The formation of formic acid upon low-temperature condensation of a methane—carbon dioxide mixture dissociated in a microwave discharge

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Formic acid was found as the main product upon low-temperature (77 K) condensation of the $CH_4 + CO_2$ mixture dissociated in the microwave discharge at a low pressure. The yield of HCOOH was studied as a function of the experimental conditions: flow rate of the initial gas mixture, CH_4 content in the initial mixture, pressure in the reactor, and output power of the microwave generator. The concentrations of H, O, OH, and O_2 in the gas phase were measured by ESR spectroscopy. Mathematical modeling of the kinetics of the gas phase chemical reactions in the connecting channel was performed. The mechanism of formic acid formation by the interaction of active species of the gas phase on the condensate surface was proposed.

Key words: electric discharge in gases, low-temperature condensation, formic acid, methane, carbon dioxide, ESR spectroscopy, atomic hydrogen, atomic oxygen, hydroxyl radicals.

Hydrogenation of carbon oxides and partial oxidation of methane are urgent problems that have recently attracted the increasing attention of researchers. It has been found in one of our previous works[1] that formic acid is the main product formed upon the low-temperature condensation of the $CO_2 + H_2$ and $CO + H_2O$ gas mixtures dissociated in the electric discharge. In this work, we used methane as the hydrogenating reagent, because the dissociation of CH_4 molecules in the discharge gives atomic hydrogen and CH_n ($n = 1—3$) radicals whose participation in the process under study could lead to the formation of acetic acid and other organic compounds with two carbon atoms.

Experimental

Experiments were carried out on a vacuum discharge-jet setup. The setup and the scheme of the reactor were described in our previous work.[2] The experimental procedure was similar to that described previously[1] with the only distinction that the appendix of a cryostat ("finger") was cooled on the inside by a liquid nitrogen stream going from bottom to top.

Stable condensation products were determined as follows. The condensate was re-frozen into a demountable trap, its content was dissolved in water, and the solution was analyzed on a Finnigan MAT ITD-850 AT GC-MS spectrometer using propionic acid as the internal standard. The conditions of GC-MS determination have been published elsewhere.[1] Only water-soluble substances were analyzed. The possibility of formation of hydrocarbons and other water-insoluble organic compounds was not studied.

In the experiments, the flow rate of the initial gas mixture was varied from 1.6 to 5.6 L h^{-1} (standard conditions), the

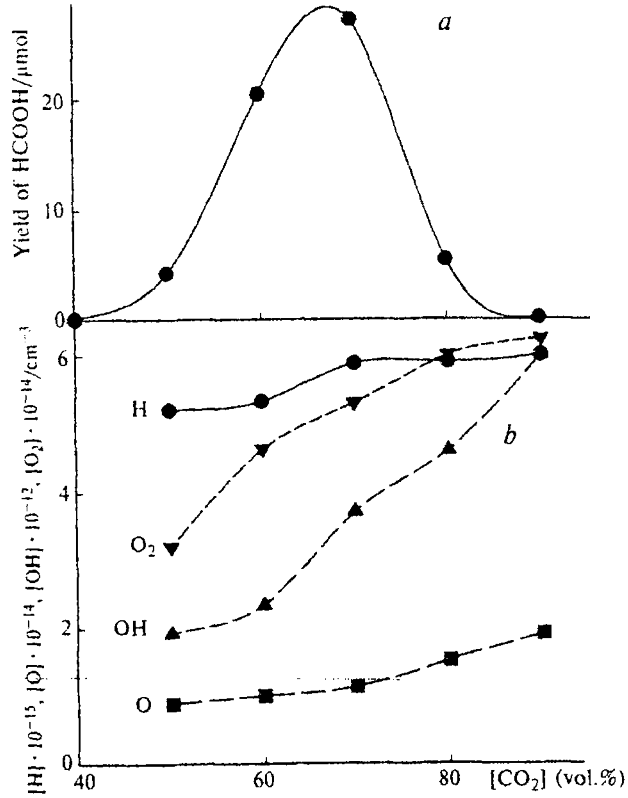

Fig. 1. Dependences of the yield of formic acid (*a*) and concentrations of H, O, O_2, and OH in the gas phase (*b*) on the composition of the initial gas mixture. Flow rate 3.2 L h^{-1} (standard conditions), pressure 1.11 Torr, and power 50 W.

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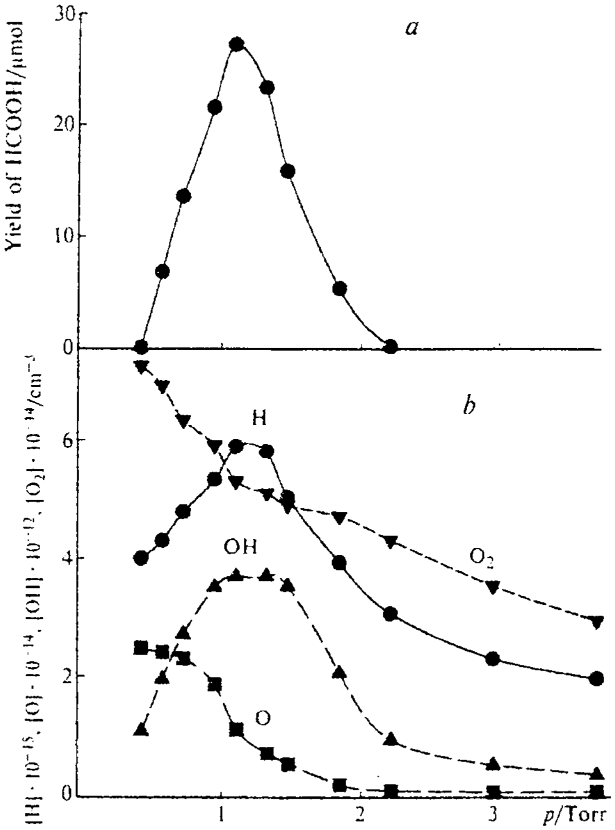

Fig. 2. Dependences of the yield of formic acid (*a*) and concentrations of H, O, O_2, and OH in the gas phase (*b*) on the pressure (*p*) in the reactor. Flow rate 3.2 L h^{-1} (standard conditions), composition of the initial gas mixture 70% CO_2 + 30% CH_4, and power 50 W.

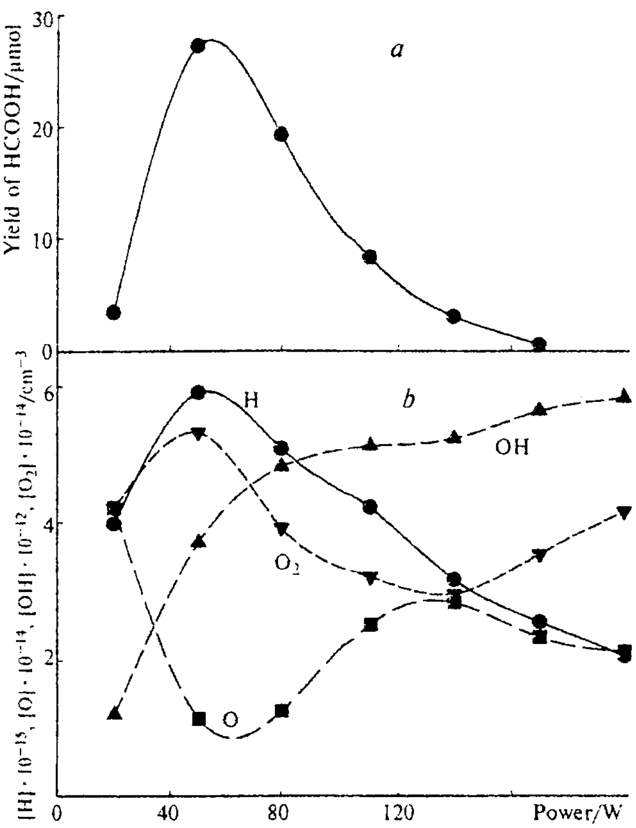

Fig. 3. Dependences of the yield of formic acid (*a*) and concentrations of H, O, O_2, and OH in the gas phase (*b*) on the output power of the microwave generator. Flow rate 3.2 L h^{-1} (standard conditions), composition of the initial gas mixture 70% CO_2 + 30% CH_4, and pressure 1.11 Torr.

content of CH_4 in the initial mixture was varied from 10 to 60 vol.%, the pressure in the reactor ranged from 0.5 to 4 Torr, and the output power of the microwave generator was varied from 20 to 200 W. The experimental results are presented in Figs. 1—4.

Results and Discussion

Formic acid is the main product of the low-temperature condensation of the $CH_4 + CO_2$ mixture dissociated in the microwave discharge. In addition, we observed insignificant amounts (1—2% of the mole content of HCOOH) of acetic acid, methanol, and formaldehyde. Apparently, the presence of acetic acid in the products indicates the participation of the CH_n radicals in the process; however, even traces of other possible products of transformations of these radicals, ethanol and acetaldehyde, were not observed.

The composition of the gas phase (the surface on which the condensation occurred was placed in the cavity of an ESR spectrometer) was studied simultaneously with the low-temperature synthesis. The dependences of the yield of the products of the low-temperature synthesis in the CH_4 + CO_2 system on the composition of the gas phase are similar to those observed for the previously studied CO_2 + H_2 system. Both systems contain significant concentrations of atomic hydrogen (10^{15}—10^{16} cm^{-3}) in the gas phase near the synthesis zone. In addition, the formation of formic acid requires the presence of O* and O_2 in the gas phase, and both an excess and a deficiency of these species relatively to some optimum value decrease the yield of HCOOH.

To estimate the concentrations of carbon-containing species (which cannot be determined experimentally) in the gas phase near the synthesis zone of C_1 compounds, we performed the mathematical modeling of the processes in the connecting channel. As a whole, the simulation procedure is similar to that described in the previous work.[2] This system differs mainly from the previously studied CO_2 + H_2 system by the uncertainty in choosing the initial concentrations of the dissociation products of CH_4 in the discharge. This problem is discussed in detail below. In addition, the functional of

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* Hereinafter unpaired electrons of free radical species are not indicated for simplicity.

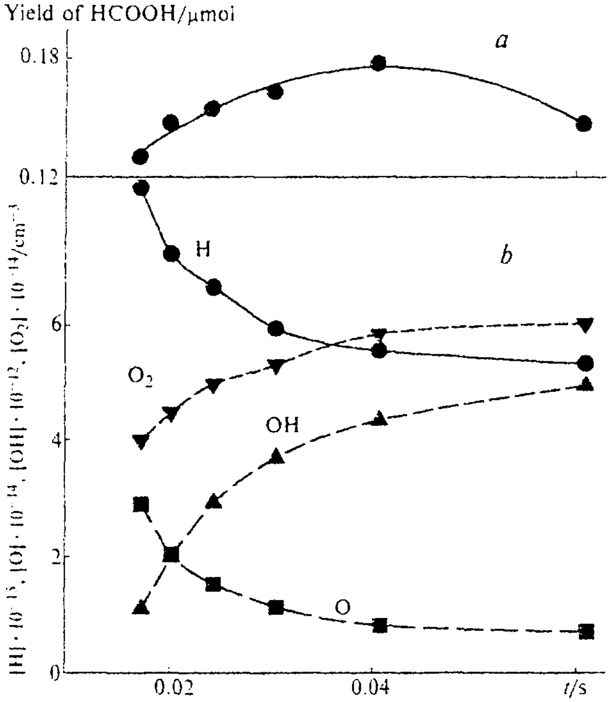

Fig. 4. Dependences of the yield of formic acid (*a*) and concentrations of H, O, O_2, and OH in the gas phase (*b*) on the contact time (*t*) in the reactor. Composition of the initial gas mixture 70% CO_2 + 30% CH_4, pressure 1.11 Torr, and power 50 W.

divergence of the experimental and calculated data was minimized only by the selection method, and the minimum set of reactions sufficient for the description of transformations in the CH_4 + CO_2 system was not determined.

The mathematical modeling of the kinetics of the gas phase reactions occurring in the connecting channel in the microwave discharge products (the output power of the microwave generator was 50 W) was carried out for a mixture of 70 vol.% CO_2 and 30 vol.% CH_4 at a pressure of 1.1 Torr and room temperature. Calculation was performed by the program described in the monograph,[3] using the experimental (see Fig. 4) and published data.[4—7] The following kinetic scheme was chosen*:

Reaction	log*K*
(1) $H + HO_2 \longrightarrow OH + OH$	−10.8
(2) $H + HO_2 \longrightarrow H_2 + O_2$	−10.9
(3) $H + HO_2 \longrightarrow H_2O + O$	−10.8
(4) $H + H + M \longrightarrow H_2 + M$	−32.1
(5) $H + OH + M \longrightarrow H_2O + M$	−29.9
(6) $H + O_2 + M \longrightarrow HO_2 + M$	−31.5
(7) $H + O + M \longrightarrow OH + M$	−31.7
(8) $O + O + M \longrightarrow O_2 + M$	−32.1
(9) $O + OH \longrightarrow H + O_2$	−10.4
(10) $O + HO_2 \longrightarrow OH + O_2$	−10.5
(11) $CH_3 + CH_3 + M \longrightarrow$ products	−27.7
(12) $CH_3 + CH_2 + M \longrightarrow$ products	−27.7
(13) $CH_3 + H_2 \longrightarrow CH_4 + H$	−11.4
(14) $CH_3 + H + M \longrightarrow CH_4 + M$	−28.4
(15) $CH_3 + O \longrightarrow HCHO + H$	−10.1
(16) $CH_3 + HCO \longrightarrow CH_4 + CO$	−11.0
(17) $CH_3 + HO_2 \longrightarrow CH_4 + O_2$	−15.9
(18) $CH_3 + OH \longrightarrow CH_2 + H_2O$	−12.7
(19) $CH_3 + HCHO \longrightarrow CH_4 + HCO$	−17.2
(20) $CH_2 + H \longrightarrow CH + H_2$	−14.1
(21) $CH_2 + CH_2 \longrightarrow$ products	−10.3
(22) $CH_2 + O \longrightarrow H + HCO$	−13.8
(23) $CH_2 + CH_2 \longrightarrow CH + CH_3$	−15.2
(24) $CH_2 + HCO \longrightarrow CH_3 + CO$	−12.3
(25) $CH_2 + H_2 \longrightarrow CH_3 + H$	−16.4
(26) $CH_2 + HCHO \longrightarrow CH_3 + HCO$	−17.2
(27) $CH + O \longrightarrow H + CO$	−10.7
(28) $CH + CO_2 \longrightarrow CO + HCO$	−16.9
(29) $CH + H + M \longrightarrow CH_2 + M$	−31.0
(30) $CH + HCO \longrightarrow CH_2 + CO$	−12.3
(31) $CH + HCHO \longrightarrow CH_2 + HCO$	−14.0
(32) $CH + O + M \longrightarrow HCO + M$	−32.8
(33) $CH + HO_2 \longrightarrow HCO + OH$	−15.2
(34) $CO + H + M \longrightarrow HCO + M$	−34.0
(35) $CO + OH \longrightarrow CO_2 + H$	−12.8
(36) $HCO \longrightarrow CO + H$	−0.2
(37) $HCO + O \longrightarrow CO_2 + H$	−12.3
(38) $HCO + O \longrightarrow CO + OH$	−10.2
(39) $HCO + H \longrightarrow CO + H_2$	−10.3
(40) $HCO + OH \longrightarrow CO + H_2O$	−10.8
(41) $HCO + HCO \longrightarrow HCHO + CO$	−11.3
(42) $HCO + HO_2 \longrightarrow HCHO + O_2$	−12.0
(43) $HCHO + H \longrightarrow HCO + H_2$	−13.5
(44) $HCHO + OH \longrightarrow HCO + H_2O$	−10.8
(45) $HCHO + O \longrightarrow HCO + OH$	−12.8
(46) $CH_3 \longrightarrow$ decay	6.0
(47) $CH \longrightarrow$ decay	6.0
(48) $O \longrightarrow O_{ads}$	1.5
(49) $H \longrightarrow H_{ads}$	0.5
(50) $H_{ads} + H \longrightarrow H_2$	−10.0
(51) $O_{ads} + O \longrightarrow O_2$	−10.0
(52) $O_2 + H_{ads} \longrightarrow HO_2$	−10.0

The results of calculation are presented in Figs. 5 and 6. The initial conditions for the O, CO, CO_2, and H species were calculated from the experimental data under the assumption of a pseudo-first order of effective decay of O and H and from the material balance. The initial concentrations of CH_n (n = 1—4) were selected during calculation using the correlation $[H]_0 = [CH_3]_0 + 2\ [CH_2]_0 + 3\ [CH]_0$. The curves presented in Fig. 5 were calculated for different initial concentrations of CH_n (Table 1). The initial concentrations of H, O, CO, and CO_2 were $1 \cdot 10^{16}$, $1.2 \cdot 10^{15}$, $1.2 \cdot 10^{15}$, and $2.42 \cdot 10^{16}$ cm^{-3}, respectively, and they were assumed to be equal to zero for the other species.

As follows from the analysis of the calculated curves, there is a narrow interval of the initial concentrations of CH_n at which an appropriate agreement with the experimental data with respect to the concentrations of H, O, OH, and O_2 is achieved. At high initial concentrations of CH_3 and CH, the calculated concentration of atomic oxygen is much lower than the experimental value. This

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* The reactions were selected by the previously described algorithm.[8]

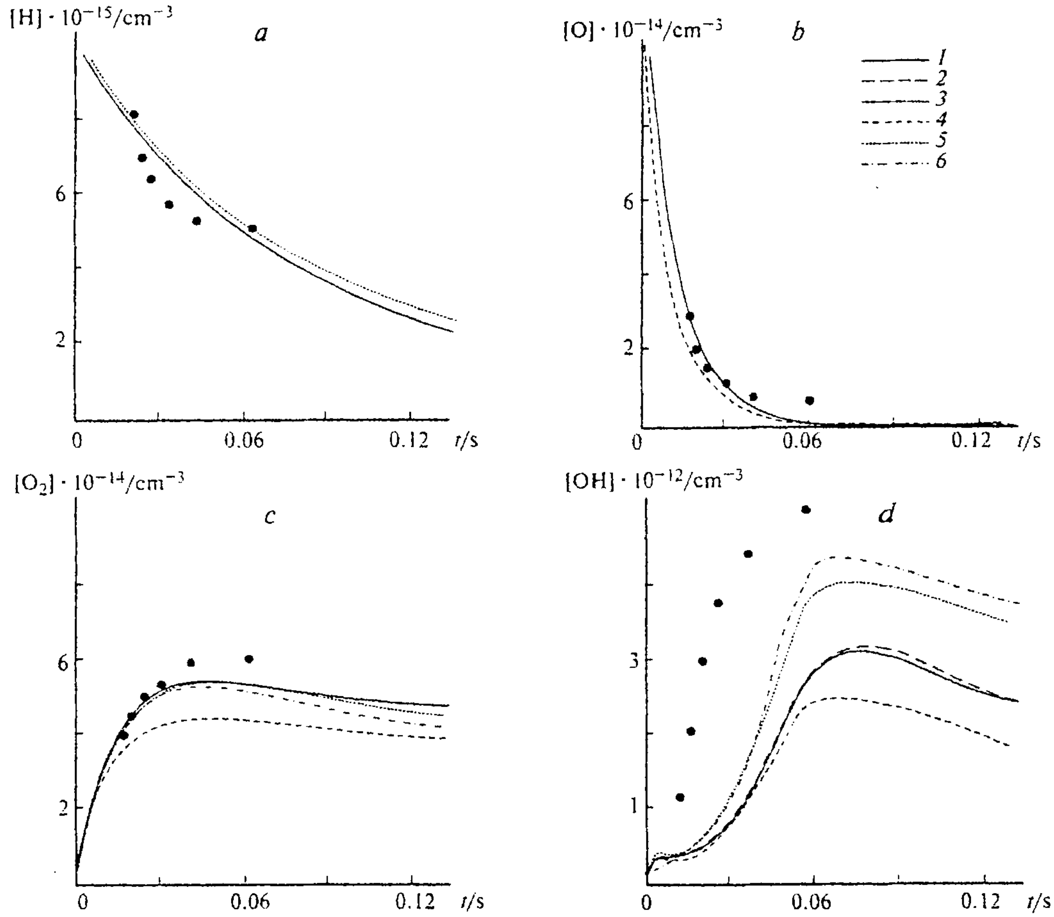

Fig. 5. Dependences of the concentrations of H (*a*), O (*b*), O_2 (*c*), and OH (*d*) on the contact time (t) in the reactor. Points indicate the experimental data, and lines are the calculation. Composition of the initial gas mixture 70% CO_2 + 30% CH_4, pressure 1.11 Torr, and power 50 W. Curves *1—6* correspond to various initial concentrations indicated in in Table 1 (some curves coincide).

is related to the occurrence of fast steps (15) and (27). Moreover, the overall decay of the CH_3 and CH species should be taken into account (reactions (46) and (47) imitate the decay of CH_3 and CH in the processes which are not shown in the scheme) to decrease their concentration in the gas phase to values that allow a satisfactory agreement with the experiment to be achieved (at the used initial concentrations of CH_n). Evidently, a decrease in the concentrations $[CH_n]$ relatively to the values corresponding to the material balance, *i.e.*, $[H]_0 > [CH_3]_0 + 2\ [CH_2]_0 + 3\ [CH]_0$, would be an alternative for the introduction of steps of efficient decay of the CH_3 and CH species. In principle, this is acceptable if we assume that efficient polymerization in the microwave discharge zone decreases $[CH_n]_0$ but has no effect on $[H]_0$. It is still impossible to choose between these two variants. The concentration $[CH_2]_0$ can vary in sufficiently broad limits. This is related to the relatively low (as compared to those of CH_3 and CH) reactivity of the CH_2 species in reactions with oxygen. In addition, the scheme ignores the heterogeneous decay of the CH_2 radical, because it has almost no effect on the concentrations of the H, O, OH, and O_2 species and, hence, we believe that step (21) adequately describes the process of its overall decay. The reactions of formation and consumption of the CH_3O_2 and CH_3O radicals are not considered in the scheme. This is related to the fact that due to the introduced overall

Table 1. Variants of the choice of the initial concentrations of CH_n (n = 1—4)

Variant	$[CH_4]_0$	$[CH_3]_0$	$[CH_2]_0$	$[CH]_0$
	cm⁻³			
1	$5 \cdot 10^{15}$	$1 \cdot 10^{15}$	$3 \cdot 10^{15}$	$1 \cdot 10^{15}$
2	$5 \cdot 10^{15}$	$5 \cdot 10^{14}$	$4 \cdot 10^{15}$	$5 \cdot 10^{14}$
3	$6 \cdot 10^{15}$	0	$2 \cdot 10^{15}$	$2 \cdot 10^{15}$
4	$1 \cdot 10^{15}$	$1 \cdot 10^{16}$	0	0
5, 6 *	$5 \cdot 10^{15}$	$1 \cdot 10^{15}$	$3 \cdot 10^{15}$	$1 \cdot 10^{15}$

* Variant *5* — reaction (52) in the form $O_2 + H_{ads} \longrightarrow OH + O$ was taken into account in the scheme; variant *6* — reaction (52) in the form $O_2 + H_{ads} \longrightarrow HO_2$ was taken into account in the scheme.

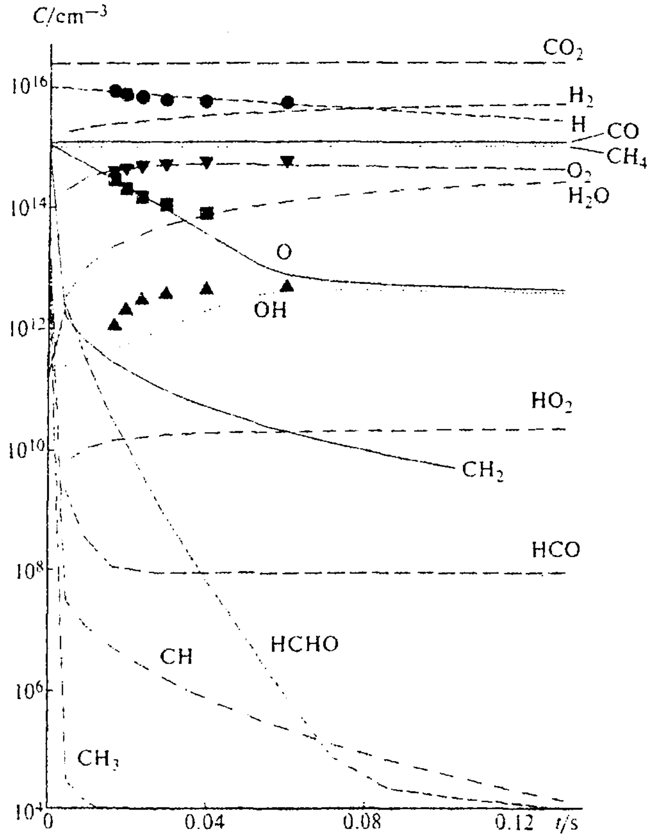

Fig. 6. Dependence of the composition of the gas phase in the connecting channel after the discharge in the $CO_2 + CH_4$ mixture on the contact time (*t*) in the reactor. Points indicate the experimental data, and lines are the calculation. Composition of the initial gas mixture 70% CO_2 + 30% CH_4, pressure 1.11 Torr, and power 50 W. The initial concentrations were chosen according to variant *6* (see Table 1).

decay of the CH_3 and CH species (steps (46), (47)), their concentrations in the gas phase become insignificant (~10^5—10^8 cm^{-3}) and, hence, the reactions of the formation of CH_3O_2 and CH_3O do not noticeably contribute to the overall process. Reaction (52) (curves *5*, *6*) does not result in significant changes in the concentrations of H, O, and O_2 but somewhat increases the yield of the OH radicals and allows the overall process of radical escape to the gas phase from the reactor walls to be taken into account.

Thus, calculation shows that the concentrations of the CH_3 and CH species in the zone of synthesis of C_1 compounds are low (~10^5—10^8 cm^{-3}). Therefore, in the $CH_4 + CO_2$ system under the experimental conditions, the CH_3 and CH radicals cannot be considered as methylating reagents. In addition, the high (relative to those of CH_3 and CH) concentration of the CH_2 species provides, most likely, the formation of an insignificant amount of acetic acid. Note that, according to calculation, the concentrations of HCO and HCHO generated in the gas phase are low and amount to ~10^9—10^{12} cm^{-3} at the outlet of the discharge zone and to ~10^7—10^8 cm^{-3} in the synthesis zone.

This implies that, as in the case of the $CO_2 + H_2$ system, HCOOH and CH_3COOH are formed heterogeneously (on the cooled surface) in the $CH_4 + CO_2$ system under the experimental conditions, and the participation of the gas-phase HCHO and HCO and CH_n radicals in the formation of C_1 and C_2 compounds is insignificant.

The scheme of formation of organic compounds in the low-temperature condensation of a $CO_2 + H_2$ mixture dissociated in electric discharges has been proposed previously.[1] The consideration presented for the substantiation of this scheme[1] is also appropriate for the $CH_4 + CO_2$ system because a resemblance of the $CH_4 + CO_2$ to the $CO_2 + H_2$ systems is observed under the conditions of our experiments. As indicated above, the composition of the gas phase and its influence on the yield of products of the low-temperature synthesis are similar in both systems. The $CH_4 + CO_2$ and $CO_2 + H_2$ condensates contain considerable amounts of the HO_2 radicals. The composition of the products of low-temperature condensation in the $CH_4 + CO_2$ system is the same as that in the $CO_2 + H_2$ system except for the fact that in the latter case, insignificant amounts of acetic acid are observed in the condensation products. To explain the formation of acetic acid, we introduced into the scheme additional stages of the interaction of the HOCO (HCO_2) and CH_2 radicals. Therefore, the scheme of formation of organic compounds under the low-temperature condensation of the $CH_4 + CO_2$ mixture dissociated in electric discharges can be presented as follows:

$$\begin{tikzcd}
CO \arrow[r, "(5')"] \arrow[dd, "(1')"] & CO_2^* \arrow[r, "(6')"] & HOCO\,(HCO_2) \arrow[r, "(7')"] \arrow[dr, "(8')"'] & HCOOH \\
 & & & CH_3COOH \\
HCO \arrow[r, "(2')"] & HCHO \arrow[r, "(3')"] & CH_2OH\,(CH_3O) \arrow[r, "(4')"] & CH_3OH
\end{tikzcd}$$

(1') $CO + H \longrightarrow HCO$;
(2') $HCO + H \longrightarrow HCHO$;
(3') $HCHO + H \longrightarrow CH_2OH\,(CH_3O)$;
(4') $CH_2OH\,(CH_3O) + H \longrightarrow CH_3OH$;
(5') $CO\,(^1\Sigma^+) + O\,(^3P) \longrightarrow CO_2^*$;
(6') $CO_2^* + H \longrightarrow HOCO\,(HCO_2)$;
(7') $HOCO\,(HCO_2) + H \longrightarrow HCOOH$;
(8') $HOCO\,(HCO_2) + CH_2 \longrightarrow$
$\longrightarrow CH_2HCOOH \longrightarrow CH_3COOH$.

In this case, all comments presented[1] for the scheme of formation of organic compounds in the $CO_2 + H_2$ system are valid.

Thus, formic acid and insignificant amounts of acetic acid, methanol, and formaldehyde are formed in the low-temperature condensation of the $CH_4 + CO_2$ mixture dissociated in the microwave discharge at a low pressure. The formation of formic acid can be rationalized in the framework of the scheme presented previously[1] for the $CO_2 + H_2$ and $CO + H_2O$ systems.

References

1. A. V. Levanov, A. R. Gromov, E. E. Antipenko, and V. V. Lunin, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 638 [*Russ. Chem. Bull.*, 2000, No. 4 (Engl. Transl.)].
2. A. V. Levanov, A. R. Gromov, E. E. Antipenko, and V. V. Lunin, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 665 [*Russ. Chem. Bull.*, 2000, No. 4 (Engl. Transl.)].
3. L. S. Polak, M. Ya. Gol'denberg, and A. A. Levitskii, *Vychislitel'nye metody v khimicheskoi kinetike* [*Calculation Methods in Chemical Kinetics*], Nauka, Moscow, 1984, 280 pp. (in Russian).
4. F. Westley, *Table of Recommended Rate Constants for Chemical Reactions Occurring at Combustion*, Nat. Bur. Stand. (U. S.), Washington, D. C., 1980, 119 pp.
5. V. Ya. Basevich, S. M. Kogarko, and M. G. Neigauz, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 42 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25** (Engl. Transl.)].
6. V. I. Vedeneev, M. Ya. Gol'denberg, N. I. Gorban', and M. A. Teitel'boim, *Kinet. Katal.*, 1988, **29**, 14 [*Kinet. Catal.*, 1988, **29** (Engl. Transl.)].
7. V. I. Vedeneev, A. A. Karnaukh, A. A. Mantashyan, and M. A. Teitel'boim, *Kinet. Katal.*, 1990, **31**, 7 [*Kinet. Catal.*, 1990, **31** (Engl. Transl.)].
8. O. Yu. Berezin, Ph.D. (Chem.) Thesis, M. V. Lomonosov Moscow State University, Moscow, 1981, 190 pp. (in Russian).

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