Kinetics and Mechanism of Catalytic Acetylene Hydrochlorination with Gaseous HCl on the Surface of Mechanically Activated K_2PdCl_4

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Abstract—The catalyst for acetylene hydrochlorination with gaseous HCl at room temperature is prepared by mechanical pretreatment of K_2PdCl_4 in an acetylene atmosphere. The rate-determining step of the reaction is the chloropalladation of π-coordinated acetylene involving an HCl molecule. As a consequence, the replacement of HCl with DCl brings about a kinetic isotope effect of 2.8 ± 0.4, which differs substantially from that observed in the protodemetalation of the intermediate palladium(II) chlorovinyl derivative yielding vinyl chloride (6.8 ± 0.6).
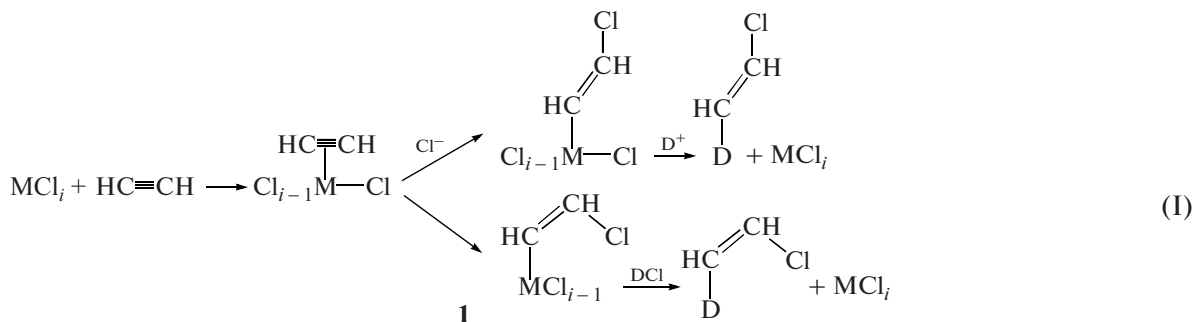
INTRODUCTION

Acetylene hydrochlorination is one of the commercial methods of vinyl chloride production. The commercial processes employ mercury(II) chloride supported on active carbon as the catalyst [1]. The reaction proceeds at appropriate rates above 100°C. However, this catalyst is unstable, which is primarily due to the loss of $HgCl_2$ because of the volatility of the salt [2]. Besides, this process contaminates the environment. The high toxicity of the mercury catalyst and its relative instability prompted us to search for other catalytic systems. Under heterogeneous conditions, Au[III] [3, 4] and Rh[III] [5] complexes on active carbon catalyze acetylene hydrochlorination, but they need

elevated temperatures (170−180°C). It has recently been discovered that acetylene hydrochlorination at room temperature is catalytically accelerated on the surface of the mechanically activated salts K_2PtCl_6 [6] and K_2PtCl_4 [7].

Acetylene activation by metal complexes [1] begins with the π-coordination of the C≡C bond to the metal. Subsequent outer-sphere attack by the nucleophile on π-coordinated acetylene yields the product of *trans*-addition of the nucleophile and metal complex to the triple bond. Attack by the coordinated nucleophile results in the *cis*-addition product. The subsequent protodemetalation of this intermediate complex affords the final product retaining the stoichiometry of the intermediate (Scheme 1).
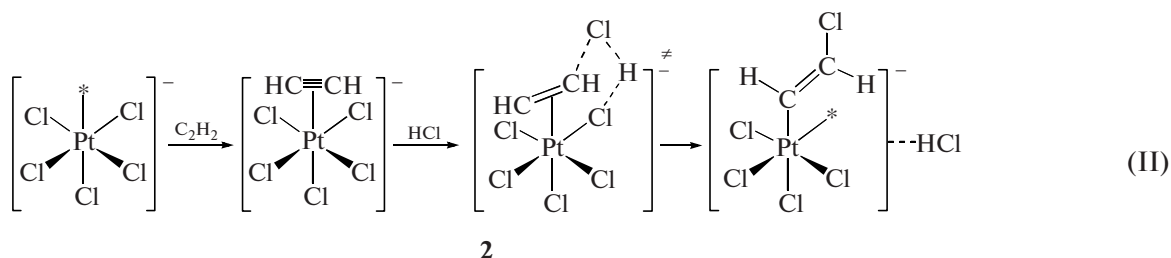

(I)

Scheme 1.

Mechanical treatment of K_2PtCl_6 in an acetylene atmosphere (system **1**) results in the formation of catalytic sites active in acetylene hydrochlorination.

These sites are topologically connected $[PtCl_5^*]^-$− $[PtC_4]^{2-}$ pairs, where $[PtCl_5^*]^-$ is a platinum(IV) com-

plex with a coordination vacancy. The stepped mechanism includes the chloroplatination of acetylene by coordinatively unsaturated platinum(IV) complexes with the intermediate formation of a platinum(IV) β-chlorovinyl derivative. It is believed that the role of the platinum(II) complexes in this system is the complement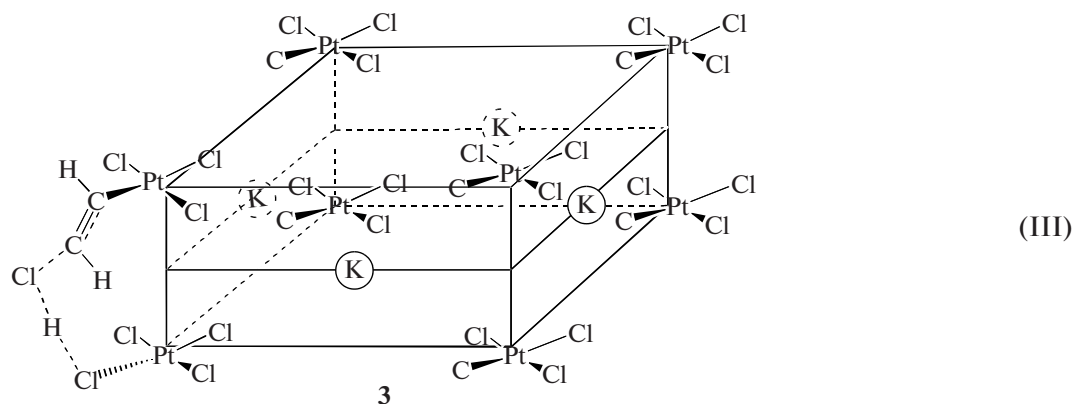ary reduction of $Pt^{IV}(CH=CHCl)$ to the corresponding platinum(II) derivative, whose protodemetalation results in the formation of vinyl chloride and in the regeneration of the active site of the catalyst. The rate-determining step of the reaction (acetylene chloroplatination) involves an HCl molecule and proceeds via a six-membered transition state as a concerted process (Scheme 2).

Scheme 2.

The mechanical activation of the platinum(II) salt K_2PtCl_4 in an acetylene atmosphere (system **2**) also affords an acetylene hydrochlorination catalyst. Under these conditions, the active sites, which are platinum(II) acetylene π-complexes [7], are formed in the surface layers. The rate-determining step of the catalytic reaction in system **2** is again the chloroplatination of π-coordinated acetylene involving an HCl molecule. The reaction proceeds as a concerted process consisting of the cleavage of the H−Cl and Pt−Cl bonds in the metal complex adjacent to the acetylene π-complex and the simultaneous formation of the intermediate platinum(II) β-chlorovinyl derivative, the coordinatively unsaturated platinum complex $[PtCl_3^*]^-$, and a new HCl molecule (Scheme 3).

Scheme 3.

The fast protodemetalation of the resulting σ-Pt−C bond by HCl completes the catalytic cycle to give the final products and the initial $[PtCl_4]^{2-}$ complex.

It could be expected that the palladium(II) chloro complex K_2PdCl_4 (system **3**), an analogue of K_2PtCl_4, will also be catalytically active in acetylene hydrochlorination under similar conditions. The purpose of this work was to verify this assumption and to study the kinetics and elucidate the mechanism of the catalytic reaction in system **3**.

EXPERIMENTAL

K_2PdCl_4 was synthesized according to a standard procedure [8] and was dried at 120−140°C for 3 days. Samples of the resulting salt (0.25 g) were subjected to mechanical treatment in an acetylene atmosphere in a closed glass vibroreactor containing glass milling bodies. For this purpose, we used an MMVE-0.005 vibrating micromill with a working frequency of 50 Hz and an amplitude of 5.5 mm, which corresponds to a specific energy intensity of $I = 15$ W/kg. The specific dose

Table 1. Dependences of the specific surface area of the K_2PdCl_4 salt and the apparent rate constant of catalytic acetylene hydrochlorination on the duration of the mechanical treatment of the catalyst (0.25 g of K_2PdCl_4)

t, min	S_{sp}, m^2/g	$k_{app} \times 10^5$, s^{-1}
0	~0.02	0
15	4.7 ± 0.5	2.3 ± 0.1
30	6.0 ± 0.6	5.9 ± 0.3
60	5.9 ± 0.6	9.0 ± 0.7
90	6.9 ± 0.7	10 ± 1
120	7.2 ± 0.7	12 ± 1

of mechanical energy absorbed by the salt powder (D_{sp}) was determined using the equation $D_{sp} = It$, where t is the activation time [9]. After the treatment, the reactor was purged successively with argon and HCl (or an HCl/DCl mixture) and sealed. Acetylene and ethane (as an internal standard) were introduced through a septum.

The reaction was carried out at 18°C. The acetylene consumption was monitored by GLC using an LKhM-8-MD chromatograph with a flame-ionization detector and a column packed with Silochrome C-120 adsorbent. The MultiChrom system (Ampersand, Russia) was used in data acquisition and processing. The relative acetylene concentration $\varphi(RH)$ was determined as the ratio of the areas of chromatographic peaks of C_2H_2 and ethane used as the internal standard. The amount of acetylene was calculated using the calibration relationship between the amount of acetylene introduced into the empty reactor and the area of the corresponding chromatographic peak.

The specific surface area of the catalyst was determined by argon desorption using the BET method.

Acetylene was prepared by a standard procedure [10], and gaseous hydrogen chloride (HCl or DCl) was obtained by the interaction of calcined KCl with H_2SO_4 or D_2SO_4. The resulting deuterium chloride was passed through the reactor and then through an IR gas cell with KBr windows at its ends, and then the cell and reactor were sealed. The mole fraction of DCl in the resulting gaseous HCl/DCl mixture was determined by IR spectrophotometry using a Bruker Tensor 27 instrument, whose software makes it possible to integrate the IR signal. The isotope composition of the HCl/DCl mixture was determined from the ratio of integrated peak intensities, taking into account that, under the same conditions, the bands of HCl are approximately twice as intense as the bands of DCl [11].
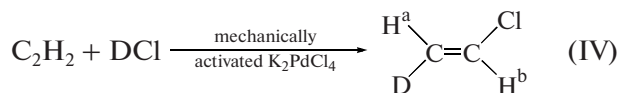
The NMR spectra of the acetylene hydrochlorination products were recorded in a deuterochloroform solution on an AVANCE-II-400 spectrometer (Bruker BioSpin GmbH) operating at 400 MHz.

RESULTS

The mechanical preactivation of dry K_2PdCl_4 in an acetylene atmosphere indeed yields a catalyst for acetylene hydrochlorination with gaseous HCl. The catalytic reaction occurs at room temperature and requires no continuous mechanical treatment. In an HCl atmosphere the rate of acetylene uptake from the gas phase of the closed reactor obeys a first-order kinetic equation. The apparent rate constant was determined as $k_{app} = -\dfrac{d[\ln\varphi(RH)]}{dt}$. The vinyl chloride yield in terms of reacted acetylene was close to 100%.

The reaction proceeds in the catalytic regime: no substantial decrease in the catalytic activity is observed after the occurrence of more than 150 catalytic cycles in terms of palladium on the salt surface, or more than 1.7 catalytic cycles in terms of the total amount of palladium.

The stereochemistry of the product resulting from acetylene hydrochlorination in a DCl atmosphere corresponds to the *trans*-addition of the chlorine and deuterium atoms to the triple bond of acetylene (the ^{1}H NMR spectrum obtained in a CDCl$_3$ solution has the following characteristics: $\delta = 5.52$ ppm (H^a) and 6.31 ppm (H^b), $J(\text{H}^a\text{H}^b) = 14.75$ Hz, and $J(\text{H}^b\text{D}) = 1.03$ Hz).

$$C_2H_2 + DCl \xrightarrow[\text{activated } K_2PdCl_4]{\text{mechanically}} \begin{array}{c} \text{H}^a \\ \diagdown \\ \text{D} \end{array} C = C \begin{array}{c} \text{Cl} \\ \diagup \\ \text{H}^b \end{array} \quad \text{(IV)}$$

Dependence of the Catalytic Activity on the Mechanical Pretreatment Time

The specific surface area and activity of the catalyst increase monotonically with the salt preactivation time (Table 1).

The plot of the specific surface area of the catalyst versus the specific dose of mechanical energy absorbed by the powder has the shape of a saturation curve (Fig. 1) and is described by the equation

$$S_{sp} = S_0 + S_{sp}^*(1 - e^{-\eta_s D_{sp}}), \qquad (1)$$

where S_0 is the specific surface area of the initial K_2PdCl_4 powder, S_{sp}^* is the limiting value of the increase in the specific surface area due to mechanical treatment, and η_s is the constant characterizing the efficiency of new surface formation (quantity inverse to the specific work of surface formation).

The increase in catalytic activity with an increase in the mechanical pretreatment time can be due to two factors, namely, an increase in the specific surface area of the salt and an increase in the surface concentration of active sites. To rule out the influence of the former factor on k_{app}, let us consider the apparent rate constant per unit area of the catalyst surface: $k^* = k_{app}/S_{sp}m$.
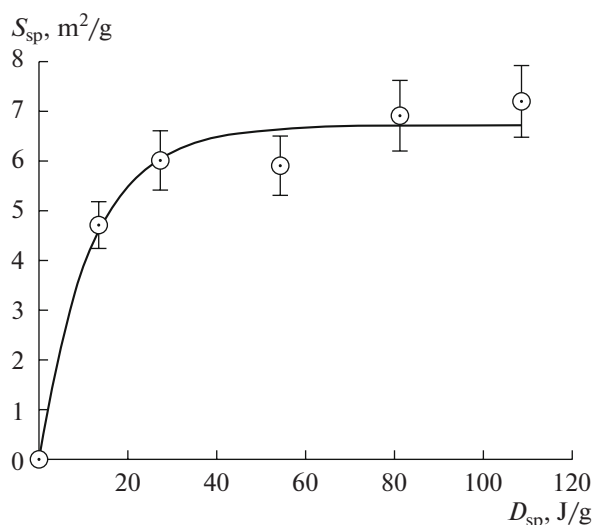
Fig. 1. Dependence of the specific surface area of the K_2PdCl_4 powder on the absorbed specific dose of mechanical energy. The points are experimental S_{sp} values, and the curve represents the data calculated using Eq. (1).

Fig. 2. Dependence of the apparent rate constant of acetylene consumption per unit area of the catalyst surface on the specific dose of mechanical energy absorbed by the K_2PdCl_4 powder. The points are experimental values, and the curve represents the data calculated using Eq. (2).

The dependence of k^* on the specific dose of mechanical energy absorbed by the powder also appears as a saturation curve with (Fig. 2) and obeys the equation

$$k^* = k^*_{max}(1 - e^{-\eta D_{sp}}), \qquad (2)$$

where k^*_{max} is the limiting value of k^* and η is the constant characterizing the efficiency of the formation of active states in the catalyst under mechanical treatment (quantity inverse to the specific work of formation of active sites in the catalyst).

The parameters of Eqs. (1) and (2) are listed in Table 2, and the earlier found S^*_{sp} and η_s values for ionic crystals of KCl [12] are given for comparison. The specific work of formation of a new surface for the K_2PdCl_4 ionic crystal (~12.5 J/g) is lower than the corresponding value for KCl (~170 J/g [12]). This result is in qualitative agreement with the expectations since the KCl crystal lattice is more compact than the K_2PdCl_4 lattice. The η_s value for K_2PdCl_4 is approximately three times larger than the η value. This means that the increase in the surface area and the formation of active sites of the catalyst are unrelated.

It follows from Table 1 that 1-h-long mechanical pretreatment is sufficient for reaching a near-limiting value of the specific surface area of the catalyst and for ensuring a fairly high catalytic activity. For this reason, subsequent experiments were carried out on the catalyst mechanically preactivated for 1 h.
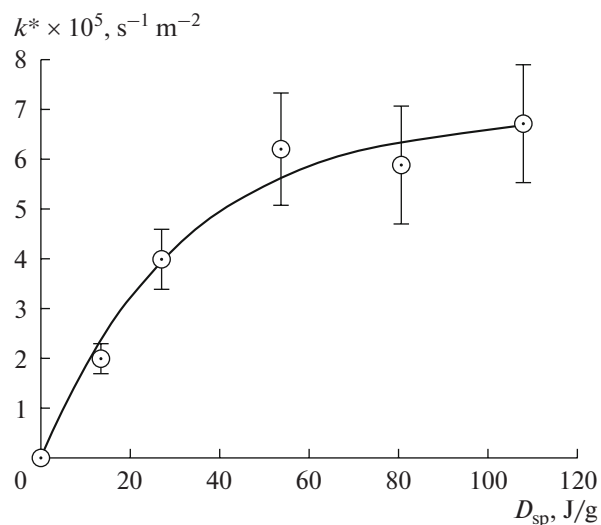
Kinetic Isotope Effect

The k_{app} values measured in an HCl atmosphere (after the reactor was purged with a fivefold volume of HCl) and at an approximately three times lower partial pressure of HCl (after the reactor was purged with 5 ml of HCl) are equal within the experimental error. This coincidence of the constants can be due to the rate-determining step occurring without HCl or to the change in the surface HCl concentration being negligible under the given conditions.[1] As will be shown below, the latter situation actually takes place.

If an HCl molecule participates in the rate-determining step, the replacement of HCl with DCl will bring about a kinetic isotope effect (KIE). We found that the reaction rate is appreciably lower when the reaction is carried out in a DCl/HCl atmosphere (Table 3). The apparent rate constants of acetylene consumption in pure DCl (k_{app}^{DCl}) are listed in Table 3. They were determined using the equation [13]

$$k_{app}^{DCl} = \frac{k_{app}^{DCl/HCl} - k_{app}\chi}{1 - \chi}, \qquad (3)$$

where $k_{app}^{DCl/HCl}$ is the apparent pseudo-first-order rate constant of acetylene consumption in the DCl/HCl atmosphere and χ is the mole fraction of HCl in the DCl/HCl mixture. Hence, $KIE = \dfrac{k_{app}}{k_{app}^{DCl}} = 2.8 \pm 0.4$. Such a noticeable isotope effect proves the participa-

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[1] This is possible, for example, in the case of the limiting Langmuir or polylayer coverage of the surface with HCl molecules.

Table 2. Values of S_{sp}^*, η_s, k_{max}^*, and η in Eqs. (1) and (2)

Crystal	S_{sp}^*, m^2/g	$\eta_s \times 10^2$, g/J	$k_{max}^* \times 10^5$, s^{-1} m^{-2}	$\eta \times 10^2$, g/J
K$_2$PdCl$_4$	6.7 ± 0.7	8 ± 2	6.8 ± 0.6	3.2 ± 0.6
KCl	0.42 ± 0.04	0.60 ± 0.05	—	—

Table 3. Dependences of the apparent rate constant of acetylene consumption and the ratio of the nondeuterated and mono-deuterated vinyl chloride yields on the mole fraction of HCl in the HCl/DCl mixture (0.25 g of K$_2$PdCl$_4$)
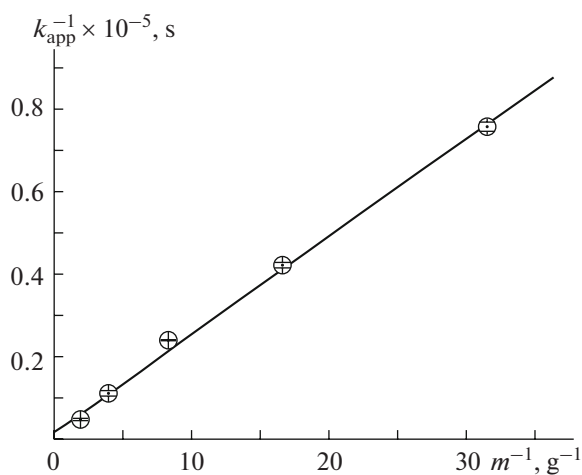
χ	$k_{app}^{DCl/HCl} \times 10^5$, s^{-1}	$k_{app}^{DCl} \times 10^5$, s^{-1}	$\dfrac{H_2C=HCl\ yield}{HDC-CHCl\ yield}$	γ
1.0	9.0 ± 0.7	—	—	—
0.53	6.2 ± 0.1	3.0	—	—
0.40	5.6 ± 0.3	3.3	—	—
0.60	—	—	9.6	6.4
0.60	—	—	11.2	7.5
0.66	—	—	12.7	6.5
Average value		3.2 ± 0.2	—	6.8 ± 0.6

tion of an HCl molecule in the rate-determining step of the reaction.

The KIE values derived from the ratio of the yields of nondeuterated and monodeuterated vinyl chlorides in the DCl/HCl atmosphere,

$$\gamma = \frac{yield\ H_2C=CHCl}{yield\ HDC=CHCl} \times \frac{1-\chi}{\chi},$$

are noticeably larger that the above value of KIE = 2.8 (Table 3).

$k_{app}^{-1} \times 10^{-5}$, s

Fig. 3. Dependence of the apparent pseudo-first-order rate constant of acetylene consumption on the catalyst weight: the linear anamorphosis of Eq. (5).

Specific Catalytic Activity

The fact that the rate of acetylene consumption in heterogeneous catalytic reaction (IV) obeys a first-order kinetic equation means that acetylene is adsorbed according to Henry's law

$$[RH]_{ads}= KP_{RH}, \qquad (4)$$

where $[RH]_{ads}$ is the surface concentration of acetylene, K is the adsorption equilibrium constant, and P_{RH} is the partial acetylene pressure. Accordingly, the true pseudo-first-order rate constant of HCl consumption (determined in the absence of a gas phase) should be related [6] to the experimental k_{app} value by the equation

$$k_{app} = \frac{k}{1 + \alpha\lambda}, \qquad (5)$$

where $\alpha = (RTK)^{-1}$, $\lambda = V_g/S_{sp}m$, V_g is the volume of the gas phase in the reactor, R is the gas constant, T is temperature, S_{sp} is the specific surface area of the catalyst, and m is the catalyst weight.

Equation (5) is in agreement with the experimental dependence of k_{app} on the catalyst weight at $k = (5 \pm 3) \times 10^{-4}$ s^{-1} and $K = (8 \pm 4) \times 10^{-10}$ mol m^{-2} Pa^{-1} (Fig. 3). Knowing the true reaction rate constant k and the acetylene adsorption equilibrium constant K, one can estimate the lower limit of the specific catalytic activity of the catalyst. At the limiting hydrogen chloride coverage of the surface (see above) and an acetylene partial pressure of 1 atm, the rate of vinyl chloride formation per square meter of the catalyst surface is $\sim 4 \times 10^{-8}$ mol m^{-2} s^{-1}. The maximum possible number of moles of palladium on a 1-m^2 area of the catalyst surface (N_{Pd}) can be estimated knowing the lattice

parameters $a = b = 7.05 \times 10^{-10}$ m and $c = 4.1 \times 10^{-10}$ m [14]:

$$N_{Pd} = \frac{1/ac}{N_a} \approx 5.7 \times 10^{-6} \text{ mol/m}^2, \qquad (6)$$

where N_a is Avogadro's number. Hence, the specific catalytic activity of the catalyst at the limiting coverage of the surface with hydrogen chloride molecules and an acetylene partial pressure of 1 atm is at least 7×10^{-3} (mol C_2H_2) (mol Pd)$^{-1}$ s^{-1}.

DISCUSSION

The kinetics of acetylene uptake from the gas phase of the closed reactor in an HCl atmosphere is described by a first-order kinetic equation, as in the case of system **1** [6]. By contrast, the amount of acetylene in system **2** decreases according to a zeroth-order equation [7]. The zeroth order with respect to acetylene in system **2** is explained [7] by fast acetylene chemisorption on the surface of the mechanically activated salt via π-coordination with the coordinatively unsaturated near-surface platinum(II) complexes. Therefore, the amount of adsorbed substrate is almost independent of its partial pressure in the gas phase. Unlike platinum(II), palladium(II) cannot form stable π-complexes [15] and is similar to platinum(IV) in this respect [15]. It is likely due to this circumstance that the same reaction order with respect to acetylene is observed in systems **1** and **3**.

Since the reaction orders with respect to acetylene in systems **1** and **3** are equal, it is possible to compare the catalytic activities of the corresponding metal complexes under the same conditions (Table 4). Clearly, the true rate constants of acetylene consumption in systems **1** and **3** are similar. Under the assumption that the electrophilic properties of metal complexes play the key role in the activation of multiple C–C bonds by these complexes, the approximate equality of the k values in systems **1** and **3** means that the platinum(IV) and palladium(II) chloro complexes have similar electrophilicities. The lower limit of the specific catalytic activity in system **3** is approximately 30 times lower, which is mainly due to the smaller acetylene adsorption equilibrium constant in this system. At equal partial pressures of acetylene, the surface substrate concentration in system **1** is one order of magnitude higher, due to which its consumption rate is higher.

Because of the stereoselectivity of reaction (IV), the outer-sphere attack of the *cis* chloride ligand on the palladium(II)–acetylene π-complex should be ruled out. By analogy with the reactions in systems **1** [6] and **2** [7], we believe that acetylene is chloropalladated by hydrogen halide. This is consistent with the fact that reaction (IV) yields only the *trans*-addition product, although system **3** does not contain "external" chloride ions in amounts comparable with the amount of the resulting vinyl chloride.[2]

Thus, HCl can participate in two reaction steps, namely, acetylene chloropalladation with the intermediate formation of the palladium(II) β-chlorovinyl derivative and the protodemetalation of the latter species. Taking into account that the protodemetalation of platinum metal σ-organic derivatives usually occur readily (see, e.g., [16, 17]), it is natural to assume that the rate-determining step of catalytic acetylene hydrochlorination in system **3** is chlorometallation involving the HCl molecule, as in systems **1** [6] and **2** [7].

This assumption provides a natural explanation for the observed substantial difference between the KIE derived from the kinetics of acetylene consumption (KIE = 2.8 ± 0.4) and that derived from the yields of the corresponding isotopomers of vinyl chloride (γ = 6.8 ± 0.6). The latter value likely refers to the protodemetalation of the intermediate palladium derivative (fast step), whereas the former refers to acetylene chloropalladation (rate-determining step).

Note that a different situation is observed in aqueous solutions [18], in which the palladium(II) chloride complexes also catalyze acetylene hydrochlorination, but only in the presence of an oxidizer (FeCl$_3$) and at elevated temperatures (above 90°C). In this case, the yield of vinyl chloride does not exceed 50%, because hydrochlorination is accompanied by acetylene oligomerization and hydration. The kinetic data obtained are explained [18] under the assumption that the acetylene chloropalladation step is quasi-equilibrium and the hydrochlorination rate is limited by the protolysis of the intermediate palladium chlorovinyl derivative. The evident cause of the differences between the homogeneous and heterogeneous catalytic reactions is that the heterogeneous system, unlike solutions, does

Table 4. True rate constants of adsorbed acetylene consumption in the absence of a gas phase, acetylene adsorption equilibrium constants, and specific catalytic activity in systems **1** and **3**

System	$k \times 10^4$, s^{-1}	$K \times 10^9$, mol m^{-2} Pa^{-1}	Specific catalytic activity, (mol C_2H_2) (mol M)$^{-1}$ s^{-1}
1 (M = Pt^{IV} [6])	4.4 ± 1.5	12 ± 6	≥0.2
3 (M = Pd^{II})	5 ± 3	0.8 ± 0.4	≥0.007

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[2] In solids, as distinct from solutions, molecular mobility is retarded and the interatomic distances in the lattice are fixed. The shortest distance between palladium complexes in the K$_2$PdCl$_4$ crystals is 4.1 Å [14]. For this reason, we do not consider the possibility of addition of halogen from an adjacent complex molecule.

not contain free nucleophiles (in our case, chloride ions) in amounts comparable with that the amount of the resulting product. As a consequence, the acetylene chloropalladation step is slow.

Since the K_2PdCl_4 and K_2PtCl_4 lattices are of the same type and have close parameters, we may assume, taking into account the KIE values in systems **2** and **3**, that the reaction mechanisms in these systems are similar. In particular, it would be expected that a transition state similar to structure (III) forms in system **3**. To confirm the reaction mechanism suggested for system **3**, it is necessary to know the nature of the active sites of the heterogeneous catalyst that result from the mechanical treatment of K_2PdCl_4. This will be the subject of our forthcoming studies.

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