The formation of formic acid upon low-temperature condensation of CO_2—H_2 and CO—H_2O gas mixtures dissociated in electric discharge

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The formation of formic acid in the low-temperature condensation of CO_2—H_2 and CO—H_2O gas mixtures dissociated in electric discharge was investigated. The gas-phase concentrations of $H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$, and O_2 were measured downstream a microwave discharge in a CO_2—H_2 mixture. Low-temperature (77 K) condensates formed from CO_2—H_2 and CO—H_2O mixtures were studied by ESR. The formation of formic acid in the CO_2—H_2 and CO—H_2O systems was found to be due to the reactions of $H^{\cdot}$, CO, $O^{\cdot}$, and O_2 on the condensate surface. A single mechanism of the formation of formic acid in the CO_2—H_2 and CO—H_2O systems was proposed.

Key words: electric discharge in gases, low-temperature condensation, formic acid, hydrogen, carbon dioxide, water, carbon monoxide, ESR, frozen radicals.

Previously[1—3] we have found that low-temperature condensation of CO_2—H_2 and CO—H_2O gas mixtures dissociated in a low-pressure electric discharge affords formic acid (the major product), methanol, and formaldehyde. This result is of interest from the viewpoint of astrochemistry and the problem of life origination because processes of this type (the formation of organic compounds in reactions on a cold surface of simple species such as $H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$, O_2, and CO deposited from the gas phase) can be regarded as models of similar structures in the cosmos (for example, on the surface of a cometary nucleus).

The purpose of this work is (1) to determine the yield of formic acid in the low-temperature condensation of a CO_2—H_2 mixture dissociated in an alternating current glow discharge (50 Hz) or a microwave discharge over the whole range of compositions of the initial mixture; (2) determination of the gas phase composition downstream a microwave discharge in CO_2—H_2 mixtures over the whole range of compositions of these mixtures; (3) ESR study of the low-temperature condensates obtained from CO_2—H_2 and CO—H_2O mixtures; (4) study of the mechanism of formation of organic compounds in the low-temperature condensation of CO_2—H_2 and CO—H_2O gas mixtures dissociated in a low-pressure electric discharge.

Experimental

The experiments were carried out using a vacuum discharge setup with two reactors. Reactor N1 (Fig. 1) was a quartz tube passing through a resonator-type discharger (1/4 wave; the design of the discharger was described previously[4]) and the cavity of a Radiopan SE/X-2547 ESR spectrometer. The cold surface (an appendix of the cryostat, *i.e.* a "finger" filled with liquid nitrogen) on which the low-temperature condensate was collected was mounted in the center of the cavity of the radiospectrometer. The design of the reactor allowed, first, determination of the concentration of atoms and radicals in the gas phase near the condensate surface and, second, detection of the radicals stabilized in the low temperature condensate. The combustion of the discharge was maintained using a Luch-11 microwave generator (frequency 2450 MHz, output power

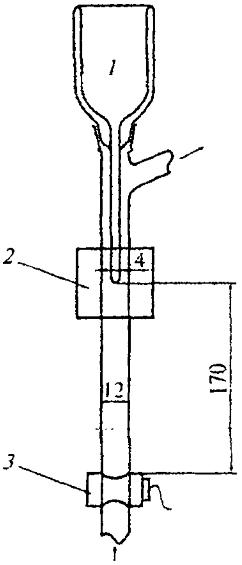

Fig. 1. Scheme of reactor N1: (*1*) Dewar vessel with liquid nitrogen, (*2*) the cavity of the ESR spectrometer, (*3*) microwave discharger connected to a microwave generator (2450 MHz, 15—150 W). The dimensions are expressed in mm.

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15—150 W). The discharge was ignited by an Iskra-1 external source. Reactor N1 was similar to that used previously,[1] except for the microwave generator parameters and the geometric dimensions.

The scheme of reactor N2, made of molybdenum glass, and the electric circuit for the glow discharge supply are shown in Fig. 2. The power is supplied by an ac source (50 Hz). During burning of the discharge, plasma is contacting with the surface cooled by liquid nitrogen. A certain difficulty in these experiments is usually brought about by the fact that the condensate is not collected on the surface cooled by liquid nitrogen but tends to accumulate on the adjacent surface having a higher temperature.[5] Reactor N2 that was used in our experiments rules out this possibility. Since the inner tube of the trap is heated by burning of the discharge, low-temperature condensation occurs exactly on the surface cooled with liquid nitrogen. Since the joint of the trap is located below the upper edge of the Dewar vessel, the joint is efficiently cooled by cold liquid nitrogen vapor; this prevents melting of the vacuum lubrication.

The stable condensation products were determined as follows. When experiments were carried out in reactor N1, the condensate was recondensed into a removable trap. In the case of reactor N2, the reactor trap in which the condensate directly formed was disconnected (heating or evaporation of the condensate from the trap were virtually absent). Then the condensate was dissolved in water or acetone and the resulting solution was analyzed by GC/MS using the method of internal standards. The internal standards were propionic acid and isobutyl alcohol. A Finnigan MAT ITD-850 AT GC/MS spectrometer, a Varian 3300 chromatograph, and 30-m long DB-1701 and DB-WAX capillary columns 0.25 mm in diameter were used. Helium was used as the carrier gas, flow rate 100 $cm^3 min^{-1}$. A solution of the condensate (1 μL) was introduced with a microsyringe into the injector heated to 250 °C. The temperature mode of the column was as follows: the initial temperature equal to 50 °C was maintained for 2 min, then the column temperature was raised to 200 °C at a rate of 10 K min^{-1}, and the column was maintained at this temperature up to the end of the analysis.

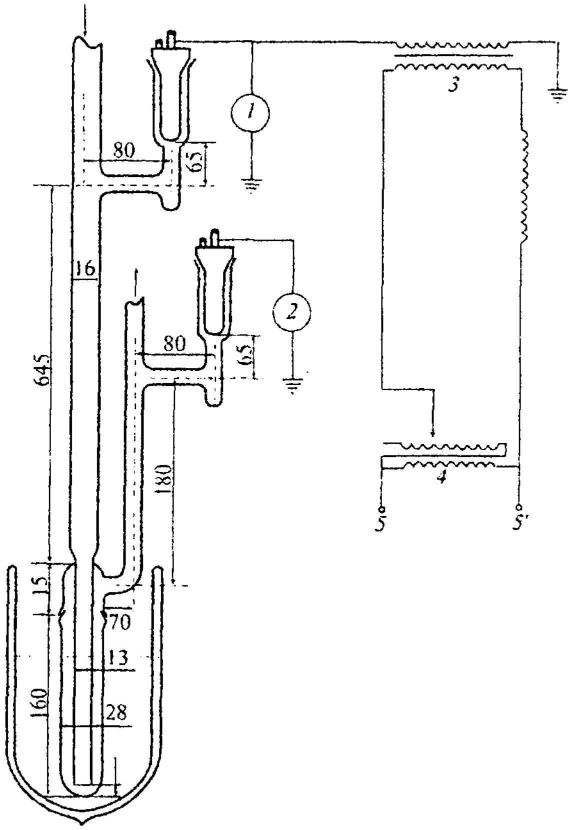

Fig. 2. Scheme of reactor N2 and electric circuit of the glow discharge supply: (*1*) S-96 kilovoltmeter, (*2*) Ts-4311 tester for measuring the current, (*3*) NOM-10 step-up transformer, (*4*) variator, (*5*), (*5'*) connection to the power supply (220 V, 50 Hz). The dimensions are expressed in mm..

The experiments in reactor N1 were carried out at a flow velocity of 3 L h^{-1} (standard conditions (sc)), a pressure of 1.2 Torr, and an output power of the microwave generator of 15 W. The distance from the area of dissociation of the gas mixture (microwave discharge) to the area of synthesis (cooled surface) was constant and equal to 17 cm. The amount of formic acid in the condensate and the contents of $H^·$, $O^·$, $OH^·$, and O_2 in the gas phase were determined as functions of the composition of the CO_2—H_2 gas mixture (no signals of free electrons or O_2 ($^1\Delta_g$) were detected in the gas phase). The condensates formed from CO_2—H_2 and CO—H_2O mixtures were studied by ESR. The experiments in reactor N2 were performed at a flow velocity of 3 L h^{-1} (sc), a pressure of 1.6 Torr, and a discharge power of 200 W. The amount of formic acid in the condensate was determined as a function of the composition of the initial CO_2—H_2 gas mixture. The duration of freezing-out in all experiments was 10 min.

Results and Discussion

The results of experiments on the determination of the composition of the gas phase and the yield of formic

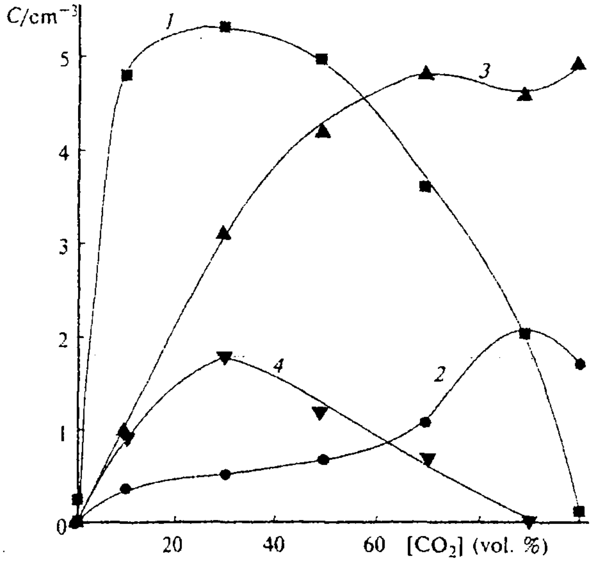

Fig. 3. Gas-phase concentrations of $[H^·] \cdot 10^{-15}$ (*1*), $[O^·] \cdot 10^{-15}$ (*2*), $[O_2] \cdot 10^{-14}$ (*3*), and $[OH^·] \cdot 10^{-12}$ (*4*) *vs* composition of the initial gas mixture. Reactor N1, flow rate 3 L h^{-1} (sc), pressure 1.2 Torr, power 15 W.

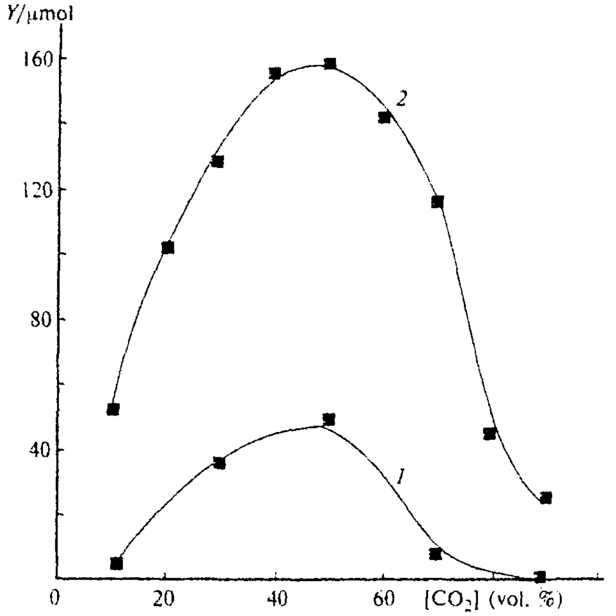

Fig. 4. Yield of formic acid (*Y*) *vs* composition of the initial gas mixture: (*1*) reactor N1, flow rate 3 L h^{-1} (sc), pressure 1.2 Torr, power 15 W; (*2*) reactor N2, flow rate 3 L h^{-1} (sc), pressure 1.6 Torr, power 200 W.

acid are presented in Figs. 3 and 4. Both in the glow and microwave discharge, the highest yield of HCOOH is attained when the initial mixture contains CO_2 and H_2 in a ratio ranging from 0.9 : 1 to 1 : 1. The lower yield of HCOOH in a microwave discharge (compared to that in glow discharge) is due to the different discharge powers.

In reactor N2, the yield of HCOOH was studied as a function of the gas flow rate and pressure in the reactor. The composition of the initial mixture was 45% CO_2 + 55% H_2 (v/v); the discharge power was 200 W. It was found that the variation of the yield of HCOOH *vs* pressure or residence time of the gas in the discharge (the residence time of the gas in the discharge *t* is inversely proportional to the gas flow rate, $v \sim 1/t$) is described by linear functions: as pressure increases from 1.3 to 3.6 Torr, the yield of HCOOH based on the initial CO_2 decreases from 1.7 to 0.7 mol. % (flow rate 2.6 L h^{-1} (sc)); as the flow rate of the initial mixture decreases from 8.1 to 1.5 L h^{-1}, the yield of HCOOH increases from 0.5 to 1.7 mol. % (pressure 2.4 Torr).

A typical ESR spectrum of the CO_2—H_2 condensate is presented in Fig. 5. In the literature,[6] these spectra are usually attributed to the $HO_2^{\cdot}$ radical in the CO_2 matrix. The number of $HO_2^{\cdot}$ radicals is great; their signal can overlap the signals of radicals present in a small amount. The dependence of the amount of $HO_2^{\cdot}$ in the codensate on the composition of the initial mixture is shown in Fig. 6. The presence of $HO_2^{\cdot}$ radicals in the condensate obtained from carbon dioxide (with CO_2 as the only initial gas) is due to the admixtures of hydrogen-containing compounds (water vapor) in the initial CO_2.

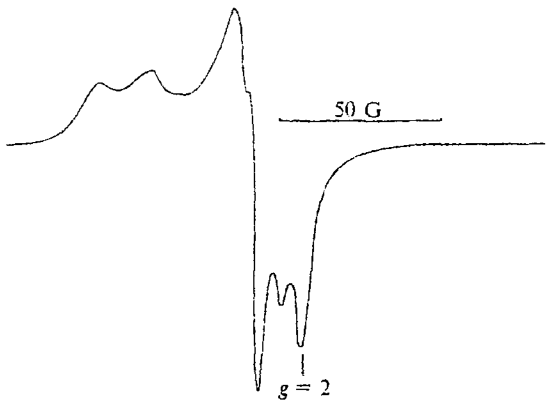

Fig. 5. ESR spectrum of the condensate prepared from the CO_2 (48% v/v)—H_2 (52% v/v) mixture at a flow rate of 3.5 L h^{-1} (sc), a pressure in the reactor of 0.8 Torr, and an output power of the microwave generator of 15 W. Relative amplification 2.

The content of $HO_2^{\cdot}$ radicals in the condensate correlates with the content of O_2 in the gas phase near the freezing-out area (except for the condensate prepared from CO_2). The generally accepted mechanism of the formation of $HO_2^{\cdot}$ in the peroxide radical condensate (PRC) includes the reaction of $H^{\cdot}$ atoms with O_2 molecules on the surface of the matrix.[5,7,8] Apparently, in our case, $HO_2^{\cdot}$ is formed by the same mechanism.

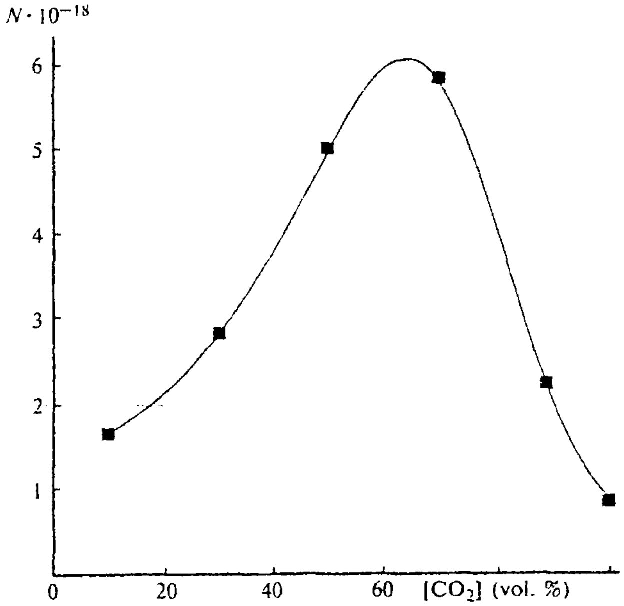

Fig. 6. Number of $HO_2^{\cdot}$ radicals (*N*) in the condensate *vs* composition of the initial gas mixture. Reactor N1, flow rate 3 L h^{-1} (sc), pressure 1.2 Torr, power 15 W.

The gas-phase concentration of $H^{\cdot}$ in $CO_2—H_2$ mixtures dissociated in the microwave discharge is approximately an order of magnitude higher than the O_2 concentration; thus, the formation of $HO_2^{\cdot}$ is limited by the concentration of O_2. In the case of carbon dioxide, the concentration of $H^{\cdot}$ is an order of magnitude lower than the concentration of O_2 and the formation of $HO_2^{\cdot}$ is limited by the concentration of $H^{\cdot}$ atoms.

The condensates formed from the $CO—H_2O$ mixture were studied by ESR spectroscopy under conditions close to those ensuring the maximum yield of HCOOH.[3] Due to the lower content of O_2 in the gas phase, the number of $HO_2^{\cdot}$ radicals in the condensate is much lower than that in the $CO_2—H_2$ system. Thus, other radicals can also be determined in the condensate. The ESR spectrum of the condensate obtained from $CO—H_2O$ (Fig. 7) exhibits a doublet with asymmetric lines (splitting 134.5 G) and a complex central signal. The doublet (lines *A* and *F*) belongs to the $HCO^{\cdot}$ radical.[9] The central signal resembles the spectrum of the $HO_2^{\cdot}$ radical in PRC matrices. An unusual feature is that the intensity of component *E* is higher than the intensity of component *D*. The central signal may be due to the overlap of the spectra of the $HO_2^{\cdot}$ radical and some other radical.

To confirm this assumption, we studied the ESR spectra of the condensates formed upon passing a mixture of hydrogen, oxygen, and HCOOH vapor through a microwave discharge. The formation of a substantial amount of $HO_2^{\cdot}$ radicals and a radical resulting from abstraction of a hydrogen atom from the formic acid molecule should be expected in this case. The spectrum recorded is shown in Fig. 8. The spectrum exhibits overlapped signals of $HO_2^{\cdot}$ and the radical derived from HCOOH. The ESR spectral pattern for the condensate from $H_2—O_2—HCOOH$ (see Fig. 8) is similar to the structure of the central signal of the ESR spectrum of the $CO—H_2O$ condensate (see Fig. 7). Thus, component *E* is due to one or several radicals formed upon decomposition of HCOOH. The reverse reactions involving these radicals should regenerate HCOOH. The spectra obtained do not permit unambiguous identification of these radicals. It can be accepted as a working hypothesis that component *E* in the ESR spectra of the condensates from $CO—H_2O$ is due to the $HOCO^{\cdot}$ radical.

It has been shown previously[2] that the yields of HCOOH and other organic compounds decreases on increasing the temperature of the cold surface. In addition, when the distance between the cold surface and the discharge is such that no atoms or radicals are present in the gas phase, these compounds are not formed. Thus, for organic compounds to appear, the system must have a cold surface accessible to atoms and radicals from the gas phase having formed in an electric discharge. The cold surface stabilizes the initial species and product molecules possessing excess energy. The products formed are then incorporated in the structure of the growing matrix and become inaccessible for the reactions with the gas-phase species, which could destroy them.

Let us determine the set of gas-phase species that can participate in the formation of organic compounds. For this purpose, we use the data[10] on the simulation of the reaction kinetics in the area downstream the discharge in a $CO_2—H_2$ mixture (composition of the initial gas mixture 25% CO_2 + 75% H_2 (v/v), pressure in the reactor 1 Torr, output power of the microwave generator 20 W). Under these conditions, the yield of formic acid exceeds 20 μmol (flow rate 3 L h^{-1}, freezing-out time 10 min). Let us consider the case where one

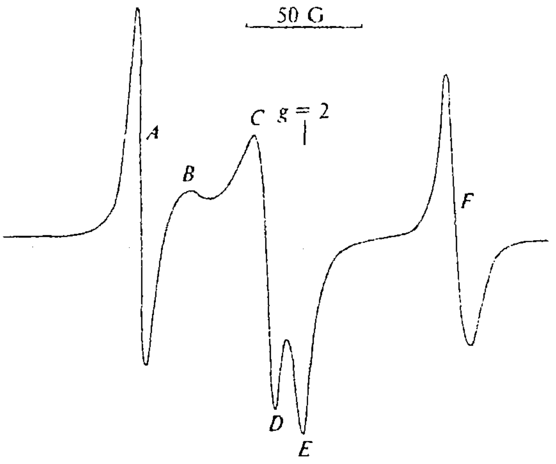

Fig. 7. ESR spectrum of the condensate obtained from the CO (56% v/v)—H_2O (44% v/v) mixture at a flow rate of 2.8 L h^{-1} (sc), a pressure in the reactor of 1.2 Torr, and an output power of the microwave generator of 15 W. Relative amplification 125.

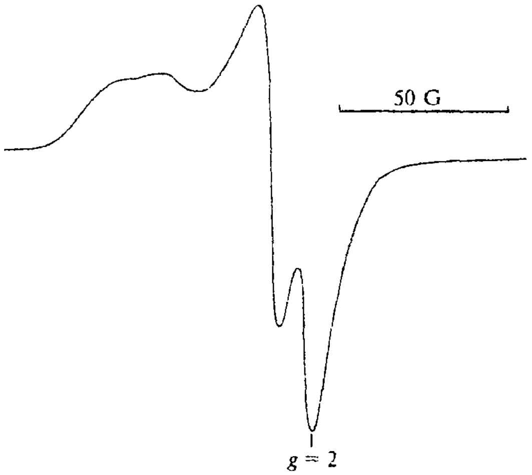

Fig. 8. ESR spectrum of the condensate obtained on treatment of formic acid vapor with the microwave discharge products (output power of the microwave generator 15 W) in an H_2 (flow rate 1.8 L h^{-1} (sc))—O_2 (flow rate 0.9 L h^{-1} (sc)) mixture. Relative amplification 1.

species in the gas phase gives rise to one HCOOH molecule in the condensate. When the flow rate is 3 L h^{-1}, the pressure in the reactor is 1 Torr, and the freezing time is 10 min, 10 μmol of HCOOH in the condensate corresponds to a concentration of $1 \cdot 10^{13}$ species cm^{-3}. Those species (atoms, radicals, molecules) whose gas-phase concentration is lower than this value cannot provide the amount of HCOOH observed experimentally.

The formation of organic compounds requires the presence of carbon-containing species near the synthesis area. As shown previously,[10] when the flow rate is 3 L h^{-1} and the pressure is 1.2 Torr, $[HCO^{\cdot}] < 4 \cdot 10^9$ cm^{-3} over the whole range of concentrations of the initial gas mixture. Thus, the gas-phase concentration of $HCO^{\cdot}$ radicals is far from being adequate to account for the amount of organic compounds formed. The gas-phase concentrations of CO and/or CO_2 suffice for explanation of the observed yields of HCOOH and other organic compounds. Carbon-containing species other than CO, CO_2, or $HCO^{\cdot}$ are virtually absent from the gas phase.[10] The estimated rates of the chemical reactions of carbon dioxide indicate that, under conditions of our experiments, this molecule is inert and the contribution of its reactions is insignificant.[10] Thus, the initial carbon-containing species serving for the formation of organic compounds under experimental conditions is the CO molecule.

In all experiments, organic compounds were formed only in the case where the gas phase near the synthesis area contained substantial concentrations of hydrogen atoms (10^{15}—10^{16} cm^{-3}) (see Fig. 3). This fact implies that organic compounds arise *via* reactions involving H atoms. However, the currently available data do not allow one to match the yield of formic acid to the concentration of a particular species detectable in the gas phase. Apparently, HCOOH is the product of a complex reaction involving several species both generated on the surface and deposited from the gas phase.

It follows from a comparison of the variation of the yield of HCOOH and gas-phase concentrations of species that the formation of HCOOH requires that oxygen-containing species ($O^{\cdot}$, O_2, $OH^{\cdot}$) be present in the gas phase. The yield of HCOOH depends on the concentrations of several species rather than a single one. The concentration of $OH^{\cdot}$ radicals does not suffice for explanation of the yields observed (it is ~5—10 times lower). In the majority of experiments, the yields of HCOOH can be interpreted by assuming that oxygen atoms coming from the gas phase participate in the low-temperature reaction. However, in some cases, the gas-phase concentration of oxygen atoms is too low. The experimental data and results of mathematical simulation indicate that the only reactive oxygen-containing species other than atomic oxygen whose gas-phase concentration can account for the observed yields of HCOOH is molecular oxygen. The overall concentration of atomic and molecular oxygen is high enough to provide for the formation of HCOOH in the yields observed in all experiments. Thus, the minimum set of gas-phase species necessary for the formation of formic acid in the low-temperature condensation includes $H^{\cdot}$ atoms, CO molecules, and oxygen-containing species $O^{\cdot}$ and O_2. Apparently, dioxygen acts as the source of $O^{\cdot}$ and $OH^{\cdot}$ in the reactions on the surface of the condensate formed:

$$H^{\cdot} + O_2 \longrightarrow HO_2,$$
$$H^{\cdot} + HO_2^{\cdot} \longrightarrow 2\ OH^{\cdot},$$
$$H^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O + O^{\cdot}.$$

Judging by the rate constants and the activation energies of these reactions in the gas phase,[11] they all could occur on the surface of the condensate at low temperatures.

The above inferences are also valid for the $CO—H_2O$ system, which largely resembles the $CO_2—H_2$ system. In fact, the compositions of products of the low-temperature condensation of these two mixtures dissociated in the microwave discharge are close. Both systems produce substantial gas-phase concentrations of hydrogen atoms (10^{15}—10^{16} cm^{-3}) and CO. The distinctive feature of the $CO—H_2O$ system is that the O_2 signal cannot be detected in the gas phase, while the signals of $O^{\cdot}$ and $OH^{\cdot}$ are at the noise level. However, one should bear in mind that the concentration sensitivity of the ESR method with respect to dioxygen under conditions of experiments with the $CO—H_2O$ mixture is ~10^{14} cm^{-3}.[12,13] The gas-phase concentration of O_2 ($1 \cdot 10^{14}$ cm^{-3}) is sufficiently high to account for the observed yields of HCOOH in all experiments in the $CO—H_2O$ system. The mechanisms of formation of organic compounds in the low-temperature condensation of $CO—H_2O$ and $CO_2—H_2$ mixtures dissociated in electric discharge might be identical.

The question arises of what are the intermediate species *en route* to the organic compounds in the low-temperature condensation. Some of these may be the radicals detected in the condensate by ESR. In addition to HCOOH, methanol and traces of formaldehyde can often be found among the condensation products. The most probable pathway to CH_3OH is successive hydrogenation of CO (*via* $HCO^{\cdot}$ and HCHO) on the cold surface:

$$CO \xrightarrow{+H^{\cdot}} HCO^{\cdot} \xrightarrow{+H^{\cdot}} HCHO \xrightarrow{+H^{\cdot}}$$
$$\longrightarrow CH_2OH^{\cdot}(CH_3O^{\cdot}) \xrightarrow{+H^{\cdot}} CH_3OH.$$

Formic acid is formed upon successive CO + O + 2 $H^{\cdot}$ interaction on the surface of the condensate. The $HOCO^{\cdot}$ ($HCO_2^{\cdot}$) radical is assumed as the intermediate species in the formation of HCOOH in our experiments. The reaction of $H^{\cdot}$ with $HOCO^{\cdot}$ ($HCO_2^{\cdot}$) should afford HCOOH. The $HOCO^{\cdot}$ ($HCO_2^{\cdot}$) radical is stable in low-temperature matrices and can be obtained in low-temperature reactions of CO.[14,15] Let us discuss the route by which the $HOCO^{\cdot}$ ($HCO_2^{\cdot}$) radical is generated in the condensate. Generally speaking, the CO + $O^{\cdot}$ + $H^{\cdot}$ interaction can follow three pathways

$$CO \xrightarrow{+O^{\cdot}} CO_2{}^{*} \xrightarrow{+H^{\cdot}} HOCO^{\cdot}\ (HCO_2{}^{\cdot}),$$

$$CO \xrightarrow{+OH} HOCO^{\cdot}\ (HCO_2{}^{\cdot}).$$

$$CO \xrightarrow{+H^{\cdot}} HCO^{\cdot} \xrightarrow{+O^{\cdot}} HOCO^{\cdot}\ (HCO_2{}^{\cdot}).$$

The $CO_2{}^{*}$ molecule is introduced in the scheme because, as noted above, carbon dioxide is nonreactive in the ground state. However, the primary products of interaction of CO with O are excited CO_2 molecules, which are highly reactive. Indeed, the gas phase reaction CO ($X^1\Sigma^+{}_g$) + $O^{\cdot}$ (^3P) involves the stage of formation of CO_2 ($^3B_2$).[16] The CO ($X^1\Sigma^+{}_g$) + $O^{\cdot}$ (^3P) reaction in the argon matrix at 18 K affords linear van der Waals complex CO ($X^1\Sigma^+{}_g$)...O (^3P); the bent CO_2 ($^3B_2$) complex is not formed due to steric restrictions.[17]

As noted above, the gas-phase concentrations of $OH^{\cdot}$ are low; therefore, the contribution of the channel

$$CO \xrightarrow{+OH^{\cdot}} HOCO^{\cdot}\ (HCO_2{}^{\cdot})$$

is insignificant. The $HCO^{\cdot}$ radical can react not only with oxygen atoms on the condensate surface but also with other species, for example, with hydrogen atoms, whose gas-phase concentration is higher. Since $H^{\cdot}$ atoms are highly reactive at low temperatures, it can be concluded that the contribution of the channel

$$CO \xrightarrow{+H^{\cdot}} HCO^{\cdot} \xrightarrow{+O^{\cdot}} HOCO^{\cdot}\ (HCO_2{}^{\cdot})$$

is also insignificant. Thus, in all probability, the reaction CO + $O^{\cdot}$ + $H^{\cdot}$ follows predominantly the following pathway

$$CO \xrightarrow{+O^{\cdot}} CO_2{}^{*} \xrightarrow{+H^{\cdot}} HOCO^{\cdot}\ (HCO_2{}^{\cdot}),$$

i.e., the formation of the $HOCO^{\cdot}$ ($HCO_2{}^{\cdot}$) radical includes the step of hydrogenation of $CO_2{}^{*}$.

Based on comparison of the data on the concentrations near the synthesis area and on the yields of organic compounds under our experimental conditions, the following scheme of formation of organic compounds can be proposed (Scheme 1, only the most probable pathways to organic compounds are indicated).

All the reactions occur on the surface of the condensate. An important role in the formation of organic compounds is played by stabilization of reactive intermediates in the matrix. The H atoms and CO molecules are deposited from the gas phase. The O atoms can either come from the gas phase or arise during the surface reactions of $H^{\cdot}$ atoms and O_2 molecules having entered from the gas phase

$$H^{\cdot} + O_2 \longrightarrow HO_2,\ H^{\cdot} + HO_2{}^{\cdot} \longrightarrow H_2O + O^{\cdot}.$$

Scheme 1

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

$$CO + H^{\cdot} \longrightarrow HCO^{\cdot}, \tag{1}$$

$$HCO^{\cdot} + H^{\cdot} \longrightarrow HCHO, \tag{2}$$

$$HCHO + H^{\cdot} \longrightarrow CH_2OH^{\cdot}\ (CH_3O^{\cdot}), \tag{3}$$

$$CH_2OH^{\cdot}\ (CH_3O^{\cdot}) + H^{\cdot} \longrightarrow CH_3OH, \tag{4}$$

$$CO\ (^1\Sigma^+) + O^{\cdot}\ (^3P) \longrightarrow CO_2{}^{*}, \tag{5}$$

$$CO_2{}^{*} + H^{\cdot} \longrightarrow HOCO^{\cdot}\ (HCO_2{}^{\cdot}), \tag{6}$$

$$HOCO^{\cdot}\ (HCO_2{}^{\cdot}) + H^{\cdot} \longrightarrow HCOOH. \tag{7}$$

With excess oxygen-containing species, destruction of carbon-containing species and products is also possible; it is not indicated in the Scheme.

Scheme 1 takes into account all the characteristic features of formation of organic compounds found experimentally.

1. Organic compounds are formed if the gas-phase concentration of $H^{\cdot}$ is rather high and exceeds substantially the concentrations of all the other reactive species. The greater part of reactions in the Scheme involves atomic hydrogen. The formation of oxygen-containing species requires excess hydrogen atoms.

2. The reactions

$$CO\ (^1\Sigma^+) + O^{\cdot}\ (^3P) \longrightarrow CO_2{}^{*},\ H^{\cdot} + O_2 \longrightarrow HO_2{}^{\cdot},$$
$$H^{\cdot} + HO_2{}^{\cdot} \longrightarrow H_2O + O^{\cdot}$$

account for the experimentally observed influence of oxygen-containing species on the yield of formic acid.

3. The different intermediate species on the pathways to formic acid and methanol stipulate the different patterns of dependence of the yields of these compounds on experimental parameters.

4. The low yields of MeOH compared to those of HCOOH are due to the facts that, first, the greater part of $HCO^{\cdot}$ radicals are destroyed in the reaction

$$HCO^{\cdot} + H^{\cdot} \longrightarrow H_2 + CO,$$

and, second, the probability of occurrence of the sequence of reactions (2), (3), and (4) (see Scheme 1) is low.

Scheme 1 interprets the characteristic features of formation of organic compounds in the experiments on the low-temperature condensation of gas mixtures containing carbon oxides. In fact, organic compounds are not formed in the CO_2—H_2O system because excess concentrations of $O^{\cdot}$ and $OH^{\cdot}$ result in the destruction of reactive carbon-containing species. In the CO—H_2 system, synthesis of organic compounds virtually does not occur because no oxygen-containing species ($O^{\cdot}$, O_2, $OH^{\cdot}$) are present in the gas phase; in addition, the matrix is not formed.

In accordance with Scheme 1, an important role in the formation of organic compounds is played by the $HO_2^{\cdot}$, $HCO^{\cdot}$, and $HOCO^{\cdot}$ ($HCO_2^{\cdot}$) radicals. The $HO_2^{\cdot}$ and $HCO^{\cdot}$ radicals were actually detected in low-temperature condensates, which confirms the validity of Scheme 1. In addition, an ESR signal that may be due to the $HOCO^{\cdot}$ ($HCO_2^{\cdot}$) radical was detected.

The results of the work show that the formation of formic acid in the low-temperature condensation of CO_2—H_2 and CO—H_2O mixtures dissociated in electric discharge proceeds upon the reactions of $H^{\cdot}$, CO, $O^{\cdot}$, and O_2, deposited from the gas phase, on the surface of the growing condensate. There are grounds for believing that reactions in the CO_2—H_2 and CO—H_2O systems follow the same mechanism.

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