# Ethylene Adsorption and Oxidation Kinetics in the Reactions with Pd(II)/SiO$_2$ and Cr(VI)/SiO$_2$: Consideration of Substrate Distribution between the Gas Phase, Silica Gel, and Reaction Centers

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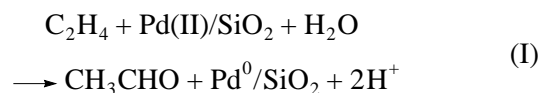
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**Abstract**—The kinetics of ethylene oxidation by PdCl$_2$ and CrO$_3$ complexes supported on silica gel (300 K, closed batch reactor) and the adsorption of C$_2$H$_4$ by silica gel and metal complex reaction centers (M$^n$) were studied. A new version of the kinetic distribution method was applied to determine the rate constants of ethylene reactions with metal complexes with consideration for the equilibrium distribution of C$_2$H$_4$ among the reactor gas phase, silica gel, and M$^n$. The rate constant of a first-order reaction with respect to Cr(VI) ($k_e$) remained constant as [M$^n$] was increased up to 0.15 mol % with the absence of detectable ethylene adsorption by chromium(VI). In the case of Pd(II)/SiO$_2$, strong ethylene adsorption by palladium(II) was found, and $k_e$ was an exponential function of [M$^n$]. This exponential function is indicative of an increase in the specific activity of Pd(II) with palladium concentration on SiO$_2$. Taking into account the adsorption of ethylene (physisorption on SiO$_2$ and chemisorption on Pd(II)), we found an analogy between the kinetic behaviors of Pd(II) in reactions with ethylene on silica gel and with ethylene and other hydrocarbons in solutions.

## INTRODUCTION

In studies of the kinetics and mechanisms of reactions between volatile substrates and metal complexes in solutions, substrate distribution between the gas phase and the solution [1] and substrate complex formation [2] are taken into account. Such methods were not applied in full measure to heterogeneous reactions. The reaction of ethylene oxidation with Pd(II) complexes supported on SiO$_2$ serves as a convenient model for using this approach to heterogeneous systems. It was studied in detail in aqueous solutions of palladium(II) chloride [2]. The oxidation of saturated hydrocarbons by palladium(II) in sulfuric acid was also studied [3]. The data obtained in these studies can be used for a comparison between homogeneous and heterogeneous palladium systems.

The silica-supported metal complex compositions of Pd(II) with redox components (V$_2$O$_5$, [V–Mo] heteropoly acids, etc.), which are responsible for the reoxidation of Pd$^0$ to Pd(II) are used in the catalytic oxidation of alkenes with oxygen [4–6]. In this case, side reactions occur along with the main reaction (acetaldehyde or butanone formation in the oxidation of ethylene or 1-butene, respectively) [4, 6]. These side reactions involve the direct interaction of a redox component with an alkene and result in products that inhibit the main reaction.

Previously [7], the kinetic distribution method [1], which is applicable to reactions in solutions, was used for studying the reaction of ethylene oxidation with palladium(II) chloride

$$C_2H_4 + Pd(II)/SiO_2 + H_2O$$

$$\longrightarrow CH_3CHO + Pd^0/SiO_2 + 2H^+ \tag{I}$$

with consideration for C$_2$H$_4$ distribution between the gas phase and silica gel. At low Pd(II) concentrations on SiO$_2$ (0–0.1 mol %), first-order and second-order reaction pathways with respect to Pd(II) were found, which are analogous to the reaction pathways of ethylene oxidation with palladium(II) in aqueous solutions [2, 8]. The specific activity of Pd(II) was changed in the presence of redox components [9]: it decreased with the retention of both pathways in the case of CuCl$_2$, whereas in an excess of an oxo component (H$_3$PMo$_{12}$O$_{40}$ or CrO$_3$) over palladium(II) only a first-order reaction pathway remained and the specific activity of Pd(II) increased with the concentration of the oxo complex.

These data were obtained without considering the effect of ethylene binding to palladium(II). The subsequent measurements performed with consideration for the complexation of ethylene demonstrated that, in the absence of redox components and at low Pd(II) concentrations, first-order and second-order reaction pathways with respect to Pd(II) made a noticeable contribution to

the reaction kinetics. Over a wider range of palladium concentrations, the effective rate constant $k_e$ was an exponential function.

Because redox components can directly react with ethylene in addition to palladium regeneration, it is important to study the kinetics and mechanisms of oxidation not only by palladium(II) but also by the redox components.

The aim of this work was to modify the "solution" distribution method as applied to heterogeneous systems and to use it for studying the kinetics of ethylene oxidation with palladium(II) chloride complexes on $SiO_2$ and, for comparison, with chromium(VI) oxo complexes taking into account ethylene adsorption (physisorption on $SiO_2$ and chemisorption on Pd(II)).

## EXPERIMENTAL

Ethylene (reagent grade) for chromatography and spectroscopy with total hydrocarbon and nonhydrocarbon impurity contents of 0.2 and 0.3 vol %, respectively, was used. The samples of Pd(II)/$SiO_2$ and Cr(VI)/$SiO_2$ with a specific surface area of $480 \pm 20$ m$^2$/g and a specific solid-phase volume of $0.50 \pm 0.02$ cm$^3$/g were prepared as described previously [7]. KSK-2.5 silica gel (with a particle size of 0.012–0.025 cm) was impregnated with hydrochloric acid (0.06 M) solutions of PdCl$_2$ (0.01 M) or CrO$_3$ (0.04 M) and an HCl solution without metal complexes and dried at 400 or 470 K in a sand bath for 2 h. The samples were loaded in a reactor after cooling at room temperature for 6 min. The amount of $H_2O$ in the samples was determined by the weight difference before and after the complete removal of water at 675 K [5]. The $H_2O$ concentration in the samples dried at 400 and 470 K and loaded in the reactor was found by this procedure to be equal to $5.0 \pm 0.5$ mol % (12% monolayer capacity at a water molecule surface area of $1 \times 10^{-15}$ cm$^2$ [5]).

To evaluate the effect of Pd(II) reduction in the reaction with ethylene on the adsorption ability and reactivity of Pd(II)/$SiO_2$, the samples dried after preparation were heated in ampules with $H_2$, and their interaction with ethylene was studied after drying in air at 400 K for 2 h. On the reduction of palladium with hydrogen, its color changed from light pink to gray and this was retained upon subsequent drying.

The adsorption of ethylene and the kinetics of its reactions with metal complexes on $SiO_2$ at 300 K were studied by measuring ethylene loss in the gas phase of shaken thermostated batch reactors with volumes of $4.9 \pm 0.1$ and $22.0 \pm 0.1$ cm$^3$. The reactors were filled with nitrogen (1 vol % $O_2$) before the experiments to standardize the gas-phase composition. Gas samples were withdrawn through gas-tight rubber septa using a syringe (0.05 cm$^3$). All experiments were performed in a 10- to 100-fold excess of Pd(II) over reacted ethylene. As a rule, the reaction rate constants $k_e$ were repro-

duced to within ±15% with the use of standard preparation procedures for measurements.

The yield of the reaction product, acetaldehyde, which is strongly adsorbed by silica gel at 300 K, was found to be equal to $80 \pm 20\%$ using calibrations at 360 K. The concentrations of ethylene and acetaldehyde in the reactor gas phase were determined by GLC analysis (an LKhM-80 Model 6 chromatograph with a flame-ionization detector) under isothermal conditions. The following two columns were used: (1) Polysorb (1 m) at 360 K and (2) 5% OV-225 on Chromaton Super (3 m) at 300 K. Along with the peak of acetaldehyde, an unidentified peak was observed, which was smaller than the peak of $CH_3CHO$ by a factor of ~5. In an excess of ethylene over Pd(II), Pd(II)/$SiO_2$ samples became gray as $C_2H_4$ was consumed; this fact is indicative of Pd(II) reduction (reaction (I)).

We did not study the products of the reaction of $C_2H_4$ with Cr(VI)/$SiO_2$. According to published data [4, 10], alkenes in the presence of $H_2O$ are oxidized by high-valence metal complexes to alcohols and *cis*-glycols.

## RESULTS AND DISCUSSION

### Adsorption Measurements

The following designations are used: $V_r$ (cm$^3$) is the reactor volume; $V$ (cm$^3$) is the volume of the gas phase in the reactor; $P$ (g) is the sample weight; $S$ (cm$^2$) is the sample surface area; $\lambda = V/S$ (cm); $N_M$ (mol) is the amount of the metal complex M$^n$ in the sample; $C_M = N_M/S$ (mol/cm$^2$); $N$ (mol) is the amount of ethylene in the reactor; $N_g$, $N_s$, and $N_c$ (mol) are the amounts of ethylene in the gas phase, on silica gel, and bound to the metal complex, respectively; $C_g = N_g/V$ (mol/cm$^3$), $C_s = N_s/S$ (mol/cm$^2$), and $C_c = N_c/S$ (mol/cm$^2$) are the bulk and surface concentrations, respectively; $k_\lambda$ (s$^{-1}$) is the measured rate constant of substrate loss from the gas phase; $k_e$ is the effective rate constant of first-order reaction with respect to Pd(II); and $k_i$ (s$^{-1}$) is the rate constant of the conversion of an intermediate complex into products.

The following two types of measurements were performed:

(1) The adsorption of $C_2H_4$ by silica gel was studied to determine the distribution coefficient $\alpha$ of ethylene between the gas phase and $SiO_2$. In a reactor with a silica gel sample of 0.28 g, the concentration of $C_2H_4$ in the gas phase linearly increased as the ethylene amount was increased from 0 to $1 \times 10^{-7}$ mol. An analogous line for an empty reactor with the same gas-phase volume ($V = 4.8$ cm$^3$) passed above the line for the reactor with $SiO_2$. This fact indicates that $C_2H_4$ is adsorbed by silica gel and the linear relation

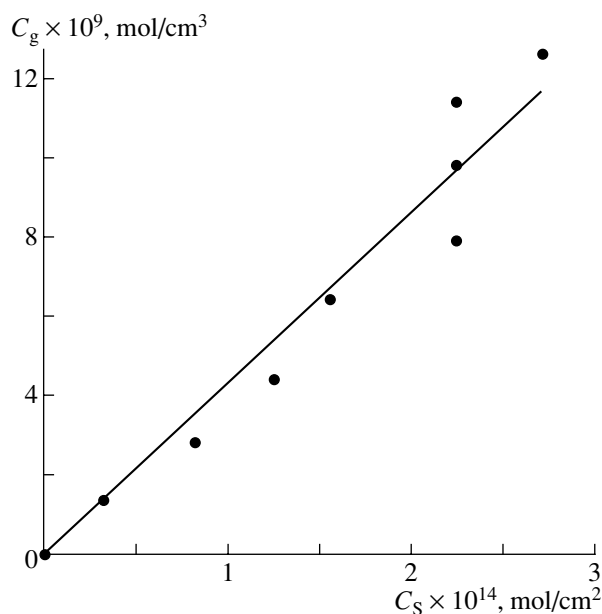$$\alpha = C_g/C_s = \text{const} \tag{1}$$

**Fig. 1.** Ethylene adsorption isotherm: a linear increase in the concentration of $C_2H_4$ in a gas phase ($C_g$) with ethylene concentration ($C_s$) on $SiO_2$. The gas-phase volume $V$ in the reactor with a $SiO_2$ sample ($p = 0.28$ g) was equal to 4.8 cm$^2$; the amount of ethylene ($N$) was increased from 0 to $1 \times 10^{-7}$ mol.



**Fig. 2.** Logarithm of the ratio between ethylene ($C_g$) and methane ($C_{gm}$) concentrations as a function of time $t$ (*1*) in the absence and (*2*) in the presence of Pd(II) on $SiO_2$; $V_r = 22.0$ cm$^3$; $SiO_2$ and Pd(II)/$SiO_2$ sample weights were equal to 0.2 g; [Pd(II)] = 0.05 mol %; $N = 2.5 \times 10^{-8}$ mol.

between the concentrations of gas-phase ($C_g$) and adsorbed ($C_s$) ethylene is obeyed (Fig. 1), which represents a linear portion of the adsorption isotherm. At 300 K, the values of $\alpha$ measured for ethylene and methane were equal to $4.4 \times 10^5$ and $9.0 \times 10^5$ cm$^{-1}$, respectively.

(2) The equilibrium consumption of $C_2H_4$ by palladium(II) was studied, and the equilibrium constant $K_s$ for the palladium complex of ethylene was determined. Methane was used as an internal standard because it does not react with Pd(II). For $V_r = 22.0$ cm$^3$, the silica gel weight $p = 0.2$ g, and $\lambda = (V/S) = 2.3 \times 10^{-5}$ cm, $N_g/N_s = \alpha\lambda = 10.1$, and the gas-phase portion of total ethylene amount is $N_g/(N_g + N_s) = 0.91$. In the absence of Pd(II) on $SiO_2$, the ethylene concentration and the value of $\log(C_g/C_{gm})$, where $C_{gm}$ is the concentration of methane in the gas phase, did not change with time (Fig. 2, straight line *1*) within the experimental error. With the same initial amount of $C_2H_4$–$CH_4$ mixture and with Pd(II)/$SiO_2$ ($p = 0.2$ g), the value of $\log(C_g/C_{gm})$ initially rapidly decreased, and then more slowly linearly decreased (Fig. 2, straight line *2*). The difference $\Delta$ between the values of $\log(C_g/C_{gm})$ extrapolated to $t = 0$ by straight lines *1* and *2* (Fig. 2) determines the additional rapid initial ethylene consumption by palladium(II) as compared with $SiO_2$. The value of $\Delta = \log[C_g(1)/C_g(2)]$, where $C_g(1)$ and $C_g(2)$ are the ethylene concentrations that correspond to straight lines *1*
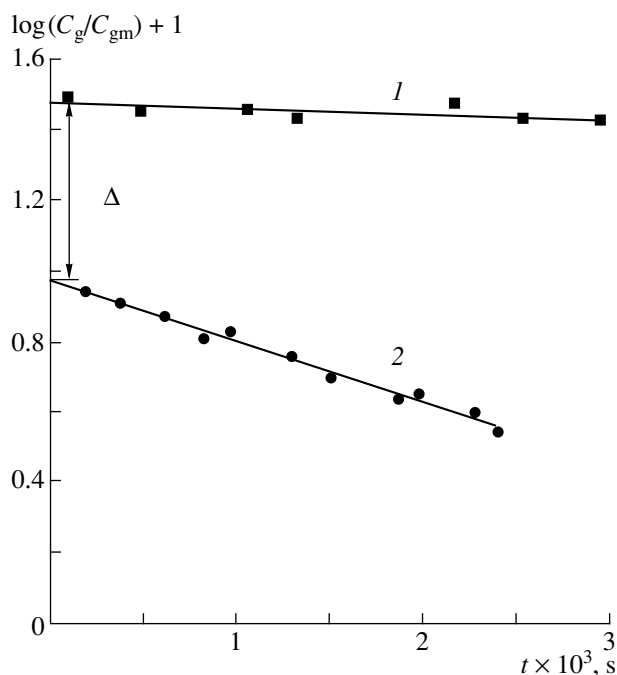
and *2* at $t = 0$, increased with Pd(II) concentration on $SiO_2$ (Table 1). The equilibrium fractions of ethylene in the gas phase ($N_g/N$) and on $SiO_2$ ($N_s/N$) calculated from the values of $\Delta$ decreased, and the fraction of $C_2H_4$ bound to palladium ($N_c/N$) increased with the amount of Pd(II) in the reactor. In this case, the equilibrium constant

$$K_s = C_c/[C_s(C_M - C_c)] \qquad (2)$$

for the ethylene complex of Pd(II) remained constant within the experimental error. The average value $K_s = (1.3 \pm 0.4) \times 10^{13}$ cm$^2$/mol was used for calculating the reaction rate constants $k_e$.

According to Fig. 2 and Table 1, the concentration of gas-phase ethylene in the presence of Pd(II) on $SiO_2$ (0.05 mol %) decreased by a factor of 3.2 because of the formation of an equilibrium ethylene complex. With the corresponding sample reduced with hydrogen, the concentration of ethylene decreased by a factor of only 1.3. Because all of the experiments were performed with a 10- to 100-fold excess of Pd(II) over ethylene, the reduction of a small portion of the Pd(II) in the course of measurements did not noticeably change the adsorption capacity of Pd(II)/$SiO_2$ samples.

As distinct from palladium samples, the initial values of $\log(C_g/C_{gm})$ for Cr(VI)/$SiO_2$ ($p = 0.2$ g; [Cr(VI)] = 0.2 mol %) and $SiO_2$ are equal to within a

5% error; this fact is indicative of the absence of the noticeable binding of ethylene to chromium(VI).

### Kinetic Measurements

The linear decrease in the value of $\log(C_g/C_{gm})$ with time, which is shown in Fig. 2, demonstrates a decrease in the ethylene concentration in the gas phase because of the oxidation with palladium(II). This decrease is described by the rate equation

$$d\ln C_g/dt = -k_\lambda \qquad (3)$$

with the rate constant $k_\lambda = 4 \times 10^{-4}$ s$^{-1}$. For the sample reduced with hydrogen and dried in air at 400 K, the value of $k_\lambda$ was found to be 10 times lower, which falls within the limits of experimental error. Because all of the kinetic measurements were performed at a constant Pd(II) concentration, Eq. (3) was obeyed in all cases. The presence of $O_2$ in the reactor had no noticeable effect on the kinetics because the reaction rate constants $k_\lambda$ in nitrogen (1 vol % $O_2$) and air atmospheres were equal within the experimental error.

### Ratio between $k_e$ and $k_\lambda$

The total amount ($N$, mol) of the substrate distributed among the gas phase (volume $V$), $SiO_2$ (surface area $S$), and a metal complex (number of moles $N_M$) in a closed reactor is

$$N = N_g + N_s + N_c = VC_g + SC_s + SC_c. \qquad (4)$$

We believe that the reaction of $C_2H_4$ with palladium(II) occurs, as in solutions, via the equilibrium intermediate $\pi$ complexes $C_2H_4$–Pd(II). Therefore, the reaction rate $dN/dt$ is proportional to the amount of these complexes ($N_c$):

$$-dN/dt = k_i N_c = k_i SC_c. \qquad (5)$$

If the presence of $M^n$ complexes has no detectable effect on the value of $S$ for a $M^n/SiO_2$ sample, the rate constant $k_i$ of the slow step of the conversion of the

$C_2H_4$–Pd(II) intermediate into products determines the value of $k_\lambda$ in accordance with the equation [11]

$$k_\lambda = k_i K_s (C_M - C_c)/(1 + \alpha\lambda + K_s(C_M - C_c)). \qquad (6)$$

Equation (6) reflects the participation of the metal complex in both the equilibrium binding of a molecule and its chemical transformation. To calculate the effective rate constant

$$k_e = k_i K_g = k_i K_s/\alpha, \qquad (7)$$

the values of $\alpha$, $\lambda$, and $K_s(C_M - C_c)$ according to Eq. (6) should be known in addition to $k_\lambda$.

In a limiting case when the main portion of the substrate is in the gas phase, $\alpha\lambda \gg 1 + K_s(C_M - C_c)$, and it follows from Eqs. (6) and (7) that at $C_M \gg C_c$ $k_\lambda$ is inversely proportional to the parameter $\lambda$:

$$k_\lambda = k_e C_M/\lambda. \qquad (8)$$

The rate constants $k_e$ can be obtained without adsorption measurements using relation (8).

Equation (6) and its limiting form (8) describe reactions that occur via equilibrium intermediate compounds of the substrate with metal complex reaction centers. For reactions with an irreversible attack of surface reaction centers by the substrate, the value of $k_\lambda$ is determined by the equation [7]

$$k_\lambda = k_e \alpha C_M/(1 + \alpha\lambda). \qquad (9)$$

As in the case of Eq. (6), relation (8) with the reaction rate constant $k_e$ as a combination of the rate constants of the irreversible steps of the reactions of gas-phase ($k_g$) and adsorbed ($k_s$) substrates with a metal complex is a limiting form of Eq. (9) at $\alpha\lambda \gg 1$ [7]. It is likely that the reaction of $C_2H_4$ with Cr(VI)/$SiO_2$ satisfies this mechanism. As mentioned above, this reaction occurs without the formation of equilibrium intermediate compounds of the substrate with the metal complex in detectable amounts, because $d^0$ ions do not form stable $\pi$ complexes with alkenes [8].

In both of the mechanisms of the interaction of substrates with metal complexes (an irreversible attack on

**Table 1.** Distribution of ethylene among the gas phase, $SiO_2$, and Pd(II) in a reactor ($V_r = 22.0$ cm$^3$, $p = 0.2$ g, and $N = 2.5 \times 10^{-8}$ mol)

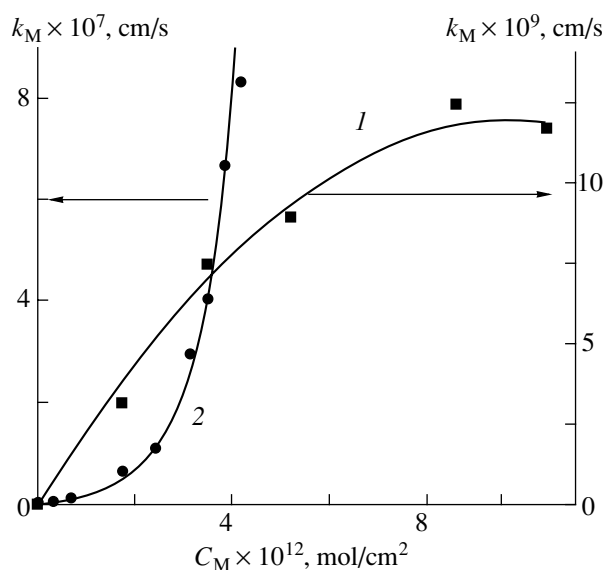| [Pd(II)], mol % | 0 | 0.01 | 0.02 | 0.03 | 0.04 | 0.05 |
|---|---|---|---|---|---|---|
| $C_M \times 10^{13}$, mol/cm$^2$ | 0 | 3.47 | 6.94 | 10.4 | 13.9 | 17.4 |
| $N_M \times 10^7$, mol | 0 | 3.33 | 6.66 | 9.99 | 13.3 | 16.6 |
| $\Delta = \log[C_g(1)/C_g(2)]$ | 0 | 0.065 | 0.24 | 0.46 | 0.42 | 0.51 |
| $N_g/N = 0.91 C_g(2)/C_g(1)$ | 0.91 | 0.78 | 0.53 | 0.31 | 0.35 | 0.28 |
| $N_s/N = N_g/(10.1N)$ | 0.09 | 0.08 | 0.05 | 0.03 | 0.04 | 0.03 |
| $N_c/N = 1 - (N_g + N_s)/N$ | 0 | 0.14 | 0.42 | 0.66 | 0.61 | 0.69 |
| $(N_c/[N_s(C_M - C_c)]) \times 10^{-13}$, cm$^2$/mol | – | 0.5 | 1.2 | 2.0 | 1.2 | 1.4 |
| $K_s \times 10^{-13}$, cm$^2$/mol (average) | 1.3 ± 0.4 | | | | | |

**Fig. 3.** Rate constants of zero-order reactions with respect to a metal complex ($k_M = k_e(C_M - C_c)$) as functions of metal complex concentration ($C_M$) on $SiO_2$: (*1*) Cr(VI) and (*2*) Pd(II). $V = 22.0$ cm$^3$, $p = 0.02$ g.

reaction centers or a reaction path via equilibrium intermediate compounds), the rate constant $k_e$, in contrast to the measured rate constant $k_\lambda$, is independent of the gas-phase volume in the reactor and the surface area of $M^n/SiO_2$, and it is an effective rate constant of substrate conversion on surface reaction centers.

### Calculation of the Rate Constants $k_e$ and $k_i$

Table 2 illustrates the calculation of effective rate constants $k_e$ for the reaction of ethylene oxidation by palladium(II) with the use of Eq. (6). As distinct from the measured rate constant $k_\lambda$, the rate constant $k_e$ remained unchanged within the experimental error as the amount of Pd(II)/SiO$_2$ in the reactor was changed by a factor of 12. Table 2 also gives the rate constant $k_i$ of conversion of the intermediate complex into reaction products, which was found by Eq. (7).

### Effect of the Concentration of $M^n$ Ions in Cr(VI)/SiO$_2$ and Pd(II)/SiO$_2$ Samples on the Rate Constants of Their Reactions with Ethylene

Figure 3 demonstrates the changes of $k_M = k_e(C_M - C_c)$ in the reactions of Cr(VI) and Pd(II) with $C_M$, as found from the values of $k_\lambda$ using Eqs. (6) and (9). Note that the plots for these complexes are dramatically different. At the linear portion of curve *1*, the reaction is of first order with respect to Cr(VI), and the rate constant is $k_e = k_1 = 1.9 \times 10^3$ cm$^3$ mol$^{-1}$ s$^{-1}$; the values of $k_e$ are lower at higher Cr(VI) concentrations.

Another behavior was observed in the reaction of C$_2$H$_4$ with Pd(II)/SiO$_2$. In this case, the value of $k_M$ rap-

idly increased with $C_M$ (curve *2*), and the reaction was of first order with respect to Pd(II) only near $C_M = 0$. The corresponding first-order reaction rate constant $k_1 = 9 \times 10^3$ cm$^3$ mol$^{-1}$ s$^{-1}$ was obtained by extrapolating $k_e = k_M/(C_M - C_c)$ to $C_M = 0$ (Fig. 4, curve *1*).

Previously [7], the values of $k_e$ for the reaction of ethylene with Pd(II)/SiO$_2$ without consideration for C$_2$H$_4$ adsorption on Pd(II) were found to linearly increase as $C_M$ was increased up to $3.47 \times 10^{-12}$ mol/cm$^2$. However, additional measurements [12] were performed at higher Pd(II) concentrations on SiO$_2$ (up to $5.2 \times 10^{-12}$ mol/cm$^2$), and ethylene binding to palladium(II) was taken into account with the use of Eq. (6). It was found that the value of $k_e$ linearly increased at the initial portion, whereas the general form of $k_e$ as a function of $C_M$ (Fig. 4, curve *2*) was the same as that illustrated by curve *1* (Fig. 4) obtained in this work. The value of $k_e = k_1 = 2.5 \times 10^4$ cm$^3$ mol$^{-1}$ s$^{-1}$ extrapolated to $C_M = 0$ by curve *2* is higher than the value of $k_1$ for curve *1* by a factor of 2.8; this is likely due to differences in the conditions of sample preparation (Fig. 4).

The analytical form of $k_e$ as a function of $C_M$,

$$k_e = k_1 \exp(bC_M), \qquad (10)$$

follows from the linear relations $\ln(k_e/k_1) = bC_M$, which are shown in Fig. 5.

Previously, deviations from the first-order reaction with respect to Pd(II) similar to those found in this work were observed in the reaction of Pd(II) with ethylene in aqueous solutions [2, 8, 13]. The first-order reaction rate constants with respect to palladium ($k_{el}$, l mol$^{-1}$ s$^{-1}$) determined at [Pd(II)] = 0–0.2 M satisfy the equation [2] (in our notation)

$$k_{el} = k_{1l}(1 + \alpha[\text{Pd(II)}]) \qquad (11)$$

and a mechanism that involves an attack on the palladium(II) $\pi$ complex with ethylene by other palladium ions at prelimiting steps. In an alternative mechanism, the substrate attacks already formed Pd(II) associates. These two mechanisms are kinetically indistinguishable [2].

Our experimental data obtained at the Pd(II) concentrations $C_M = (0–1.0) \times 10^{-12}$ mol/cm$^2$ (Fig. 4) obey the same equation (the first two members of function $k_e$ (cm$^3$ mol$^{-1}$ s$^{-1}$) expanded in a series)

$$k_e = k_1(1 + bC_M), \qquad (12)$$

which is indicative of a kinetic analogy between the homogeneous and heterogeneous reactions of Pd(II) with ethylene.

Another example of an analogy between the kinetic behavior of Pd(II) on a surface and in solutions is represented by Eq. (10) and the exponential relation [3]

$$k_{el} = k_{1l} \exp(B[\text{Pd}]) \qquad (13)$$

for the rate constant (first-order reaction with respect to Pd(II)) of the oxidation of saturated hydrocarbons in
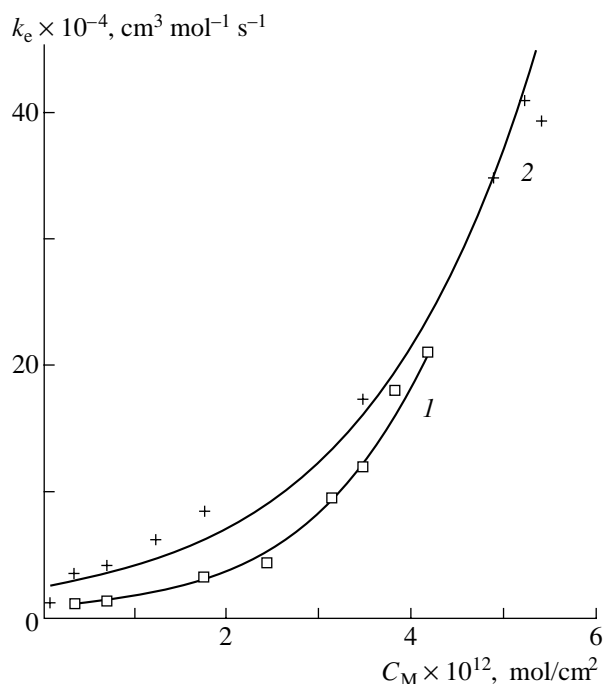
**Fig. 4.** Rate constants of first-order reactions with respect to Pd(II) ($k_e$) as functions of $C_M$: (*1*) $V = 22.0$ cm$^3$; $p = 0.02$ g; in solutions used for impregnating SiO$_2$, [HCl] = 0.06 M and [PdCl$_2$] = 0.01 M; the samples were dried at 400 K; (*2*) $V = 6.7$ cm$^3$; $p = 0.01$ g; in solutions used for impregnating SiO$_2$, [HCl] = 0.03 M and [PdCl$_2$] = 0.01 M; the samples were dried at 470 K.



**Fig. 5.** Linear relations between $\ln(k_e/k_1)$ and $C_M$ (straight lines *1* and *2* correspond to curves *1* and *2* in Fig. 4). The coefficients of linear correlation are $R$ = (*1*) 0.99 and (*2*) 0.94. The constant *b* is equal to $7.6 \times 10^{11}$ or $5.4 \times 10^{11}$ cm$^2$/mol for lines *1* and *2* (Figs. 4 and 5), respectively.

sulfuric acid (80–90 wt %) at [Pd(II)] = 0–0.1 mol/kg. An increase in $k_{el}$ in accordance with Eq. (13) was interpreted as a result of the joint electrophilic effects of Pd(II) ions on a hydrocarbon molecule in the active complex [3].

It is likely that detailed information on deviations from the first order with respect to Pd(II) in its reactions with hydrocarbons can be obtained from the studies of the composition [14] of palladium complexes on SiO$_2$ (under reaction conditions) by IR spectroscopy w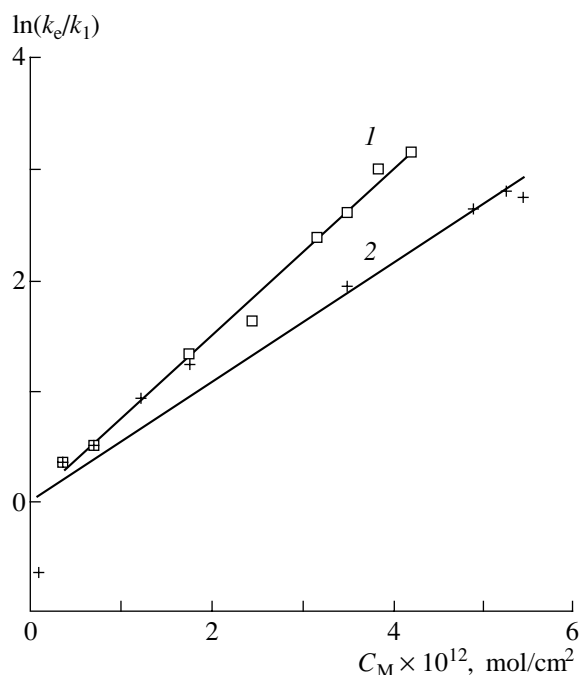ith the use of CO as a probe. The mechanism of CO oxidation by supported palladium(II) complexes was studied using this approach [15].

The considered interaction of C$_2$H$_4$ with Pd(II)/SiO$_2$ includes the noticeable physical adsorption of ethylene by silica gel; the rapid equilibrium formation of stable C$_2$H$_4$–Pd(II) complexes on SiO$_2$, which are probably similar to $\pi$ complexes in solutions (chemisorption); and the comparatively slow conversion of these complexes into reaction products. The rate constant $k_\lambda$ of ethylene loss from the gas phase due to a reaction, which was determined by Eq. (3), depends on the reaction volume, the surface area of a Pd(II)/SiO$_2$ sample, and the adsorption capacities of SiO$_2$ and Pd(II). This

**Table 2.** Calculation of the rate constants $k_e$ and $k_i$ ($V_r = 22.0$ cm$^3$, $N = 1.0 \times 10^{-8}$ mol, $C_M = 3.47 \times 10^{-13}$ mol/cm$^2$, $\alpha = 4.4 \times 10^5$ cm$^{-1}$, $K_s = 1.3 \times 10^{13}$ cm$^2$/mol, and $N_c/N_s = C_c/C_s = K_s(C_M - C_c) = 4.5$)

| Weight of Pd(II)/SiO$_2$, g | 0.02 | 0.03 | 0.05 | 0.10 | 0.20 | 0.24 |
|---|---|---|---|---|---|---|
| $N_M \times 10^7$, mol | 0.33 | 0.50 | 0.83 | 1.67 | 3.33 | 4.0 |
| $S \times 10^{-5}$, cm$^2$ | 0.96 | 1.44 | 2.40 | 4.80 | 9.60 | 11.5 |
| ($\lambda = V/S$) $\times 10^5$, cm | 23.0 | 15.3 | 9.2 | 4.6 | 2.3 | 1.9 |
| $N_g/N_s = \alpha\lambda$ | 101 | 67.3 | 40.5 | 20.2 | 10.1 | 8.3 |
| $k_\lambda \times 10^4$, s$^{-1}$ | 0.18 | 0.26 | 0.30 | 0.70 | 1.12 | 1.80 |
| $[k_\lambda(1 + N_g/N_s + N_c/N_s)/(\alpha[C_M - C_c])] \times 10^{-4}$, cm$^3$ mol$^{-1}$ s$^{-1}$ | 1.3 | 1.2 | 0.9 | 1.2 | 1.1 | 1.6 |
| Average value of $k_e \times 10^{-4}$, cm$^3$ mol$^{-1}$ s$^{-1}$ | 1.2 ± 0.1 | | | | | |
| ($k_i = \alpha k_e/K_s$) $\times 10^4$, s$^{-1}$ | 4.0 | | | | | |

constant is not the rate constant of the reaction of the substrate distributed among the gas phase, the surface, and the reaction centers. The rate constant $k_e$ (Eq. (6)) should be considered as a quantitative measure of the rate of these reactions. An approach based on this equation allowed us to study the role of the adsorption of a gaseous substrate by the surface of a support and by supported metal complexes in the reaction mechanism. Consideration of the adsorption revealed an analogy between the kinetic behavior of Pd(II) in the reactions with ethylene on silica gel and with ethylene and other hydrocarbons in solutions.

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