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Abstract

Full Text

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MECHANISM OF THE REACTIONS OF METHANE CONVERSION BY CARBON DIOXIDE

Methane and carbon dioxide, as chemical raw materials, can be obtained in practically unlimited quantities, with comparatively small expenditures of energy and capital investment. In this connection, the problem of carrying out, under industrial conditions, the process of methane conversion by carbon dioxide to obtain a mixture of carbon monoxide and hydrogen gases suitable for chemical synthesis has long attracted the attention of investigators. For the successful solution of this problem, a deep study of the kinetics and mechanism of this reaction is necessary.

The kinetics and mechanism of the reactions of thermal decomposition of methane, especially the reactions of its interaction with molecular and atomic oxygen, have been studied in considerable detail and summarized in the well-known monographs of N. N. Semenov ([1]) and V. Ya. Shtern ([2]). There are significantly fewer works on the study of the reactions of methane interaction with carbon dioxide, and especially on the mechanism of this process. The mechanism of this reaction was partially analyzed in works ([3,4]).

On the basis of literature data and our experiments, an analysis has been carried out of the elementary reactions of the interaction of methane with carbon dioxide and their thermal effects; on this basis a monoradical chain mechanism of the process is shown, in which it proceeds with the least expenditure of heat; consequently, this mechanism is the most probable or principal one.

The reaction of methane conversion by carbon dioxide to hydrogen and carbon monoxide in general form may be represented by the following equation:

$$\mathrm{CH_4} + \mathrm{CO_2} = 2\mathrm{CO} + 2\mathrm{H_2} - 59.1\ \mathrm{kcal/mol} \quad (\Delta H^0_{298} = 59.1).$$

The reaction proceeds at temperatures above 900° and with a significant endothermic effect, which at the present time has been established sufficiently well from data on the enthalpies of the final and initial substances and is equal to 59.1 kcal/mol ([5]).

In considering the elementary reactions of this process it should be noted that there are both specific reactions and reactions common to the process of methane interaction with oxygen. The formation in this process of methyl, methoxyl, and formyl monoradicals, as well as formaldehyde, is generally accepted and has been quite convincingly proven ([1,2]). In the reaction of methane conversion by carbon dioxide these radicals are also inevitably formed, which may serve as evidence of the commonality of certain elementary reactions of methane oxidation regardless of the source of oxygen.

The elementary reactions of the process of methane interaction with carbon dioxide may be represented by the following scheme:

		ΔH^0_{298}, kcal/mol	ε, kcal/mol
1.	$CH_4 = \dot{C}H_3 + \dot{H}$	+103	
2.	$\dot{C}H_3 + OCO = CH_3\dot{O} + CO$	+36.2	38.7
3.	$CH_3\dot{O} = H_2CO + \dot{H}$	+17.0	24.3
4.	$H_2CO = \dot{H}CO + \dot{H}$	+77	(77)
5.	$\dot{H}CO = \dot{H} + CO$	+34	37.0
6.	$4\dot{H} = 2H_2$	−208.4	–
	$CH_4 + CO_2 = 2CO + 2H_2$	+58.8	–

Reaction 6 is written in general form only for summing all the reactions and their thermal effects. Taking into account the insufficient accuracy of the data on bond-dissociation energies in radicals ([6,7]), the error obtained in the calculations, amounting to 0.3 kcal/mole, between the thermodynamic data and the bond-dissociation energies in molecules and radicals is quite permissible. This circumstance gives grounds for asserting that the adopted values of the bond-dissociation energies in molecules and radicals are close to the true values, and further refinements of them cannot introduce large changes.

For reaction 4, the abstraction of a hydrogen atom from formaldehyde, Steacie ([8]) gives an activation energy equal to 78 kcal/mole, which practically corresponds to the energy of detachment of a hydrogen atom.

In the scheme presented for the radical mechanism of reactions involving interaction and decomposition of molecules and radicals, the most difficult stage is the decomposition reaction of methane with formation of a methyl radical and atomic hydrogen, requiring 103 kcal/mole. The activation energy of this process under homogeneous conditions is approximately equal to this value; consequently, the reaction proceeds only at high temperatures. However, this reaction may be initiated by the wall, and still more so by catalysts, with a smaller expenditure of energy, and then the possibilities for its occurrence increase. The second difficult stage of the mechanism is reaction 4, decomposition of formaldehyde with formation of a formyl radical and atomic hydrogen, requiring a heat expenditure of 77 kcal/mole. This reaction may also be accelerated on the surface of a solid body or through interaction of formaldehyde with atomic hydrogen according to the scheme

		ΔH^0_{298}, kcal/mole	ε, kcal/mole
7.	$H_2CO + \dot{H} = \dot{H}CO + H_2$	−27.2	4.7,

which is exothermic.

Reaction 6, the interaction of hydrogen atoms with formation of molecular hydrogen, cannot proceed for the reason that the concentration of atomic hydrogen in the gas, in comparison with the other gas components, is very small throughout the entire process, and also because of the large exothermic effect, which causes the reverse process of decomposition of the hydrogen molecule. As is known, recombination of hydrogen atoms is possible only in a triple collision of two hydrogen atoms with an inert gas molecule or with a wall, which remove the energy released.

The atomic hydrogen formed in elementary reactions readily interacts with a methane molecule, with formation of molecular hydrogen and a methyl radical. The reaction proceeds with a small exothermic effect and an activation energy amounting to approximately 11 kcal/mole. This reaction serves as a link in the main chain of the monoradical chain unbranched mechanism of the interaction of methane with carbon dioxide according to the scheme:

		ΔH^0_{298}, kcal/mole	ε, kcal/mole
8.	$CH_4 + \dot{H} = \dot{C}H_3 + H_2$	−1.2	11.2
2.	$\dot{C}H_3 + OCO = CH_3\dot{O} + CO$	36.2	38.7
3.	$CH_3\dot{O} = H_2CO + \dot{H}$	17.0	24.3
7.	$H_2CO + \dot{H} = \dot{H}CO + H_2$	−27.2	4.7
5.	$\dot{H}CO = \dot{H} + CO$	34	37
	$CH_4 + CO_2 = 2CO + 2H_2$	58.8	

For reaction 8, the interaction of methane with atomic hydrogen, Steacie ([8]) gives a general summary of data on the activation energy, which vary from 4.1 to 15.6 kcal/mole, but the main part of the data is around

11 kcal/mol. This is in good agreement with calculations by the equation of N. N. Semenov ([1]).

In the main chain of the radical-chain mechanism of reactions (8, 2, 3) for the conversion of methane by carbon dioxide, the most difficult is the reaction of interaction of methyl with carbon dioxide, with formation of methoxyl and carbon monoxide. It requires 36.2 kcal/mol of heat and, evidently, determines the rate of the process of methane conversion by carbon dioxide.

Proceeding from the relationship between the thermal effect and the activation energy of radical reactions established by N. N. Semenov ([1]), let us approximately determine the activation energies of the elementary reactions of the main chain of the process. For activation of the reaction of methane with atomic hydrogen, 11.2 kcal/mol is required; for activation of methyl with carbon dioxide, 38.7 kcal/mol is necessary; and for the decomposition reaction of methoxyl, 24.3 kcal/mol. Consequently, the occurrence of a radical-chain mechanism of the process of interaction of CH_4 with CO_2 is possible at comparatively low temperatures. The difficulty lies in the initial generation of atomic hydrogen and the methyl radical.

It may be supposed that under certain conditions the process of further decomposition of methane can proceed with formation of the methylene biradical, which then interacts with carbon dioxide according to the schemes:

$$10.\quad \dot{C}H_3 = \ddot{C}H_2 + \dot{H} - 92.0\ \text{kcal/mol},$$

$$11.\quad \ddot{C}H_2 + OCO = H_2CO + CO - 8.3\ \text{kcal/mol}.$$

Subsequently, the process is carried out by the reactions given above.

In this scheme of interaction and decomposition of the initial and intermediate reaction products to $\dot{H}$ and carbon monoxide, the most difficult is reaction 10, for which 92.0 kcal/mol of heat must be supplied.

In a complex gaseous mixture of initial, intermediate, and final reaction products, as well as of various radicals, other intermediate reactions are also possible, but they cannot be of great importance, since a greater expenditure of heat is required for this.

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