The kinetics of chemical reactions in the products of dissociation of the CO_2—H_2 gas mixture in microwave discharge

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The yields of hydrogen atoms, oxygen atoms and molecules, and hydroxyl radicals after a microwave discharge in the mixture of CO_2 and H_2 were measured by ESR spectroscopy in a flow-type system. A mathematical model of the kinetics of chemical reactions downstream the microwave discharge was devised. The concentrations of particles that cannot be detected under our experimental conditions were estimated.

Key words: electric discharge in gases, chemical kinetics, hydrogen, carbon dioxide, ESR spectroscopy, hydrogen atoms, oxygen atoms, hydroxyl radicals.

Our earlier studies[1—4] have shown that low-temperature condensation of CO_2—H_2 mixtures dissociated in low-pressure electric discharge affords C_1 organic compounds. The composition of the products of low-temperature condensation is determined by the composition of the gas phase near the cold surface. In this study, we performed mathematical simulation of the kinetics of reactions involved in the dissociation of the CO_2—H_2 gas mixture in a microwave discharge and estimated the concentrations of species that cannot be detected experimentally.

Experimental

The experiments were carried out using a vacuum discharge flow setup (Fig. 1) at a pressure of 1 Torr in a quartz reactor. The initial gas mixture was 25% (v/v) CO_2 + 75% (v/v) H_2. The discharge was maintained by a microwave generator "Luch-58.1" (frequency 2350 Hz) with an output power of 20 W. A resonator-type adjustable discharger was used, whose design had been described previously.[5] The discharge was ignited using an external "Iskra-1" source. The gas-phase concentrations of paramagnetic species were measured using an SE/X-2542 ESR spectrometer by standard procedures.[6]* An H_{001} cylindrical resonator with a through-hole inner diameter of 18 mm was used.

The concentration of paramagnetic species was studied as a function of residence time in the reactor (τ), *i.e.*, the time it takes for a particle to fly from the end of the discharge zone (from the microwave discharger because the height of the discharge zone was restricted by the discharger height) to the center of the cavity of the ESR spectrometer. The τ value was varied by changing the flow rate v. The change in v was considered to have no effect on the concentration of species coming out of the discharge. The experimental conditions were chosen in such a way that the distribution of concentrations would be described by differential equations of chemical kinetics.[9]

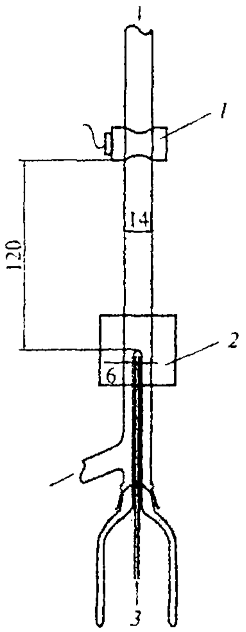

Fig. 1. Reactor scheme: (*1*) microwave discharger connected to a microwave generator (2350 MHz, 20—200 W); (*2*) ESR cavity; (*3*) supply of liquid nitrogen. The dimensions are expressed in mm.

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* Experimental values of the concentration sensitivity for an RE-1306 ESR spectrometer are as follows: for a pressure of 1 Torr and optimized detection conditions, $H^\cdot$, 10^{11} cm^{-3}; $O^\cdot$, $3 \cdot 10^{10}$ cm^{-3}; $OH^\cdot$, 10^{10} cm^{-3}; O_2, $3 \cdot 10^{13}$ cm^{-3} (Ref. 7); for a pressure of 2 Torr, $H^\cdot$, $5 \cdot 10^{12}$ cm^{-3}; $O^\cdot$, $2 \cdot 10^{12}$ cm^{-3}; $OH^\cdot$, $2.5 \cdot 10^{11}$ cm^{-3}; O_2, $7.5 \cdot 10^{14}$ cm^{-3}.[8]

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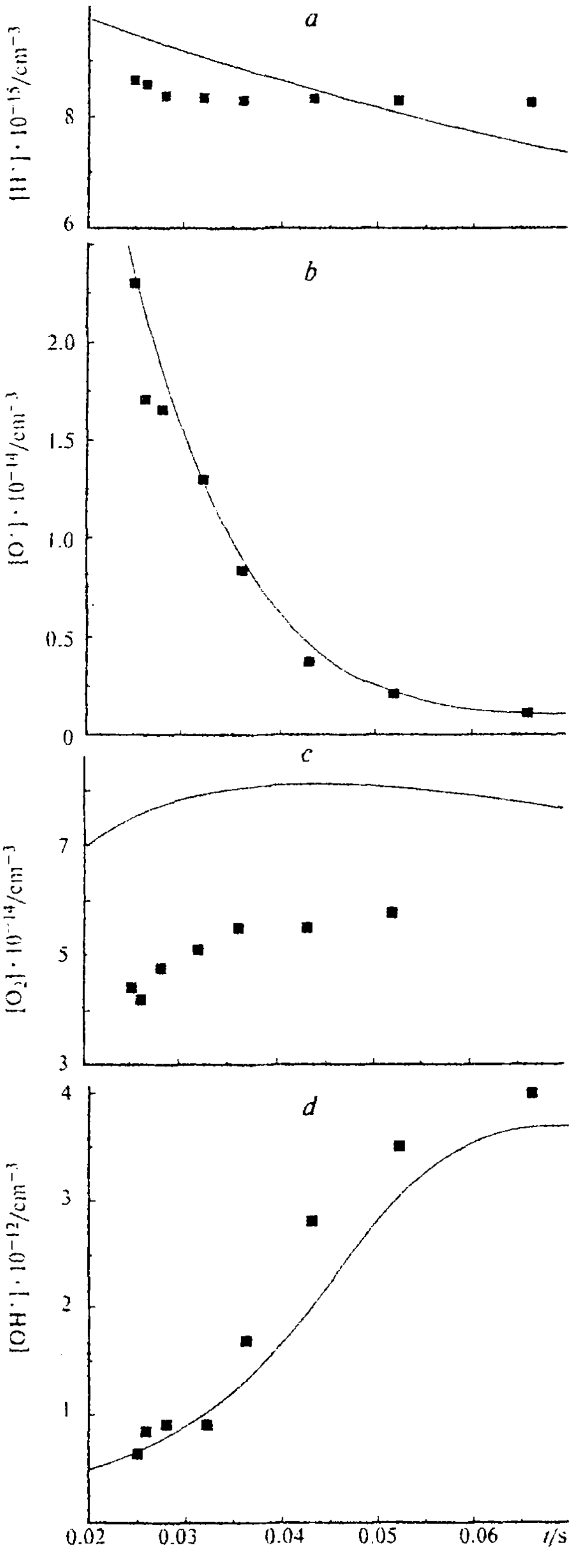

Fig. 2. Concentrations of $\mathrm{H}^{\cdot}$ (*a*), $\mathrm{O}^{\cdot}$ (*b*), $\mathrm{O_2}$ (*c*), and $\mathrm{OH}^{\cdot}$ (*d*) *vs* residence time in the reactor. Dots correspond to experimental data, lines show the results of calculations. Initial mixture 25% $\mathrm{CO_2}$ + 75% $\mathrm{H_2}$ (v/v), pressure 1 Torr, power 20 W.

The gas phase was found to contain $\mathrm{H}^{\cdot}$ and $\mathrm{O}^{\cdot}$ atoms, $\mathrm{OH}^{\cdot}$ radicals, and dioxygen in the ground state $^3\Sigma_g^-$. No signals of singlet oxygen $\mathrm{O_2}(^1\Delta_g)$ or free electrons were detected. The experimental dependences of the concentrations of $\mathrm{H}^{\cdot}$, $\mathrm{O}^{\cdot}$, $\mathrm{OH}^{\cdot}$, and $\mathrm{O_2}$ on the residence time are shown in Fig. 2. These curves were used to carry out mathematical simulation of the reaction kinetics in the products of discharge in a $\mathrm{CO_2}$—$\mathrm{H_2}$ mixture.

Mathematical simulation of the reaction kinetics

The mathematical model was constructed in the following way. A set of reactions known to contain all the steps that can occur in the system considered (primary set) was specified. Using rough estimate of the reaction rates, the primary set was reduced to the initial set. Subsequently, the rates of the reactions included in the initial set were estimated based on experimental data. The reactions characterized by the lowest rates were rejected until the removal of a reaction resulted in an increase in the discrepancy between experimental results and those calculated in terms of the model. This procedure gave a set of steps sufficient to describe processes in the system in question.

As the primary set of chemical reactions, we employed gas-phase reactions of $\mathrm{H}^{\cdot}$, $\mathrm{O}^{\cdot}$, $\mathrm{O_2}$, $\mathrm{O_3}$, $\mathrm{OH}^{\cdot}$, $\mathrm{HO_2}^{\cdot}$, $\mathrm{H_2O}$, $\mathrm{H_2O_2}$, CO, $\mathrm{CO_2}$, $\mathrm{CH_3}^{\cdot}$, $\mathrm{CH_4}$, $\mathrm{HCO}^{\cdot}$, $\mathrm{H_2CO}$, $\mathrm{MeO}^{\cdot}$, MeOH, and HCOOH. The rate constants were taken from reference books.[10–12] The initial set, containing much fewer reactions than the primary set, was obtained from the primary set by a previously reported algorithm.[13] The rate constant of the fast reaction

$$\mathrm{O}^{\cdot} + \mathrm{H}^{\cdot} + \mathrm{M} \longrightarrow \mathrm{OH}^{\cdot} + \mathrm{M}$$

is known only for the 1500—2000 K temperature range.[10] We took this value for room temperature. Since the rate of termolecular recombination increases upon decrease in the temperature, the value employed, $k = 2.2 \cdot 10^{-32}$ cm^6 (molecule^2 s)$^{-1}$, is the lower limit of the rate constant at room temperature.

The rate constants for the heterogeneous decay of some species and the initial concentrations serve as the mathematical model parameters. The effective constant for heterogeneous decay and the initial concentrations of $\mathrm{H}^{\cdot}$ and $\mathrm{O}^{\cdot}$ can be estimated from the dependences of the concentrations of these species on the residence time. For this purpose, the change in the concentrations of $\mathrm{H}^{\cdot}$ and $\mathrm{O}^{\cdot}$ was assumed to be determined by the pseudo-first-order decay. This assumption allows one to find the first approximation for more accurate determination of the constants and the initial concentrations. The microwave discharge was regarded only as the source of $\mathrm{H}^{\cdot}$, $\mathrm{O}^{\cdot}$, and CO species. Knowing the composition of the initial mixture and the concentrations of $\mathrm{H}^{\cdot}$ and $\mathrm{O}^{\cdot}$ at the outlet of the discharge, one can find the initial concentrations of $\mathrm{H_2}$, $\mathrm{CO_2}$, and CO. The initial concentrations of the other species were taken to be zero.

An important role in this type of systems is played by reactions occurring on the reactor surface (usually this is the decay of active species). The heterogeneous decay of $\mathrm{H}^{\cdot}$, $\mathrm{O}^{\cdot}$, $\mathrm{OH}^{\cdot}$, and $\mathrm{HO_2}^{\cdot}$ on glass and quartz surfaces is described by a first-order equation.[14] The rate constants for the heterogeneous decay depend on numerous parameters; these constants should be determined from experimental data for each system and each reactor. The determination of the first approximations for the constants for heterogeneous decay of the $\mathrm{H}^{\cdot}$ and $\mathrm{O}^{\cdot}$ atoms is described above; for $\mathrm{OH}^{\cdot}$ [15] and $\mathrm{HO_2}$,[14] published data were used.

The heterogeneous decay of the $O^{\cdot}$ atoms in a CO_2 glow discharge occurs[16] at the same sites where CO molecules are adsorbed. The constant for the heterogeneous decay of the $O^{\cdot}$ atoms is inversely proportional to the concentration of CO in the gas phase. In addition, the heterogeneous reaction

$$CO + O^{\cdot} \longrightarrow CO_2$$

can occur on the same sites; the rate of this reaction exceeds the rate of homogeneous recombination

$$CO + O^{\cdot} + M \longrightarrow CO_2 + M.$$

The initial approximation for the rate constant for the heterogeneous reaction

$$CO + O^{\cdot} \longrightarrow CO_2$$

was estimated using the value found previously.[16]

The set of reactions sufficient for describing the experimental kinetic curves (*i.e.*, for constructing the model of the process) was determined using the following algorithm.

1. A set of reactions known to include all the processes occurring in the system in question was specified (the initial model). The initial approximations of the constants for heterogeneous decay and for the starting concentrations were specified.

2. The constants of the heterogeneous decay were determined by minimization of the functional

$$J\{\log k\} = \sum_{j=1}^{m} \sum_{i=1}^{N} \left(\frac{C_{ji}^{\exp}}{C_{ji}\{\log k\}} - \frac{C_{ji}\{\log k\}}{C_{ji}^{\exp}} \right)^2,$$

where $\{\log k\} = \{\log k_H, \log k_O, \log k_{OH}, \log k_{HO_2}, \log k_{CO+O}\}$ is the set of logarithms of the constants for heterogeneous decay, $C_{ji}^{\exp}$ is the measured concentration of a *j*th substance ($H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$, O_2) at instant t_i, and $C_{ji}\{\log k\}$ is the concentration of a *j*th substance at instant t_i calculated in terms of the model. The direct kinetic problem was solved using the program described previously.[17] The functional was minimized using the coordinate descent and gradient methods.[18] This step affords either the numerical values for unknown rate constants or the ranges containing the true values of these constants. Only upper estimates can often be found for unknown rate constants. Values lower that these estimates do not influence the functional.

In the majority of cases, inverse problems of this type have a non-unique solution.[19] The use of published data on the possible values for unknown constants allows one to avoid blunders and to determine correctly the upper limits of the contributions of the corresponding reactions.

3. If further variation of the constants does not result in a decrease in the functional, variation of the initial concentrations was carried out by the trial-and-error method.

4. Let us define the contribution of an *i*th reaction by the expression

$$\left(\sum_i \int_0^T W_i(t)\mathrm{d}t \right)^{-1} \int_0^T W_i(t)\mathrm{d}t,$$

where W_i is the rate of an *i*th reaction and $T = 0.2$ s in our case. The contributions of reactions were calculated by solving the direct kinetic problem using a program described previously.[17] The constants found at the third step of the procedure were used to calculate the contributions. If only the range of values is available for a constant, the upper estimate was employed. Reactions with small contributions were removed from the set.

Table 1. Heterogeneous chemical reactions included in the initial set

Reaction	log*k*	Ref.
$H^{\cdot} \longrightarrow 0.5\ H_2$	0.0	This work
$O^{\cdot} \longrightarrow 0.5\ O_2$	1.8	This work
$OH^{\cdot} \longrightarrow$ Products	1.0	15
$HO_2^{\cdot} \longrightarrow$ Products	1.0	14
$CO + O^{\cdot} \longrightarrow CO_2$	−17.0	16

Steps 2—4 were repeated until the minimum set of reactions describing adequately the experimental kinetic curves was obtained. At every stage of steps 2—4, fulfillment of the following condition was checked: the value of the functional at a given stage should not be greater than that at the previous stage.

The species included in the initial model and the starting concentrations of these species are presented below.

Species	C_0/cm^{-3}	Species	C_0/cm^{-3}
H_2	$1.925 \cdot 10^{16}$	O_2	0
$H^{\cdot}$	$1.1 \cdot 10^{16}$	H_2O	0
$OH^{\cdot}$	0	$HO_2^{\cdot}$	0
CO_2	$6.45 \cdot 10^{16}$	H_2O_2	0
CO	$1.8 \cdot 10^{15}$	O_3	0
$O^{\cdot}$	$1.8 \cdot 10^{15}$	$HCO^{\cdot}$	0
M	$3.3 \cdot 10^{16}$	HCOH	0

Only the initial concentrations of the $H^{\cdot}$ atoms and H_2 molecules were varied at step 3 of the simulation. The heterogeneous chemical reactions included in the initial set and the upper estimates of the rate constants for heterogeneous reactions obtained after steps 1—3 have been accomplished for the first time are presented in Table 1.

Results and Discussion

The calculated and experimental concentrations of $H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$, and O_2 are presented in Fig. 2. Generally, the model describes adequately the experimental kinetic curves. This model predicts a somewhat faster consumption of hydrogen atoms than is observed experimentally even though the heterogeneous decay is neglected. In addition, the model gives overstated concentrations of dioxygen. The calculated concentrations of $OH^{\cdot}$ are somewhat understated, due to the fact that, as noted above, the rate constant for the reaction

$$O^{\cdot} + H^{\cdot} + M \longrightarrow OH^{\cdot} + M$$

at room temperature is higher than the value given in Table 2. It should be specially noted that the model describes correctly the qualitative characteristics (the S shape) of the time variation of the concentration of the $OH^{\cdot}$ species. The $OH^{\cdot}$ radical is the only intermediate species detected experimentally. The fact that the calculated and experimental characteristics for the variation of $[OH^{\cdot}]$ *vs* *t* coincide indicates a satisfactory accuracy of the experimental data and confirms once again the adequacy of the model.

Table 2. Chemical reactions whose contribution exceeds 0.1% and the corresponding rate constants

Reaction	log*k*
$O^{\cdot} \longrightarrow 0.5\ O_2$ (1)	1.8
$H^{\cdot} + H^{\cdot} + M \longrightarrow H_2 + M$ (2)	−32.1
$H^{\cdot} + O_2 + M \longrightarrow HO_2^{\cdot} + M$ (3)	−31.5
$O^{\cdot} + OH^{\cdot} \longrightarrow H^{\cdot} + O_2$ (4)	−10.4
$O^{\cdot} + H^{\cdot} + M \longrightarrow OH^{\cdot} + M$ (5)	−31.7
$H^{\cdot} + HO_2^{\cdot} \longrightarrow OH^{\cdot} + OH^{\cdot}$ (6)	−10.8
$H^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O + O^{\cdot}$ (7)	−10.8
$H^{\cdot} + HO_2^{\cdot} \longrightarrow H_2 + O_2$ (8)	−10.9
$CO + OH^{\cdot} \longrightarrow CO_2 + H^{\cdot}$ (9)	−12.8
$H^{\cdot} + OH^{\cdot} + M \longrightarrow H_2O + M$ (10)	−29.9
$OH^{\cdot} + H_2 \longrightarrow H_2O + H^{\cdot}$ (11)	−14.2
$O^{\cdot} + O^{\cdot} + M \longrightarrow O_2 + M$ (12)	−32.1
$O^{\cdot} + HO_2^{\cdot} \longrightarrow OH^{\cdot} + O_2$ (13)	−10.5
$HCO^{\cdot} + H^{\cdot} \longrightarrow CO + H_2$ (14)	−10.3
$CO + H^{\cdot} + M \longrightarrow HCO^{\cdot} + M$ (15)	−34.0
$OH^{\cdot} \longrightarrow$ Products (16)	1.0
$OH^{\cdot} + OH^{\cdot} \longrightarrow H_2O + O^{\cdot}$ (17)	−11.8
$O^{\cdot} + H_2 \longrightarrow OH^{\cdot} + H^{\cdot}$ (18)	−17.5
$H^{\cdot} + OH^{\cdot} \longrightarrow H_2 + O^{\cdot}$ (19)	−15.4

Figure 3 shows the calculated concentrations of the species included in the model. Note that in the range of τ studied, heterogeneous decay of $OH^{\cdot}$ and $HO_2^{\cdot}$ can be neglected. The reactions whose contributions exceed 0.1% are listed in Table 2 in the order of decreasing contribution. Reactions (1)—(11) (see Table 2) constitute the minimum set that describes adequately the experimental curves; together with the corresponding rate constants, they represent the mathematical model of the kinetics of reactions in the reactor. The only intermediate species whose concentration cannot be determined experimentally and whose reactions have a substantial influence on the concentrations of $H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$, and O_2 is the $HO_2^{\cdot}$ radical. The reactions of H_2O_2, $HCO^{\cdot}$, O_3, and HCOH have no effect on the $H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$, and O_2 concentrations.

The concentrations of $HO_2^{\cdot}$ and $HCO^{\cdot}$ can be estimated using the method of steady-state concentrations. By equating the rates of formation (of $HO_2^{\cdot}$, reaction (3), and $HCO^{\cdot}$, reaction (15)) and decay (of $HO_2^{\cdot}$, reactions (6)—(8), and $HCO^{\cdot}$, reaction (14)), we have

$$[HO_2^{\cdot}] = k_3[M][O_2]/(k_6 + k_7 + k_8),$$

$$[HCO^{\cdot}] = k_{15}[M][CO]/k_{14}.$$

Substitution of $[O_2] = 5 \cdot 10^{14}$ cm^{-3} and $[CO] = 1.8 \cdot 10^{15}$ cm^{-3} gives $[HO_2^{\cdot}] \approx 1 \cdot 10^{10}$ cm^{-3} and $[HCO^{\cdot}] \approx 1 \cdot 10^{8}$ cm^{-3}, which is in good agreement with the simulation results. A change in the composition of the gas phase can increase contributions of some other reactions of the formation and decay of $HO_2^{\cdot}$ and $HCO^{\cdot}$; this has to be taken into account in the estimation of $[HO_2^{\cdot}]$ and $[HCO^{\cdot}]$ by the method of steady-state concentrations. Our estimates show that, when the proportion of CO_2 in the initial mixture increases, reactions (3) and (15) remain the main pathways of the formation of $HO_2^{\cdot}$ and $HCO^{\cdot}$, respectively, while the decay of these radicals contains greater contributions of step (13) and the reaction $O^{\cdot} + HCO^{\cdot} \longrightarrow OH^{\cdot} + CO$ (log$k = -10.2$). To estimate the concentrations over the whole range of compositions of the initial CO_2—H_2 mixture, one should use reactions (3), (6), (7), (8), and (13) for $HO_2^{\cdot}$ and reactions (14), (15), and $O^{\cdot} + HCO^{\cdot} \longrightarrow OH^{\cdot} + CO$ for $HCO^{\cdot}$. The concentrations determined in this way are the upper estimates because heterogeneous decay of radicals is neglected.

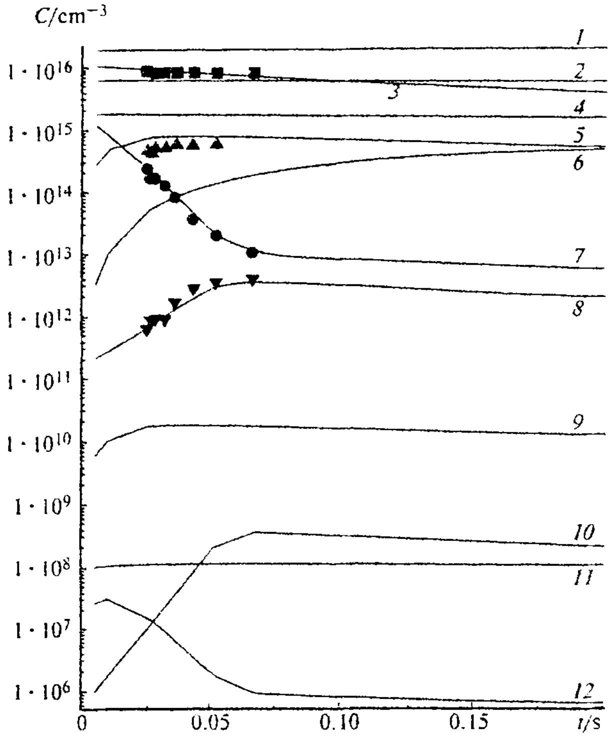

Fig. 3. Gas-phase concentrations (C) of H_2 (*1*), CO_2 (*2*), H (*3*), CO (*4*), O_2 (*5*), H_2O (*6*), $O^{\cdot}$ (*7*), $OH^{\cdot}$ (*8*), $HO_2^{\cdot}$ (*9*), H_2O_2 (*10*), HCO (*11*), and O_3 (*12*) in the zone downstream the discharge in the CO_2—H_2 mixture *vs* residence time in the reactor. Dots correspond to experimental data; lines show the results of calculations. Initial mixture 25% CO_2 + 75% H_2 (v/v), pressure 1 Torr, power 20 W.

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