Mass spectrum of the gaseous reaction product, m/z (I_{rel} (%)): 51 (CD_3CDHCD_3 [M^+]) (9.7), 50 ($CD_3CH_2CD_3$ [M^+] and $CD_3CDHCD_3 - H$) (29.7), 49 (31.7), 48 (4.9), 47 (15), 46 (16.1), 45 (21.5), 44 (5), 43 (4.1), 42 (25.2), 41 (12.8), 40 (8.5), 39 (2.4), 38 (5.5), 34 (10.8), 33 ($CD_3CDHCD_3 - CD_3$) (85.3), 32 ($CD_3CH_2CD_3 - CD_3$) (100), 31 (62.7), 30 (74.9), 29 (48.1), 28 (23.1), 27 (9.8), 26 (2.5).

Mass spectrum of the gaseous reaction product in the absence of ester **1**, m/z (I_{rel} (%)): 51 (CD_3CDHCD_3 [M^+]) (10.8), 50 ($CD_3CH_2CD_3$ [M^+] and $CD_3CDHCD_3 - H$) (28.5), 49 (25.4), 48 (7.1), 47 (17.6), 46 (20.9), 45 (25.2), 44 (6.8), 43 (5.4), 42 (33.2), 41 (16.2), 40 (11.6), 39 (3.1), 38 (7.6), 34 (14.1), 33 ($CD_3CDHCD_3 - CD_3$) (100), 32 ($CD_3CH_2CD_3 - CD_3$) (85.9), 31 (67.9), 30 (75.7), 29 (53.3), 28 (31.4), 27 (12.3), 26 (3.6).

(*E*)-1-(2-Chloroethyl)-2-methylcyclopropanol was obtained by a similar procedure in 51% yield from ester **1** (0.61 mL, 4.5 mmol), $(Pr^iO)_4Ti$ (0.15 mL, 0.5 mmol), and Grignard reagent obtained from 2-bromopropane (1 mL, 10 mmol) and Mg (0.5 g, 21 mg-at.) in Et_2O (6 mL). ^1H NMR ($CDCl_3$), δ: 0.12 (t, 1 H, J = 5.5 Hz); 0.83—0.98 (m, 2 H); 1.02 (s, 3 H); 1.92—2.18 (m, 2 H); 2.28 (br.s, 1 H); 3.77 (t, 2 H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.2, 19.4, 20.5, 36.7, 42.0, 57.2.

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Formation of formic and acetic acids by low-temperature condensation of a mixture of methane and water vapor dissociated in MW discharge

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Formic and acetic acids are formed by the low-temperature (77 K) condensation of a mixture of methane and water vapor dissociated by MW discharge at a low pressure. The effect of experimental conditions on the yield of HCOOH and AcOH was studied under different experimental conditions. The yields of H˙, OH˙, and O_2 from MW discharge in the CH_4+H_2O mixture were determined by ESR in the gas-phase under the experimental conditions used to synthesize HCOOH and AcOH. The kinetics of the gas phase reactions in the connecting channel was simulated. The mechanism of formation of HCOOH and AcOH through the interaction of active species from the gas phase on the condensate surface was suggested.

Key words: electric discharge in gases, low-temperature condensation, formic acid, acetic acid, methane, water, ESR in gas phase, hydrogen atoms, oxygen atoms, hydroxyl radicals.

Low-temperature condensation (LTC) of gas mixtures dissociated by electric discharges is a unique method for synthesis of inaccessible compounds, for example, higher hydrogen polyoxides H_2O_3 and H_2O_4 (Ref. 1).

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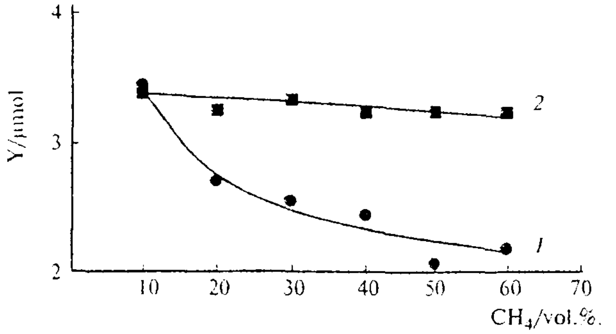


Fig. 1. Yields (Y) of formic and acetic acids as functions of the composition of the starting gas mixture. *1*, HCOOH; and *2*, MeCOOH. Flow rate 2.5 L h^{-1} (standard conditions), pressure 1 Torr, power 20 W.

Formic acid is formed in LTC of CO_2+H_2, $CO+H_2O$ (Ref. 2), and CH_4+CO_2 (Ref. 3) mixtures dissociated by low-pressure discharges.

Experimental

Experiments were carried out with a vacuum discharge setup. The detailed description of the reactor design and procedures of experiment and analysis of products will be given in the publications that follow.[2—4]

In experiments, the flow rate of the initial mixture of gases was varied from 1.0 to 2.5 L h^{-1} (standard conditions), the content of CH_4 in the initial mixture was maintained between 0.5 and 1.7 Torr, and the output power of the MW generator was kept between 20 and 200 W.

Results and Discussion

Formic and acetic acids are the products of LTC of the CH_4+H_2O mixture dissociated by MW discharge. The yields (Y) of the acids as a function of the composition of the starting gas mixture is shown in Fig. 1. When the fraction of methane increases in the starting mixture, the yield of formic and acetic acids increases. The highest yield of the acids (~0.2% calculated from the CH_4 introduced) is observed for the initial mixture containing 10 vol.% methane. At high concentrations of methane, a polymer film is formed on the reactor walls in the discharge region. In addition, the formation of by-products, in particular, hydrocarbons, was observed. Therefore, further experiments were carried out with a gas mixture containing 10 vol.% CH_4.

The yields of formic and acetic acids and gas-phase concentrations of H$^{\cdot}$, OH$^{\cdot}$, and O_2 as functions of the output power of the MW generator (*W*) are presented in Fig. 2. It can be seen that an increase in the discharge power to 140 W results in the selective formation of HCOOH (2 mol.% with respect to methane). Molecular oxygen is observed in the gas phase near the synthesis

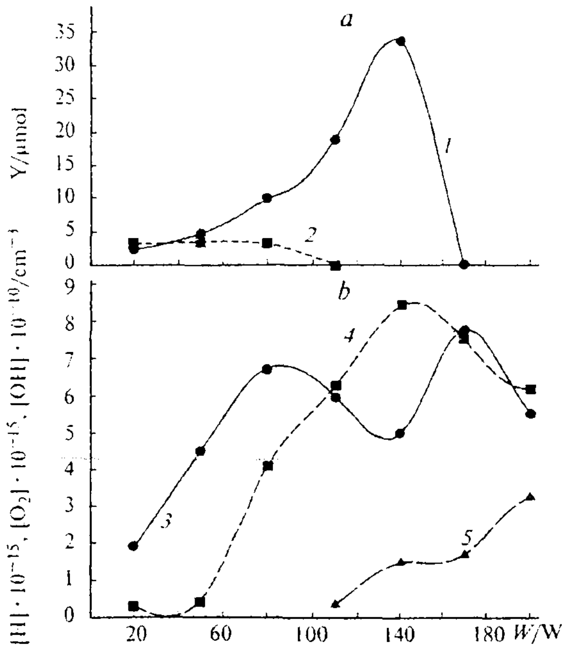


Fig. 2. Yields (Y) of formic and acetic acids (*a*) and concentrations of H$^{\cdot}$, OH$^{\cdot}$, and O_2 in the gas phase (*b*) as functions of the output power of the MW generator. *1*, HCOOH; *2*, AcOH; *3*, H$^{\cdot}$; *4*, OH$^{\cdot}$; and *5*, O_2. Flow rate 2.5 L h^{-1} (standard conditions), composition of the starting gas mixture 90 vol.% H_2O + 10 vol.% CH_4, pressure 1 Torr.

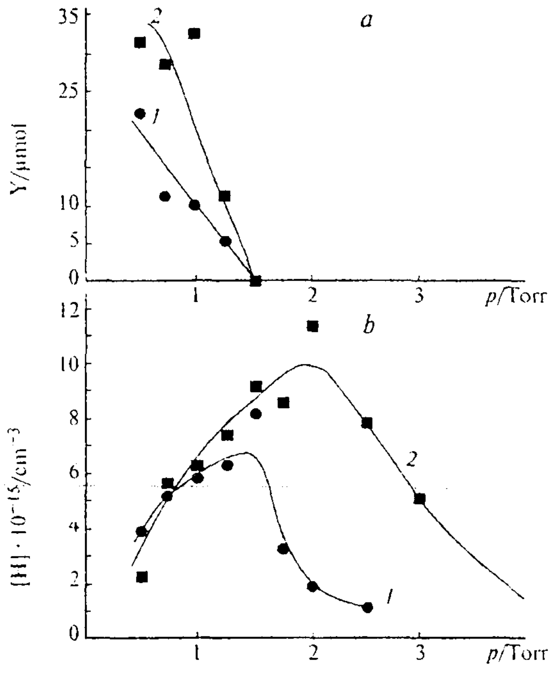


Fig. 3. Yield (Y) of formic acid (*a*) and concentration of H$^{\cdot}$ in the gas phase (*b*) as functions of the pressure in the reactor. Flow rate 2.5 L h^{-1} (standard conditions), composition of the starting gas mixture 90 vol.% H_2O + 10 vol.% CH_4, power 80 (*1*) and 140 (*2*) W.

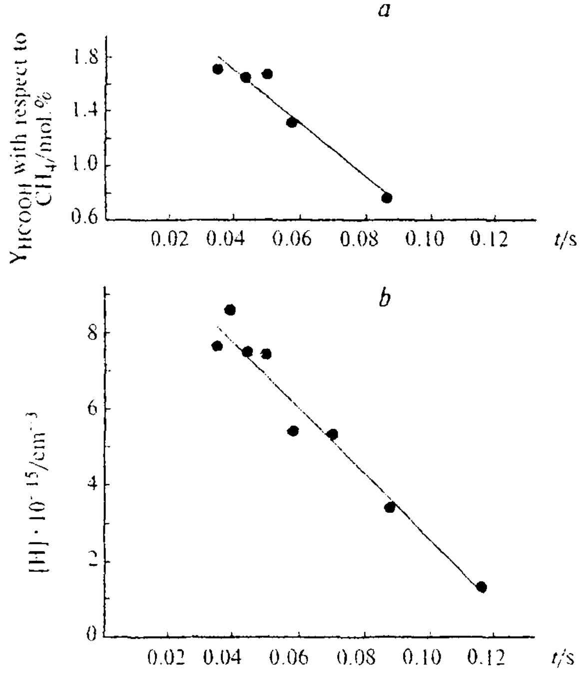


Fig. 4. Yield of formic acid (*a*) and concentration of H$^\cdot$ in the gas phase (*b*) as functions of the contact time in the reactor. Composition of the starting gas mixture 90 vol.% H_2O + 10 vol.% CH_4, p = 1 Torr, power 140 W.

zone at a output power higher than 100 W. The appearance of O_2 indicates that the degree of dissociation of water vapor increases as the output power of the MW generator increases. Oxygen appears in the gas phase when MeCOOH formation ceases. The absence of significant amounts of O atoms in the gas phase ([O$^\cdot$] is lower than the detection level of an ESR spectrometer) indicates that the discharge leads to considerable dissociation of CH_4. Evidently the O atoms disappear in very fast reactions with Me and CH$^\cdot$ radicals.

The influence of the pressure and flow rate on the yield of HCOOH and concentration of H atoms in the gas phase is shown in Figs. 3 and 4.

To obtain more complete information on the concentrations of species in the gas phase and nature of processes occurring in the connecting channel, we performed a mathematical simulation of the gas phase chemical reactions that proceed in the connecting channel in the products of MW discharge (output power 140 W) in a mixture of 90 vol.% H_2O and 10 vol.% CH_4 at 1 Torr and room temperature. In the kinetic study of the dependence of the gas phase composition on the contact time in the reactor, only H atoms were reliably detected (see Fig. 4); therefore, the simulation has, to a great extent, a qualitative character. The procedure of simulation is presented in the later work.[5]

Based on the results of simulation (Fig. 5) and experimental data (see Figs. 2—4), we can draw some conclusions on the processes occurring in the zone of discharge and connecting channel. Dissociation of the H_2O and CH_4 molecules occurs in the discharge zone. The OH$^\cdot$ and O$^\cdot$ species enter into fast reactions with Me, CH_2, and CH. As a result, considerable amounts of CO and CO_2 are present at the output of the discharge zone, whereas the concentrations of OH$^\cdot$, O$^\cdot$, Me, CH_2, and CH, primary products of dissociation of the starting gases, remain low. In addition, a polymer film appears on the reactor wall. Large amounts of H atoms are formed at the outlet of the discharge zone, and their decay occurs comparatively slowly; therefore, the concentration of H$^\cdot$ in the connecting channel is 10^{16}—10^{15} cm^{-3}. Considerable concentrations of O_2 molecules, which are mainly formed in the heterogeneous recombination of O atoms, are observed at the end of the discharge zone.

Thus, the H_2, CO, O_2, and CO_2 molecules, H$^\cdot$ radicals, and unreacted CH_4 and H_2O are the main dissociation products yielded from the CH_4+H_2O mixture by MW discharge. Due to a low reactivity of H_2, CO_2, CH_4, and H_2O, chemical processes in the connecting channel involving these molecules can be neglected.

The results of mathematical simulation and experimental data suggest that the formation of HCOOH and AcOH in the experiment occurs on the cool surface of the condensate. CO, which is formed in the gas phase in the reaction of dissociation of the feeding gases, is the

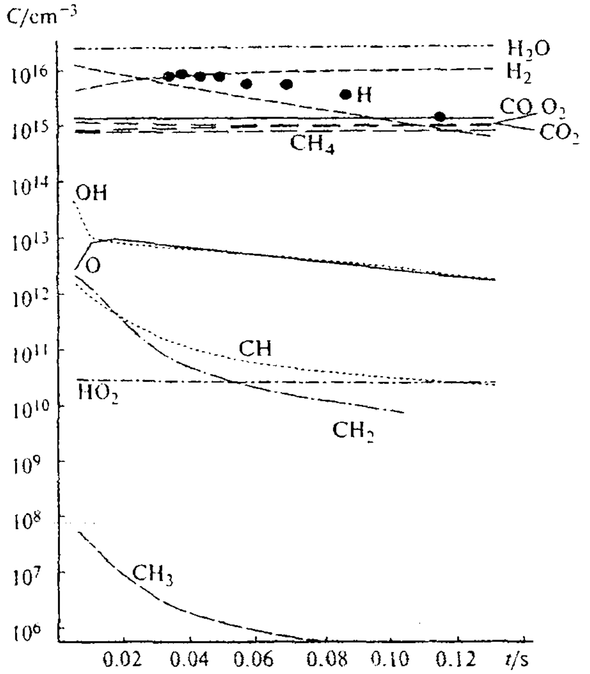
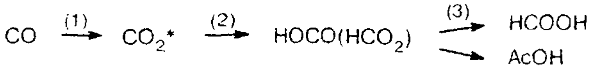


Fig. 5. Results of mathematical simulation of the gas phase composition in the zone after discharge in the CH_4+H_2O mixture at different contact times in the reactor. Points are experimentally determined concentrations of H atoms. Composition of the starting gas mixture 90 vol.% H_2O + 10 vol.% CH_4, p = 1 Torr, power 140 W.

precursor of organic acids. Thus, the mechanism of formation of organic compounds by LTC in the CH_4+H_2O system is the same as that in the CO_2+H_2, $CO+H_2O$ (Ref. 2), and CH_4+CO_2(Ref. 3) systems. It can be presented by the following scheme:



$$CO \xrightarrow{(1)} CO_2{}^{*} \xrightarrow{(2)} HOCO(HCO_2) \begin{cases} \xrightarrow{(3)} HCOOH \\ \xrightarrow[(4)]{} AcOH \end{cases}$$

$$CO(^1\Sigma^+) + O(^3P) \longrightarrow CO_2{}^{*} \qquad (1)$$

$$CO_2{}^{*} + H \longrightarrow HOCO(HCO_2) \qquad (2)$$

$$[HCO_2]^{\cdot} + H \longrightarrow HCOOH \qquad (3)$$

$$[HCO_2]^{\cdot} + CH_2 \longrightarrow CH_2HCOOH \xrightarrow{+H} AcOH \qquad (4)$$

The O atoms are mainly formed during the surface chemical reactions of H atoms and O_2 molecules coming from the gas phase: $H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$, $H^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O^{\cdot}$. Note that significant amounts of $HO_2^{\cdot}$ radicals were detected by ESR in the CH_4+H_2O condensate. In excess of oxygen-containing species, the destruction of carbon-containing radicals and products can occur (it is not shown in the scheme). Methane serves as a source of carbon oxides and hydrocarbon radicals for the formation of MeCOOH (reaction (4)).

When the fraction of water (a source of oxygen-containing species) in the starting mixture increases, the amount of the $HCO_2^{\cdot}$ radical, the precursor of formic and acetic acids, increases. At the same time, the concentration of hydrocarbon radicals participating in the formation of acetic acid decreases in the gas phase. As a result, the yield of HCOOH increases and that of AcOH remains unchanged (see Fig. 1).

The degree of water dissociation increases with an increase in the discharge power. Mathematical simulation shows that an increase in the concentrations of products of water dissociation results in an increase in the concentrations of oxygen-containing species. In this way, the amount of $HCO_2^{\cdot}$ radicals increases in the condensate and the concentrations of hydrocarbon radicals in the connecting channel decrease. In fact, the concentration of O_2 in the gas phase increases considerably with an increase in the output power (see Fig. 2). As a result, when the power increases, initially the yield of HCOOH increases and the yield of MeCOOH remains unchanged. Further increase in the power results in the disappearance of AcOH, since the hydrocarbon radicals disappear in the gas phase due to an increase in the concentration of oxygen-containing species. Then HCOOH disappears, because the excessive concentrations of oxygen-containing species result in the decomposition of the $HOCO^{\cdot}$ ($HCO_2^{\cdot}$) radical on the surface of the condensate that formed (see Fig. 2).

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