\cdot10^{9}$	96	—
8a	$CH_3O+H \rightleftarrows H_2CO+H_2$	81	$6\cdot10^{10}$	0	[51]	$1.8\cdot10^{10}$	81	—
9a	$CH_3O+O_2 \rightleftarrows H_2CO+HO_2$	25	$6\cdot10^{9}$	5.3	[51]	$2.8\cdot10^{8}$	30.5	—
1.16	$H_2CO+H+M \rightleftarrows CH_3O+M$	22	$1.2\cdot10^{8}T$	6.4	—	$2\cdot10^{12}$	30	[51]
1d	$C_2H_2+O \rightleftarrows CO+CH_2$	73	$2\cdot10^{10}$	3.2	[54]	$5.2\cdot10^{9}$	78	—
2d	$C_2H_2+OH \rightleftarrows CO+CH_3$	56	$7.8\cdot10^{9}$	4.64	[55]	$3.3\cdot10^{10}$	62	—
6e	$C_2H+H+M \rightleftarrows C_2H_2+M$	128	—	—	—	$6\cdot10^{9}$	96	[56]
7e	$C_2H+H_2 \rightleftarrows C_2H_2+H$	25	—	—	—	$6\cdot10^{9}$	20	[56]
8e	$C_2H+O_2 \rightleftarrows CO+HCO$	214	$6\cdot10^{9}$	0	[56]	—	—	—
3d	$C_2H_2+O_2 \rightleftarrows CH_2+CO_2$	81	$6\cdot10^{10}$	40	—	$3.4\cdot10^{11}$	122	—
1b	$C_2H_4+O \rightleftarrows CH_3+HCO$	43	$6\cdot10^{9}$	0.7	[57]	$5\cdot10^{7}$	46	—
2b	$C_2H_4+OH \rightleftarrows CH_3+H_2CO$	15	$4.5\cdot10^{9}$	0.9	[58]	$1.4\cdot10^{9}$	17.4	—
3b	$C_2H_3+H_2 \rightleftarrows C_2H_4+H$	1	$5.8\cdot10^{8}$	12.8	—	$6\cdot10^{9}$	12	[57]
4b	$C_2H_3+HO_2 \rightleftarrows C_2H_4+O_2$	57	$1.4\cdot10^{8}$	−0.2	—	$6\cdot10^{9}$	54	[57]
5b	$C_2H_2+H_2 \rightleftarrows C_2H_4$	41	$2.9\cdot10^{4}$	0	—	$1.7\cdot10^{12}/T$	42	[59]
6b	$C_2H_3+O \rightleftarrows CH_2+CO$	117	$6\cdot10^{9}$	0	[57]	$2.1\cdot10^{9}$	116	—
7b	$C_2H_3+OH \rightleftarrows CH_2+HCO$	48	$6\cdot10^{9}$	0	[57]	$1.5\cdot10^{9}$	46	—
8b	$C_2H_3+H \rightleftarrows C_2H_2+H_2$	63	$6\cdot10^{9}$	0	[57]	$6.3\cdot10^{9}$	62	—
9b	$C_2H_3+O_2 \rightleftarrows C_2H_2+HO_2$	7	$6\cdot10^{9}$	10	[57]	$1.8\cdot10^{9}$	15	—
30c	$C_2H_3+OH \rightleftarrows C_2H_2+H_2O$	78	$6\cdot10^{9}$	0	[64]	$2.3\cdot10^{10}$	76	—
31c	$C_2H_3+O \rightleftarrows C_2H_2+OH$	61	$6\cdot10^{9}$	0	[64]	$2.8\cdot10^{9}$	60	—
2e	$CH_3+CH_3 \rightleftarrows C_2H_4+H_2$	55	$2\cdot10^{13}$	38	[60]	—	—	—
3e	$C_2H_4+H+H \rightleftarrows CH_3+CH_3$	48	—	—	—	$6\cdot10^{10}$	41.6	[60]
2c	$CH_3+CH_3 \rightleftarrows C_2H_6$	83	$8.4\cdot10^{9}$	0	[61]	$1\cdot10^{13}$	83	—
3c	$C_2H_6+OH \rightleftarrows C_2H_5+H_2O$	20	$1.8\cdot10^{11}$	4	[62]	$1.6\cdot10^{11}$	24	—
4c	$C_2H_5+H \rightleftarrows C_2H_6+H_2$	5	$7.4\cdot10^{10}$	9.6	[63]	$1.4\cdot10^{10}$	14.2	—
5c	$C_2H_5+O \rightleftarrows C_2H_6+OH$	3	$4.6\cdot10^{9}$	4	[64]	$3.8\cdot10^{6}$	7.0	—
6c	$C_2H_5+HO_2 \rightleftarrows C_2H_6+O_2$	51	$3.2\cdot10^{6}$	−1.2	—	$6.9\cdot10^{9}$	50	[64]
7c	$C_2H_5+H_2O_2 \rightleftarrows C_2H_6+HO_2$	11	$4.9\cdot10^{9}$	8	—	$6\cdot10^{8}$	19	[64]

Table 1 (cont'd.).

No. of reaction	Reaction	h, kcal mol^{-1}	Forward reaction			Reverse reaction		
			A, mol litre^{-1}s^{-1}	E, kcal mol^{-1}	Refs.	A, mol litre^{-1}s^{-1}	E, kcal mol^{-1}	Refs.
8c	$C_2H_5+OH\rightleftarrows CH_3O+CH_3$	4	$3\cdot10^{10}$	0	[64]	$8\cdot10^{9}$	1.4	—
9c	$C_2H_5+H\rightleftarrows CH_3+CH_3$	15	$4\cdot10^{10}$	0	[65]	$6.7\cdot10^{7}$	12.6	—
10c	$C_2H_5+H\rightleftarrows CH_4+CH_2$	32	$6\cdot10^{9}$	6	[64]	$3.3\cdot10^{8}$	36	—
11c	$C_2H_5+O\rightleftarrows CH_3+H_2CO$	88	$6\cdot10^{9}$	0	[64]	$2.1\cdot10^{8}$	80	—
12c	$C_2H_5+O_2\rightleftarrows CH_2O+H_2CO$	55	$6\cdot10^{9}$	10	[64]	$1.7\cdot10^{8}$	62	—
13c	$C_2H_5+O_2\rightleftarrows CH_3CHO+OH$	61	$6\cdot10^{9}$	10	[64]	$3.2\cdot10^{8}$	72	—
14c	$CH_3CHO+OH\rightleftarrows CH_3CO+H_2O$	23	$3.4\cdot10^{10}$	4	[66]	$3\cdot10^{10}$	28	—
15c	$CH_3CHO+H\rightleftarrows CH_3CO+H_2$	8	$6\cdot10^{9}$	3.4	[66]	$1.1\cdot10^{9}$	12.2	—
16c	$CH_3CHO+O\rightleftarrows CH_3CO+OH$	6	$1.1\cdot10^{10}$	2.8	[67]	$9.1\cdot10^{8}$	9.4	—
17c	$CH_3+CO_2+OH\rightleftarrows CH_3CHO+O_2$	11	$7.4\,T$	26.8	[64]	$6\cdot10^{8}$	20	—
18c	$CH_3CO+HO_2\rightleftarrows CH_3CHO+O_2$	48	$1.6\cdot10^{7}$	−17.2	—	$3\cdot10^{8}$	30	[64]
19c	$CH_3CO+H_2O_2\rightleftarrows CH_3CHO+HO_2$	8	$4.9\cdot10^{6}$	−0.8	[64]	$6\cdot10^{6}$	6	—
20c	$CH_3+HCO+M\rightleftarrows CH_3CHO+M$	68	$7.9\cdot10^{4}\,T$	−20	—	$2\cdot10^{14}$	52	[64]
21c	$CH_3+CO\rightleftarrows CH_3CO$	8	$1.5\cdot10^{2}\,T$	6.8	—	$2\cdot10^{10}$	16	[68]
22c	$CH_3CO+H\rightleftarrows CH_3+CHO$	27	$6\cdot10^{9}$	4.80	[64]	$6.6\cdot10^{7}$	28	—
23c	$CH_3CO+O\rightleftarrows CH_2O+CO$	87	$6\cdot10^{9}$	0	[64]	$1.6\cdot10^{10}$	84	—
24c	$C_2H_5+OH\rightleftarrows C_2H_4+H_2O$	85	$6\cdot10^{9}$	0	[64]	$7.2\cdot10^{8}$	80	—
25c	$C_2H_5+H\rightleftarrows C_2H_4+H_2$	70	$6\cdot10^{9}$	0	[64]	$1.6\cdot10^{9}$	66	—
26c	$C_2H_5+O\rightleftarrows C_2H_4+OH$	68	$6\cdot10^{9}$	0	[64]	$6.9\cdot10^{8}$	64	—
27c	$C_2H_4+H+M\rightleftarrows C_2H_5+M$	33	$3\cdot10^{2}\,T$	2	—	$6\cdot10^{9}$	40	[64]
28c	$C_2H_5+O_2\rightleftarrows C_2H_4+HO_2$	14	$6.9\cdot10^{9}$	8	[64]	$4.5\cdot10^{8}$	18	—
1e	$C_2H_5+H_2\rightleftarrows CH_3+CH_4$	12	$8.7\cdot10^{10}$	9	—	$6.9\cdot10^{9}$	21	[56]
4e	$C_2H_5+H\rightleftarrows C_2H_6$	98	—	—	—	$1\cdot10^{13}$	98	[56]
2.1	$CH_2NH_2+O\rightleftarrows CH_2NH+OH$	15	$1.45\cdot10^{10}$	2.57	[69]	$2.4\cdot10^{9}$	17.5	—
2.2	$CH_2NH_2+OH\rightleftarrows CH_2NH+H_2O$	32	$6.1\cdot10^{9}$	0.45	[70]	$9.5\cdot10^{8}$	32	—
2.3	$CH_2NH_2+H\rightleftarrows CH_2NH+H_2$	17	$6.3\cdot10^{10}$	5.3	[71]	$2.1\cdot10^{10}$	22	—
2.4	$CH_3+NH_2\rightleftarrows CH_2NH_2$	81	$5.8\cdot10^{8}\,T$	9.4	—	$1\cdot10^{16}$	84.4	[72]
2.5	$CH_2NH+HO_2\rightleftarrows CH_2NH_2+O_2$	39	$5.5\cdot10^{8}$	−0.85	—	$6\cdot10^{9}$	39	[69]
2.6	$CH_2NH+O\rightleftarrows CH_2O+NH$	14	$6\cdot10^{10}$	0	[69]	$1.5\cdot10^{9}$	14	—
2.7	$CH_2NH+OH\rightleftarrows CH_4+HNO$	40	$6\cdot10^{9}$	0	[69]	$3.2\cdot10^{9}$	40	—
2.8	$CH_2NH+H\rightleftarrows CH_3+NH_2$	15	$6\cdot10^{10}$	0	[69]	$5.3\cdot10^{7}$	14	—
2.9	$CH_2NH+O_2\rightleftarrows CH_2O+HNO$	12	$6\cdot10^{9}$	4	[69]	$3.1\cdot10^{8}$	15	—
2.10	$NH_2+H+M\rightleftarrows NH_3+M$	104	$3.2\cdot10^{8}\,T$	−15	—	$1.2\cdot10^{18}$	91	[73]
2.11	$NH_2+HO_2\rightleftarrows NH_3+O_2$	56.5	$2.5\cdot10^{8}$	−1.4	—	$6.9\cdot10^{8}$	56	[69]
2.12	$NH_2+OH\rightleftarrows NH_3+O$	2.5	$5.7\cdot10^{7}$	1.6	—	$1\cdot10^{9}$	4.8	[74]
2.13	$NH_2+O\rightleftarrows HNO+H$	25	$6\cdot10^{9}$	0	[69]	$3.8\cdot10^{9}$	25	—
2.14	$NH_2+NO\rightleftarrows N_2+H_2O$	120	$1.1\cdot10^{9}$	0	[75]	$1.4\cdot10^{10}$	122	—
2.15	$NH_2+NH_2\rightleftarrows NH_3+NH$	15	$6\cdot10^{10}$	10	[69]	$4.3\cdot10^{11}$	25	—
2.16	$NH_2+NH\rightleftarrows NH_3+N$	21	$6\cdot10^{10}$	4	[69]	$2.8\cdot10^{12}$	26	—
2.17	$NH_2+OH\rightleftarrows NH_3+H_2O$	14.5	$3.2\cdot10^{9}$	1.84	[76]	$2\cdot10^{9}$	15.6	—
2.18	$NH_2+H\rightleftarrows NH_3+H_2$	0	$2.7\cdot10^{10}$	17.4	[73]	$3.6\cdot10^{9}$	15.2	—
2.19	$HNO+OH\rightleftarrows NO+H_2O$	69	$6\cdot10^{8}$	0	[69]	$1.3\cdot10^{9}$	70	—
2.20	$NH+NO\rightleftarrows N_2+OH$	93	$1\cdot10^{9}$	0	[77]	$6.6\cdot10^{9}$	94	—
2.21	$HNO+O\rightleftarrows NO+OH$	52	$6\cdot10^{9}$	0	[78]	$1.3\cdot10^{9}$	53	—
2.22	$NH+O_2\rightleftarrows NO+OH$	50	$5.1\cdot10^{8}$	0	[79]	$3.1\cdot10^{8}$	50	—
2.23	$NH+OH\rightleftarrows NO+H_2$	69	$1.6\cdot10^{8}\,T^{0.86}$	1.5	[55]	$2.5\cdot10^{9}\,T^{0.86}$	70	—
2.24	$NH+H\rightleftarrows N+H_2$	20	$6\cdot10^{10}$	4.2	[69]	$2.5\cdot10^{11}$	25	—
2.25	$NH+O\rightleftarrows N+OH$	18	$6\cdot10^{10}$	5	[69]	$1.1\cdot10^{11}$	24	—
2.26	$HNO+H\rightleftarrows NO+H_2$	55	$6\cdot10^{10}$	0	[69]	$2.8\cdot10^{10}$	55	—
2.27	$NH+NH\rightleftarrows NH_2+N$	6.8	$6\cdot10^{10}$	8	[69]	$3.9\cdot10^{11}$	15	—
2.28	$CH_2+NH\rightleftarrows HN+H_2$	117	$6\cdot10^{10}$	0	[69]	$1.5\cdot10^{12}$	116	—
2.29	$CH_2+N\rightleftarrows HCN+H_2$	118	$6\cdot10^{10}$	0	[80]	$2.9\cdot10^{11}$	115	—
2.30	$CH+NH_2\rightleftarrows HCN+H_2$	153	$6\cdot10^{9}$	0	[69]	$5.7\cdot10^{11}$	154	—
2.31	$CN+H+M\rightleftarrows HCN+M$	122	$1.83\cdot10^{6}\,T$	−9.4	—	$5.8\cdot10^{13}$	117	[81]
2.32	$CN+H_2O\rightleftarrows HCN+OH$	4	$5.1\cdot10^{9}$	4.1	[69]	$6\cdot10^{9}$	10.5	—
2.33	$CN+H_2\rightleftarrows HCN+H$	19	$6\cdot10^{10}$	5.3	[82]	$3.6\cdot10^{11}$	27	—
2.34	$CN+OH\rightleftarrows HCN+O$	21	$1.32\cdot10^{-1}\,T^{2.286}$	−18.2	—	$1.79\,T^{2.286}$	5.2	[83]
2.35	$CN+O_2\rightleftarrows CO+NO$	106	$6\cdot10^{9}$	0	[69]	$6.8\cdot10^{9}$	110	—
2.36	$CN+OH\rightleftarrows CO+NH$	57	$6\cdot10^{9}$	0	[69]	$1.6\cdot10^{10}$	60	—
2.37	$CN+O\rightleftarrows CO+N$	74	$6\cdot10^{9}$	0	[69]	$3\cdot10^{10}$	78	—
2.38	$CN+NO\rightleftarrows CO+N_2$	149	$7.2\cdot10^{7}$	0	[84]	$1.3\cdot10^{9}$	154	—
2.39	$CN+NH_3\rightleftarrows HCN+NH_2$	18.5	$6\cdot10^{8}$	6.9	[85]	$4.8\cdot10^{8}$	27	—
2.40	$HCN+OH\rightleftarrows NH_2+CO$	24	$6\cdot10^{8}$	6	[69]	$4.2\cdot10^{9}$	31	—
2.41	$HCN+NH\rightleftarrows CH_2+N_2$	30	$6.8\cdot10^{8}$	0	—	$2.8\cdot10^{9}$	30	[86]
2.42	$N+HCN\rightleftarrows CH+N_2$	2	$7.2\cdot10^{9}$	9.3	[87]	$8\cdot10^{8}$	11	—
1.3	$NO+HO_2\rightleftarrows NO_2+OH$	8	$8.7\cdot10^{8}$	0	—	$6\cdot10^{9}$	8	[88]
1.4	$NO_2+H\rightleftarrows NO+OH$	29	$2.9\cdot10^{10}$	0	[88]	$3.5\cdot10^{8}$	29.4	—
1.5	$NO+O+M\rightleftarrows NO_2+M$	72	$5.8\cdot10^{4}\,T$	−8.6	—	$1.1\cdot10^{13}$	65	[89]
1.6	$NO_2+O\rightleftarrows NO+O_2$	46	$1\cdot10^{10}$	0.6	[89]	$2.2\cdot10^{9}$	46	—
1.7	$NO+NO+O_2\rightleftarrows NO_2+NO_2$	26	$4.9\,T$	−0.6	—	$4\cdot10^{9}$	27	[89]
1.8	$NO+NO_3\rightleftarrows NO_2+NO_2$	23	$1.5\cdot10^{7}$	1.3	—	$7.8\cdot10^{8}$	24	[89]
1.9	$NO_2+O+M\rightleftarrows NO_3+M$	49	$2.8\cdot10^{7}\,T$	−7.8	—	$1\cdot10^{14}$	43	[89]
1.10	$NO+O_2+M\rightleftarrows NO_3+M$	3	$7.65\,T$	−1.7	—	$1.2\cdot10^{8}$	3.2	[89]
1.11	$CH_3+NO_2\rightleftarrows CH_3O+NO$	18	$1.3\cdot10^{10}$	0	[90]	$2.46\cdot10^{10}$	18	—
1.12	$N+NO\rightleftarrows N_2+O$	75	$2.75\cdot10^{10}$	0.5	—	$5\cdot10^{10}$	75	[91]
1.13	$N+O_2\rightleftarrows NO+O$	32	$1\cdot10^{10}$	7.5	[55]	$2\cdot10^{9}$	39.4	—
1.14	$NO+NO\rightleftarrows N_2+O_2$	43	$1.41\cdot10^{12}$	85	[91]	$2.85\cdot10^{13}$	128	—
1.15	$N+OH\rightleftarrows NO+H$	49	$4\cdot10^{10}$	0	[92]	$1.5\cdot10^{11}$	48.6	—
1.1	$NO_2+OH+M\rightleftarrows HNO_3+M$	48	—	—	—	$6\cdot10^{11}$	30.1	[88]
1.2	$OH+HNO_3\rightleftarrows NO_3+H_2O$	18	$5.4\cdot10^{7}$	0	[93]	—	—	—

*The reactions are grouped in terms of substances; the numbering used in the original papers has been retained.

**The combination of the Arrhenius parameters of these processes selected for the description of cold flames.[94]

The mechanisms indicated above describe satisfactorily the course of the reaction in an atomic-oxygen hydrogen flame when oxygen atoms and molecular hydrogen are rapidly mixed in the stream.[95] An important part of the scheme, particularly at pressures close to and above the second limit, are reactions involving hydrogen peroxide.[96] The latter is formed during the oxidation of H_2 as an intermediate and the allowance for such reactions makes it possible to achieve a satisfactory agreement between the calculated and experimental second ignition limits.[96]

A fairly universal DKM, describing the hydrogen oxidation and combustion reaction over a wide range of temperatures, pressures, and mixture compositions, should apparently contain a greater number of elementary steps than in the calculations quoted above. It should consist of at least three parts including (a) chain initiation, propagation, branching, and linear termination processes when the rate of termination is proportional to the concentration of the active centre (with a power exponent of unity under all conditions), (b) quadratic termination processes the rate of which is proportional to the square of the concentration of the active centre, i.e. recombination reactions (at high concentrations of the active species at high temperatures and for high degrees of combustion), and (c) reactions involving hydrogen peroxide, which make a large contribution at high pressures.

A fairly detailed mechanism, incorporating more than 20 processes satisfying the above requirements, has been described in a number of communications[2,97-99] (the first 22 forward and reverse processes in Table 1). The validity of this DKM has been tested by a series of calculations modelling the self-ignition and combustion in the spreading flame.

In self-ignition, the initial reaction stage is not outwardly manifested in any way and a sharp increase in the rate of reaction and evolution of heat, passing into explosion, are observed only after a certain time, called the self-ignition delay, has elapsed. Calculation of the self-ignition delay time makes it possible to follow the initial stages of the reaction, where the concentration of the initial reactants hardly changes.

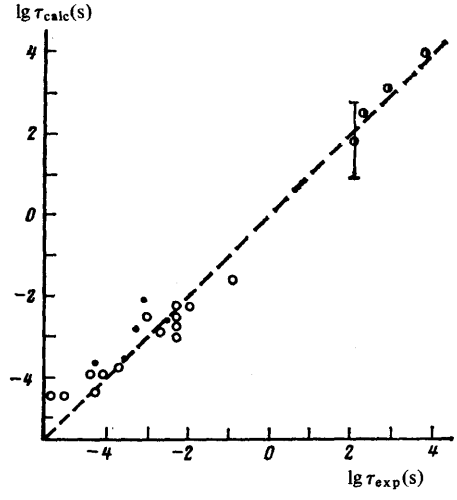


Figure 2. Comparison of the calculated[30,46,97,98] and experimental self-ignition delays; $[H_2]_0$ = 1–8%, $[CH_4]_0$ = 2–33%, $[O_2]_0$ = 1–67%, T = 696–2130 K, P = 0.167–5 atm (according to the data in Refs. 100–112).

An example of a comparison of hydrogen ignition delays, measured and calculated on the basis of the DKM on the assumption that a purely branched chain process takes place, is given in Fig. 2 (filled symbols). The delays were calculated with the aid of a standard program by solving a system of material balance equations (I). A sharp increase in the rate of the chemical reaction, indicating the occurrence of self-ignition, was adopted as a criterion at the end of the delay. The experimental data refer to the temperature range 979–2130 K and the pressure range 0.23–5 atm. Evidently the discrepancy between the measured and calculated delay does not exceed one order of magnitude.

We shall now proceed to the examination of reactions in a mixture containing hydrogen peroxide as the initial reactant. Since hydrogen peroxide occurs in the DKM (Table 1), the latter can be used without any changes. The mechanisms of the reactions of H_2O_2 have been investigated in a number of studies. Thus the rate constant for reaction (-28) has been determined[113] for the conditions prevailing at the beginning of the thermal decomposition of H_2O_2 (Table 1). In another study[32] the investigation was carried out under flow conditions at low pressures. The authors determined the important rate constants for reactions of H_2O_2 with hydrogen and oxygen atoms. Under these constants, calculations have been performed[27] on the basis of the DKM for the conditions of the experiment adopted in previous calculations.[32,113] Thus the experimental[32] and calculated concentrations of H_2, H, O, O_2, H_2O, and H_2O_2 in the reaction of H_2O_2 with O (453 K, 0.124 atm) were compared; a comparison was also made of the experimental[113] and calculated $[H_2O_2]$ and $[HO_2]/[H_2O_2]_0$ in the H_2O_2 decomposition reaction (1060 K, 6.2 atm) as a function of the reaction time and of the yield of H_2O_2 as a function of its initial concentration in the reaction of the peroxide with the products of a discharge in a hydrogen–oxygen mixture containing hydrogen atoms {$[H]_0$ = 0.04%} and hydroxy-radicals {$[OH]_0$ = 0.0114%} at 803 K, a pressure of 0.01 atm, and for a reaction time of 1.7 ms. It was found that the calculations permit a qualitatively correct description of the course of the reaction of H_2O_2 in the temperature range 453–1060 K and in the pressure range 0.01 to 6.2 atm.

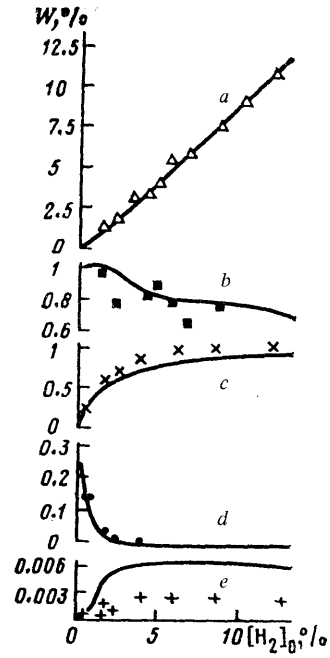


Figure 3. Dependence of the yield of the reaction products on the initial H_2 concentration for the oxygen atomic flame with hydrogen;[28] $[O]_0$ = 0.5%, $[O_2]_0$ = 0.82%, T = 1169 K, P = 0.01 atm, t = 2.5 ms: symbols—experiment; lines—calculation; *a*) H_2; *b*) O_2; *c*) H; *d*) O; *e*) OH.

It has been shown[27] that failure to take into account the reactions of hydrogen peroxide at 803–1038 K near the ignition peninsula in the combustion of hydrogen–oxygen mixtures can lead to appreciable errors, but at temperatures above 1200 K these reactions can be disregarded.

As the kinetics and rate constants for different stages are refined, it becomes possible to obtain a more accurate and reliable description of the hydrogen combustion process. This can be seen from the comparison of the calculated and experimental yields of the products obtained for the atomic-oxygen hydrogen flame[28] (Fig. 3).

The results of numerous studies on the mechanism of the combustion of hydrogen are also presented in a review,[114] in a monograph,[115] a number of communications,[116–118] etc. They consider the mechanisms involving virtually the same reactions as those listed in Table 1. Thus one may note the unity of the views of different investigators concerning the principal processes in the DKM of the oxidation of hydrogen. We may also note that algorithms have been proposed in a number of studies, for example in Refs. 115 and 116, for the identification of the reactions important under the specific conditions considered and for the construction of abbreviated kinetic schemes.

III. C_1–C_2 HYDROCARBONS AND METHANOL

1. The Combustion of Methane

The experience gained in the study of the mechanism of the combustion of hydrogen has shown that the chemical reaction can be described with a satisfactory accuracy under most varied conditions. The next step as regards complexity involves the construction of the DKM for the oxidation and combustion of methane (including the combustion of carbon monoxide and formaldehyde appearing as intermediates).

Extensive experimental data on the kinetics of the oxidation of methane, referring mainly to the region of low temperatures (below 900 K), have been examined in monographs and communications.[1,6,12,13,111,112,119,120]

On the basis of data for the low-temperature oxidation and high-temperature processes in flames, a number of workers[43,48,121–123] demonstrated that reactions involving the active centres of the hydrogen–oxygen flame (OH, H, and O) and molecular hydrogen play an important role in the conversion of methane. Thus, according to Westenberg and Fristrom,[121] the methane oxidation reaction# in the flame proceeds as follows:

$$CH_4+OH\rightarrow CH_3+H_2O, \quad (31)$$

$$CH_4+O\rightarrow CH_3+OH, \quad (35)$$

$$CH_3+O_2\rightarrow H_2CO+OH, \quad (57)$$

$$H_2CO+OH\rightarrow HCO+H_2O. \quad (43)$$

$$HCO+OH\rightarrow CO+H_2O, \quad (68)$$

$$CO+OH\rightarrow CO_2+H, \quad (21)$$

$$H+H_2O\rightarrow OH+H_2, \quad (-1)$$

$$O+H_2\rightarrow OH+H, \quad (-6)$$

$$OH+OH\rightarrow H_2O+O, \quad (9)$$

$$H+O_2\rightarrow OH+O, \quad (-4)$$

$$O+O+M\rightarrow O_2+M. \quad (12)$$

#Here and henceforth the numbers of reactions are given in accordance with Table 1.

The basis of the mechanism formulated here is the reactions of the active centres O and OH with the initial methane and the reactions ensuring the degenerate chain branching by hydrogen. The principal direction of the transformation corresponds to the sequence

$$CH_4\rightarrow CH_3\rightarrow H_2CO\rightarrow HCO\rightarrow CO\rightarrow CO_2.$$

Molecular hydrogen and water also appear during the reaction.

Quantitative calculations, carried out approximately within the framework of the mechanism described above, enabled a number of workers[124–126] to describe satisfactorily the experi-experimental data.

In a number of studies[30,97–99] an attempt was made also simultaneously to elucidate to what extent the reaction scheme based on a mechanism similar to that described above but including a greater number of possible elementary steps with participation of species involved in the scheme proposed by Westenberg and Fristrom[121] may be universal. It is essential to elucidate also the contributions of these new reactions to the DKM and to determine whether their introduction is really necessary. The scheme under test is wholly based on the DKM of the oxidation of hydrogen and numerous probable but as yet uninvestigated reactions of the radicals generated during the combustion of methane (CH_3, CH_2, CH, and HCO) have been introduced. The possible elementary steps were selected taking into account their probable rates on the basis of the following rules: all reactions (apart from several active centre initiation reactions) with a high activation energy were excluded; also excluded were almost all the reactions accompanied by a change in multiplicity (in conformity with the Wigner rule). Analysis showed that the methane oxidation pathway leading to the final product involving the CH species is less probable than other possible pathways and this species and its reactions were not therefore included in the scheme.

Ultimately the kinetic mechanism incorporating processes ranging from (1) to (74) in Table 1 was adopted. It does not include several well known reactions. Among them in the recombination of methyl radicals with formation of ethane, which takes place in accordance with the equation

$$CH_3+CH_3\rightarrow C_2H_6. \quad (2c)$$

Analogous processes lead to the formation of other hydrocarbons. These reactions are followed by the interactions of hydrocarbons with the active centres, etc. Allowance for all these reactions entailed a very great increase in the complexity of the mechanism. In the proposed scheme chain termination as a result of the recombination of methyl radicals is simulated by reaction (42).

The rate constants were taken from the literature sources and, when these were lacking, the activation energy was determined from semiempirical formulae:[1] for exothermic reac-reactions, $E = 11.5 - 0.25h$ for $h \leq 46$ and $E = 0$ for $h > 46$; for endothermic reactions, $E = 11.5 + 0.75h$ (h is the heat of reaction in kcal mol^{-1} [127]). The pre-exponential factor A for a bimolecular reaction is approximately 10^{-11} cm^3 molecule^{-1} s^{-1} (6×10^9 litre mol^{-1} s^{-1}). The values of A and E for the reverse reactions have been calculated from the equilibrium constants given by Gurvich et al.[127] If the activation energy for the endothermic process is smaller than h for the reaction, then the activation energy for the reverse process is found to be negative. In this case an extremely high rate constant may be obtained at low temperatures. This is a consequence of the deviation of the temperature variation of the rate constant from the Arrhenius straight line and must be taken into account in the calculations at low temperatures. Naturally, the parameters of the rate constants thus obtained

constitute only an extremely rough and approximate estimate. The values of A and E obtained in the calculations have been corrected when necessary. Clearly, in the presence of a large number of roughly estimated parameters the correction can also be fairly approximate. The total number of elementary reactions in the initial version of the DKM reached 86 (the forward and reverse processes).[30]

The DKM obtained was tested primarily in the calculation of the arrest of the self-inflammation over a wide range of initial conditions: temperatures from 979 to 2130 K, pressures from 0.167 to 3 atm (Fig. 2, open symbols). At the same time, the yields of products in the shock tube and in the atomic flame of methane were modelled. The products formed in such a flame (0.01 atm) have been analysed in greater detail by Basevich et al.[37]

Comparison of all these calculations with experiments yielded yielded more or less satisfactory results. An acceptable agreement has been obtained in the description of the propagation of the methane flame.[128] In the latter case the calculation was performed using Eqn. (III) on the assumption of a stepwise temperature rise in the combustion zone:

$$x<0,\ T=T_0\ ,$$
$$x\geqslant 0,\ T=T_c.$$

The values of T_C and the rates of propagation of the flame were specified on the basis of experimental data.[129] Account was taken only of reactions which make the greatest contribution to the process under specific conditions of the calculation.

The extension of the DKM described above to the low-temperature region did not require any fundamental changes.[46] It has been possible to calculate the reaction half-lives in satisfactory agreement with experiment up to hundreds of minutes (Fig. 2, half-filled symbols). The processes significant for the DKM, whose contribution to the yield of products throughout the range of calculated conditions is either between 10 and 100% (approximately 30–40 elementary steps including certain forward and reverse reactions) or between 1 and 10% (a further approximately 30 processes) have been selected on the basis of the calculations performed. If account is taken of the possible occurrence of the above reactions in the forward and reverse directions, then one obtains 2×55 processes including also processes (5d) and (4d), which were added later—see below. We may note that the processes have been selected by Basevich et al.[46] by comparing the integrals of the rate of reaction over the periods covered by the calculation:

$$I=\int_{\tau} w_i\,dt\ . \qquad (V)$$

Such comparison showed that methane is consumed mainly in the processes

$$CH_4+OH\rightarrow CH_3+H_2O \qquad (31)$$

and

$$CH_4+H\rightarrow CH_3+H_2. \qquad (33)$$

The main source of H atoms is the reaction

$$H_2+OH\rightarrow H_2O+H\ . \qquad (1)$$

Water is formed in the reactions

$$CH_4+OH\rightarrow CH_3+H_2O, \qquad (31)$$

$$H_2CO+OH\rightarrow HCO+H_2O, \qquad (43)$$

and

$$H_2+OH\rightarrow H_2O+H. \qquad (1)$$

Carbon monoxide is obtained in the processes

$$HCO+M\rightarrow H+CO+M \qquad (-66)$$

and

$$HCO+O_2\rightarrow CO+HO_2\ , \qquad (70)$$

while carbon dioxide is produced in the reactions

$$CO+OH\rightarrow CO_2+H, \qquad (21)$$

and

$$CO+HO_2\rightarrow CO_2+OH. \qquad (24)$$

The greatest yield of hydrogen is obtained from the process

$$CH_4+H\rightarrow CH_3+H_2\ . \qquad (33)$$

Degenerate branching takes place at the H_2O_2, H_2, and H_2CO molecules. After the selection of the leading reactions steps, it was found that at 700–1000 K the rate of branching is a maximum due to the process

$$H_2O_2+M=OH+OH+M\ , \qquad (-28)$$

while at $T > 1200$ K the main branching process becomes the reaction

$$H+O_2=OH+O. \qquad (-4)$$

The addition of reactions (87)–(91) and (2c) from Table 1 to the kinetic scheme for the combustion of methane proposed by Basevich et al.[46] makes it possible to model, on the basis of Eqns. (I) and (II), the reaction in the region of cold flames and the cold-flame flash[94] observed by Vanpee[130] (here it is necessary to take into account the thermal regime in the reaction). Furthermore, it is necessary to modify the Arrhenius parameters of the rate constants for stage (57) which had given rise to doubts (the new values are $A = 1.56 \times 10^9$ litre $mol^{-1}\ s^{-1}$ and $E = 25$ kcal mol^{-1}). Analysis of the solution showed[94] that the mechanism of the cold flame includes the initial activation of the oxidation reaction and subsequent inhibition owing to the thermal decomposition of the peroxy-radical, the formation of formaldehyde from the latter, and the interaction of formaldehyde with the leading active centres. Additional tests showed that the changes in the kinetic parameters introduced for the description of the cold flame do not affect the calculated characteristics of the reaction outside this region.

Criteria have been proposed[131] for the estimation of the accuracy of the calculations based on the DKM for the combustion of methane. Quantities characterising the deviation of the experimental parameters X_{exp} from the calculated X_{calc}, i.e.

$$pM = \lg(X_{calc}/X_{exp})$$

have been calculated for the eight DKM for the oxidation of methane proposed in the literature. The induction period, the coefficient in the exponent defining the growth of the concentration of CO_2 during the induction period (β_{CO_2}), and the analogous coefficient for the chemiluminescence of the excited radical CH* (β_{CH^*}) and the CO molecule (β_{CO}) (Table 2) were adopted as the parameters. The values of pM obtained,[132] corresponding to the DKM for the oxidation of methane proposed by Basevich et al.[46], are presented in Table 2; the average logarithm of the deviation of the calculated quantities is 0.03 and the mean square logarithm of the deviation is 0.33 (the deviation corresponds to a coefficient of ~2). In general, these deviations are not worse than the values calculated by Olsen and Gardiner[131] especially since the experimental parameters selected by the authors[131] were in no way optimised.

Table 2. Comparison of the calculated and experimental parameters of the oxidation of methane.

Parameter X	T, K	P, atm	Composition, % (remainder-Ar)			Value of X		pM	
			CH_4	CO	O_2	experiment*	calculation (Ref.132)	from Ref.132	from Ref.131
τ, s	1750	0.28	1.67	—	3.33	$1.38\cdot10^{-3}$	$0.34\cdot10^{-3}$	−0.61	−0.72÷0.56
τ, s	2000	0.33	1.67	—	3.33	$3.2\cdot10^{-4}$	$0.7\cdot10^{-4}$	−0.66	
τ, s	2000	0.15	0.05	4.32	2.13	$3.3\cdot10^{-4}$	$2.5\cdot10^{-4}$	−0.12	−0.8÷0.08
β_{CO_2}, s^{-1}	2000	0.15	0.05	4.32	2.13	$4.6\cdot10^{3}$	$9.6\cdot10^{3}$	0.32	
β_{CH^*}, s^{-1}	1800	1.5	1	—	1	$2.6\cdot10^{5}$	$2.6\cdot10^{5}$	0	−0.3÷1.0
β_{CH^*}, s^{-1}	2400	1.9	1	—	1	$7.15\cdot10^{6}$	$7.3\cdot10^{6}$	−0.02	
$[CO][O]$, mol^2cm^{-6}	2195	1.43	1	2	2	$3.8\cdot10^{-16}$	$1.8\cdot10^{-16}$	−0.31	−0.3÷0.3
Δt_{max}, s	2195	1.43	1	2	2	$2.1\cdot10^{-6}$	$5\cdot10^{-6}$	0.38	
β_{CO}, s^{-1}	1600	1.14	0.21	1.06	19.5	$3.0\cdot10^{4}$	$6.1\cdot10^{4}$	0.31	−0.04÷0.6
β_{CO}, s^{-1}	1600	1.13	0.02	1.03	19.4	$1.2\cdot10^{4}$	$2.2\cdot10^{4}$	0.27	
$d[CH_3]/dt$, mol $cm^{-3}s^{-1}$	1600	10	1	—	2	$1.8\cdot10^{-6}$	$3.2\cdot10^{-6}$	0.25	0.08÷2.13
$d[CH_3]/dt$, mol $cm^{-3}s^{-1}$	1820	10	1	—	2	$3.9\cdot10^{-4}$	$3.5\cdot10^{-4}$	−0.05	
$\Delta[CH_4]_{rel}$	2200	0.25	9	—	1	0.017	0.0081	−0.32	−0.8÷0.02
$\Delta[CH_4]_{rel}$	2500	0.25	9	—	1	0.01	0.014	0.15	

Notation: τ is the induction period, Δt_{max} the time from the start of the reaction until the attainment of $\{[CO][O]\}_{max}$, and $\Delta[CH_4]_{rel}$ is the change in the relative concentration after $(0.2-2)\times10^{-4}$ s.

*According to Olson and Gardiner.[131]

A kinetic mechanism of the combustion of methane has also been described in other communications,[117,133–137] etc.

2. Combustion of Methyl Alcohol

The study of the combustion of CH_3OH is important intrinsically and also because methanol is usually formed as a side product in the combustion of methane and other hydrocarbons. A possible mechanism of the oxidation of methanol has been examined[51] in relation to its flame with atomic oxygen. We shall now turn to the kinetics of this process.

In the primary step of the interaction of oxygen atoms with methanol, the CH_2OH radical and the hydroxylradical are apparently formed.[138,139] Formaldehyde, which has also been considered[140] as a primary product, appears in our view in a subsequent elementary step involving the interaction of CH_2OH with O and H atoms, with the hydroxylradical, and molecular oxygen. Qualitatively the same picture holds also in the case where the methoxyradical is obtain instead of the alcohol radical.

There are no grounds for the belief that the subsequent course of the reactions of formaldehyde and the resulting molecular hydrogen involves any specific stages characteristic solely of the oxidation of methanol. It most probably involves the same processes by which they react as intermediates in the oxidation of methane. This has been confirmed by the study of the characteristic features of the formation of carbon monoxide, hydroxylradicals, and atomic hydrogen in the course of the O + CH_3OH reactions.

Thus, a quantitative description of the interaction of methanol with oxygen atoms requires the addition of the processes specified above of the reactions of methanol and the radical [Table 1, reactions (1a)–(9a)]. Among these reactions, at the beginning of the investigation[51] only the rate constants for reactions (1a) and (3a) were known. For the remaining seven reactions, the rate constants were adopted on the basis of semiempirical estimates. In the CH_3OH reaction mechanism these processes are then followed[51] by the reactions of formaldehyde and its formyl radical, carbon monoxide, and hydrogen. At sufficiently high temperatures, this mechanism presupposes the occurrence of a chain reaction, formaldehyde and hydrogen playing the role of intermediates ensuring degenerate branching.

On the basis of this mechanism, kinetic calculations have been made of the yields of all the analysed reaction products at a constant temperature and pressure.[51] Qualitative agreement between calculation and experiment has been observed. The maximum coefficient of deviation does not exceed 5.

The calculations performed make it possible to estimate the role of individual steps in the overall mechanism of the oxidation of CH_3OH.[51] We shall now consider the reactions of methanol and its radical. The interaction of CH_3OH with with oxygen atoms [reaction (1a)] initiates oxidation and its rate determines to a large extent also the degree of reaction. However, the reactions of CH_3OH with OH [reaction (2a)] and H [reaction (3a)], formed during the reaction, also influence the yields of all the products although to a much smaller extent. Thus an increase of the rate constant k_{2a} by an order of magnitude alters the yield of H_2CO, CO, and H by 5–9%. The increase of the rate constant k_{3a} (according to the data of Aders[141]) alters the yields of H_2CO, CO, and H_2 by 5–20%. The yields of all the products depend especially strongly on the rate constants for the reactions of CH_2OH with O, H, and OH; when these quantities are varied within the limits of one order of magnitude, the corresponding yields change from several to hundredths per cent. The reaction of CH_2OH with O_2 is less important: the analogous change in the constant alters the yields of products by less than 10%. The high activation energies for reactions (−4a) and (−5a) show that they can play a significant role only in the absence of initiation and at high temperatures. Calculations have shown that, under the given conditions, the reactions of hydrogen peroxide also influence the yields of all the products albeit only slightly.[51]

The kinetic mechanism of the combustion of methanol has likewise been considered in other studies.[137,142,143]

3. The Combustion of Acetylene

Kinetic mechanisms of the oxidation of acetylene have been proposed in a number of studies (for example in Refs.144 to 147) and the rate constants of certain elementary stages have been determined. Although these mechanisms differ, they also have much in common. According to the majority of investigators, the main reactions involving the consumption of acetylene in the combustion of weak mixtures are

$$O+C_2H_2 \rightarrow CO+CH_2 \qquad (1d)$$

and

$$OH+C_2H_2 \rightarrow CO+CH_2 . \qquad (2d)$$

In addition, there is no doubt that other reactions in which acetylene is consumed also occur, in particular, the reaction of H atoms with C_2H_2. Presumably the kinetics of the subsequent reactions of the carbon monoxide and methyl and methylene radicals formed in the stages (1d) and (2d) are similar to those which obtain in the combustion of methane. This makes it possible to construct a theoretical scheme for the oxidation of acetylene–oxygen mixtures, based on the general ideas concerning the combustion of methane, which is sufficiently complete for the description of all the main reaction products.[49] However, this scheme is unsuitable for the description of the combustion of rich mixtures of acetylene and of its cracking, since this process includes heterogeneous stages which have not been investigated.

According to Basevich et al.[49], the combustion of acetylene begins with two reactions in which it is consumed [reactions (1d) and (2d)] and this is followed by branching as a result of the reactions

$$CH_2+O_2 \rightarrow CO+OH+H \qquad (5d)$$

and

$$CH_2+O_2 \rightarrow CO_2+2H \qquad (4d)$$

(see Table 1). The second reaction has been discussed in the literature (for example, in Refs.147 and 148). Calculations have shown[49] that the inclusion of even one of them ensures the necessary rate of propagation of the flame. The subsequent part of the mechanism corresponds to the DKM for methane [reactions (1)–(14), (14a), (17), (17a), (17d), (19), (21), (24), (26), (27), (28), (29a), (30)–(33), (35), (42)–(45), (46a), (47), (48), (54), (57), (59), (66), (68), (69), (70), (70a), (83), and (1d)–(5d) in Table 1].

This mechanism is applicable also in the region of relatively low temperatures, since the reactions of hydrogen peroxide, which play an appreciable role in the region $T < 1200$ K, are fairly completely represented here. Table 1 also indicates the Arrhenius parameters of the rate constants for reactions (1d) and (2d) taken from the literature. The rate constants for reactions (5d) and (4d) were selected by calculation. A stepwise temperature rise in the reaction zone is postulated. The calculations were performed for the conditions used in the study of Eberius et al.[147], in which the yields of the final and intermediate products generated in a planar acetylene flame were obtained. In these experiments the conditions were as follows: $[C_2H_2]_0 = 7.2\%$, $[O_2]_0 = 89.2\%$, the remainder comprising He and Ar; $P = 0.0144$ atm and $T = 960$ K. It follows from the comparison of the experimental and calculated[49] profiles that, when no account is taken of reactions (5d) and (4d), it is essential to adopt a somewhat high rate constant for the reaction

$$CO+OH \rightarrow CO_2+H. \qquad (21)$$

On the other hand, if one adopts an "average" rate of reaction (21) with the Arrhenius parameters $A = 2.9 \times 10^9$ litre mol^{-1} s^{-1} and $E = 5.7$ kcal mol^{-1},[34] then it is necessary to include step (5d) or (4d) with a fairly high rate constant (~1.8×10^8 litre mol^{-1} s^{-1}). It is noteworthy that the inclusion of reaction (5d) or (4d) in the methane oxidation mechanism hardly affects the calculated rate of combustion of methane, since in this case the formation of CH_2 is a side reaction.

The calculated and experimental concentrations of the products in the reaction zone agree well with one another and one may conclude that the mechanism is reliable and that the choice of reaction rate constants is correct. One can also conclude that the mechanisms of the oxidation of acetylene and methane are similar, which permits the use of a single approach to their description.

The kinetic mechanism of the combustion of acetylene has also been described in other communications.[117,137,149,150]

4. The Combustion of Ethylene

Experiments have shown[151–153] that the C=C bond is broken in the oxidation of ethylene by oxygen atoms and that products characteristic of the combustion of methane are formed. This makes it possible to construct a theoretical scheme for the combustion of a weak ethylene–oxygen mixture which is sufficiently complete for the description of the yields of all the main reaction products.[57] A broader and more detailed mechanism of the reaction, necessary for the description of the combustion of rich mixtures, remains, however, outside such a scheme.

The most probable primary steps in this reaction involve the interaction of C_2H_4 with oxygen atoms and hydroxyl radicals. The former is apparently the main reaction, since in weak mixtures the concentration of atomic oxygen is usually highest. According to the literature,[151–153] the reaction of C_2H_4 with oxygen atoms proceeds in accordance with the equation

$$C_2H_4+O \rightarrow CH_2+HCO. \qquad (1b)$$

The less important reactions of C_2H_4 have also been less thoroughly investigated. The reaction of C_2H_4 with OH is of this kind and three possible pathways have been proposed for it:[57]

$$C_2H_4+OH \rightarrow CH_2+H_2CO , \qquad (2b)$$

$$C_2H_4+OH \rightarrow CH_4+HCO , \qquad (2b')$$

$$C_2H_4+OH \rightarrow C_2H_2+H_2O . \qquad (2b'')$$

Analytical data have shown[151] that the formation of acetylene C_2H_2 and of the vinyl radical C_2H_3 has been observed in the combustion of ethylene. As already mentioned, the main pathway in the reaction of C_2H_4 in weak mixtures apparently leads immediately to the rupture of the C=C bond, it follows that the formation of C_2H_2 and C_2H_3 is a side process. For this reason, without risking the distortion of the overall picture of the oxidation of C_2H_4, one may attempt to describe in a general form the kinetics of their formation and consumption which have been investigated to only a fairly slight extent. Certain possible reaction pathways, proposed previously by various investigators, were selected for a quantitative test,[57] namely the formation of C_2H_3 via reactions (2b'') and

$$C_2H_4+H \rightarrow C_2H_3+H_2 , \qquad (-3b)$$

$$C_2H_4+O_2 \rightarrow C_2H_3+HO_2 \qquad (-4b)$$

and its consumption via the reactions

$$C_2H_3+O \rightarrow CH_2+CO , \qquad (6b)$$

$$C_2H_3+OH \rightarrow CH_2+HCO , \qquad (7b)$$

$$C_2H_3+H\rightarrow C_2H_2+H_2\,, \qquad (8b)$$

$$C_2H_3+O_2\rightarrow C_2H_2+HO_2\,. \qquad (9b)$$

The possible ethylene decomposition reaction

$$C_2H_4+M\rightarrow C_2H_2+H_2+M\,. \qquad (-5b)$$

must be added to the last two reactions, which lead to the formation of acetylene.

The Arrhenius parameters of the reaction rate constants, which in general differ from one another, were known for only three of the processes enumerated above [reactions (1b), (2b), and (5b)]. The values of *A* and *E* for reaction (1b) were taken from Basevich et al.[57], who obtained them by averaging the data from a number of studies;[151-153] those for reaction (2b) were taken from Greiner's data[58] and those for reaction (-5b) were obtained from Kozlov and Knorre[59] (Table 1). Semiempirical estimates were adopted for the remaining reactions. C_2H_2, CH_4, CH_3, H_2CO, HCO, CO, H_2, HO_2, and H_2O, whose further reactions were considered above, are formed in the reactions enumerated. For this reason, the subsequent part of the mechanism involves the DKM for acetylene and methane [in the study of Basevich et al.[57] these were reactions (1b)–(9b), (1d), (2d), (5d), (1)–(14), (14a), (17), (17a), (17d), (19), (21), (24), (26), (27), (28), (29a), (30), (31)–(35), (38), (39), (40), (42)–(45), (46a), (47), (48), (50), (53)–(57), (59), (65), (66)–(69), (70), (70a), (71), (72), (74), (83), (86) from Table 1].

The kinetic curves were calculated[57] for the experimental conditions adopted by Peeters and Mahnen,[151] who provided the most detailed data on the compositions of the ten final and intermediate products generated in a planar ethylene plane. The conditions in these experiments were as follows: $[C_2H_4]_0 = 6.55\%$, $[O_2]_0 = 33.45\%$, $P = 0.0535$ atm, and $T = 1900$ K. The calculated and experimental concentrations agreed in order of magnitude, the agreement being best on the assumption of a single channel in reaction (2b). Hence one may conclude that the reliability of the reaction mechanism underlying the calculation is fairly high.

Naturally the analytical results depend to a large extent on the choice of the reactions and rate constants; however, despite this they are of interest. The contributions of different elementary processes can be most conveniently estimated from the integral *I* [see Eqn.(V)]. The main pathway leading to the consumption of ethylene is, as was in fact assumed, reaction (1b); reaction (2b) has the lowest rate. The replacement of reaction (2b) by (2b′) makes the calculated concentration of methane higher by almost two orders of magnitude. The reaction pathway (2b″) yields a calculated concentration $[C_2H_3]$ twenty times higher than the experimental value. If account is taken only of the interaction of C_2H_4 with O and OH [reactions (1b) and (2b)] and at the same time all the processes associated with the reactions of C_2H_3 and C_2H_2 [(3b)–(9b), (1d), and (2d)], then one obtains in this instance the concentrations of products which agree in order of magnitude with their experimental values {naturally in this calculation it is assumed that $[C_2H_3] = [C_2H_2] = 0$}.

The main process responsible for the appearance of acetylene is

$$C_2H_4+M\rightarrow C_2H_2+H_2+M\,, \qquad (-5b)$$

while the reaction

$$C_2H_4+H\rightarrow C_2H_3+H_2 \qquad (-3b)$$

is responsible for the appearance of the C_2H_3 radical. The main processes leading to their consumption are respectively

$$C_2H_2+O\rightarrow CH_2+CO \qquad (1d)$$

and

$$C_2H_3+O_2\rightarrow C_2H_2+HO_2\,. \qquad (9b)$$

It is important to note that the fastest branching process under the given conditions, as in the vast majority of cases of high-temperature oxidation of hydrocarbons, is the reaction

$$H+O_2\rightarrow OH+O, \qquad (-4)$$

while the main source of hydrogen atoms is the process

$$HCO+M\rightarrow H+CO+M. \qquad (-66)$$

Examination of the overall results of the calculations and their comparison with kinetic data for methane and acetylene flames apparently permit the conclusion that the mechanisms of the combustion of various hydrocarbons are very similar and that hydrogen plays an important role as an intermediate oxidation product.

The kinetic mechanism of the combustion of ethylene has also been considered in other communications,[117,137,154,155] etc.

5. The Combustion of Ethane

The search for reaction schemes describing the combustion of all the more complex hydrocarbons (C_2H_6, C_3H_8, etc.) is important for both chemical kinetics and for practical purposes. The proposed mechanisms are apparently still not yet sufficiently schematic and are conventional in character. The mechanism of the combustion of ethane must naturally include the scheme for the oxidation of yet another stable intermediate—acetaldehyde.

At an early stage of the development of the DKM, two more or less detailed mechanisms of the combustion of ethane were proposed and analysed quantitatively. In one of them,[156] the dissociation of the carbon–carbon bond with formation of methyl radicals was considered as the primary step:

$$C_2H_6\rightarrow CH_3+CH_3\,. \qquad (-2c)$$

The formation of CH_3 is characteristic also of the oxidation of methane. The author[156] therefore assumed that the subsequent reactions fully correspond to the mechanism of the oxidation of CH_4. The arbitrary nature of this solution is evident, because the rate of decomposition of C_2H_6 can in general be lower than the rate of its reaction with the principal active centres of the reaction—the hydroxylradical OH and the H and O atoms. In a second study[157] the primary reactions considered in the oxidation of ethane involved its interaction with OH, H, O, and O_2, leading to the abstraction of a hydrogen atom and the formation of hydrocarbon molecules and radicals, which in their turn react in the same way. According to this mechanism,[157] the carbon chain is ruptured only in the interaction of the C_2H_2 and C_2H formed with O and O_2 respectively, which leads to the appearance of CH_2, CO, and CHO. Thus the extremely probable reactions of the ethyl radical, which involve the rupture of the C–C bond or the formation of oxygen-containing species, were altogether excluded from consideration.

The mechanism of the combustion of ethane considered below was proposed by Basevich and Kogarko[64] and is based on the probable analogy of the mechanisms of the combustion of C_2H_6 and CH_4; in it additional allowance was made for a large number of reactions proposed previously by various workers, including those associated with acetaldehyde [Table 1, reactions (2c)–(28c)]. In the first six reactions [reactions (2c)–(7c)], the decomposition of ethane as well as the formation of ethyl radicals are postulated. Next, in contrast to the study of Cooke and Williams,[157] certain possible reaction pathways, involving the interaction of C_2H_5 with OH, H, and O and leading to the rupture of the C–C bond and the formation of alkyl radicals and oxygen-containing species [reactions (8c)–(11c)], were introduced.

When the reaction of C_2H_5 with the O_2 proceeds by analogy with the reaction between CH_3 and O_2, it can afford CH_3CHO and OH or, when the C–C bond is ruptured, H_2CO and CH_3O are formed [reactions (12c) and (13c)]. It has been suggested that CH_3CHO then reacts with dissociation of the C–C bond [reactions (–17c) and (–20c)] and with abstraction of the latter in the unimolecular reaction (–21c) or in reactions with H and O [reactions (22c) and (23c)]. The next group of reactions [reactions (24c)–(28c)] agrees in broad outline with the direction of the transformation via ethylene described by Cooke and Williams.[157]

All the processes described above result in the formation of products (H_2, H_2O_2, H_2CO, HCO, CH_4, CH_3, CH_2, CH_3O, C_2H_4, and CO) which also occur in the mechanisms of the combustion of CH_4, CH_3OH, C_2H_2, and C_2H_4; the list of the elementary processes involved in the oxidation of C_2H_6 should therefore be supplemented by the reactions of the latter compounds.

Table 1 indicates the Arrhenius parameters of the rate constants for the above reactions. The values of *A* and *E* were taken from the literature sources quoted, were selected in the calculations, or were estimated approximately from semiempirical formulae.

At sufficiently high temperatures, the mechanism proposed presupposes the occurrence of a branched chain reaction, hydrogen playing the role of the intermediate ensuring degenerate branching.

Calculations[64] have been carried out for two main versions. In the first account was taken of all the reactions involved in the mechanism. In order to elucidate whether the ethane dehydrogenation pathway[157] is the rate determining pathway in ethane combustion and whether the experimentally observed reaction products can be formed, in principle, without following this pathway, in the second version of the calculation all the reactions of the ethyl radical leading to the formation of ethylene were excluded. For the eight products investigated, a qualitative agreement has in general been observed between calculation and experiment.

The published literature data make possible an additional test of the mechanism considered. It follows from the theoretical analysis of the results of experimental studies of the atomic oxygen flame of ethane,[158] the oxidation of CH_3.CHO,[159,160] and the ignition delays[157,161,162,163] that the oxidation pathway involving the reactions of C_2H_5 with dissociation of the C–C bond and the formation of alkyl radicals and oxygen-containing species is entirely feasible, like the dehydrogenation pathway. The simultaneous occurrence of the reaction via both channels is extremely likely; however, it is difficult to trace the details of the process by observing the overall kinetics. Judging from the value of the integral *I*, the main substances participating in the reaction (substances whose concentrations are comparable in order of magnitude with the concentrations of the initial compounds consumed and of their reaction partners) are, according to the second version of the calculation, C_2H_6, OH, H, O, HO_2, HCO, CH_3, H_2, H_2O, H_2O_2, CO, CO_2, H_2CO, C_2H_5, O_2, and CH_4. Considerations of the values of *I* permits the conclusion that ethane is consumed mainly in its reaction with OH, H, O, and M. On self-ignition at low temperatures, the highest branching rate is given by the process

$$H_2O_2+M\rightarrow OH+OH+M, \qquad (-28)$$

while at high temperatures (>1200 K) the reaction is

$$H+O_2\rightarrow OH+O. \qquad (-4)$$

The dissociation of the C–C bond in the atomic flame takes place via the reaction

$$C_2H_5+O\rightarrow CH_3+H_2CO, \qquad (11c)$$

while in the remaining cases it occurs in the reactions of C_2H_5 with O_2 and OH and in the decomposition of CH_3CHO. Atomic hydrogen is formed in the reaction

$$O+OH\rightarrow O_2+H \qquad (4)$$

or in the decomposition of the formyl radical,

$$HCO+M\rightarrow H+CO+M, \qquad (-66)$$

while molecular hydrogen is formed in the reaction of H with C_2H_6, CH_4, and H_2CO. Water appears as a result of the reactions of C_2H_6, H_2, and H_2CO with OH; carbon monoxide is produced by the reaction of HCO with O_2 and M, and carbon dioxide is formed by the reaction of CO with OH and HO_2. Thus the reaction mechanism is in many respects similar to the mechanism of the combustion of CH_4, by analogy with which it has in fact been constructed.

The lack of experimental data at the present time precludes a rigorous selection of the reaction pathways and of all the elementary steps. Table 1 does not include many of the known reactions. There is no doubt that the mechanism discussed must be regarded as preliminary, requiring confirmation and refinement on the basis of a wide variety of experimental data.

The kinetic mechanism of the combustion of ethane has also been analysed in other studies,[137,164,165] etc.

IV. NITROGEN-CONTAINING COMPOUNDS

Methylamine is the simplest amine among those used in the combustion technology independently or as a fuel additive. The knowledge of the mechanisms of the combustion of such compounds is essential for the description of the energy evolution and for the understanding of the kinetics of the formation of the final products, some of which are environmentally undesirable.

The H–C–N–O system is very complex but the availability of data on the kinetics of the combustion of H_2 and C_1–C_2 hydrocarbons with O_2 justifies attempts to construct the combustion mechanism also in this involved case. The construction of a mechanism of the combustion of methylamine is considered below in relation to the atomic oxygen flame.[69] The initial endeavour of the authors[69] to make do with a small number of reactions was unsuccessful; for this reason, subsequently their efforts were directed to the construction of a more or less detailed mechanism.

By analogy with many of the known reactions involving oxygen atoms, one can assume that the abstraction of a hydrogen atom from the molecule being oxidised is extremely probable in the primary step. The C–H bond (93.7 kcal mol^{-1}) is stronger than the N–H bond (87.2 kcal mol^{-1}).[166] One can therefore postulate that the hydrogen abstraction reaction proceeds in accordance with the equation

$$O+CH_3NH_2\rightarrow CH_2NH+OH. \qquad (2.1)$$

The hydroxylradical formed in reaction (2.1) and the atomic hydrogen obtained via the reaction

$$O+OH\rightarrow O_2+H \qquad (4)$$

can react with the initial molecules in the processes

$$OH+CH_3NH_2\rightarrow CH_2NH+H_2O, \qquad (2.2)$$

$$H+CH_3NH_2\rightarrow CH_2NH+H_2. \qquad (2.3)$$

The reactions involving the generation of active centres, i.e.

$$CH_3NH_2\rightarrow CH_3+NH_2, \qquad (-2.4)$$

$$CH_3NH_2+O_2\rightarrow CH_2NH+HO_2. \qquad (-2.5)$$

may be important for self-ignition at high temperatures and in the presence of O_2. Further reactions can be represented only very tentatively. Atomic oxygen and also H, OH, and O_2 can give rise ultimately to species of the type CH_3, CH_3O, CH_4, HNO, NH, and NH_2 on interaction with CH_3NH. However, there are no objective criteria which would make it possible to discover, on the basis of the available experimental data, the processes leading to their formation. For this reason, the reactions presented below should probably be regarded as overall processes:

$$CH_3NH+O\rightarrow CH_3O+NH\,, \qquad (2.6)$$

$$CH_3NH+OH\rightarrow CH_4+HNO\,, \qquad (2.7)$$

$$CH_3NH+H\rightarrow CH_3+NH_2\,, \qquad (2.8)$$

$$CH_3NH+O_2\rightarrow CH_3O+HNO\,. \qquad (2.9)$$

Starting with the set of species formed in these reactions, it is possible to formulate the subsequent processes (they are also included in Table 1). The reactions of CH_4 and CH_3 in the presence of atomic oxygen were considered earlier in the methane oxidation scheme and, together with the corresponding parameters, they can be usefully adopted as a component of the mechanisms investigated. This also applies to the reactions of the CH_3O radical.

The reactions of the NH, NH_2, and HNO species formed in the processes enumerated above have also been frequently considered by various investigators (for example, by Albers et al.[78]). The rate constants for some of them are known and are presented in Table 1 [see reactions (2.10) to (2.27)]. They include processes involving the possible formation of NH_3. This part of the scheme should describe also the oxidation of NH_3 constituting, together with the reactions in the H–O system, an important part of the DKM for the H–N–O system.

The combustion of rich mixtures of hydrocarbons, particularly nitrogen-containing hydrocarbons, is known to be accompanied by the formation of HCN and NH_3.[167] HCN is formed in large amounts also when NH_3 is added to hydrocarbons. Consequently one may assume that the interaction of the NH_2, N, and NH species, characteristic of the combustion of ammonia, with intermediates in the combustion of hydrocarbons, can also lead to the formation of HCN, as in the combustion of amines, including CH_3NH_2. Part of the kinetic scheme describing the formation of HCN and its oxidation reactions actually corresponds tentatively to this feature [see Table 1, reactions (2.28)–(2.40)].

Reactions (2.41) and (2.42), put forward by Fenimore,[167] make it possible to explain the formation (in the reverse reaction) of HCN and the so called "fast" NO in hydrocarbon flames. On the one hand, atmospheric nitrogen and, on the other, the CH_2 and CH species participate in these processes. The first species occurs in the methane oxidation scheme; the appearance of the second and its consumption were described by reactions (95)–(99), which constitute the continuation of the methane part of the scheme (see the first half of Table 1). The Arrhenius parameters of these processes are indicated on the basis of the estimates of Basevich et al.[50]

Processes responsible for the formation of NO in the high-temperature oxidation of methane in air [reactions (1.12) to (1.15)] (the so called extended Zel'dovich mechanism[168]) are characteristic of this species. Reactions (1.3)–(1.10) take place over a wide temperature range and lead to the formation and decomposition of NO.[89] Reaction (1.11) should also be apparently included here.

Basevich et al.[69] used as far as possible the rate constants for the forward or reverse reactions available in the literature (for the relevant references, see Table 1); in certain cases the Arrhenius parameters were estimated semiempirically. After the initial selection, the parameters listed in Table 1 were used in all subsequent calculations.

The mechanism examined was used[69] in the calculations of the kinetics of the combustion of CH_3NH_2 in an atomic oxygen flame and a fairly satisfactory agreement between experiment and calculations was achieved.

The proportions of the principal reaction products (other than CH_3NH_2, O, and O_2), whose final concentration amounted to not less than 10% of the CH_3NH_2 consumed, can be calculated. These products include H_2, CO, H, CH_4, NO, H_2O, H_2CO, N_2, and NH_3, which are thus the principal species of the kinetic scheme for the given conditions.

Next, the contribution of each elementary step to the reactions of CH_3NH_2 and the individually selected reaction components was calculated.[69] The primary reaction (2.1) involves the consumption of 12–20% of oxygen atoms. The relative contribution of reactions (2.2) and (2.3), involving the consumption of CH_3NH_2 by reaction with OH and H, to its overall reaction is 22–45%. Nitric oxide is formed mainly via the reactions

$$N+OH\rightarrow NO+H\,, \qquad (1.15$$

$$N+O_2\rightarrow NO+H\,, \qquad (1.13$$

and also

$$HNO+O\rightarrow NO+OH\,, \qquad (2.21$$

$$NH+OH\rightarrow NO+H_2\,. \qquad (2.23$$

The contributions of these reactions diminish in the above order but have similar magnitudes. The contributions of the reactions

$$CH_3+N\rightarrow HCN+H_2\,, \qquad (2.29)$$

$$CH_2+NH\rightarrow HCN+H_2 \qquad (2.28$$

to the formation of HCN are also virtually within the limits of one order of magnitude. In the processes indicated above, the reactions

$$NH+H\rightarrow N+H_2\,, \qquad (2.24)$$

$$NH+O\rightarrow N+OH\,, \qquad (2.25)$$

$$NH_2+NH\rightarrow NH_3+N\,, \qquad (2.16)$$

$$NH+NH\rightarrow NH_2+N \qquad (2.27)$$

play the role of the source of atomic nitrogen. NH_3 is formed via the reactions

$$NH_2+HO_2\rightarrow NH_3+O_2\,, \qquad (2.11)$$

$$NH_2+H_2\rightarrow NH_3+H\,. \qquad (-2.18)$$

The rapid reaction

$$NH_2+OH\rightarrow NH_3+O \qquad (2.12)$$

is ineffective owing to the faster occurrence of the reverse process.

A satisfactory agreement has also been found on comparing the calculated and experimental data obtained under the conditions of atmospheric flames[167,169] and experiments with added ammonia.[170]

The insufficiency of experimental data and the complexity of the system considered preclude at the present time a rigorous selection of reaction pathways and all the elementary steps. Table 1 does not include many of the known reactions. There is no doubt that the mechanism discussed should be regarded as a first approximation. This applies especially to the part described by Eqns. (2.6)–(2.9). It is necessary to refine the character of the process and the reaction rate constant.

A kinetic mechanism of the combustion of nitrogen-containing compounds have also been proposed in other studies,[171,172] etc.

The kinetics of combustion in the H–C–N–O system have found an application in the analysis of the environmental consequences of combustion processes and in the search for possible ways of reducing the concentrations of harmful products. Two main reactions leading to the formation of nitric oxide from atmospheric nitrogen [(1.12) and (1.13)] were found to be unspecified in a fundamental study.[168] As already stated, the above mechanism[168] is usually considered jointly with the rapid reaction (1.15). The contribution of reaction (1.15) to the formation of NO has been shown by calculations to be frequently not inferior to the contribution of reaction (1.13) and is sometimes even greater.[173] Under practical conditions, the NO concentration can reach hundredths and thousandths of parts per million owing to the relatively high temperatures and long (more than 0.1 s) residence times of the gas at high temperatures. In the absence of nitrogen in the fuel itself, the above mechanism of the formation of NO is the main one.

Under laboratory conditions, which are distinguished as a rule by low temperatures (<2000 K) and short residence times of the gas (less than 10–20 ms), the yield of NO amounts to several, several tens, and (rarely) 100 parts per million. Under these conditions, the approximations underlying the theory[168] are insufficiently valid and for this reason differences are observed between the theoretical and experimental nitric oxide concentrations: there is insufficient time for the attainment of equilibrium and the actual concentrations of atomic oxygen can exceed significantly those corresponding to thermodynamic equilibrium. Calculations using the DKM have shown that more NO is usually obtained under these conditions.[174–176] However, this applies solely to hydrocarbons. The calculations for hydrogen–air flames have fully confirmed the theoretical and experimental data,[168] which indicates the possibility of excluding the reaction zone from consideration. The calculations have also shown that, up to pressures of 100 atm, the amount of NO formed in the reaction zone of the H_2 flame even at an initial temperature of 600 K is extremely insignificant owing to the short residence times.

Under laboratory conditions, the abrupt formation of nitric oxide in the reaction zone on combustion of hydrocarbons was first observed by Fenimore.[173] It was noted that, under the experimental conditions, the formation of NO includes two stages: the rapid stage in the reaction zone and the slow stage in the flame gases. The mechanism of the formation of NO via reactions (1.12)–(1.15) operates in both stages. The authors[177] concluded that in the case of hydrocarbons the mechanism (1.12)–(1.15) describes the combustion of weak mixtures with a coefficient of the excess of air $\alpha \geq 1.3$.

Data for rich mixtures with a large discrepancy between the unduly low calculated and experimental NO concentrations, indicating that the mechanism of the formation of nitrogen oxide is in this instance apparently more complex and is not confined to the scheme (1.12)–(1.15), have been frequently quoted in the literature. Special experiments have been carried out,[178] in which the yields of NO were compared under identical conditions in hydrogen–oxygen–nitrogen flames without and with addition of acetylene. In the latter case more nitric oxide is formed and there is reason to believe that its formation is promoted by the reactions of hydrocarbon radicals with nitrogen (Table 1, DKM for the H–C–N–O system), although these NO formation pathways have not as yet been adequately investigated. We may note that the concentrations of "fast" NO do not exceed 100 to 120 p.p.m.[179] In the latter studies the authors specially optimise the experimental conditions in order to obtain the maximum yield of this species.

Finally, there exists yet another source of the formation of nitrogen oxides on combustion. This is the nitrogen which forms part of the composition of fuel and impurity molecules. Experiments have shown[180] that, depending on the combustion conditions and the composition of the fuel mixture, between 10 and 90% of the fuel nitrogen is converted into nitric oxide; the remainder (in rich mixtures) forms ammonia and HCN as well as nitrogen molecules (see the above scheme for the H–C–N–O which was formulated to account for the formation of NO from the fuel nitrogen, requires a more detailed specification and justification. The possible role of N atoms in this process, which have been discovered by Basevich et al.[69], has also been pointed out by Miller et al.[172]

V. THE APPLICATION OF H_2O_2 AND HNO_3 AS OXIDANTS

The use of hydrogen peroxide as oxidants instead of oxygen is based on the relative ease of its thermal decomposition with formation of two hydroxylradicals. The oxidation of the corresponding mixtures begins at the temperature of the onset of appareciable decomposition of hydrogen peroxide.[9] It was stated above that hydrogen peroxide is an essential component of the DKM of the oxidation of hydrogen and hydrocarbons and the kinetic mechanism where H_2O_2 functions as the oxidant is therefore identical with the mechanism of the reaction in the oxygen system.

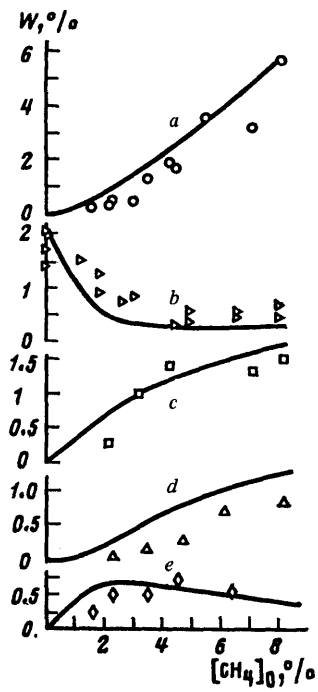


Figure 4. Dependence of the yield of the products of the reaction of CH_4 with HNO_3 on the initial methane concentration;[88] $[HNO_3]_0 = 7\%$, $T = 1067$ K, $P = 0.01$ atm, $t = 5$ ms: symbols—experiment; lines—calculation; *a*) CH_4; *b*) NO_2; *c*) CO; *d*) H_2; *e*) CO_2.

The calculated and experimental data were compared under flow conditions for the CH_4–H_2O_2 [33] and H_2–H_2O_2 [28] systems. The presence of a certain initial concentration $[O_2]_0$ as a consequence of the presence of O_2 in liquid H_2O_2, which,

when vaporised by bubbling, generated the necessary H_2O_2 concentration in the gas phase, was noted in the experiments. A satisfactory agreement between the experimental and calculated data was achieved in both cases.

Nitric acid also readily decomposes with formation of nitrogen dioxide and a hydroxylradical[181,182] and is therefore used as the oxidant.[183,184] The hydroxylradical obtained reacts again with nitric acid to form the highly reactive NO_3 radical and water [reactions (1.1) and (1.2) in Table 1]. Examination of the above processes together with the DKM for the H–N–O system made it possible to analyse the kinetics of the interaction of hydrogen with nitric acid.[28] The reaction proceeds fairly rapidly but, as a consequence of the high rate of destruction of OH, H, and O in the gas samples of the EPR spectrometer due to the presence of nitrogen-containing products, the concentration of these radicals could not be recorded.

Certain experimental data referring to the reaction of CH_4 with HNO_3 under flow conditions are presented in Fig.4.[88] The reaction begins at the temperature corresponding to the onset of the decomposition of HNO_3. The calculated kinetic curves describe satisfactorily the experimental relations obtained when the initial methane content is varied.

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The theoretical studies described above were not the only ones performed with the aid of the DKM. They have been used to calculate the ignition delays, the rates of propagation and the stabilisation limits of flames, in the study of promotion and chemi-ionisation phenomena and of the composition of the products in the technological formation of acetylene and the synthesis gas from methane, in the estimation of the concentrations of various environmentally undesirable components, and in other cases, including the conditions in a turbulent medium. The results of the available calculations demonstrate their more or less satisfactory agreement with experimental data. The specific DKM presented in Table 1 serves merely as the first approximation and requires further refinement.

The first stage in the construction of the detailed kinetic mechanisms, where their possibilities and the accuracy of the calculations based on them have become clear has apparently now been completed. The next stage in the construction of the DKM will probably involve a careful analysis of the individual elementary steps and the real reaction channels and also an increase in the accuracy of the estimation of the rate constants. The aim of this stage will be a transition from qualitative estimates obtained nowadays to a quantitatively accurate *a priori* calculation.

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