

Model of the Catalytic Reaction $2\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$ with the Participation of Molecules in a Precursor State

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Abstract—The absence of experimental evidence for the occurrence of the catalytic reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ on platinum in accordance with the Langmuir–Hinshelwood mechanism was established. It was found that the heterogeneous process can be described more adequately and its nature can be better understood with consideration for chemical transformations involving molecules in a precursor state in a model of the above reaction. The inverse kinetic problem was solved. It was found that the model in which an unambiguously specified set of rate constants for the elementary steps of the reaction was used provided an opportunity to describe experimental data obtained by various authors concerning the oxidation of hydrogen on platinum over the detonating gas pressure range 10^{-3} – 10^5 Pa. The signs of the occurrence of heterogeneous reactions by an adsorption mechanism were found.

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INTRODUCTION

Relaxation methods, which provide information on the kinetics of elementary chemical and physical steps with nonequilibrium energy distribution over internal degrees of freedom in the system, are widely used in the studies of chemical reaction mechanisms. Kinetic spectroscopy techniques with the time resolution $\Delta t = 10^{-5}$ – 10^{-14} s are frequently applied to consider chemical phenomena in homogeneous media. The non-steady-state investigation techniques, including the temporal analysis of products (TAP) and steady-state isotope transient kinetic analysis (SSITKA), which are used in the studies of heterogeneous chemical reactions at interfaces between solids and gases, are characterized by much lower time resolution of no higher than $\Delta t = 10^{-3}$ – 10^{-5} s. Therefore, elementary surface processes with short characteristic times (with the participation of highly reactive intermediate substances), which occur in the course of heterogeneous chemical reactions, remain comparatively poorly known.

To obtain direct data on the participation of incident molecules from a gas atmosphere in a heterogeneous chemical reaction, their flow should be modulated with the time resolution $\Delta t \ll \tau$, where $\tau < 10^{-5}$ s is the lifetime of molecules in a precursor state on the surface. Such investigation techniques are currently unavailable. If the surface coverage (θ) with chemisorbed particles is much lower than unity under reaction conditions (low pressures and high temperatures), a number of signs suggests the occurrence of a heterogeneous process by the Eley–Rideal (ER) collision mechanism [1–5]. However, the experimentally obtained kinetic parameters do not provide an opportunity to determine

whether the reaction really occurs by a collision mechanism or whether the product is formed by the interaction of molecules in a precursor state with chemisorbed particles. If $\theta \approx 1$ (high pressures and low temperatures), the cross sections of chemical transformations by the collision mechanism are negligibly small, and only adsorbed particles participate in final product formation, as exemplified in a number of heterogeneous chemical reactions [6–13]. These particles can occur in chemisorbed or precursor states. However, experimental tests capable of unambiguously determining the states of adsorbed molecules that participate in chemical transformation events do not exist (the exception is provided by heterogeneous atomic recombination reactions [10]). The mechanism of a heterogeneous chemical reaction could be determined by comparing alternative models that imply the participation of either chemisorbed molecules or the molecules in a precursor state in product formation events. However, an analysis of models of this kind is absent from the literature.

Problems in the interpretation of heterogeneous chemical reaction mechanisms can be illustrated using the oxidation of CO and (or) H_2 with molecular oxygen on palladium and platinum as an example. These reactions are characterized by the signs of both the ER collision mechanism and the Langmuir–Hinshelwood (LH) adsorption mechanism. For example, the application of the molecular beam method to study the reaction $\text{CO} + \text{O}_2$ demonstrated that a dramatic drop in the concentration of CO in a gas atmosphere was synchronously accompanied by a rapid change in the rate of oxidation followed by a slow change [14, 15]. The rapid and slow responses were attributed to the ER collision

mechanism and the change in the rate of interaction between adsorbed particles (the LH mechanism), respectively. On the other hand, under the action of a beam of CO (or O₂) molecules on adsorbed O₂ (or CO) molecules, the reaction did not begin immediately and its rate reached a maximum after an induction period [6]. According to Engel and Ertl [6], this finding casts doubt on the conclusion [14, 15] that CO molecules that collide with a surface are converted into CO₂ with a probability close to unity by the collision mechanism, and the adsorption mechanism is preferred. At the same time, Engel and Ertl [6] did not satisfactorily explain the published results [14, 15].

Let us consider the results of studies of the catalytic reaction of hydrogen oxidation $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ on platinum [16–24]. The experimental data were interpreted with the use of both the ER collision mechanism and the LH adsorption mechanism. Chemisorbed H, O, OH, H₂, O₂, and H₂O₂ species were considered as intermediate substances. Only a limited range of experimental results was described satisfactorily. The problem of bridging a pressure gap remained unsolved; that is, a single model applicable to all of the data obtained both under high-vacuum conditions and at moderate and high pressures in a gas mixture was not developed. The reason for a decrease in the probability of formation of H₂O molecules by the collisions of H₂ molecules by several orders of magnitude on going from low to high pressures [22, 23] was not found. The isotope effect, which manifested itself in a decrease in the rate of reaction upon the replacement of H₂ molecules with D₂, was not explained [17, 24]. There is no adequate interpretation of data obtained at high pressures (10⁴–10⁵ Pa) [17].

Boudart et al. [22, 23] explained their experimental results by a considerable decrease in the surface coverage with oxygen as the pressure of a mixture was increased. However, the surface coverage depends on the parameters of elementary processes that occur in the system. It is likely that these parameters can be changed because of the formation of oxides on the surface; however, this explanation seems inappropriate with an excess of hydrogen in the mixture. The occurrence of an isotope effect [17] implies the participation of hydrogen in rate-controlling steps of the reaction. In an excess of oxygen, this effect can be explained by the occurrence of the reaction by the ER collision mechanism. However, this explanation is unsuitable in a large excess of hydrogen because the reaction is of first order with respect to oxygen under these conditions [17]; that is, the process is limited by the supply of O₂ molecules to the surface. Khar'kovskaya et al. [17] related a change in the rate of reaction with increasing partial pressures of hydrogen and oxygen to uncontrollable changes in the catalyst composition under the action of a reaction atmosphere.

The possibility of describing the results [16–24] with the use of a model based on the ER and LH mech-

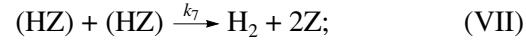
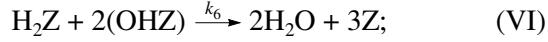
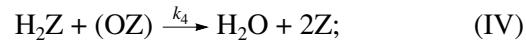
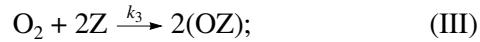
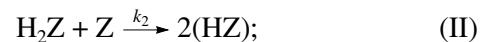
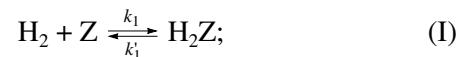
anisms, in which the parameters of elementary steps depend on surface composition, is questionable. In this work, we used another approach. We used another model, in which the effect of surface coverage on the reaction parameters was considered secondary and not responsible for the main characteristics of a chemical process. In this model, the signs of the ER and LH mechanisms are present but characteristic steps of the forms A + (BZ) \longrightarrow AB + Z and (AZ) + (BZ) \longrightarrow AB + 2Z, where (AZ) and (BZ) are chemisorbed molecules, AB is the product of the heterogeneous reaction, and Z is the adsorption center, were absent.

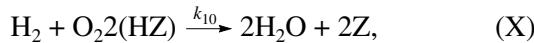
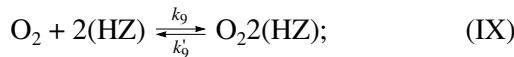
It is well known that reactant molecules can be retained on the catalyst surface by a weak or strong bond; in this case, weakly bound species are reactive [7–10, 25]. We assume that, in the oxidation of hydrogen by molecular oxygen on platinum, H₂ molecules in a precursor state are reactive and the chemical transformations of chemisorbed molecules do not have a noticeable effect on the overall rate of reaction. In this case, as will be demonstrated below, the results [16–24] obtained at 293–603 K and gas mixture pressures of 10³–10⁵ Pa, which correspond to bridging a pressure gap, can be explained.

REACTION MODEL AND ITS USE IN THE INTERPRETATION OF EXPERIMENTAL DATA

It is well known that the molecules of hydrogen and oxygen are adsorbed on the surface of platinum to undergo dissociation into atoms (reversibly in the case of hydrogen or irreversibly in the case of oxygen) [26–28]. In the oxidation of hydrogen on platinum, adsorbed OH species are formed, the surface concentration of which depends on the partial pressures of hydrogen and oxygen. Water molecules were not detected on the surface. The presence of water vapor had no effect on the rate of reaction [18].

We consider that the following processes are predominant in the course of a heterogeneous reaction of hydrogen oxidation on the surface of platinum:





where H_2Z and $\text{O}_2\text{2}(\text{HZ})$ are the molecules of hydrogen and oxygen, respectively, in a precursor state; (HZ) , (OZ) , and (OHZ) are chemisorbed species; k_1 – k_{10} are the rate constants of corresponding reactions, where $k_1 = h_1 P_1$, $k_3 = h_2 P_2$, $k_8 = h_3 P_1$, $k_9 = h_4 P_2$, and $k_{10} = h_5 P_1$; P_1 and P_2 are the partial pressures of hydrogen and oxygen, respectively; and h_1 – h_5 are coefficients. Steps (I), (II), and (IV) were written taking into account the circumstance that the chemisorption of hydrogen on platinum occurs through a precursor state [29]. Step (III) is irreversible because the catalyst temperature is $T < 700$ K [27, 28]. The probability of reverse reactions (IV) and (VI) occurring is negligibly small. The irreversibility of step (V) and the disregard of the step $(\text{HZ}) + (\text{OHZ}) \rightarrow \text{H}_2\text{O} + 2\text{Z}$ should be considered as an approximation to decrease the number of model parameters. Steps (VIII)–(X) are included in order to interpret the results obtained at high pressures. As will be demonstrated below, the probability of these steps is low at low pressures and they have no effect on the rate of reaction. It is likely that reactions (III) and (VIII)–(X) provide a simplified description of real multistep processes with the participation of O_2 and H_2 molecules in precursor states. In this case, reactions (IX) and (X) can compete with the analogous processes $\text{O}_2 + (\text{HZ}) = \text{O}_2(\text{HZ})$, $\text{H}_2 + \text{O}_2(\text{HZ}) + (\text{HZ}) \rightarrow 2\text{H}_2\text{O} + 2\text{Z}$, and $\text{O}_2(\text{HZ}) + (\text{HZ}) = \text{O}_2\text{2}(\text{HZ})$. The predominance of these latter does not significantly affect the results obtained below.

Steps (I)–(III), (V), and (VII) involved in model (I)–(X) were detected experimentally; steps (IV) and (VI) correspond to the ER collision mechanism; reaction (VIII) can be considered a competitive step with respect to multistep process (I), (II), and (V); steps (IX) and (X) are hypothetical. The absence of adequate justification for including steps (IX) and (X) should be considered a disadvantage of the model. However, it is justified by the fact that these steps correspond to the concept of the participation of molecules in a precursor state in surface chemical transformations.

Let us consider that the number of adsorption sites and the constants k_1 – k_{10} are independent of the degree of surface coverage. Then, the rate equations that describe the behavior of system (I)–(X) have the form

$$\dot{n}_1 = k_1 n - k'_1 n_1 - k_2 n_1 n - k_4 n_1 n_3 - k_6 n_1 n_4^2; \quad (1)$$

$$\dot{n}_2 = 2k_2 n_1 n - k_5 n_2 n_3 - 2k_7 n_2^2 - 2k_9 n_2^2 + 2k'_9 n_5; \quad (2)$$

$$\dot{n}_3 = 2k_3 n^2 - k_4 n_1 n_3 - k_5 n_2 n_3 - 2k_8 n_3^2; \quad (3)$$

$$\dot{n}_4 = k_5 n_2 n_3 - 2k_6 n_1 n_4^2 + 2k_8 n_3^2; \quad (4)$$

$$\dot{n}_5 = k_9 n_2^2 - k'_9 n_5 - k_{10} n_5; \quad (5)$$

$$n_1 + n_2 + n_3 + n_4 + n = 1, \quad (6)$$

where $n_1 = [\text{H}_2\text{Z}]$, $n_2 = [(\text{HZ})]$, $n_3 = [(\text{OZ})]$, $n_4 = [(\text{OHZ})]$, and $n_5 = [\text{O}_2\text{2}(\text{HZ})]$ are the degrees of surface coverage with intermediate substances, and $n = [\text{Z}]$ is the fraction of unoccupied surface. In this case, the rate of reaction is equal to $J = k_4 n_1 n_3 + 2k_6 n_1 n_4^2 + 2k_{10} n_5$.

In our subsequent considerations, we consider the activation-free adsorption of hydrogen and oxygen on platinum [26–28]. We believe that the activation energies of processes (I)–(IV), (VI), and (VIII)–(X) with the participation of H_2 and O_2 molecules, either incident from a gas atmosphere or preadsorbed, are low. In this case, an approximation in accordance with which the values of k_i other than k_5 and k_7 do not depend on surface coverage and temperature is physically substantiated. To compare Eqs. (1)–(6) with experimental data, we consider the dependence of the rate of reaction on the partial pressure of a reactant (at a constant pressure of the other reactant) $J(P_1)$ and $J(P_2)$ [17, 18, 21] obtained in experiments performed under steady-state conditions at pressures $P = 10^{-3}$ – 10^5 Pa in the gas mixtures and temperatures $T = 293$ – 603 K.

Let us solve the inverse kinetic problem: we numerically solve Eqs. (1)–(6) under steady-state conditions ($\dot{n}_i = 0$) on the condition that the shapes of theoretical and experimental curves coincide (the rate of reaction is expressed in arbitrary units). In this case, we assume that the parameters k_i other than k_7 do not depend on experimental conditions. The constant k_7 was considered temperature-dependent (we found that the dependence of k_5 on temperature and surface coverage can be ignored for the consistency of the model and the experimental data). A satisfactory agreement between theoretical and experimental curves, which were obtained with the use of polycrystalline platinum as a catalyst (Figs. 1–4), was reached at the following parameters (the values of k_i are expressed in s^{-1} ; P_1 and P_2 are expressed in Pa):

$$\begin{aligned} k_1 &= 1.22 \times 10^7 P_1, & k'_1 &= 4 \times 10^{12}, & k_2 &= 10^9, \\ k_3 &= 2.6 \times 10^3 P_2, & k_4 &= 2 \times 10^9, & k_5 &= 2 \times 10^3, \\ k_6 &= 10^{12}, & k_8 &= 8.62 P_1, & k_9 &= 97 P_2, \\ k'_9 &= 7.65 \times 10^7, & k_{10} &= 10^3 P_1. \end{aligned} \quad (7)$$

The values of k_7 (their numerical values are specified in figure captions) found under various experimental conditions obey the equation

$$\begin{aligned} k_7 &= 1.5 \times 10^9 \exp[-E_7(RT)^{-1}], \\ E_7 &= 65(1 - 0.5\bar{n}_2) \text{ kJ/mol}, \end{aligned} \quad (8)$$

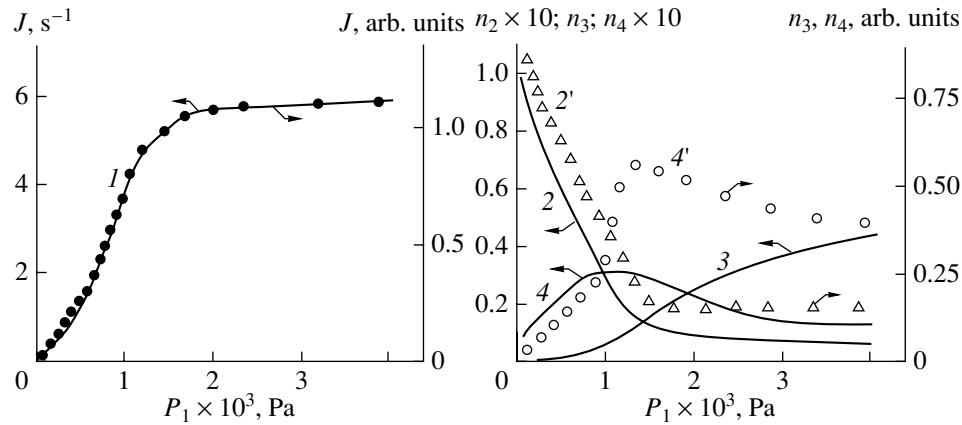


Fig. 1. Dependence of (1) the rate of hydrogen oxidation on platinum and the surface coverage with the species (2, 2') (OZ), (3) (HZ), and (4, 4') (OHZ) on the partial pressure of hydrogen at the constant pressure of oxygen $P_2 = 1.5 \times 10^{-3}$ Pa ($T = 603$ K; $k_7 = 3.5 \times 10^{-3}$ s^{-1}). Points and solid lines refer to experimental results [18] and calculation data, respectively.

where $\bar{n}_2 \approx n_{2\max} - n_{2\min}$; $n_{2\max}$ and $n_{2\min}$ are the maximum and minimum values of n_2 , respectively, over a known range of changes in P_1 or P_2 (for example, see Fig. 5 and curve 3 in Fig. 1). It is well known that, in an atmosphere of pure hydrogen ($P_2 = 0$), the activation energy of desorption of H_2 molecules is independent of the surface coverage of platinum with hydrogen and equal to 65 ± 2 kJ/mol at $n_2 < 0.5$; however, it decreased several times with increasing n_2 , when $0.5 < n_2 < 1$ [26, 27]. Analytical expression (8) was postulated based on experimental data [26, 27], and the numerical values of parameters that appear in this expression were determined by solving the inverse kinetic problem. The most serious simplification in the model under consideration is the use of an averaged value of E_7 in Eq. (8) and the neglect of the function $k_7(n_2)$ in Eq. (2). Note that the

numerical values of k_1' and k_9 (7) allow one to interpret the precursor states H_2Z and O_2Z (HZ) (see reactions (I) and (IX)) as physical adsorption states. However, the problem of the true nature of these states cannot be solved in the framework of the model under consideration.

Check that the numerical values of k_1 , k_2 , and k_3 (7) are consistent with the results of adsorption measurements. Let us use the equalities $k_3 = h_2 P_2 = 0.25 n_g v \sigma_2$, where n_g is the concentration of oxygen molecules in a gas phase; v is the average thermal velocity of these molecules; σ_2 is the capture cross section of O_2 molecules into a chemisorbed state. Then, $\sigma_2 = 9.7 \times 10^{-16}$ cm^2 . On the other hand, knowing the sticking coefficient k_s of O_2 molecules on platinum equal to 0.1–0.4 [28], we obtain a similar value of σ_2 : $\sigma_2 = k_s N_0^{-1} \approx 10^{-15}$ cm^2 , where N_0

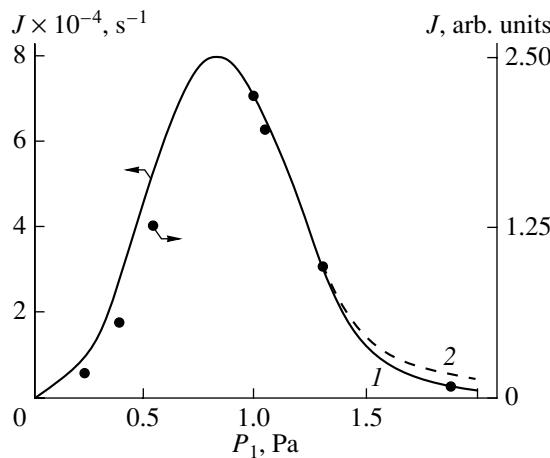


Fig. 2. Dependence of the rate of hydrogen oxidation on platinum on the pressure of hydrogen at $P_2 = 2.8$ Pa, $T = 293$ K, and $k_7 = (1) 10^{-2}$ or (2) 1 s^{-1} . Points refer to experimental data [21].

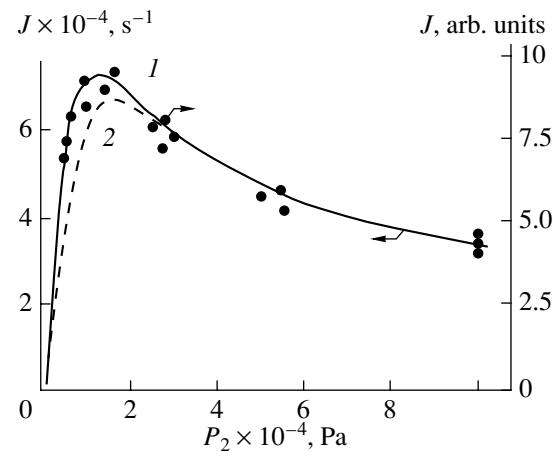


Fig. 3. Dependence of the rate of hydrogen oxidation on platinum on the pressure of oxygen at $P_1 = 545$ Pa and $k_7 = (1) 4.6 \times 10^3$ (453 K) or (2) 4×10^2 s^{-1} (393 K). Points refer to experimental data [17].

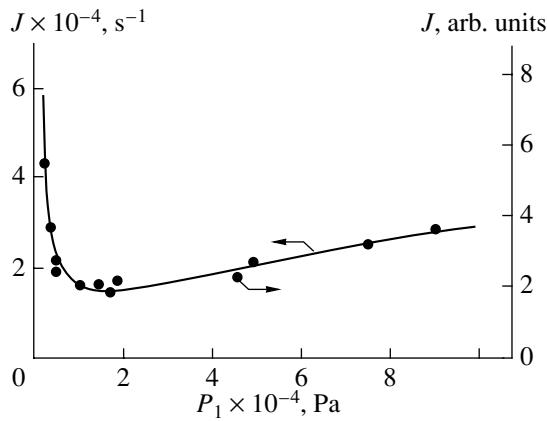


Fig. 4. Dependence of the rate of hydrogen oxidation on platinum on the pressure of hydrogen at $P_2 = 273 \text{ Pa}$, $T = 453 \text{ K}$, and $k_7 = 2.7 \times 10^5 \text{ s}^{-1}$. Points refer to experimental data [17].

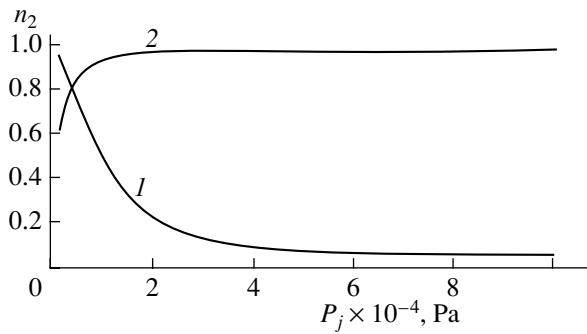


Fig. 5. Dependence of the surface coverage of platinum with hydrogen on (1) the partial pressure of oxygen in a gas mixture at $T = 453 \text{ K}$, $P_1 = 545 \text{ Pa}$, and $k_7 = 4.6 \times 10^3 \text{ s}^{-1}$ and (2) the partial pressure of hydrogen at $T = 453 \text{ K}$, $P_2 = 273 \text{ Pa}$, and $k_7 = 2.7 \times 10^5 \text{ s}^{-1}$.

is the concentration of adsorption sites for O_2 molecules ($N_0 \approx 2 \times 10^{14} \text{ cm}^{-2}$ [6, 27]). The sticking coefficient k_s of H_2 molecules on transformation into a chemisorbed state is (see reactions (I) and (II)) $k_s = k_2 \sigma_1 N_0 (k'_1)^{-1}$, where σ_1 is the capture cross section of H_2 molecules with transformation to the state H_2Z . With the use of the adsorption parameters of hydrogen molecules on platinum $k_s \approx 0.1$ and $N_0 \approx 2 \times 10^{14} \text{ cm}^{-2}$ [27] and the value $k'_1 = 4 \times 10^{12} \text{ s}^{-1}$, we find $k_s \approx 10^9 \text{ s}^{-1}$, which is consistent with the value of k_2 in expression (7).

Then, we derive an analytical expression for the reaction rate J under steady-state conditions ($\dot{n}_i = 0$) and compare it with experimental data. The quantities n_i and J are considered to have steady-state values. Taking into account a weak bond of hydrogen molecules in a precursor state to the surface, we consider that the condition $k'_1 \gg k_2 + k_4 + k_6 n_4$ is fulfilled. Then, in accordance with Eq. (1), $n_1 \equiv k_1 n (k'_1)^{-1}$. We use the condition $n_1 \ll n_2 + n_3$, which is true at any pressures P_1 and P_2 according to the results of a numerical solution of Eqs. (1)–(6) with parameters (7) and (8). Let us assume that $n_2 = an$ and $n_3 = bn$, where a and b are quantities that depend on the reaction rate constants k_1 – k_{10} . Substituting these expressions into Eqs. (2)–(6), we obtain

$$\begin{aligned} n &= (1 - n_4)(1 + a + b)^{-1}, \\ n_4 &= -0.5c + (0.25c^2 + c)^{1/2}, \\ c &= k'_1(k_5ab + 2k_8b^2)(2k_1k_6)^{-1}(1 + a + b)^{-1}; \end{aligned} \quad (9)$$

$$\begin{aligned} r - k_5ab - (2k_7 + p)a^2 &= 0, \\ s - qb - k_5ab - 2k_8b^2 &= 0, \quad s = 2k_3, \\ r = 2k_1k_2(k'_1)^{-1}, \quad q &= k_1k_4(k'_1)^{-1}, \\ p = 2k_9k_{10}(k'_9 + k_{10})^{-1}. \end{aligned} \quad (10)$$

Using expressions (3)–(5), we find

$$\begin{aligned} J &= k_4n_1n_3 + 2k_6n_1n_4^2 + 2n_{10}n_5 \\ &= pn_2^2 + 2k_3n^2 = (s + pa^2)(1 - n_4)^2(1 + a + b)^{-2}, \end{aligned}$$

where $n_4 \ll 1$ in accordance with (7) and (9).

Let us consider the region of low pressures corresponding to the condition $2k_7 \gg p$ (where the effect of processes (VIII)–(X) on the rate of reaction is negligibly small). In an excess of hydrogen in the mixture ($r \gg s$), an approximate solution to Eqs. (10) has the form $a \approx r^{1/2}(2k_7)^{-1/2}$ because, in this case (when $r \gg s$), the following inequalities, which were obtained by identical transformations, are valid: $2k_7a^2 \gg s$, $2k_7a(q + k_5a) \gg sk_5$, $2k_7a \gg bk_5$, and $2k_7n_2 \gg k_5n_3$. Hence, according to Eq. (2), we obtain $2k_2n_1n \approx 2k_7n_2^2$ and $a \approx r^{1/2}(2k_7)^{-1/2}$. In this case, the rate of reaction is

$$J \approx s(1 - n_4)^2(1 + r^{1/2}(2k_7)^{-1/2})^{-2}, \quad (11)$$

$$r \gg s, \quad 2k_7 \gg p.$$

In the case of $r \ll 2k_7$ (when $P_1 \ll k_7k'_1(h_1k_2)^{-1}$), according to (11), we have $J \approx s \sim P_2$. In another limiting case ($r \gg 2k_7$) $J \approx 2k_7sr^{-1} \sim P_1^{-1}P_2$.

Then, let us assume that the following inequalities are valid: $r < s$, $A \ll B$, and $C \ll D$, where $A = 4(2k_7 + p)rq^2$, $B = k_5^2(s - r)^2$; $C = 8sk_8$, and $D = (q + k_5a)^2$. In this case (low pressures), with the use of expressions (10), we find

$$a \equiv r q k_5^{-1} (s-r)^{-1},$$

$$J \approx s(1-n_4)^2 [1 + r q k_5^{-1} (s-r)^{-1} + (s-r) q^{-1}]^{-2}, \quad (12)$$

$$r < s, \quad A \ll B, \quad C \ll D.$$

In an excess of oxygen in the mixture ($r \ll s$), expression (12) takes the form $J \approx q^2 s^{-1} \sim P_1^2 P_2^{-1}$. Testing the functions $J(P_1)$ and $J(P_2)$, which correspond to expression (12), for extrema on condition that $n_4 \ll 1$, we find that the dependence of the rate of reaction on the pressure of hydrogen at a constant pressure of oxygen exhibits a maximum at $P_1 = P_{1m}$; in this case,

$$P_{1m} \equiv 2k_2 k_5 k'_1 s k_4^{-2} h_1^{-1} r_m^{-1} (s r_m^{-1} - 1) (2s r_m^{-1} - 1)^{-1}, \quad (13)$$

$$n_4 \ll 1,$$

whereas the dependence of the rate of reaction on the pressure of oxygen at a constant pressure of hydrogen reaches a maximum at $P_2 = P_{2m}$; in this case,

$$P_{2m} \equiv [k_5 (q-r) (s_m - r)^2 + r q^2 (3s_m - r)]$$

$$\times (2k_5 h_2)^{-1} (s_m - r)^{-2}, \quad (14)$$

$$n_4 \ll 1,$$

where $r_m = 2k_2 h_1 (k'_1)^{-1} P_{1m}$ and $s_m = 2h_2 P_{2m}$.

Let us consider the region of high pressures in the mixture, when the rate of reaction at the degree of surface coverage with chemisorbed species close to 1 depends on processes (VIII)–(X). In the case that the inequalities $s \gg r$ and $C \gg D$ are valid (a large excess of oxygen in the mixture), based on Eqs. (10), we obtain $b \equiv s^{1/2} (k_8)^{-1/2}$. In this case,

$$J \equiv s(1-n_4)^2 b^{-2} \equiv 2k_8 = 2h_3 P_1, \quad (15)$$

$$s \gg r, \quad C \gg D.$$

If the inequalities $r \gg s$ and $p \gg 2k_7$ are valid (an excess of hydrogen in the mixture at high gas pressures), with the use of Eqs. (10), we find $a \equiv r^{1/2} p^{-1/2}$. In this case,

$$J \equiv p = 2k_{10} (k'_9 + k_{10})^{-1} h_4 P_2, \quad (16)$$

$$r \gg s, \quad p \gg 2k_7.$$

Consequently, at high pressures, the rate of reaction increases in accordance with a linear law as the partial pressure of a reactant is increased (at a constant pressure of the other reactant). This is consistent with experimental results [17], which were obtained at a pressure of 10^4 – 10^5 Pa in the mixture.

Unlike models based on the ER and LH mechanisms [16–24], mechanism (I)–(X) allowed us to interpret published results [17, 22, 23]. As the pressure $P = P_1 + P_2$ is increased (at a constant ratio P_1/P_2), according to expressions (9) and (10), the value of a monotonically increases, whereas the values of b and c do not increase. The rate of reaction either does not increase or does

decrease with P (see expressions (11) and (12)). Therefore, under conditions of going from low pressures $P = P_1$ (when $a = a_1 \ll 1$) to high pressures $P = P_{10}$ (when $a = a_{10} \gg 1$) at unchanged values of k'_1, k_2, k_4 – k_7 , and h_i , the probability of chemical transformations on the collision of a gas molecule with the surface decreases by a factor of $a_{10}^2 = 10^3$ – 10^4 (cf. the ratios J/P_1 in Figs. 1–4). This result is due to the blocking of the surface with chemisorbed molecules; it allows us to explain the effect experimentally observed by Boudart et al. [22, 23].

The rate constants of reactions depend on the frequencies of vibrational motions or collision frequencies, which are proportional to the velocities of translational motion of particles that participate in chemical transformations. Therefore, we can assume that $k_1 \sim m^{-1/2}$, $k'_1 \sim m^{-1/2}$, $k_4 \sim m^{-1/2}$, $k_7 \sim m^{-\alpha}$, $k_8 \sim m^{-1/2}$, and $k_{10} \sim m^{-1/2}$, where m is the mass of a hydrogen atom, and α varies from 0.5 to 1. In the case of low pressures in an excess of oxygen in the mixture ($r \ll s$), using expression (12), we find that $J \equiv q^2 s^{-1} = k_1^2 k_4^2 (k'_1)^{-2} s^{-1} \sim m^{-1}$. Analogously, in an excess of hydrogen ($r \gg s$), from Eq. (11), we obtain $J \approx 2k_7 s r^{-1} = k_7 k'_1 s (k_1 k_2)^{-1} \sim m^{-\alpha}$. In the case of high pressures, using Eqs. (15) and (16), we find that $J \sim m^{-1/2}$ (on the condition that $k_{10} \ll k'_9$ in (16)). These results are consistent with the experimentally observed [17] decrease in the rate of reaction by a factor of 1.3–2 upon the replacement of H_2 molecules by D_2 .

Let us compare approximate expressions (11) and (12) for the rate of reaction, which are applicable to the case of low pressures, with experimental results obtained at the pressure $P \approx 10^{-3}$ Pa in the mixture [18]. The function $J(P_1)$ contains a segment of initial growth and a region in which the rate of reaction does not depend on the pressure of hydrogen (see Fig. 1, curve 1). In the former segment (where $r < s$), in accordance with expression (12), the condition $J \sim P_1^2 P_2^{-1}$ is fulfilled; in the latter segment (where $r > s$), in accordance with expression (11), $J \sim P_1^0 P_2$. The extent of the former segment is proportional to P_2 . These theoretical relationships are consistent with experimental data [18]. These data [18] are also consistent with the shapes of theoretical curves for $n_3(P_1)$ and $n_4(P_1)$ (cf. curves 2 and 2' or 4 and 4' in Fig. 1).

At the pressure $P \approx 1$ Pa in the mixture, the curves of $J(P_1)$ and $J(P_2)$ pass through a maximum [20, 21] (e.g., see Fig. 2). As calculated, the surface coverage with chemisorbed hydrogen monotonically increases to approach 1 (Fig. 5) with the partial pressure of hydrogen at a fixed pressure of oxygen. That is, the presence of a maximum and a descending segment in the curve of $J(P_1)$ is due to surface blocking with hydrogen. The presence of a maximum in the curve of $J(P_2)$ can be explained in an analogous manner. The theoretical

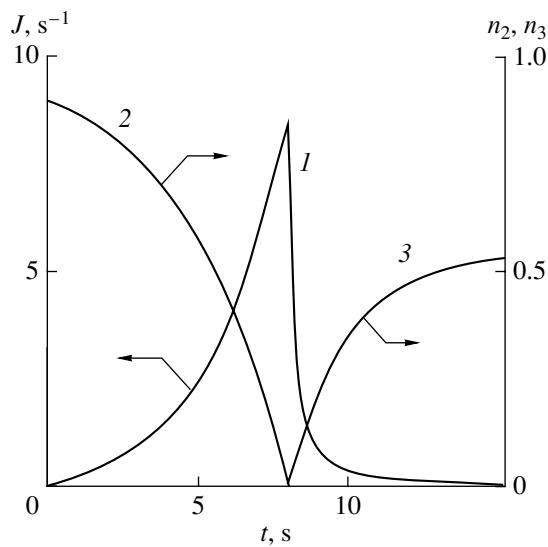


Fig. 6. Time changes in (1) the rate of H_2O formation and the surface concentrations of (2) (OZ) and (3) (HZ) species on platinum in the interaction of adsorbed oxygen ($n_3(0) = 0.9$) with H_2 molecules incident from a gas phase. $P_1 = 5 \times 10^{-5} \text{ Pa}$; $P_2 = 0$; $k_7 = 10^{-1} \text{ s}^{-1}$.

functions $J(P_1)$, $J(P_2)$, and $J(P)$, which correspond to expressions (11)–(14), are consistent with experimental data [20, 21]: (1) in an excess of oxygen ($r \ll s$; $J \approx q^2 s^{-1} \sim P_1^2 P_2^{-1}$), the order with respect to hydrogen is equal to 2; (2) in an excess of hydrogen ($r \gg s$; $J \approx 2k_7 s r^{-1} \sim P_2 P_1^{-1}$), the order with respect to oxygen is equal to 1; (3) in an excess of hydrogen or oxygen, the reaction is slowed down; (4) the curves of $J(P_1)$ and $J(P_2)$ pass through a maximum, and the position of this maximum corresponds to an excess of oxygen in the mixture (see Fig. 2); (5) the value of P_{1m} depends on only the ratio P_1/P_2 rather than the individual partial pressures of hydrogen and oxygen (see expressions (13)); (6) in experiments with stoichiometric mixtures (when the condition $J \approx 2k_7 s r^{-1} \sim P_2 P_1^{-1}$ is fulfilled), the rate of reaction does not depend on the pressure P of the mixture.

In the case of an excess of oxygen ($s \gg r$) at medium pressures ($p \sim k_7$), if the condition $D \gg C$ is fulfilled, in accordance with Eqs. (10), we find that $a \approx r^{1/2}(p + 2k_7)^{-1/2}$ and $b \approx sq^{-1}$. In this case, the expression for the rate of reaction takes the form $J \approx s[1 + r^{1/2}(p + 2k_7)^{-1/2} + sq^{-1}]^{-2}$. The function $J(P_2)$, which follows from this expression, exhibits a maximum at the oxygen pressure

$$P_{2m} \approx \frac{1 + r^{1/2}(p + 2k_7)^{-1/2}}{2h_2q^{-1} - 2h_4k_{10}r^{1/2}(k_9 + k_{10})^{-1}(p + 2k_7)^{-3/2}},$$

$$s \gg r, \quad D \gg C.$$

The constant k_7 increases with temperature (see expression (8)), and a maximum in the curve of $J(P_2)$ shifts

toward a lower excess of oxygen (cf. curves in Fig. 3 calculated at two different values of k_7). This result is consistent with experimental data [17].

Figure 6 exemplifies the numerical solution of differential Eqs. (1)–(5) with parameters (7) and (8). In the interaction of H_2 molecules incident from a gas phase with preadsorbed O_2 molecules ($P_2 = 0$), the reaction did not come into play immediately and its rate reached a maximum after an induction period. This was due to an increase in the rate of reaction as the chemisorbed O_2 molecules that blocked the surface were removed. By this is meant that, in fact, there is no experimental evidence for the occurrence of the reaction by the LH adsorption mechanism because analogous data [6, 27, 28] were used for substantiating models based on the LH mechanism; however, we see that these data cannot be interpreted unambiguously. After “switching off” the flow of H_2 molecules ($P_1 = 0$), the rate of reaction stepwise (in a time of $\sim 10^{-12} \text{ s}$) decreased to zero; this is a sign of the ER mechanism.

According to the results of a computer simulation, analogous non-steady-state processes, which are characterized by the presence of signs of the ER and LH mechanisms, take place in the occurrence of the catalytic reaction $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ with the participation of CO molecules in a precursor state. Thus, contradictions between experimental results [6, 14, 15] occur only as a consequence of the unjustified use of the ER and LH mechanisms for interpreting experimental data.

The analysis performed indicates that unambiguous criteria should be developed for determining the mechanism of a heterogeneous reaction with the use of experimental tests.

SIGNS OF THE ADSORPTION MECHANISM

Let a catalytic reaction occur by the LH adsorption mechanism; then, its rate at an arbitrary point in time is

$$J = \mu v \theta_1^\beta \theta_2^\lambda, \quad (17)$$

where v is the reaction rate constant; λ and β are the stoichiometric coefficients of the reaction step responsible for the formation of product molecules; θ_1 and θ_2 are the surface coverages with intermediate substances that participate in product formation; μ is a coefficient that takes into account the possibility of the two-dimensional condensation of a reaction intermediate and the occurrence of chemical transformations at the boundary of the islands of chemisorbed particles, $\mu \approx (R^2 - R_1^2)R^{-2} = (2L - 1)L^{-2}$ (here, $R = La_0$ is the radius of islands, a_0 is the crystal lattice parameters, L is an integer number, $R_1 = (L - 1)a_0$). Let us write differential rate equations that describe time changes in the surface coverage with intermediate substances and analyze a non-steady-state process that occurred after an abrupt decrease of the pressure of the reaction mixture to zero using these rate equations (this can be performed exper-

imentally by using a molecular beam or passing an inert gas through the reactor). In this case, summing the left-hand and right-hand sides of the rate equations, we obtain the inequality

$$-\frac{d\theta(t)}{dt} > (\beta + \lambda)J(t), \quad t \geq t_0, \quad (18)$$

where θ is the surface coverage with intermediate substances, and t_0 is the point in time of an abrupt decrease in the pressure of the reactant mixture to zero. If conditions (17) and (18) are fulfilled, the reaction occurs by the LH adsorption mechanism. A violation of inequality (18) at the point in time $t = t_0$ corresponds to the participation of species in a precursor state or molecules incident from a gas atmosphere in the reaction. For estimations, it is convenient to use the dimensionless parameter $\chi = (\beta + \lambda)J_0\tau_0\theta_0^{-1}$, where J_0 and θ_0 are the rate of reaction and the surface coverage with intermediate substances, respectively, at the point in time $t = t_0$; τ_0 is the time constant of the relaxation of θ . If the LH mechanism takes place, $\chi < 1$. For the catalytic reactions $\text{H} + \text{H} \longrightarrow \text{H}_2$, $\text{O} + \text{O} \longrightarrow \text{O}_2$, and $\text{CO} + \text{O} \longrightarrow \text{CO}_2$, the parameter χ is equal to 10^3 – 10^4 ; by this is meant that species in a precursor state participate in these reactions [10]. We do not know analogous data for other heterogeneous reactions.

Thus, as a result of this study, we found an agreement between model (I)–(X) for the reaction of hydrogen oxidation on polycrystalline platinum and experimental data obtained at the pressure $P = (10^{-3}$ – $10^5)$ Pa in the detonating mixture over the temperature range 293–603 K [16–24]. An accidental coincidence between the results that follow from the model with unambiguously chosen parameters (7) and (8) and many independent experimental data obtained by various authors under different conditions is improbable.

In this work, we did not consider a heterogeneous–homogeneous mechanism of hydrogen oxidation, which likely involves the desorption of hydrogen atoms from the surface of platinum and the development of a radical-chain process in the volume of a gas phase [30]. The region of parameters in which critical effects (multiplicity of steady states etc.) occur was not studied because critical effects experimentally observed in many cases were not caused by purely kinetic reasons. Model (I)–(X) does not take into account the effect of surface coverage with intermediate substances on the rate constants of reactions. Moreover, it includes steps (IX) and (X), the participation of which was not experimentally substantiated directly. Nevertheless, the number of experimental regulations and numerical data described in terms of the proposed model is much higher than the number of parameters of the model. Consequently, it is believed that the catalytic activity of platinum in the chemical reaction $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ is due to the fact that its surface traps H_2 molecules incident from a gas atmosphere and converts them into a

precursor state. Because of this, the effective cross section of the chemical process dramatically increases. Thus, the concept of the high reactivity of weakly bound hydrogen in the processes of hydrocarbon hydrogenation on the surface of platinum [7, 8] can be extended to the case of the catalytic oxidation of hydrogen.

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