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Heterogeneous Chemiluminescence of Crystallophosphor Catalysts in the CO + O Mixture

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Abstract—The results of the study of stationary and relaxation characteristics of heterogeneous chemiluminescence (HCL_{CO+O}) of such crystalophosphor catalysts as CaO–Bi and Zn_2SiO_4–Mn are presented. Chemiluminescence was excited by the products of the dissociation of the CO, CO_2, or O_2 + CO + Ar mixture. The excitation of (HCL_{CO+O}) generally follows the Eley–Rideal mechanism, that is O + CO–L ⟶ CO_2–L + $h\nu$ or CO + O–L ⟶ CO_2–L + $h\nu$, where L denotes a lattice. The stepwise kinetic mechanism of HCL_{CO+O} excitation is suggested. The cross-sections and quantum yields of CO oxidation on the surface of CaO–Bi and Zn_2SiO_4–Mn are determined.

INTRODUCTION

Heterogeneous chemical reactions on the surfaces of solid catalysts can excite chemiluminescence in infrared, visible, and even in ultraviolet regions (heterogeneous chemiluminescence, HCL) [1]. This enables the study of heterogeneous reactions by highly sensitive spectral methods. HCL of solids is well known and systematically studied. This HCL is initiated during the heterogeneous recombination of free atoms (H, O, and N and radicals [2]), which became a model chemical reaction. HCL in the reactions of H_2, CH_3OH, CO, and NO oxidation on MgO and NiO was also observed [3, 4]. However, these processes were not systematically studied.

This work presents the results of the study of carbon monoxide oxidation reactions by atomic and molecular oxygen. This catalytic reaction became a classical model object in heterogeneous catalysis (like the recombination of atoms). In addition, this reaction is important for practical applications: carbon monoxide oxidation in catalytic filters and the oxidation of organic compounds. It was found that the reaction CO + O is efficient in inducing HCL_{CO+O} for the following reasons. The elementary act of this reaction is exothermic. For example, the heat of this reaction on Cu_2O is >3 eV [5]. In this process, vibrationally excited CO_2^v molecules with an excitation energy of up to 2.6 eV localized on asymmetric stretching of the molecule ((009) level) are formed [6]. According to our idea [7], under certain conditions, this vibrational energy can be efficiently transformed into the energy of electronic excitation of the surface or near-surface luminescence centers.

In the elementary act of the reaction CO + O, not only CO_2^v molecules but also electronically excited CO_2^v molecules ($CO(^1\Sigma_g^+) + O(^3P) \longrightarrow CO_2(^3B_2, {}^1B_2)$) are formed. The probability of the later process is high. This is due to the fact that the formation of the ground state of ($^1\Sigma_g^+$) CO_2 molecule, when the reactants move along the coordinate of the reaction CO + O is spin forbidden [8]. CO_2^e molecules can relax with radiation (CO_2^e–L ⟶ CO_2–L + $h\nu$, where L denotes the lattice) or without it, but with energy transfer to the surface centers of luminescence. The rate constant of the gas-phase radiative reaction CO + O is $k_{CO+O} = 2 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} [9, 10]. This value is higher than the value of the rate constant for oxygen ($k_{O+O} = 2.3 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}) by an order of magnitude. The possibility for the radiative stabilization of the excited surface centers or the products of heterogeneous CO oxidation on the surface of solids is confirmed by the observation of HCL accompanying this reaction.

HCL_{CO+O} is a light indicator of the heterogeneous CO + O reaction, and permits us to obtain information on the elementary act of this reaction, its mechanism, the rate constants and cross-sections of various steps of reactions. This is necessary to better understand the role of nonequilibrium states in catalytic reactions.

EXPERIMENTAL

HCL_{CO+O} of crystallophosphor catalysts was studied in CO oxidation by oxygen in a high-vacuum setup ($P_{res} \leq 6 \times 10^{-6}$ Pa) with an oil-free pump. A flow reactor with a constant concentration of the components of

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exciting gas over the sample was used. Atomic oxygen was generated in an electrode-free high-frequency discharge (the frequency was 39 MHz and the power was 80 W). The following gases dissociated in the discharge: CO and CO_2 and the mixtures CO + O_2, CO_2 + O_2, and 2% O_2 + 80% CO + 18% Ar (argon was used as a high-purity buffer gas). The products of dissociation diffused to the sample.

The distance between a discharge and a luminophore was >40–60 cm to exclude the access of ions and vibrationally and electronically excited molecules from the discharge zone to the sample. The relaxation of excited molecules and the neutralization of ions were promoted by the presence of an argon buffer atmosphere and a small diameter (<2 cm) of tube for the supply of the gaseous reactants to the sample. Note that the character of experimental results did not change if a hot rhodium film is used for the dissociation of molecules. This result was expected because the states of O_2^e'(Δ_g, Σ_g^+, and others) cannot excite Mn^{2+}- and Bi^{3+} centers of luminescence in a visible spectral range and do not affect the kinetics of the heterogeneous processes on Zn_2SiO_4–Mn and CaO–Bi luminophores due to insufficient energy.

The luminescence was measured using two methods: by the measurement of the integral luminescence intensity and by the luminescence spectra (with an MDR-23 monochromator). Powdered samples were deposited onto a microheater for indirect heating. The microheater was made of a 10 μm thick permalloy covered by a thin film of SiO_2. The system of temperature stabilization assured a constant temperature of the sample with an accuracy of ±1 K at 293–700 K and the possibility of measuring the thermal effect of the reaction on the surface of catalytic phosphors. These measurements were carried out simultaneously with the measurement of the intensity of HCL_{CO+O}.

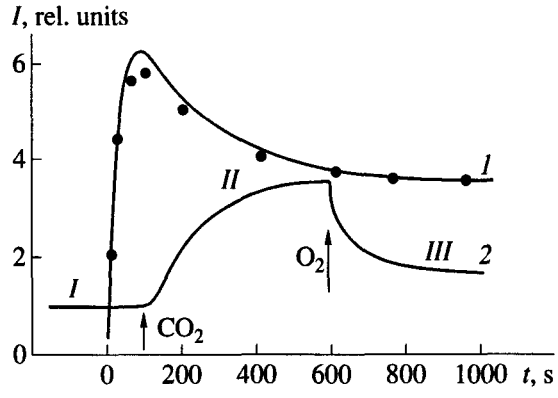

Fig. 1. Kinetics of Zn_2SiO_4–Mn HCL: (*1*) HCL in the products of CO_2 dissociation (HCL_{CO+O}) (points correspond to the experimental values), (*2*) HCL in a high-frequency discharge in O_2 (HCL_{CO+O}, part *I*), and after the substitution of O_2 by CO_2 (HCL_{CO+O}, part *II*), and after the substitution of CO_2 by O_2 (HCL_{CO+O}, part *III*). T = 550 K.

RESULTS AND DISCUSSION

More than 60 luminophore samples of various classes were studied. The luminescence of carbonates, chalcogenides, sulfides, and phosphates was not detected. The brightest luminescence was observed for CaO–Bi, Zn_2SiO_4–Mn, Y_2O_3–Eu, Y_2O_3–Bi, and AlN–Mn. The intensity of luminescence reaches a value of 10^{10}–10^{11} quanta cm^{-2} s^{-1}. The number of quanta radiated in one act of CO oxidation is $\eta = 10^{-4}$–10^{-3} (η is the quantum yield of HCL_{CO+O}). The experimental study of HCL_{CO+O} characteristics was carried out at a temperature corresponding to the maximum HCL intensity.

At T > 400 K, the short-wave part of HCL spectra of CaO–Bi and Zn_2SiO_4–Mn samples at excitation by oxygen (HCL_O) and UV irradiation have the same elementary band with λ_{max} = 400 nm (CaO–Bi) and with λ_{max} = 525 nm (Zn_2SiO_4–Mn). The HCL spectrum has two additional (compared to photoluminescence spectrum) bands with λ_{max} = 525 nm and 590 nm for CaO–Bi and one additional band with λ_{max} = 655 nm for Zn_2SiO_4–Mn. The HCL spectra of Zn_2SiO_4–Mn and CaO–Bi measured in the CO + O mixture ($HCL_{O,CO+O}$) contain pronounced bands of ions/activators with λ_{max} = 400 nm (Bi^{3+}) and λ_{max} = 525 nm (Mn^{2+}) observed at photoexcitation. These HCL spectra also contain bands with λ_{max} = 590 nm (CaO–Bi) and λ_{max} = 675 nm (Zn_2SiO_4–Mn) typical of surface center excitation. Note that HCL_{CO+O} lines are somewhat broadened compared to photoluminescence spectra.

The initial segment of the kinetic curve of HCL_{CO+O} flare-up in the products of the dissociation of CO_2 (CO + O) on the clean surface in a high-frequency discharge is linear. This is due to the two-step Eley-Rideal mechanism of CO oxidation and HCL_{CO+O} excitation (Fig. 1, curve *1*). The intensity of HCL_{CO+O} is 2–3 times higher than the intensity of HCL_{CO+O} (HCL in the mixture O + O_2) (Fig. 1, curve *2*). This agrees with the results of the study of the photoinduced recombination of CO + O and O + O, where the rate constant of the photoinduced recombination k_{O-O} is one order of magnitude lower than the k_{CO-O} [9, 10].

Figure 2 (curve *1*) shows the intensity of HCL_{CO+O} as a function of the flux density of oxygen atoms $I(j)$ (j_O and j_{CO} are the densities of O and CO fluxes; $j_{CO} = \alpha j_O$; for the discharge in CO_2, $\alpha \approx 1$). The curve was measured by the responses of the HCL_{CO+O} intensity when the power of a high-frequency discharge was discretely increased [2]. At low j, the function $I(j)$ is nonlinear.

If chemiluminescence is excited by the products of CO dissociation (HCL_{CO}), the intensity of HCL_{CO} (Fig. 2, curve *2*) associated with the oxidation of CO by oxygen atoms on the surface of phosphors is lower than at the excitation in the products of CO_2 dissociation by one

order of magnitude. This is due to the low degree of CO dissociation in a high-frequency discharge (≤0.1%). The yield of oxygen atoms in a high-frequency discharge in CO is comparable to the yield of nitrogen atoms in a high-frequency discharge in N_2 (0.1–0.2%) [11, 12]. The order of the stationary intensity of HCL_{CO} with respect to the flux density of oxygen atoms in the discharge in CO is higher than unity at low j (Fig. 2, curve 2). This is due to the two-step mechanism of the process of HCL_{CO} excitation which largely occurs according to the equation CO +O–L ⟶ CO_2–L + $h\nu$ even with a high excess of CO molecules (j_{CO} is higher than j_O by a factor of ~10^3).

The addition of O_2 accelerates CO–L oxidation and leads to an increase in the intensity of HCL_{CO+O}. In the discharge in the 2% O_2 + 80% CO + 18% Ar mixture, the intensity of HCL is proportional to the flux density of oxygen atoms (Fig. 2, curve 3). The excitation is probably associated with the reaction O + CO–L. The surface coverage remains virtually constant at a high excess of CO compared to the concentration of the oxygen atoms ($j_{CO} \gg j_O$).[1] This situation resembles the adsorption luminescence in oxygen [13]. The difference is that the adsorption of oxygen atoms takes place on CO–L with the formation of volatile product CO_2, but not on the surface defects.

Thermal power of the chemical reaction (ΔW) at HCL_{CO} was measured simultaneously with the intensity of HCL_{CO} (Fig. 3, curves 1 and 2). After "dark" pauses Δt (Δt is time when the high-frequency discharge was switched off), there is no correlation between the functions $\Delta W(t)$ and $I(t)$. This is due to two reactions of CO oxidation: CO + O–L ⟶ CO_2–L and O + CO–L ⟶ CO_2–L. The first reaction is efficient in the activation of HCL_{CO}, the second is less efficient but more exothermic. In addition, the rate of the second reaction increases with an increase in the duration of a dark pause due to an increase in the surface coverage by CO–L molecules during the pause.

The simultaneous measurement of the intensity of HCL_{CO+O} and thermal power of the reaction at the discharge in the 2% O_2 + 80% CO + 18% Ar mixture showed that the behavior after dark pauses is similar to the behavior of HCL_{CO} (Fig. 3, curves 3 and 4). Like HCL_{CO}, the intensity of HCL_{CO+O} does not become equal to zero immediately after the discharge is switched off, but it slowly decreases due to the oxidation of CO by O–L atoms on the surface. When the discharge is switched on after a long dark pause ($\Delta t \geq 100$ s) the thermal power of the reaction dramatically increases. This is accompanied by a slow increase in the HCL_{CO+O} intensity. Like HCL_{CO}, different behavior of $\Delta W(t)$ and $I(t)$ immediately after the high-frequency discharge is switched on is associated with the

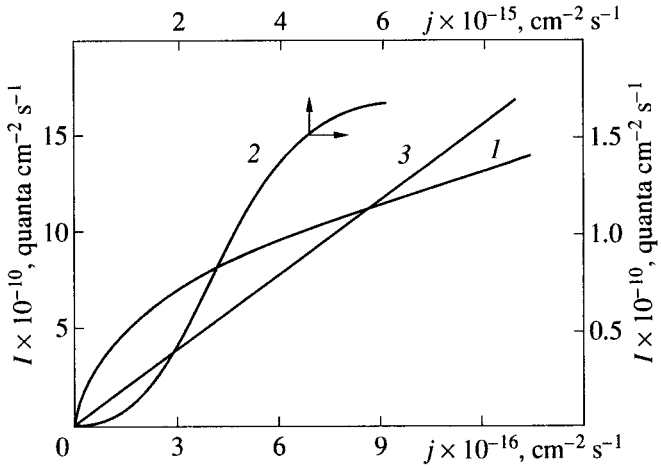

Fig. 2. The intensity of HCL on Zn_2SiO_4–Mn as a function of oxygen atom flux density. HCL is excited by the products of the dissociation of (1) CO_2, (2) CO, and (3) the mixture of 2% O_2 + 80% CO + 18% Ar. T = 550 K, P_{tot} = 2.5 Pa.

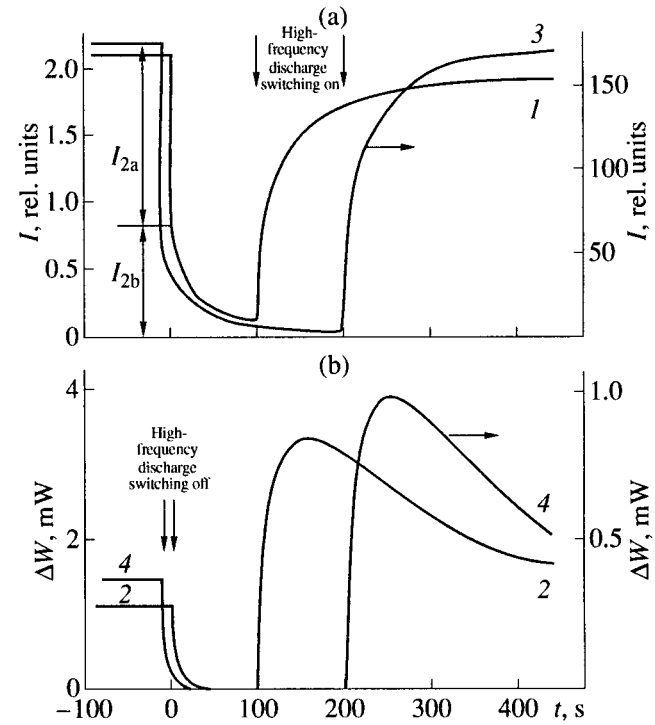

Fig. 3. (a) The intensity of HCL and (b) the thermal power ΔW before and after dark pauses at the excitation of HCL on CaO–Bi by the products of the dissociation of (1, 2) CO (P_{CO} = 2.5 Pa, $j_{CO} = 7.6 \times 10^{18}$ cm^{-2} s^{-1}) and (3, 4) the mixture of 2% O_2 + 80% CO + 18% Ar (P_{tot} = 2.5 Pa). T = 510 K.

surface coverage by CO–L during a dark pause. However, the reaction O + CO–L ⟶ CO_2–L + $h\nu$, which begins after switching the discharge on, is characterized by a one order of magnitude lower quantum yield than the reaction CO + O–L ⟶ CO_2–L + $h\nu$. Therefore, initially, the quantum yield of HCL_{CO+O} is low.

[1] Note that the flux density of oxygen atoms in the discharge in the mixture 2% O_2 + 80% CO + 18% is higher than in pure CO by about one order of magnitude.

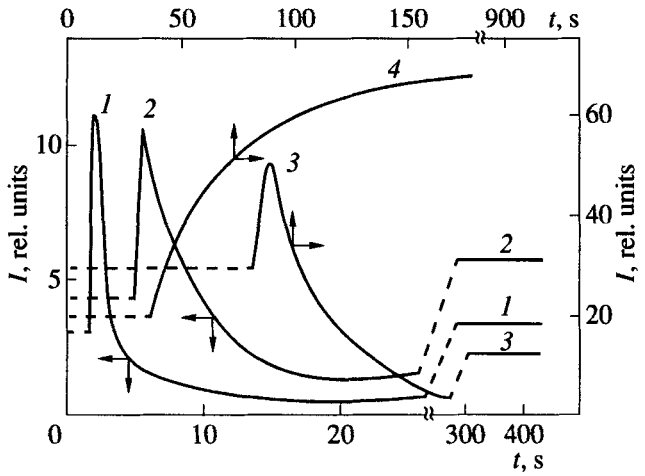

Fig. 4. The flash of HCL on the samples of (*1*, *2*) Zn_2SiO_4–Mn and (*3*, *4*) CaO–Bi after the supply of (*1*) O + O_2 with preliminary adsorption of CO, (*2*) CO with preliminary adsorption of O (discharge in CO), (*3*) CO (10% CO in O_2) with preliminary adsorption of O, and (*4*) 10% O_2 in the discharge in CO. T = 550 K.

To determine the roles of oxygen atoms and CO molecules in HCL_{CO+O}, we studied the HCL of phosphors excited by various products of discharge (Fig. 4). Curve *2* in Fig. 4 refers to CO adsorption at a high-frequency discharge in CO. The degree of CO dissociation is low, and the density of the oxygen atom flux is equal to 10^{-3} of the flux of CO molecules. Therefore, during the initial period (t < 20 s), it is only possible to consider the recombination of adsorbed oxygen atoms with CO. However, after a rather long time (t > 300 s), a new equilibrium in the system is attained. This equilibrium corresponds to the HCL in the products of high-frequency discharge in CO. The luminescence of phosphor at t > 300 s is associated with the supply of oxygen atoms from the discharge and with their adsorption. The addition of 10% CO to O_2 in a high-frequency discharge initially leads to the flash of luminescence, then the intensity of luminescence decreases (Fig. 4, curve *3*). The flash of luminescence is probably due to the fast oxidation of CO by O–L atoms, whereas a further decrease in the intensity results from the lack of oxygen for CO oxidation. This assumption is also confirmed by an increase in the intensity of HCL after the addition of 10 % O_2 to CO in a high-frequency discharge (Fig. 4, curve *4*).

Note the discrepancy between the data presented in curves *1* and *4* (Fig 4). These curves correspond to the Zn_2SiO_4–Mn and CaO–Bi luminophores, respectively. The discrepancy of the results shows that the efficiency of the reaction O + CO–L $\longrightarrow$ CO_2–L + $h\nu$ on CaO–Bi is relatively low as compared to the reaction on Zn_2SiO_4–Mn and that the efficiency of CaO–Bi excitation by oxygen atoms following the recombination mechanism O + O–L $\longrightarrow$ O_2–L + $h\nu$ is high.

The relatively low intensity of the flash of luminescence of Zn_2SiO_4–Mn (Fig 1, curve *2*, *II*) as compared to the intensity of luminescence in Fig. 4 (curve *2*) is associated with the much lower CO concentration obtained in the first case by a high-frequency discharge in CO_2.

To find the contribution of the molecular gas component to the intensity of HCL, the intensity of HCL flash without a high-frequency discharge was measured in the interaction of different molecules on the surface. For this purpose, one of the gases was adsorbed on the sample surface (marked by symbol L), and then the other gas was added to the reactor. The luminescence flash in the reaction O + CO–L was more intense than in the reactions O_2 + CO–L or N_2O + CO–L by a factor of 10^5–10^6. The higher intensity of HCL_{CO+O} can be due not only to the higher exothermic effect of this reaction, but also to a much higher cross-section of the reaction O + CO–L as compared to the cross-sections of the reactions of O_2 and N_2O molecules with CO–L.

KINETIC MECHANISM OF HCL_{CO+O} EXCITATION

Kinetic mechanism of the excitation of HCL_{CO+O} includes the following reactions

$$O + L \underset{\nu_{-1}}{\overset{\nu_1}{\rightleftharpoons}} O\text{–}L; \qquad \text{(Ia)}$$

$$O + CO\text{–}L \xrightarrow{\nu_2, \eta_{2a}} CO_2\text{–}L + h\nu; \qquad \text{(IIa)}$$

$$O_2 + L \underset{\nu_{-3}}{\overset{\nu_3}{\rightleftharpoons}} O_2\text{–}L; \qquad \text{(IIIa)}$$

$$O + O\text{–}L \xrightarrow{\nu_4, \eta_{4a}} O_2\text{–}L + h\nu^2, \qquad \text{(IVa)}$$

$$CO + L \underset{\mu_{-1}}{\overset{\mu_1}{\rightleftharpoons}} CO\text{–}L; \qquad \text{(Ib)}$$

$$CO + O\text{–}L \xrightarrow{\mu_2, \eta_{2b}} CO_2\text{–}L + h\nu; \qquad \text{(IIb)}$$

$$CO_2 + L \underset{\mu_{-3}}{\overset{\mu_3}{\rightleftharpoons}} CO_2\text{–}L; \qquad \text{(IIIb)}$$

where ν_i, ν_{-i}, μ_i, μ_{-i} are the probabilities of the respective reactions per unit time, η_{2a}, η_{2b}, η_{4a} are the quantum yields of different reaction steps. For ν_i, ν_{-i}, μ_i, and μ_{-i} we have: $\nu_4 = \sigma_4 j_O$, $\nu_1 = \sigma_1 j_O$, $\nu_2 = \sigma_2 j_O$, $\nu_3 = \sigma_3 j_{O_2}$, $\mu_1 = \delta_1 j_{CO}$, $\mu_2 = \delta_2 j_{CO}$, $\mu_3 = \delta_3 j_{CO_2}$, $\nu_{-1} = \nu_{0,-1}\exp(-E_{O_2}/kT)$, $\nu_{-3} = \nu_{0,-3}\exp(-E_{O_2}/kT)$, $\mu_1 = \mu_{0,-1}\exp(-E_{CO_2}/kT)$, $\mu_{-3} = \mu_{0,-3}\exp(-E_{CO_2}/kT)$ where σ_i and δ_i are the cross-sections of the respective reactions, $\nu_{0,-1}$ and $\mu_{0,-1}$ are the frequency factors, E_{O_2}, and E_{CO_2} are the activation energies of O_2 and CO_2 desorption; j_O, j_{CO}, j_{O_2}, and j_{CO_2}

[2] The experimental intensity of luminescence in reactions (Ia) and (IIIa) is lower than in reactions (IIa) and (IIb) by 2–3 orders of magnitude. Therefore, adsorption luminescence due to the reactions (Ia) and (IIIa) was not taken into account in our model.

are the densities of the O, CO, O_2, and CO_2 fluxes, respectively.

Let us use the following notation for the surface concentrations at the initial time t: $\longrightarrow N(t)$, O–L $\longrightarrow N_1(t)$, O_2–L $\longrightarrow N_2(t)$, CO–L $\longrightarrow n_1(t)$, and CO_2–L $\longrightarrow n_2(t)$; where N_0 is the initial surface concentration of adsorption sites.

The system of kinetic differential equations describing the stepwise mechanism (Ia)–(IVa), (Ib)–(IIIb) can be written as

$$\left.\begin{aligned} dN/dt &= -(\nu_1 + \mu_1 + \nu_3 + \mu_3)N + \nu_{-1}N_1 \\ &+ \mu_{-1}n_1 + \nu_{-3}N_2 + \mu_{-3}n_2; \\ dN_1/dt &= \nu_1 N - (\nu_4 + \nu_{-1} + \mu_2)N_1; \\ dN_2/dt &= \nu_3 N + \nu_4 N_1 - \nu_{-3}N_2; \\ dn_1/dt &= \mu_1 N - (\mu_{-1} + \nu_2)n_1; \\ dn_2/dt &= \mu_3 N + \mu_2 N_1 + \nu_2 n_1 - \mu_{-3}n_2. \end{aligned}\right\} \quad (1)$$

The analysis of kinetic and stationary characteristics of HCL with the system (1) is complicated due to the great number of unknown parameters. Theoretical dependencies cannot practically be applied for the analysis of the experimental results. Therefore, let us consider the most interesting limit cases.

HCL in the 2% O_2 + 80% CO + 18% Ar ($j_{CO} \approx 10^2 j_O$, $j_{O_2} \neq 0$, $j_{CO_2} = 0$. Mass spectrometric measurements of thermally and electronically stimulated desorption from Zn_2SiO_4–Mn and CaO–Bi demonstrate strong adsorption of CO and O and reversible adsorption of CO_2, which is insignificant at 550 K. In the 2% O_2 + 80% CO +18% Ar mixture the concentration of CO_2 outside the discharge zone is low, and CO_2 adsorption can be neglected ($\mu_3 = 0$, reaction (IIIb)). In this mixture, the desorption of O and CO can also be neglected due to the high heats of adsorption ($\nu_{-1} = \mu_{-1} = 0$). Thus, system (1) can be simplified, and its solution for the intensity of HCL_{CO+O} according to (IIa), (IVa), and (IIb) can be written as follows

$$I(t) = \eta_2\nu_2 n_1(t) + (\eta_{2b}\mu_2 + \eta_{4a}\nu_4)N_1(t);$$

$$I(t) = N_0\sum_{i=1}^{3}[\exp(r_i t)] \times [A_i\mu_1(\eta_{2b}\nu_2 + \eta_{4a}\nu_4) + B_i\eta_{2b}\mu_2\nu_1] + I_\infty, \quad (2)$$

where r_i, A_i, and B_i are the functions of parameters ν_i and μ_i and I_∞ is the stationary intensity of HCL.

The kinetic curve for $I(t)$ can have more than one extremum. In the initial moment, when oxygen atoms are supplied to the surface covered by CO–L, the luminescence is associated with reaction (IIa). The intensity of HCL_{CO+O} after the initial flash ($t = t_0$, $n_1(t_0) = n_{10}$, $N_1(t_0) = N_{10}$) decreases exponentially

$$I(t) = I_0\exp(-j_O\sigma_2 t), \text{ where } I_0 = n_{10}\eta_{2a}\sigma_2 j_O. \quad (3)$$

Comparison of equation (3) with the experiment (Fig. 4, curve *1*) shows that $\nu_2 = \sigma_2 j_O = 0.6\ s^{-1}$ ($j_O = 10^{17}\ cm^{-2}\ s^{-1}$). Therefore, $\sigma_2 = 6 \times 10^{-18}\ cm^2$ is the cross-section of the reaction of CO–L oxidation by oxygen atoms on the surface of Zn_2SiO_4–Mn.

Let us estimate the quantum yield of HCL_{CO+O} η_{2a} in reaction (IIa) (O + CO–L) on the surface of Zn_2SiO_4–Mn using the expression [14]

$$\eta_{2a} = I(j_O)/Kn_1\sigma_2 j_O. \quad (4)$$

It is possible to obtain from the experiment that $I(j_O) = 10^{11}$ quanta $cm^{-2}\ s^{-1}$ at $j_O = 10^{17}\ cm^{-2}\ s^{-1}$ and $\nu_2 = \sigma_2 j_O = 0.6\ s^{-1}$. If the coefficient of surface roughness $K \approx 30$ and $n_1 \approx N_0 = 10^{14}\ cm^{-2}$, we obtain $\eta_{2a} \approx 10^{-4}$.

The situation taking place during dark pauses (Fig. 3) is interesting. The intensity of HCL decreases initially jumpwise after switching off the discharge. This is due to the disappearance of oxygen atoms in the gas phase ($j_O = 0$) and the cessation of reaction (IIa). Then, the intensity of HCL decreases according to the exponential law $I(t) = I_0\exp(-\mu_2 t)$ as a result of a decrease in the oxygen atom concentration on the surface (reaction (IIb)). Reaction (Ia) does not have a significant effect because $\mu_2 \gg \nu_{-1}$. $\mu_2 = 0.02\ s^{-1}$ corresponds to the experiment with CaO–Bi (Fig. 3, curve *3*). Therefore, at $j_{CO} = 8 \times 10^{18}\ cm^{-2}\ s^{-1}$, the cross-section of reaction (IIb) (CO + O–L) is $\delta_2 = 2.5 \times 10^{-21}\ cm^2$. The coverage of the surface by oxygen atoms at the initial moment after a dark pause can be described by the equation

$$N_1(t) = N_0[\mu_{-1}/(\mu_{-1} + \mu_{-2})][1 - \exp(-\nu_1 t)]. \quad (5)$$

A change in the HCL_{CO+O} intensity with time after switching on the high-frequency discharge after a dark pause is described by the equation $I(t) = I_{2a} + I_{2b}[1 - \exp(-\nu_1 t)]$, where I_{2a} and I_{2b} are the intensities of luminescence in reactions (IIa) and (IIb). The values of $\nu_1 = 8.33 \times 10^{-3}\ s^{-1}$ and $\sigma_1 \approx 8 \times 10^{-19}\ cm^2$ (the cross-section of oxygen atom adsorption on CaO–Bi) correspond to the experiment.

HCL in the Products of CO dissociation ($j_{CO} \approx 10^3 j_O$, $j_{O_2} = j_{CO_2} = 0$). Neglecting reactions (IIIa), (IIIb), and (IVa) ($\nu_3 = \mu_3 = \nu_4 = 0$) and taking into account that the surface coverage by CO ($j_{CO} \gg j_O$, n_1, $n_2 \gg N_1$, N_2) is stationary, it is possible to rewrite the system of kinetic equations (1) as follows

$$\left.\begin{aligned} dn_1/dt &= \mu_1 N - (\mu_{-1} + \nu_2)n_1 \\ dn_2/dt &= \nu_2 n_1 - \mu_{-3}n_2 \\ N_0 &= N + n_1 + n_2. \end{aligned}\right\} \quad (6)$$

The solution to (6) for the stationary case shows that the intensity of HCL_{CO} weakly depends on the density of the CO flux (j_{CO})

$$I(j) \approx I(j_O, j_{CO}) = \frac{N_0\eta_{2a}\mu_{-3}\delta_1\sigma_2 j_{CO} j_O}{\delta_1\sigma_2 j_{CO} j_O + \delta_1\mu_{-3} j_{CO} + \sigma_2\mu_{-3} j_O + \mu_{-1}\mu_{-3}} \approx \frac{N_0\eta_{2a}\mu_{-3}\sigma_2 j_O}{\sigma_2 j_O + \mu_{-3}}.$$

In the experiment, a virtually linear increase in $I(j)$ is observed at moderate CO pressures. This corresponds to $\mu_3 \gg \nu_2$; that is, CO_2 desorption is quite fast. In this case, from the solution to system (6), it is possible to determine the initial (I_0) and stationary (I_∞) intensities of HCL_{CO}

$$I_0 = N_0\eta_{2a}\sigma_2 j_O\mu_1/(\mu_1 + \mu_{-1}); \quad I_\infty = N_0\eta_{2a}\sigma_2 j_O\mu_1/(\mu_1 + \nu_2). \tag{7}$$

According to (7) and from the experiment (Fig. 4, curve *1*) we have

$$I_\infty/I_0 = (\mu_1 + \mu_{-1})/(\mu_1 + \nu_2) \approx \mu_1/\nu_2 = \delta_1 j_{CO}/\sigma_2 j_O \geq 0.3.$$

It is possible to estimate from this equation the cross-section of CO adsorption on Zn_2SiO_4–Mn $\delta_1 = I_\infty\sigma_2 j_O/I_O j_{CO} \approx 2 \times 10^{-21}$ cm^2. We consider the case of CO supply to the surface covered by O–L atoms in a similar way (Fig. 4, curve *2*), $I_\infty/I_0 \approx \nu_1/\mu_2 \approx 0.5$. In this case, the cross-section of oxygen atom adsorption on Zn_2SiO_4–Mn is equal to $\sigma_1 = \delta_2 I_\infty j_{CO}/I_O j_O \approx 1.2 \times 10^{-18}$ cm^2.

CO supply to the surface of Zn_2SiO_4–Mn covered by oxygen atoms leads to a flash of luminescence followed by an exponential decrease in its intensity (Fig. 4, curve *2*)

$$I(t) = I_0\exp(-j_{CO}\delta_2 t), \quad \text{where} \quad I_0 = N_{10}\eta_{2b}\delta_2 j_{CO}.$$

We obtained experimentally that $\mu_2 = \delta_2 j_{CO} = 0.33$ s^{-1} ($j_{CO} = 7.6 \times 10^{18}$ cm^{-2} s^{-1}). Therefore, the cross-section for reaction (IIb) (CO + O–L) on Zn_2SiO_4–Mn is $\delta_2 = 4.3 \times 10^{-20}$ cm^2. The oxygen atoms are the lattice constituents interacting with the surface stronger than CO. This decreases the cross-section of reaction (IIb) compared to reaction (IIa) ($\delta_2/\sigma_2 \approx 7.2 \times 10^{-3}$).

Let us estimate the quantum yield of reaction (IIb) (CO + O–L). According to the definition, $\eta_{2b} = I_{CO}/KN_1\delta_2 j_{CO}$. Taking into account that $K = 30$, $N_1 \approx 10^{-2}N_0 \approx 10^{12}$ cm^{-2}, $\delta_2 = 4.3 \times 10^{-20}$ cm^2, $j_{CO} \approx 10^3 j_O$, and $I_{CO} = 10^{10}$ quanta cm^{-2} s^{-1} (Fig. 2, curve *2*), we obtain $\eta_{2b} \approx 10^{-3}$. That is the quantum yield of HCL in reaction (IIb) (CO + O–L) is an order of magnitude higher than the quantum yield of reaction (IIa) (O + CO–L).

HCL in the products of CO_2 dissociation ($j_{CO} \approx j_O \ll j_{CO_2}$, $j_{O_2} = 0$). The mechanism of HCL_{CO_2} excitation includes the same steps as the mechanism of excitation of HCL_{CO+O} (reactions (Ia)–(IVa) and (Ib)–(IIIb)) excluding (IVa) (O + O–L), whose probability is low under the experimental conditions). Neglecting the desorption of oxygen atoms O–L $\longrightarrow$ O + L ($\nu_{-1} = 0$) we obtain the system of equations describing HCL_{CO_2}

$$\left.\begin{aligned} dN_1/dt &= \nu_1 N - \mu_2 N_1 \\ dn_1/dt &= \mu_1 N - (\mu_{-1} + \nu_2)n_1 \\ dn_2/dt &= \mu_3 N + \mu_2 N_1 + \nu_2 n_1 - \mu_{-3} n_2 \end{aligned}\right\} \tag{8}$$

If CO_2 desorption does not limit the process of CO oxidation (μ_{-3} is high), we obtain

$$I(t) = [N_0/(r_1 - r_2)] \times [A_1(1 - \exp(r_1 t)) - A_2(1 - \exp(r_2 t))], \tag{9}$$

where $r_{1,2} = -\lambda \pm (\lambda^2 - \mu)^{1/2}$; $2\lambda = \mu_{-1} + \mu_1 + \mu_2 + \nu_1 + \nu_2$; $\mu = \mu_1\mu_2 + (\nu_1 + \mu_2)(\nu_2 + \mu_{-1})$.

$$A_{1,2} = \mu_1\nu_2\eta_{2a}(1 + \mu_2/r_{1,2}) + \mu_2\nu_1\eta_{2b}(1 + (\mu_{-1} + \nu_2)/r_{1,2}).$$

Expression (9) with the corresponding parameters ($I(t) = 5.5\exp(-5.43 \times 10^{-3}t) - 9\exp(-3 \times 10^{-2}t) + 3.5$) correctly describes the kinetics of HCL_{CO+O} in the products of CO_2 dissociation (Fig. 1, curve *1*).

In the steady state ($dN_1/dt = dn_1/dt = dn_2/dt = 0$; $j_O = j_{CO}$) the solution to system (8) is

$$I(j) = \frac{N_0\delta_2\mu_{-3} j_O[\eta_{2a}\delta_1\delta_2 j_O + \eta_{2b}\sigma_1\delta_2(\mu_{-1} + \sigma_2 J_O)]}{A j_O^2 + B j_O + C} \tag{10}$$

where $A = \sigma_1\sigma_2\delta_2 + \delta_1\delta_2\sigma_2$, $B = \delta_2\sigma_2(\mu_3 + \mu_{-3}) + \delta_1\delta_2\mu_{-1} + \mu_{-3}(\delta_1\delta_2 + \sigma_1\sigma_2)$, and $C = \mu_{-1}\mu_{-3}\sigma_1 + \mu_{-1}\delta_2(\mu_3 + \mu_{-3})$. Qualitatively, expression (10) does not contradict the experiment (Fig. 2, curve *1*).

Nonstationary methods for the study of HCL_{CO+O}. Let us consider the response of luminescence system to a jump in power of high-frequency discharge. This jump leads to a change in the CO and O concentrations in the products of CO_2 dissociation. The proportion of CO and O concentrations remains approximately constant in this case. However, the jump in the power of high-frequency discharge in CO or in the 2% O_2 + 80% CO + 18% Ar mixture leads to an increase in the concentration of oxygen atoms, but the concentration of CO remains virtually constant.

The intensity of HCL_{CO+O} is equal to

$$I = \eta_{2a}\nu_2 n_1 + \eta_{2b}\mu_2 N_1 \equiv I_{2a} + I_{2b},$$

where I_{2a} and I_{2b} are the intensities of luminescence in reactions (IIa) (O + CO–L) and (IIb) (CO + O–L). After a power jump of the discharge in CO and after a change

in the flux density of (mostly) oxygen atoms j_O (by the value of Δj_O), we obtain ($t = 0$): $I = I_{2a}(1 + \Delta j_O/j_O) + I_{2b}$.

The HCL_{CO+O} intensity (I_{2a}) can be determined using a dark pause, which is switching off of the oxygen atom supply for a short during period Δt. I_{2b} remains virtually unchanged during this period, but I_{2a} decreases dramatically (Fig. 3). In this case, we have $\Delta I_{2a}/I_{2a} = \Delta j_O/j_O$. This enables the experimental determination of the function $I(j)$ (Fig. 2, curve *2*).

When HCL_{CO+O} is excited by the products of discharge in CO_2 $j_{CO} \approx j_O$. Therefore, $I = j_O(\eta_{2a}\sigma_2 n_1 + \eta_{2b}\delta_2 N_1)$, and an increase in j_O by Δj_O leads to a stepwise increase in the intensity of HCL by a factor of $(1 + \Delta j_O/j_O)$. That is, $I = I_0(1 + \Delta j_O/j_O)$. The measurements of jumps (ΔI) of the value of I allows us to determine the function $I(j)$, that is the stationary intensity of HCL as a function of oxygen atom (or CO molecule) flux density in CO_2 dissociation (Fig. 2, curve *1*).

During the dark pause when $j_O = 0$ and the CO flux remains constant, a decrease in the intensity of luminescence is exponential in the products of the dissociation of CO or the $O_2 + CO + Ar$ mixture

$$I(t) = I_{2a,0}\exp[-(\nu_{-1} + \mu_2 + k_{surf} n \nu_{1,0})t]$$

where $n_{1,0}$ is the surface concentration of CO–L, which remains constant during the pause and k_{surf} is the constant of second order reaction

$$O\text{–}L + CO\text{–}L \xrightarrow{k_{surf}\cdot\eta} CO_2\text{–}L + h\nu.$$

If O and CO are removed simultaneously during the dark pause from the gas-phase products of CO_2 dissociation, a decrease in the HCL intensity is determined only by the second-order reaction mentioned above. This reaction make a much lower contribution to the total intensity of HCL ($\ll 1\%$) compared to the collisional mechanism (reactions (IIa) and (IIb)). In this case, a decrease in the HCL intensity is described by the equation

$$I(t) = k_{surf}\eta(n_{1,0}/N_{1,0}) \times \frac{(n_{1,0} - N_{1,0})^2 \exp[(n_{1,0} - N_{1,0})k_{surf}t]}{[(n_{1,0}/N_{1,0})(\exp(n_{1,0} - N_{1,0})k_{surf}t) - 1]^2}. \quad (11)$$

Thus, nonstationary methods for the HCL study in multicomponent mixtures suggested in this work enable the estimation of the contributions of various reactions to the total intensity of HCL and the determination of cross-sections of reactions and the quantum yields of HCL.

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