Academician of the Academy of Sciences of the Uzbek SSR N. V. LAVROV, I. G. PETRENKO

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Abstract

Full Text

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MECHANISM OF THE REACTIONS OF METHANE CONVERSION BY WATER VAPOR

The chemical processes of the interaction of methane with water vapor for the purpose of obtaining synthesis gas—a mixture of hydrogen and carbon monoxide—have been studied for a long time. This is explained by the relative cheapness and availability of the starting substances and by the need to develop economically advantageous methods for obtaining mixtures of gases suitable for chemical synthesis.

A considerable number of works on the study of methane conversion by water vapor has been published in the literature, but among them there are few works devoted to studying the mechanism by which this process proceeds.

Thus, for example, in the work of A. Leibush and co-workers ([1], [2]) a mechanism of methane conversion by water vapor is proposed, based on the scheme of thermal decomposition of methane according to Kassel ([3]). Each of the products of this decomposition, beginning with methane, interacts with water vapor with the formation of carbon monoxide and hydrogen. Thus, it is assumed that two main directions of reactions occur—the thermal decomposition of methane and the interaction of methane and its products with water vapor. This reaction mechanism cannot be accepted, since part of the reactions is not elementary and is not justified energetically.

The conversion of methane by water vapor to hydrogen and carbon monoxide is described by the following equation:

$$CH_4 + H_2O = CO + 3H_2 - 49.3 \text{ kcal/mol.}$$

The heat effect of this process has been established from data on the enthalpies of the initial and final reaction products and is equal to 49.3 kcal/mol ([4]), which is evidently sufficiently accurate. This value may be taken as the basis for calculating and checking the heat effects of elementary reactions using data on the energies of bond rupture of atoms in molecules and radicals ([5]-[7]).

Analysis of the literature data and of the heat effects of various variants of elementary reactions shows that the process of interaction of methane with water vapor proceeds by a radical mechanism and may be represented by the following stages:

		$\Delta H°_{298}$, kcal/mol	ϵ, kcal/mol
1.	$CH_4 = \dot{C}H_3 + \dot{H}$	103	(103)
2.	$\dot{C}H_3 + H_2O = H_3COH + \dot{H}$	30.5	34.3
3.	$H_3COH = H_2\dot{C}OH + \dot{H}$	92	(92)
4.	$H_2\dot{C}OH = H_3\dot{C}O$	8	17.5
5.	$H_3\dot{C}O = H_2CO + \dot{H}$	17	24.3
6.	$H_2CO = H\dot{C}O + \dot{H}$	77	(77)
7.	$H\dot{C}O = CO + \dot{H}$	34	37.0
8.	$6\dot{H} = 3H_2$	−312.6	–
	$CH_4 + H_2O = CO + 3H_2$	48.9	–

The errors in the calculations amount to 0.4 kcal/mol, which is quite permissible for insufficiently accurate values of the bond-rupture energies in radicals. Reaction (8) is given in a general form for summing the heat effects

effects. In reality, atomic hydrogen is consumed mainly in reactions that determine the radical-chain mechanism of the process. The activation energies (ε) of the reactions are given according to the approximate equation of N. N. Semenov (^{5}).

Of this scheme, the most difficult is reaction (1), the decomposition of methane with formation of the methyl radical and atomic hydrogen. Obviously, this reaction can be initiated only at high temperatures or under conditions of catalytic action by a solid surface, and subsequently methane reacts with hydrogen atoms. Reaction (3), the decomposition of methanol, also proceeds with a large endothermic effect. Therefore there are grounds to believe that methanol also interacts mainly with atomic hydrogen, forming water vapor and methyl, or else molecular hydrogen and the methanol radical, according to the scheme:

		ΔH^0_{298}, kcal/mol	ε, kcal/mol
9.	$H_3COH + \dot{H} \quad = \quad H_2\dot{C}OH + H_2 + 12.2$ kcal/mol	−12.2	20.7

The course of the methane conversion reaction with water vapor in the presence of catalysts, according to our ideas, should, bypassing the complex stage of methanol formation and decomposition,

$$10. \quad H_2O + [K]^* = [K]O + H_2$$

$$11. \quad [K]O + \dot{C}H_3 = \dot{O}CH_3 + [K]$$

and then the process of decomposition of $\dot{O}CH_3$ and other intermediate compounds proceeds according to equations (5, 6, 7, and 8).

The hydrogen formed in the elementary reactions readily reacts with a methane molecule, forming molecular hydrogen and the methyl radical.

$$12.\quad CH_4 + \dot{H} = \dot{C}H_3 + H_2 + 1.2\ \text{kcal/mol}$$

Reaction (12) proceeds with a small exothermic effect and an activation energy approximately equal to 11 kcal/mol. This reaction serves as a link in the main chain of the monoradical, chain, unbranched mechanism of the interaction of methane with water vapor, which in its final form may be represented by the following scheme:

				ΔH^0_{298}, kcal/mol	ε, kcal/mol
12.	$CH_4 + \dot{H}$	=	$\dot{C}H_3 + H_2$	−1.2	11.2
2.	$\dot{C}H_3 + H_2O$	=	$H_3COH + \dot{H}$	30.5	34.4
9.	$H_3COH + \dot{H}$	=	$H_2\dot{C}OH + H_2$	−12.2	20.7
4.	$H_2\dot{C}OH$	=	$H_3\dot{C}O$	8.0	17.5
5.	$H_3\dot{C}O$	=	$H_2CO + \dot{H}$	17	24.3
13.	$H_2CO + \dot{H}$	=	$H\dot{C}O + H_2$	−27.2	4.7
7.	$H\dot{C}O$	=	$\dot{H} + CO$	34	37
	$CH_4 + H_2O$	=	$CO + 3H_2$	48.9	

The decomposition of formaldehyde into radicals (6) also requires a considerable amount of heat. This reaction stage can also be considerably accelerated by means of atomic hydrogen according to scheme 13, in which 27.2 kcal/mol of heat is released.

For the activation energy of the decomposition reaction of the formyl radical (7) with formation of carbon monoxide and an atomic hydrogen atom, Stisi (8) gives a value of 14 kcal/mol, which is clearly underestimated. The energy of rupture of the bond of the hydrogen atom with carbon in formyl exceeds this value by more than a factor of two.

* [K]—catalyst.

If the first reaction of formation of methyl radicals and atomic hydrogen is not taken into account—a reaction which, evidently, is accelerated under heterogeneous conditions—the rate of the overall process is governed by reactions (7) and (2) of the interaction of methyl with water vapor, with the expenditure of 30.5 kcal/mol of heat. According to N. N. Semenov’ s equation, the activation energy of this reaction is 34.4 kcal/mol and, consequently, it can proceed at comparatively low temperatures.

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