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Academician of the Academy of Sciences of the Uzbek SSR N. V. Lavrov, I. G. Petrenko

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Abstract

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THE MECHANISM OF METHANE COMBUSTION AT ELEVATED TEMPERATURES

The course of the reactions of complete combustion of methane, i.e., the interaction of methane with oxygen with the ultimate formation of carbon dioxide and water vapor, is accompanied by the liberation of a considerable amount of heat. Calculations carried out using the latest data on the enthalpies of the initial and final reaction products (^{1}) have shown that in the process of complete combustion of methane, 191.8 kcal/mole of heat is evolved. A large number of works have been devoted to the study of the mechanism by which this important chemical process proceeds, the most complete results of which are given in well-known monographs ($^{2-4}$). A rather detailed analysis of various schemes for methane oxidation is also given in the work (^{5}). It has been convincingly shown that, in the process of methane interacting with oxygen, intermediate compounds and radicals are formed, and the reactions proceed by a chain mechanism. The more complicated question has proved to be which particular elementary chemical reactions take place under these conditions.

Three schemes of the mechanism of methane oxidation have become most widespread: those proposed by Norrish (^{6}), B. Lewis and G. Elbe (^{7}), and N. N. Semenov (^{2}), which were developed mainly for low-temperature processes. In the first two schemes there are reactions that are not elementary, and reactions that require the expenditure of a considerable amount of heat. In addition, they are not carried through to the final reaction products, and there are no calculations of the thermal effects of the individual stages of the proposed process mechanism. Therefore, at present these two schemes cannot be accepted. The scheme proposed by N. N. Semenov is the most complete and convincing, but it was proposed for low-temperature processes and is not carried through to the final reaction products.

It seems to us that, in developing various schemes for a complex chemical process, it is necessary to take into account the thermal effects of the elementary reactions, their balancing, and consistency with thermodynamic calculations of the change in the enthalpy of the system; and the scheme must be carried through to the final reaction products.

As a result of an analysis of various schemes of the reaction mechanism for the complete oxidation of methane and of elementary reactions, a scheme has been proposed for the high-temperature oxidation of methane with formation of the final reaction products—carbon dioxide and water vapor—based on N. N. Semenov' s scheme with some additions. In doing so, the thermal effects of the elementary reactions have been obtained from new initial data (^{8}), and approximate activation energies of elementary radical reactions have been obtained from the equations proposed by N. N. Semenov (^{2}). The most difficult is the initial process of radical formation. It is assumed that at the beginning the radicals are generated as a result of the interaction of methane molecules with oxygen, with formation of the methyl radical and the hydroperoxide radical:

$$CH_4 + O_2 = \dot{C}H_3 + H\dot{O}_2; \quad H = 56 \text{ kcal/mole.}$$

Since this reaction requires an expenditure of 56 kcal/mole of heat, and its activation energy must be still higher, it proceeds only in the initial moment, before the onset of the radical-chain mechanism, in the course of which complete consumption of methane also takes place. Consequently, the specific weight of this reaction in the overall mechanism of all elementary reactions must be comparatively small. The proposed tentative mechanism of methane combustion at elevated temperatures is as follows.

1. The process of chemical interaction of methane with oxygen is combined with separate stages of the thermal decomposition of methane.
2. Methane combustion is subdivided into three stages:

a) incomplete combustion of methane to formaldehyde ($CH_4 + O_2 = H_2CO + H_2O + 73.4$ kcal/mol);

b) destruction of formaldehyde as a result of thermal decomposition and the action of oxygen;

c) afterburning of the combustible substances formed during the destruction of formaldehyde to CO_2 and H_2O.

At elevated temperatures (above 800°), methane cracking reactions begin to proceed at appreciable rates. Chain initiation may be represented as follows:

$$CH_4 = \dot{C}H_3 + \dot{H} - 103 \text{ kcal/mol.}$$

In the presence of oxygen the reaction proceeds

$$\dot{H} + O_2 = HO_2 + 47 \text{ kcal/mol,}$$

$$HO_2 = \dot{O}H + \dot{O} - 64.9 \text{ kcal/mol.}$$

Subsequently, the process of high-temperature oxidation of methane proceeds according to the following radical-chain scheme:

		ΔH^0_{298}, kcal/mol	ε, kcal/mol
1.	$\dot{C}H_3 + O_2 = CH_3 + \dot{O}\dot{O}$	26.1	31.1
2.	$CH_4 + \dot{O} = \dot{C}H_3 + \dot{O}H$	0.7	12.1
2^{I}.	$CH_4 + \dot{O}H = \dot{C}H_3 + H_2O$	-16.2 $(-15)^2$	7.4 $(8.0)^4$
3.	$CH_3\dot{O} + O_2 = CH_2O + HO_2$	-28.0	4.5
3^{I}.	$CH_3\dot{O} = CH_2O + \dot{H}$	17.0	24.3
3^{II}.	$CH_3\dot{O} + \dot{O}H = CH_2O + H_2O$	-100.2	≈ 0
3^{III}.	$CH_3\dot{O} + HO_2 = CH_2O + H_2O_2$	-70.5	≈ 0
4.	$CH_2O + \dot{O}H = \dot{C}HO + H_2O$	-42.2 $(-37)^2$	1.0
4^{I}.	$CH_2O = \dot{C}HO + \dot{H}$	77.0	(77)
4^{II}.	$CH_2O + \dot{H} = \dot{C}HO + H_2$	-27.2	4.7 $(3.6)^4$
4^{III}.	$CH_2O + O_2 = \dot{C}HO + HO_2$	-30.0 $(32)^2$	$(46)^3$
4^{IV}.	$CH_2O + HO_2 = \dot{C}HO + H_2O_2$	-12.5	8.4
5.	$\dot{C}HO + HO_2 = CO + H_2O_2$	-55.5	≈ 0
5^{I}.	$\dot{C}HO + O_2 = CO + HO_2$	-13.0	≈ 7.9
5^{II}.	$\dot{C}HO = CO + \dot{H}$	34.0	37.0 $(14)^4$
5^{III}.	$\dot{C}HO + \dot{O}H = CO + H_2O$	-85.2	≈ 0
5^{IV}.	$\dot{C}HO + \dot{H} = CO + H_2$	-70.2	≈ 0 $(5)^4$
6.	$CO + H_2O_2 = CO_2 + H_2O$	-92.9	–
6^{I}.	$CO + \dot{O}H = CO_2 + \dot{H}$	-24.9	5.3
6^{II}.	$CO + HO_2 = CO_2 + \dot{O}H$	-62.3	≈ 0
6^{III}.	$CO + \dot{O} = CO_2$	-127.2	≈ 0
(1—6)	$CH_4 + 2O_2 = CO_2 + 2H_2O$	-191.8	–

Thus, the results of calculating the thermal effects of the elementary reactions of the high-temperature interaction of methane and oxygen with the formation of carbon dioxide and water vapor, as well as calculations of the change in the total enthalpy of the process, gave sufficiently concordant results. This indicates that the thermal effects of the elementary reactions adopted in the calculations are sufficiently accurate, and the errors cannot be too···

large. The scheme also gives possible additional reactions, marked with an index, which may also occur in the process under consideration. Of the main scheme, only reaction (1) is the most endothermic, with a heat expenditure of 26.1 kcal/mole, and it basically determines the rate of the overall process. For reaction (2), only 0.7 kcal/mole of heat is expended, while all the other four are exothermic. In accordance with the indications of N. N. Semenov, it may be assumed that reaction (1) proceeds with the formation of an intermediate compound–methyl peroxide (CH_3OO), which then isomerizes into the compound (CH_2OOH), with subsequent detachment of the hydroxyl group from this radical and formation of formaldehyde. There are grounds to believe that this pathway may further reduce the endothermicity of this group of reactions.

It should also be noted that in a complex system consisting of more than two dozen different types of molecules and radicals, other elementary reactions are possible, in particular chain-termination reactions on the walls of the combustion chamber; but it is obviously always necessary to distinguish side reactions, whose specific weight is comparatively small, from the principal elementary reactions leading to the complete conversion of the initial substances into the final products of the process. At high temperatures, the process of oxidation of formaldehyde proceeds simultaneously according to two overall schemes:

7. $2CH_2O + O_2 = 2CO + 2H_2O + 2 \times 50.95$ kcal/mole decomposition of CH_2O in the presence of oxygen)

8. $CH_2O = CO + H_2 - 6.8$ kcal/mole (thermal decomposition of CH_2O).

Reaction (8) proceeds through the following intermediate stages:

	ΔH°_{298}, kcal/mole	ε, kcal/mole
$CH_2O = \dot{C}HO + \dot{H}$	77.0	(77)
$CH_2 + \dot{H} = \dot{C}OH + H_2$	−27.2	4.7
$\dot{C}HO = CO + \dot{H}$	34.0	37
$\dot{C}HO+\dot{H} = CO+H_2$	−70.2	$\simeq 0$
$2CH_2O = 2CO + 2H_2$	13.6	

The ratio between CO and H_2 in the products of methane combustion will depend on the rate of reactions (7 and 8) in the temperature interval under study.

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Note: Figure translations are in progress. See original paper for figures.

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