



# Acetylene catalytic hydrochlorination over mechanically pre-activated $K_2PdCl_4$ salt: A study of the reaction mechanism <sup>☆</sup>

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## ABSTRACT

Mechanical pre-grinding of solid  $K_2PdCl_4$  in a vibratory micromill under acetylene or propylene atmosphere leads to the formation of catalyst for acetylene hydrochlorination by gaseous HCl. The active sites of the heterogeneous catalyst are Pd(II) chloro complexes with a coordination vacancy, capable reversibly form  $\pi$ -acetylene complexes. The HCl molecules participate in two steps of the reaction: acetylene chloropalladation (rate-limiting step) forming intermediate  $\sigma$ -chlorovinyl Pd(II) derivative and protonolysis of the last one.

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## 1. Introduction

Vinyl chloride is a monomer for industrially important polymeric material polyvinyl chloride, and catalytic hydrochlorination of acetylene is one of the methods for manufacture of vinyl chloride on an industrial scale. Commercial processes use  $HgCl_2$  supported on carbon [1–3], but this catalyst is highly toxic and shortly lived due to loss of mercuric chloride [4] encouraging to search for nonmercuric catalytic systems. It was recently found a few catalytic systems for acetylene hydrochlorination under heterogeneous conditions. Chloro  $Au^{III}$  complexes supported on carbon display high activity at high temperature (170–180 °C) [5,6]. Acetylene catalytic hydrochlorination occurs at ambient temperature over mechanically pre-activated  $K_2PtCl_6$  [7] (system 1) and  $K_2PtCl_4$  [8] (system 2) complexes. Recently, we have found [9] that the palladium(II) chloro complex  $K_2PdCl_4$ , an analogue of  $K_2PtCl_4$ , is

also catalytically active for acetylene hydrochlorination under similar conditions.

The ideas for mechanisms of acetylene catalytic hydrochlorination at least under homogeneous conditions are well developed [10]. The reaction (Scheme 1) begins with  $\pi$ -coordination of C–C triple bond to a metal center (steps 1–2). Further attack by external nucleophile on a  $\pi$ -coordinated acetylene (step 3) yields an intermediate product of *trans*(anti)-addition of a nucleophile and metal complex to the triple bond. An intermediate product of *cis*(sin)-addition is formed in case of attack by a coordinated nucleophile (step 3'). Protonolysis of these intermediates (step 4) gives rise to the final products with the same stereochemistry.

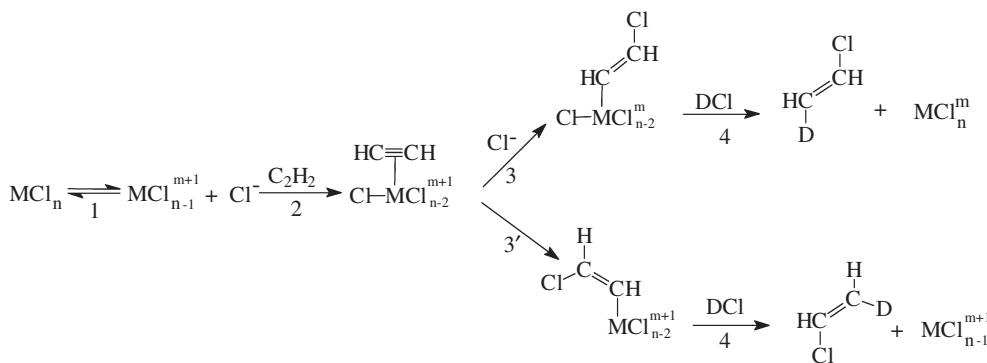
Reasoning from relations between homogeneous and heterogeneous catalysis, it could be expected that heterogeneous catalytic hydrochlorination of acetylene is controlled by the same mechanism. However, some questions regarding mechanistic details of heterogeneous reaction arise. For example, how does the chlorometallation step 3 occur in the absence of free chloride ions as external nucleophiles under heterogeneous conditions? Or how does chloro ligands dissociation (step 1) occur in the absence of solvation?

In this paper, a study of the reaction mechanism of acetylene heterogeneous catalytic hydrochlorination over mechanically pre-activated  $K_2PdCl_4$  salt (system 3) is presented.

<sup>☆</sup> Dedicated to Professor Christian Bruneau, University of Rennes, France, on the occasion of his 60th birthday.

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**Scheme 1.** The reaction mechanism for homogeneous acetylene catalytic hydrochlorination [10].

## 2. Experimental

### 2.1. Catalyst preparation and characterization

The palladium salt  $K_2PdCl_4$  was prepared according to standard techniques [11] and was recrystallized and preliminary dried for 3 days in a desiccator at 120 °C before use. The increase in the drying time did not considerably influence the kinetics of the reaction. All further manipulations with the salt were carried out in a dry glove box.

The  $K_2PdCl_4$  (0.25 g) powder was pre-ground before a run in a vibroreactor containing grinding bodies made of glass. A vibratory micromill MMVE-0.005 was used with specific power intensity ca.  $I = 15$  W/kg. The specific dose of mechanical energy, which consumed by powder, was determined [12] as  $D = I \cdot t$ , where  $t$  is the time of mechanical treatment. Specific area of the powders was determined by BET procedure from argon desorption.

The X-ray diffraction study was performed with DRON-3 instrument in monochrome  $Cu\ K\alpha$  irradiation using Ni-filter.

The X-ray photoelectron spectroscopy (XPS) measurements were performed using an EC-2402 instrument equipped with energy analyzer PHOIBOS-100\_SPECS and ion gun IQE-11/35. The slow electron gun FG-15/40 was used for compensation of dielectric surface charging. The spectra were excited by  $Mg\ K\alpha$  ( $E = 1253.6$  eV,  $P = 300$  W) irradiation.

The surface morphology of salt samples was observed by scanning electron microscopy (SEM) JSM-6490LV (JEOL, Japan). The elemental analysis of powders performed using a SEM instrument equipped with energy-dispersive X-ray spectrometer INCA Penta Fet  $\times 3$  (OXFORD Instrument, England).

### 2.2. Gaseous substrates preparation

Acetylene was prepared according to the standard techniques [13]. Gaseous HCl (DCl) was obtained by the reaction of calcinated KCl and  $H_2SO_4$  ( $D_2SO_4$ ). The gases obtained were dried over  $P_2O_5$  or calcinated  $CaCl_2$  before use. Preparation of pure isotopomer DCl is difficult because of fast isotope exchange with traces of moisture. The released gaseous HCl/DCl mixture was collected in thoroughly dried syringe of 50-ml capacity. The reactor and IR gas cuvette with windows made of KBr were preliminary cleaned out by blowing through with dry argon. Then, they were filled in by the HCl/DCl mixture. The DCl content in a DCl/HCl mixture was estimated as a ratio of integral intensities of IR bands corresponding to DCl to HCl stretching vibrations. We took into consideration that at the same conditions the intensity of HCl band is approximately twice as high as for DCl band [14]. The Bruker Tensor 27 instrument was used for determining isotope content in the HCl/DCl mixture.

### 2.3. Chemisorption of active gases by the catalyst

Gaseous CO was obtained by the reaction of formic acid with  $H_2SO_4$  at 80 °C [13]. After the mechanical treatment was stopped, the reactor containing  $K_2PdCl_4$  powder was blown through with dry argon, and then with 60 ml of CO and was hermetically sealed off. After 1.5 h, the solid content of the reactor was poured out. The DRIFT-spectra for mechanoactivated  $K_2PdCl_4$  powders in the mixture with  $BaF_2$  were registered. The Bruker Tensor 27 instrument equipped with diffuse reflection of light device Specac was used.

The reactor containing  $K_2PdCl_4$  salt mechanically pre-activated under acetylene was cleaned out by blowing through with dry argon. Then, it was filled up with 10  $\mu$ l of pyridine and sealed up. After an hour, the salt was poured out of the reactor, and the weighted powder was dissolved in 1 M solution DCl in  $D_2O$ . The  $^1H$  NMR-spectra of pyridinium chloride were registered using AVANCE-II-400 spectrometer (Bruker BioSpin GmbH) operating at 400 MHz. Sodium benzoate was used as an internal weight standard.

### 2.4. Kinetics of acetylene hydrochlorination monitoring

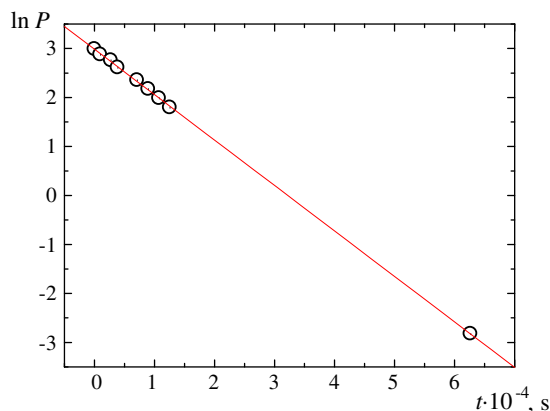
The reactions were carried out in a closed reactor of 13.7 ml capacity. The reactor containing mechanically pre-activated catalyst was blown through with dry argon. Then, it was filled with gaseous HCl and closed with a rubber seal. After that, ca. 1 ml of acetylene was fed into reactor through a rubber seal. All the reactions were carried out at 18 °C and continuous shaking providing a kinetic mode for the reactions passing. Acetylene consumption and vinyl chloride accumulation were monitored by GLC using an LKhM-8-MD chromatograph with a flame-ionization detector and equipped with data acquisition system MultiChrom Ampersand. The sampling of the gas phase was performed by means of a dosing syringe with the fixed volume through the rubber gasket.

## 3. Results

### 3.1. Reaction kinetics and selectivity

The mechanical pre-activation of dry  $K_2PdCl_4$  salt (system 3) under acetylene atmosphere produces a catalyst for acetylene hydrochlorination with gaseous HCl. Acetylene hydrochlorination proceeds very slowly on the surface of  $K_2PdCl_4$  salt, which was mechanically pre-activated in the air. Preliminary mechanical treatment of  $K_2PdCl_4$  under acetylene or propylene is necessary to get the active catalyst.

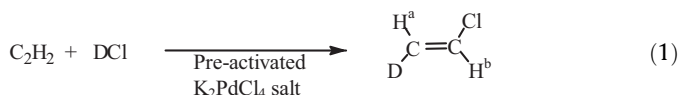
The catalytic reaction occurs at ambient temperature and requires no continuous milling. In an excess of HCl, the rate of acetylene uptake from the gas phase of the closed reactor follows the first-order kinetic equation  $k_{ap} = -\frac{d(\ln P)}{dt}$  ( $P$  is a partial pressure of



**Fig. 1.** Typical kinetics for acetylene uptake from the closed reactor under excess of HCl; the linear anamorphosis of the first-order rate law.

acetylene) (Fig. 1) as in the system 1. The vinyl chloride yield based on the amount of acetylene consumed in the reaction is close to 100%. In contrast to the system 2 [8], the mechanically pre-activated  $K_2PdCl_4$  salt invokes hydrochlorination of a double bond as well, for example, the reaction of propylene yields *iso*-propyl chloride.

Acetylene hydrochlorination reaction proceeds in the catalytic mode: no substantial decrease in the catalytic activity is observed after realization of more than 150 catalytic cycles (TON) in terms of surface palladium atoms, or more than 1.7 catalytic cycles in terms of the bulk palladium. The stereochemistry of the product resulting from acetylene deuteriochlorination corresponds to the *trans* (anti)-addition<sup>1</sup> of the chlorine and deuterium atoms to the triple bond of acetylene (Eq. (1)) just as in the systems 1 and 2.



The  $k_{ap}$  values determined at ca. 1 atm partial pressure of HCl and at approximately three times lower partial pressure of HCl are equal within the limits of experimental error. This coincidence of the  $k_{ap}$  values can be a consequence of HCl molecules nonparticipation in the rate-limiting step of the reaction; otherwise, the alternation of surface HCl concentration under these conditions should be neglected.<sup>2</sup> As will be shown below (Section 3.3), the latter situation actually takes place.

### 3.2. Preparation and characterization of the catalyst

#### 3.2.1. Formation of the catalyst in the course of $K_2PdCl_4$ mechanical pre-activation

The specific surface area of the catalyst increases monotonically with the duration of pre-grinding of the salt (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 saturation curve (Fig. 2) and is described by the equation

$$S_{sp} = S_0 + S_{sp}^* (1 - e^{-\eta_s D_{sp}}), \quad (2)$$

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, and  $\eta_s$  is inverse value of specific work for a new surface formation.

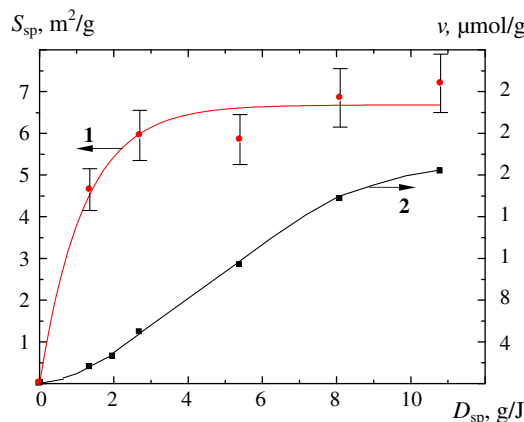
<sup>1</sup> <sup>1</sup>H-NMR in  $CDCl_3$  solution,  $\delta$ , ppm: 5.52 ( $H^a$ ), 6.31 ( $H^b$ );  $J(H^aH^b) = 14.75$ ,  $J(H^bD) = 1.03$  Hz.

<sup>2</sup> This is possible, for example, in the case of ultimate Langmuir's or multilayer surface filling with HCl molecules.

**Table 1**

Dependence of the specific surface area of the  $K_2PdCl_4$  salt and the apparent rate constant of catalytic acetylene hydrochlorination on the duration of mechanical pre-activation of the catalyst (0.25 g of  $K_2PdCl_4$ ).

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



**Fig. 2.** The dependence of the catalyst surface area  $S_{sp}$  and the quantity  $v$  of the vinyl chloride liberated in the course of  $K_2PdCl_4$  powder pre-grinding under acetylene on the specific dose of mechanical energy  $D_{sp}$  absorbed by the powder.

**Table 2**

Values of  $S_{sp}^*$ ,  $\eta_s$ ,  $k_{max}^*$ , and  $\eta$  in Eqs. (2) and (4).

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)
$K_2PdCl_4$	$6.7 \pm 0.7$	$8 \pm 2$	$6.8 \pm 0.6$	$3.2 \pm 0.6$
$K_2PtCl_6$ [20]	$17.3 \pm 0.3$	$6 \pm 1$	–	–
KCl [15]	$0.42 \pm 0.04$	$0.60 \pm 0.05$	–	–

The parameters of Eq. (2) are listed in the Table 2, and the earlier found  $S_{sp}^*$  and  $\eta_s$  values for ionic crystals of KCl [15] and  $K_2PtCl_6$  [16] are given for a comparison. The values for specific work of a new surface formation for the  $K_2PdCl_4$  (~12.5 J/g) and  $K_2PtCl_6$  (~16.7 J/g) ionic crystals are close to each other and significantly lower than for KCl (~170 J/g). The latter result is in qualitative agreement with the expectations since the KCl lattice is more compact than the  $K_2PdCl_4$  and  $K_2PtCl_6$ .

A mechanical treatment of the  $K_2PdCl_4$  powder under acetylene (propylene) is accompanied by vinyl (*iso*-propyl) chloride liberation in a trace amount. The source of chlorine atom, which is a part of chlorine-containing organic compounds formed, can be only  $K_2PdCl_4$  complexes. It means that stoichiometric consequence of such a tribochemical reaction is the formation of palladium(II) complexes with a deficit of chloro ligands ( $Pd^+$ ) besides of the above-mentioned organic products.

The typical kinetic curve for vinyl chloride accumulation is S-shaped (Fig. 2). In the beginning of the grinding, the induction period is observed. This initial section of the curve corresponds to the period when absorbed mechanical energy is transformed mainly in the channel of surface development. The vinyl chloride accumulation in the course of mechanical treatment occurs more efficiently after attainment of the ultimate value of the catalyst specific surface.

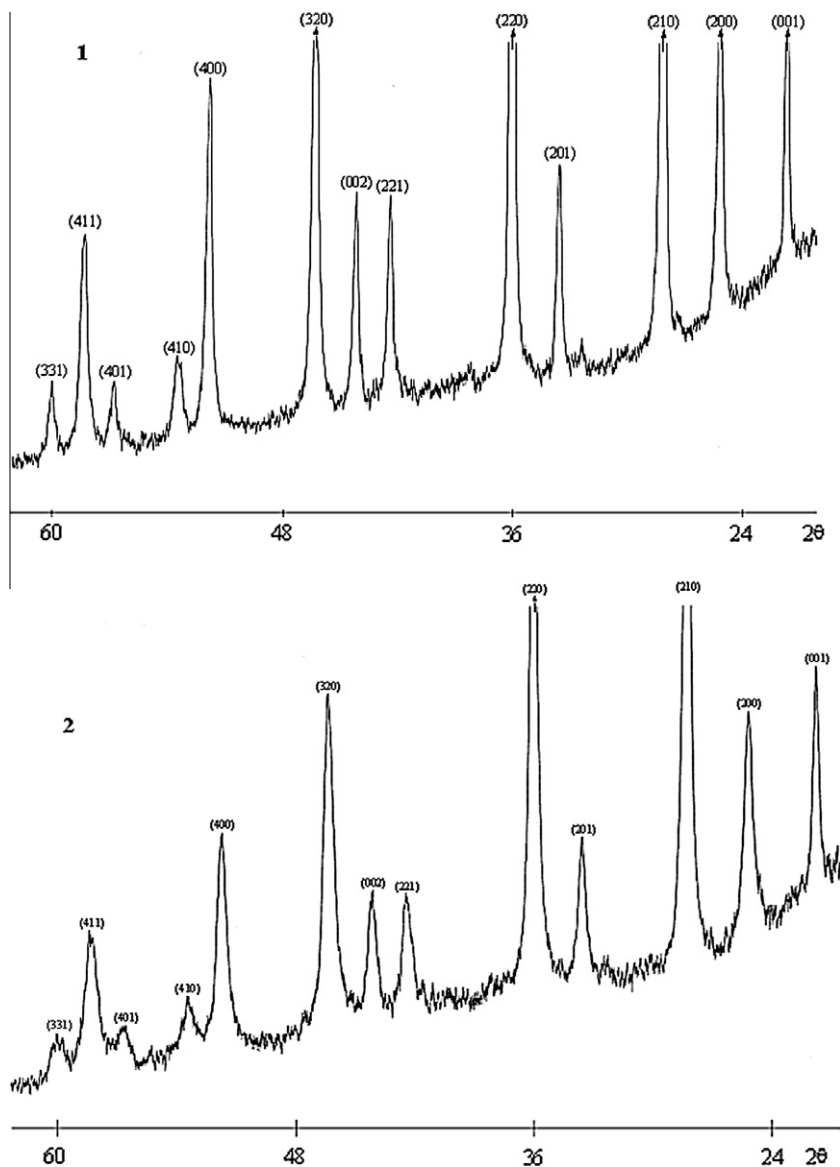


Fig. 3. Diffraction pattern for polycrystalline  $K_2PdCl_4$  samples mechanically pre-treated in air (sample 1) and acetylene (sample 2).

### 3.2.2. X-ray diffraction

The X-ray diffraction patterns (Fig. 3) for  $K_2PdCl_4$  samples mechanically activated in the air (sample 1) and acetylene (sample 2) contain all that Bragg's reflections that are characteristic for the single phase  $K_2PdCl_4$  salt. From comparison of X-ray diffraction patterns, it follows that the dispersive medium content does not influence the sample texture: pre-treatment under acetylene leads merely to decrease the granule's size and partial amorphization of near-surface layers. The estimation from the broadening of diffraction peaks according to Scherrer method gives decrease in crystallite size approximately by a factor of 1.6 for the sample 2 in comparison with the sample 1.

### 3.2.3. Scanning electron microscopy (SEM)

Mean sizes of powder particles in the samples 1 and 2 were 220 and 160 nm correspondingly. The difference in particles sizes by a factor ca. 1.4 fits with approximately twofold increase in specific surface area of the sample 2 in comparison with the sample 1. This result is similar to the one, which was obtained by X-ray diffraction method. The latter is indicative of similarity in the change of sizes of crystallites and powder micro particles.

It follows from the data of energy-dispersive X-ray spectrometry that elements intrinsic to  $K_2PdCl_4$  salt are present in the composition of the catalyst samples. The ratio  $\beta$  of atomic chlorine/palladium content in the surface layers of the catalyst monotone decreases with increase in duration of mechanical pre-activation of the initial salt under acetylene (Table 3). With the assumption that each of the formed palladium complexes  $Pd^*$  has lost no more than one chloro ligand, the fraction of such species on the surface of the catalyst,  $\varepsilon = \frac{N(Pd^*)}{N(Pd^*) + N(PdCl_4^{2-})}$ , equals to  $(4 - \beta)$ . The  $\varepsilon$  value depends on specific dose of mechanical energy absorbed by the powder according to the equation

$$\varepsilon = \varepsilon_{\max}(1 - e^{-\eta\varepsilon D_{sp}}), \quad (3)$$

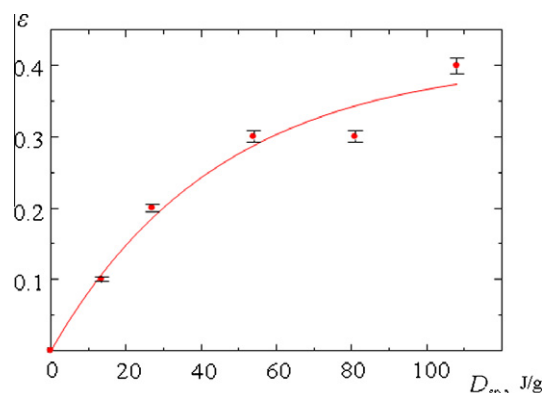
where  $\varepsilon_{\max}$  is the ultimate value of  $\varepsilon$ ,  $\eta\varepsilon$  is a quantity inverse to specific work of formation of palladium(II) complexes with a deficit of chloro ligands. Eq. (3) is in agreement with the experimental dependence of  $\varepsilon$  values on the specific dose of absorbed by the catalyst mechanical energy at  $\eta\varepsilon = (2.2 \pm 0.6) \times 10^{-2} \text{ g/J}$  (Fig. 4).

**Table 3**

Dependence of the ratio of chlorine/palladium content in the surface layers of the catalyst ( $\beta$ ), the quantity of chemisorbed pyridine ( $\nu(\text{PyH})$ ), and the value of IR band integral absorbance of chemisorbed carbon monoxide ( $A$ ) on the duration of mechanical pre-activation of the catalyst (0.25 g of  $\text{K}_2\text{PdCl}_4$ ).

$t$ (min)	$\beta$	$\nu(\text{PyH})$ (mmol/g)	$A$
0	–	–	–
15	$3.9 \pm 0.1$	$20 \pm 2$	$5.3 \pm 0.5$
30	$3.8 \pm 0.1$	$35 \pm 4$	$10.1 \pm 1.0$
60	$3.7 \pm 0.1$	$54 \pm 5$	$10.4 \pm 1.0$
90	$3.7 \pm 0.1$	$55 \pm 5$	$12.1 \pm 1.2$
120	$3.6 \pm 0.1$	$70 \pm 7$	–
60 <sup>a</sup>	$3.9 \pm 0.1$	–	–

<sup>a</sup> Mechanical pre-activation of the catalyst in air atmosphere.



**Fig. 4.** The dependence of the parameter  $\varepsilon$  on the specific dose of mechanical energy  $D_{sp}$  absorbed by the powder.

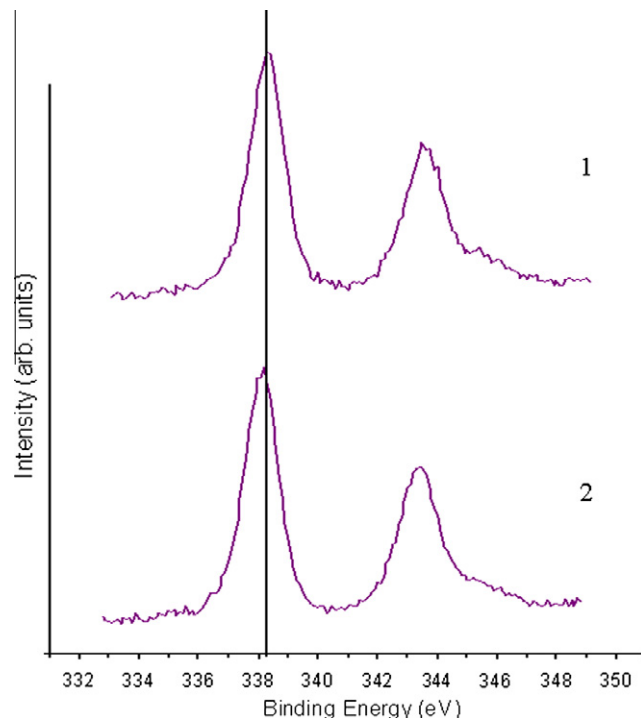
### 3.2.4. X-ray photoelectron spectrometry (XPS)

The X-ray photoelectron spectra for Pd3d-level of palladium atoms for  $\text{K}_2\text{PdCl}_4$  samples mechanically activated in the air (sample 1) and acetylene (sample 2) are presented in Fig. 5. The spectra contain well-resolved spin doublets corresponding to  $\text{Pd}3d_{5/2}$ - and  $\text{Pd}3d_{3/2}$ -levels of palladium atoms. The positions of peaks maxima for the two samples virtually coincide. The binding energy ( $E_b$ ) of  $\text{Pd}3d_{5/2}$ -level (338.3 eV) in the both samples corresponds to the palladium 2+ oxidation state. It follows from the ratio of integral intensities for Cl2p- and Pd3d-level photoelectron peaks ( $2.6 \pm 0.1$  for the sample 2 and  $3.0 \pm 0.1$  for the sample 1) that atomic ratio for Cl and Pd elements in the surface layers is less for the sample 2 in comparison with the sample 1. This result is in qualitative agreement with the above-mentioned data, obtained by means of energy-dispersive X-ray spectrometry. These results, which were obtained by different methods, within the range of experimental errors coincide quantitatively as well. The ratio  $\beta$  of the concerned elements (Table 3) is larger for the sample 2 in  $1.1 \pm 0.1$  (data of energy-dispersive X-ray spectrometry) and  $1.2 \pm 0.1$  (data of XPS) times.

### 3.2.5. Chemisorption of active gases by the catalyst surface

Palladium complexes  $\text{Pd}^+$  formed on the  $\text{K}_2\text{PdCl}_4$  surface in the course of mechanical pre-treatment can be metal complexes with a coordination vacancy. Otherwise, they could be four coordinated palladium(II) complexes, which contain bridged chloro ligands or ligands different from chloride ions. To discriminate these possibilities, it is feasible, for example, to expose the fresh surface of the pre-activated catalyst to an atmosphere of gases, molecules M of which are able to occupy a coordination vacancy forming strong complexes.<sup>3</sup> In the system 2, we used acetylene as such a gas [8],

<sup>3</sup> Chloro ligand substitution by M molecule we regard as improbable in the absence of solvation of the liberating chloride ion.



**Fig. 5.** The Pd 3d-level XPS-spectrum of palladium atoms for  $\text{K}_2\text{PdCl}_4$  samples mechanically activated in air (sample 1) and acetylene (sample 2).

and the band at  $2095\text{ cm}^{-1}$  corresponding to C–C triple bond stretching vibration was observed in the DRIFT spectrum. In case of palladium complexes, the last band was not found, conceivably, because of relative instability of  $\pi$ -acetylene palladium(II) chloro complexes [17]. So, in the present study, we used carbon monoxide or pyridine vapor as such a gas molecules M of which can be chemisorbed by surface palladium complexes with coordination vacancy forming stable  $[\text{PdCl}_3\text{M}]^-$  species.

The above-mentioned chemisorption really takes place. The following two bands at  $1907\text{ cm}^{-1}$  and  $1972\text{ cm}^{-1}$  corresponding to C–O bond stretching vibration were found in the DRIFT-spectrum for the catalyst sample that has being exposed to carbon monoxide atmosphere. The DRIFT-spectrum of the same sample but aged for 8 h at  $120\text{ }^\circ\text{C}$  or for 6 months at ambient temperature contains the only band at  $1907\text{ cm}^{-1}$ . Thus, the higher-frequency band can be attributed to C–O bond stretching vibration of physisorbed CO molecules and the band at  $1907\text{ cm}^{-1}$  to C–O bond stretching vibration of carbonyl ligands. The value  $A$  of the last band integral absorbency monotonically increases with increase in specific dose of mechanical energy absorbed by the catalyst (Table 3).

Pyridine, which has been adsorbed on the surface of mechanically pre-treated  $\text{K}_2\text{PdCl}_4$  salt, was identified by  $^1\text{H}$  NMR in the form of pyridinium cation after extraction by 1 M solution of DCl in  $\text{D}_2\text{O}$ . The quantity  $\nu(\text{PyH})$  of pyridine adsorbed by 1 g of pre-ground palladium salt within experimental errors was the same for freshly prepared and aged for 1.5 h at  $120\text{ }^\circ\text{C}$  samples, and this indicates a strong binding of pyridine by the surface. The  $\nu(\text{PyH})$  value increases with increase in duration of the catalyst pre-activation (Table 3). To exclude an influence of the catalyst surface area rise on pyridine adsorption, let us consider the value  $\nu(\text{PyH})$  attributed to the surface unit, that is, the surface concentration of pyridine,  $c = \nu(\text{PyH})/S_{sp}$ . The last value linearly depends on the parameter  $\varepsilon$  (Fig. 6). There is a linear correlation between the values of integral absorbency  $A$  of chemisorbed CO stretching vibration and  $\nu(\text{PyH})$  (Fig. 7) as well.

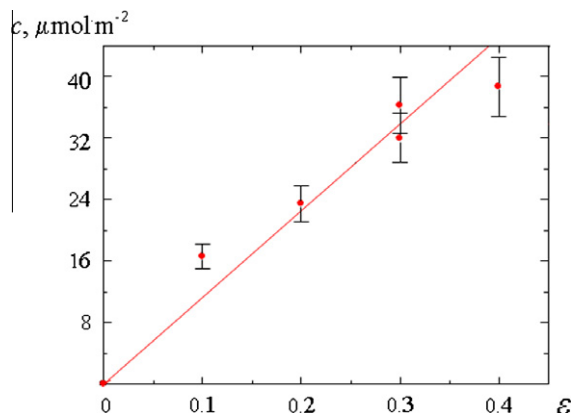


Fig. 6. The linear dependence of the surface concentration of chemisorbed pyridine  $c = \nu(\text{PyH})/S_{sp}$  on the  $\varepsilon$  parameter.

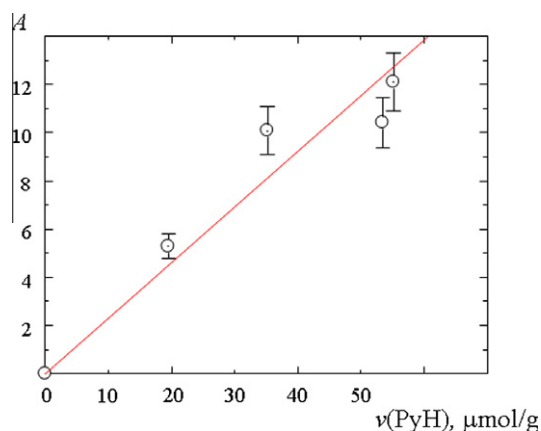


Fig. 7. The linear correlation between value of integral absorbance  $A$  of chemisorbed CO stretching vibration and the quantity of chemisorbed pyridine  $\nu(\text{PyH})$ .

These observations are in accordance with the assumption that palladium complexes with a deficit of chloro ligand  $\text{Pd}^+$  correspond to palladium(II) species with coordination vacancy.

### 3.2.6. Dependence of the catalyst activity on the duration of $\text{K}_2\text{PdCl}_4$ salt pre-grinding

The activity of the formed catalyst increases monotonically with increase in the salt pre-grinding continuance (Table 1). To rule out the influence of increase in the specific surface area of the catalyst on the values of apparent rate constant for acetylene consumption  $k_{ap}$ , let us consider the apparent rate constant per unit area of the catalyst surface, that is, the apparent value for specific catalytic activity,  $k^* = k_{ap}/S_{sp} \cdot m$ .

The dependence of  $k^*$  values on the specific dose of mechanical energy absorbed by the catalyst appears as a curve with saturation (Fig. 8) and obeys the equation

$$k^* = k_{\max}^* (1 - e^{-\eta D_{sp}}), \quad (4)$$

where  $k_{\max}^*$  is the limiting value for  $k^*$  and  $\eta$  is a quantity inverse to the specific work of active sites formation on the surface of the catalyst. The parameters of Eq. (4) are listed in the Table 2. The values of the constants  $\eta$  and  $\eta_\varepsilon$  within experimental errors coincide.

It follows from the Table 1 that 1-h-long mechanical pre-activation is sufficient for reaching a near-limiting value of specific surface area of the catalyst and for ensuring a fairly high catalytic activity. For this reason, subsequent experiments were carried

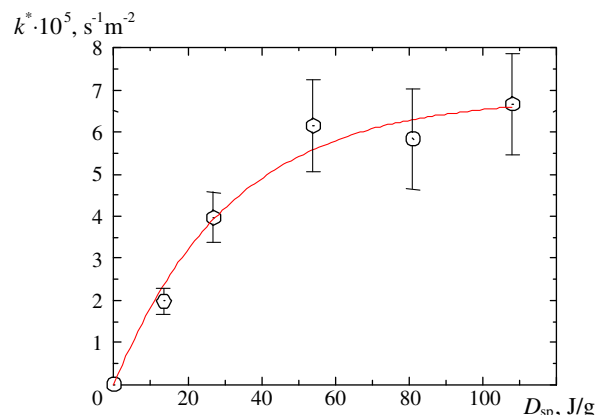


Fig. 8. The dependence of  $k^*$  value of the apparent rate constant per unit surface area of the catalyst on the specific dose  $D_{sp}$  of mechanical energy absorbed by the catalyst in the course of pre-grinding.

out with the catalyst samples, which have been mechanically pre-activated for 1 h.

### 3.3. Kinetic isotope effects

If HCl molecules are involved in the rate-determining step, the replacement of HCl with DCl will bring about a kinetic isotope effect. We found that the reaction rate is appreciably lower when the reaction is carried out in a DCl/HCl atmosphere (Table 4). The value of apparent rate constant  $k_{ap}^{\text{DCl}} = (3.2 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$  for acetylene consumption in DCl atmosphere was calculated from the equation [18] (Fig. 9)

$$k_{ap}^{\text{DCl}} = \frac{k_{ap}^{\text{DCl/HCl}} - k_{ap}\chi}{1 - \chi}, \quad (5)$$

where  $\chi$  is mole fraction of HCl in the DCl/HCl mixture. Hence,  $\text{KIE} = \frac{k_{ap}^{\text{DCl}}}{k_{ap}} = 2.8 \pm 0.4$ . Such a noticeable value for isotope effect proves the participation of a hydrochloric acid molecule in the rate-determining step of the overall catalytic reaction.

It is noticeable that the KIE value  $\gamma$  derived from the ratio of nondeuterated<sup>4</sup> and monodeuterated vinyl chloride yields in the DCl–HCl atmosphere

$$\gamma = \frac{\text{yield of } \text{H}_2\text{C}=\text{CHCl}}{\text{yield of } \text{HDC}=\text{CHCl}} \cdot \frac{1 - \chi}{\chi} \quad (6)$$

$\gamma = 6.8 \pm 0.7$  is noticeably larger than the above value of  $\text{KIE} = 2.8$  (Table 4).

### 3.4. Estimation of the TOF value

Acetylene does not react either with HCl molecules or with  $\text{Cl}^-$  and  $\text{H}^+$  solvated ions in the absence of a catalyst: acetylene C–C triple bond should be activated by coordination to a metal center [1,10] for the reaction progress. So, the Eley–Rideal mechanism for the reaction (1) with acetylene reacting directly from the gas phase, without adsorbing, could be excluded. If that is the case, the first-order kinetic in  $\text{C}_2\text{H}_2$  means that acetylene is adsorbed according to Henry's law  $[\text{C}_2\text{H}_2]_{\text{ads}} = K \cdot P$ , where  $[\text{C}_2\text{H}_2]_{\text{ads}}$  is the surface concentration of acetylene,  $K$  is the adsorption equilibrium constant.

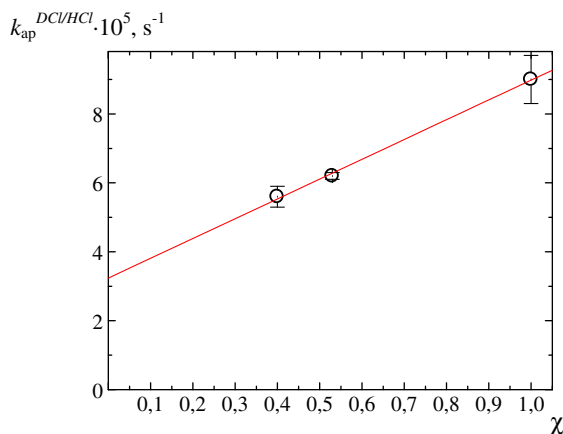
The experimentally measured values for apparent rate constant  $k_{ap}$  for acetylene consumption from the gas phase of closed reactor

<sup>4</sup> In independent experiments was shown that  $\text{C}_2\text{H}_3\text{Cl}$  does not undergo isotope-scrambling reaction with DCl under used conditions.

**Table 4**

Dependence of the apparent rate constant of acetylene consumption and the ratio of the nondeuterated and monodeuterated vinyl chloride yields on the value  $\chi$  of HCl mole fraction in the HCl/DCl mixture (0.25 g of  $K_2PdCl_4$ ).

$\chi$	$k_{ap}^{DCl/HCl} \times 10^5 \text{ (s}^{-1}\text{)}$	$\frac{H_2C=CHCl \text{ yield}}{HDC=CHCl \text{ yield}}$	$\gamma$
1.0	$9.0 \pm 0.7$	–	–
0.53	$6.2 \pm 0.1$	–	–
0.40	$5.6 \pm 0.3$	–	–
0.60	–	9.6	6.4
0.60	–	11.2	7.5
0.66	–	12.7	6.5
Average value	–	–	$6.8 \pm 0.7$



**Fig. 9.** The dependence of apparent rate constant  $k_{ap}^{DCl/HCl}$  for the reaction in DCl/HCl atmosphere on the mole fraction  $\chi$  of HCl in the DCl/HCl mixture.

depends on the ratio of gas phase volume and surface area of the catalyst. The true (i.e., in the absence of a gas phase) pseudo-first-order (excess of HCl) rate constant of acetylene uptake  $k$  is related to the experimental  $k_{ap}$  value by the equation [7]

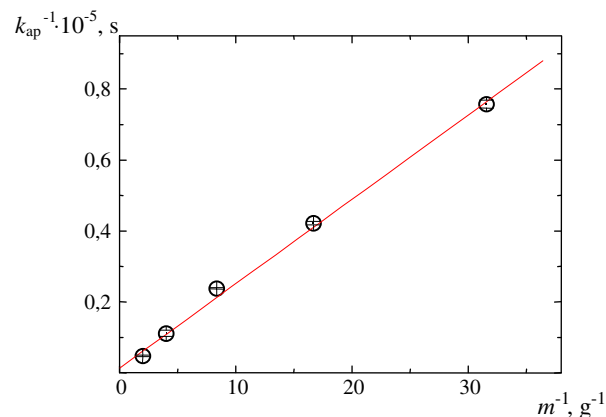
$$k_{ap} = \frac{k}{1 + \alpha\lambda}, \quad (7)$$

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 the temperature,  $S_{sp}$  is specific surface area of the catalyst, and  $m$  is the catalyst weight. Eq. (7) is in agreement with the experimental dependence of  $k_{ap}$  on the catalyst weight at  $k = (5 \pm 3) \times 10^{-4} \text{ s}^{-1}$  and  $K = (8 \pm 4) \times 10^{-10} \text{ mol m}^{-2} \text{ Pa}^{-1}$  (Fig. 10). Accomplishment of the Eq. (7) confirms the assumption that acetylene molecules undergo the reaction (1) when been adsorbed.

Let us use  $k$  and  $K$  values obtained above for the inferior limit of TOF magnitude estimation. The rate of vinyl chloride formation on  $1 \text{ m}^2$  of catalyst surface is  $k \cdot K \cdot P \sim 4 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$  in the case when the surface is covered by a monolayer (or multiplayer) of HCl molecules (see Section 3.1), and the partial pressure of acetylene is 1 atm. The superior limit for the number  $N_{pd}$  of palladium atoms located on  $1 \text{ m}^2$  of catalyst surface can be estimated from the lattice parameters  $a = b = 7.05 \times 10^{-10} \text{ m}$  and  $c = 4.1 \times 10^{-10} \text{ m}$  [19]:

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

where  $N_a$  is Avogadro's number. Hence, the inferior limit for the TOF value is equal to ca.  $7 \times 10^{-3} \text{ (mol C}_2\text{H}_2) \cdot (\text{mol Pd})^{-1} \text{ s}^{-1}$  in the case when the surface is covered by a monolayer (or multiplayer) of HCl molecules and the partial pressure of acetylene is 1 atm.



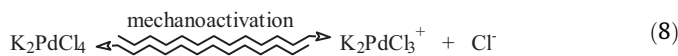
**Fig. 10.** The dependence of  $k_{ap}$  value on the mass of the catalyst. The linear anamorphosis of Eq. (7).

## 4. Discussion

### 4.1. The nature of the catalytic active sites

The following results seem to be essential for identification of the nature of the catalytic active sites. (1) The active catalyst is formed in the course of  $K_2PdCl_4$  solid salt pre-grinding under acetylene (propylene) but not in the air. (2) Such a mechanical treatment does not change the oxidation state of near-surface palladium complexes but leads to the formation of palladium(II) chloro complexes with a coordination vacancy,  $Pd^*$ . (3) There is a linear correlation between the apparent values for specific catalytic activity  $k^*$  and the values  $\varepsilon$  of the fraction of the surface  $Pd^*$  complexes (Fig. 11).

These results are consistent with the assumption that mechanical activation of  $K_2PdCl_4$  solid salt leads to the formation of active sites, which are palladium(II) species with coordination vacancy, and interstitial chloride ions:



The same kind of surface defects, that is, complexes with a coordination vacancy, are generated in the course of mechanical grinding of the similar  $K_2PtCl_4$  or  $K_2PtCl_6$  solid salts [20].

The  $K_2PdCl_4$  salt grinding under acetylene (propylene) as compared with air creates higher surface concentration of species with coordination vacancy owing to shift of the Eq. (8) to the right because of tying up of chloride-ions in the corresponding chlorine-containing organic compounds (vinyl chloride or *iso*-propyl chloride). Probably, this is a reason for the differences in catalytic activities of  $K_2PdCl_4$  salt pre-activated under above-mentioned "active" gases and in the air. The question concerning the origin of hydrogen atom, which is a part of the formed vinyl chloride (*iso*-propyl chloride) in the tribochemical reaction of acetylene (propylene) with  $K_2PdCl_4$ , remains open. The source of these H atoms could be, for example, water molecules adsorbed on the surface. In this case, the formation of deuterated vinyl chloride could be expected in the presence of  $D_2O$  vapor. But, we failed to detect the deuterated product in the tribochemical reaction of acetylene with  $K_2PdCl_4$  and  $D_2O$  vapor<sup>5</sup>: the formed vinyl chloride did not contain deuterium atom. Nevertheless, such an outcome could be a consequence of high kinetic isotope effect for monodeuterated vinyl chloride formation in the tribochemical reaction and low total yield of the accumulating products.

<sup>5</sup> 1  $\mu\text{l}$  of  $D_2O$  was injected into vibroreactor before grinding.

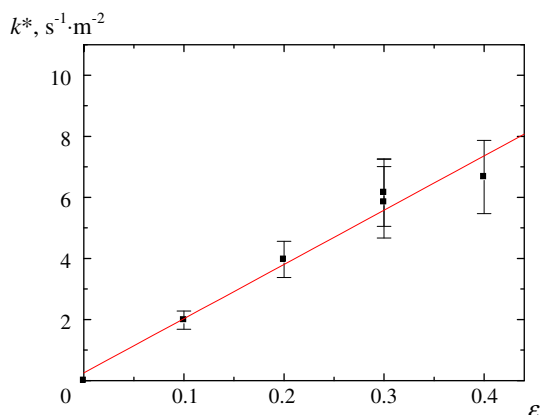


Fig. 11. Linear correlation between  $k^*$  values and the fraction  $\epsilon$  of the surface palladium complexes with a deficit of chloro ligands.

#### 4.2. Kinetics of the reaction

Both acetylene and HCl adsorb, and the adsorbed molecules undergo the bimolecular reaction (1) but they do not compete for the same sites on the catalyst surface: otherwise, the values of apparent rate constant for acetylene uptake would be different at different partial pressures of HCl. The nature of the active sites of the catalyst provides an explanation of that apparent contradiction. Because of their local positive charge, the surface complexes with a coordination vacancy electrostatically attract polar HCl molecules getting covered with them (Scheme 2). But, hydrochloric acid molecules in contrast to acetylene cannot be coordinated to the metal center occupying coordination vacancy. On the other hand,  $\pi$ -acetylene complex formation does not change the charge of the site and, therefore, does not diminish electrostatic interaction of it with HCl molecules. So, hydrochloric acid and acetylene molecules are adsorbed at the same sites and do not compete because of different mechanisms of their adsorption: nonpolar acetylene molecules are bound by donor–acceptor interaction with the metal center, and polar HCl molecules are bound by electrostatic forces. The following mechanism (Scheme 2) is consistent with the first order in acetylene, zero order in HCl, and also with DCI isotope effect.

The first order in acetylene (excess of HCl) is observed in the systems 1 [7] and 3 in contrast to the system 2, where kinetics of acetylene consumption follows the zero-order rate law [8]. The zero order in acetylene for the system 2 was explained by fast acetylene chemisorption through its bonding in  $\pi$ -complex by  $\text{Pt}^{\text{II}}$

species with a coordination vacancy. In this case, the surface concentration of the chemisorbed substrate is almost independent of acetylene partial pressure providing the zero-order rate law for acetylene uptake. Unlike  $\text{Pt}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$  chloro complexes do not form stable  $\pi$ -complexes [17] and are similar to  $\text{Pt}^{\text{IV}}$  chloro complexes in this regard. This provides an explanation for the same reaction order regarding acetylene in the systems 1 and 3.

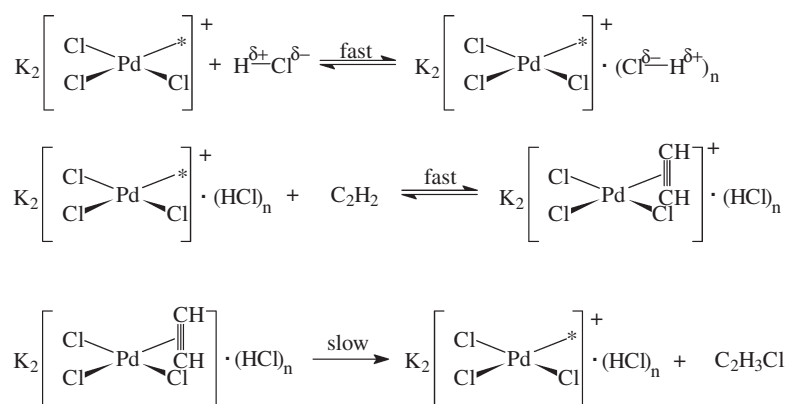
Since the reaction order in acetylene for the systems 1 and 3 is the same, it is possible to compare the catalytic activities of the corresponding metal complexes under the same conditions (Table 2). Clearly, the true rate constants  $k$  for acetylene consumption in the systems 1 and 3 are similar. Under assumption that electrophilic properties of metal complexes play a key role in the multiple C–C bonds activation, the approximate equality of the  $k$  values in the systems 1 and 3 means that the  $\text{Pt}^{\text{IV}}$  and  $\text{Pd}^{\text{II}}$  chloro complexes possess similar electrophilic reactivities. The inferior limit for the specific catalytic activity in the system 3 is approximately 30 times lower because of less acetylene adsorption equilibrium constant in this system. At equal partial pressure of acetylene, the surface substrate concentration in the system 1 is one order of magnitude higher providing greater consumption rate.

Pre-ground palladium(II) chloro complexes in contrast to platinum(II) are able to activate double C–C bonds as well. This is obviously a consequence of higher electrophilic reactivity of  $\text{Pd}^{\text{II}}$  as compared with  $\text{Pt}^{\text{II}}$  chloro complexes.

#### 4.3. Reaction mechanism and kinetic isotope effect values

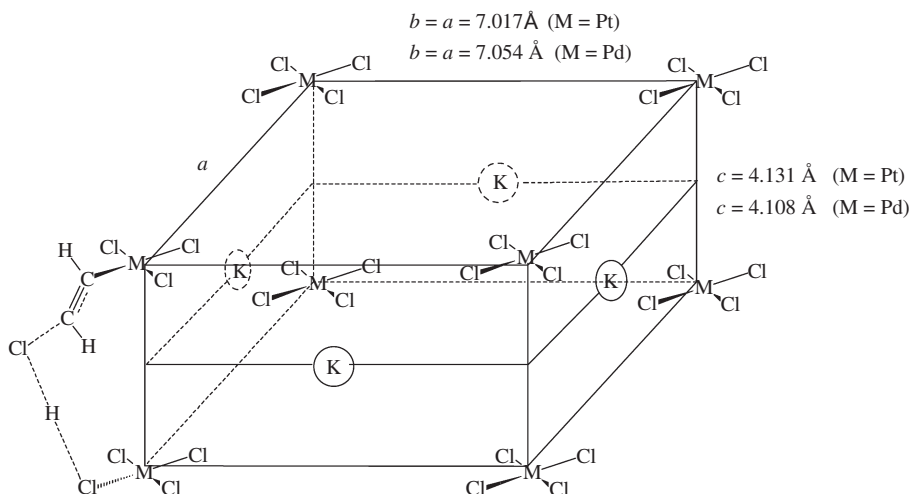
To explain the reaction (1) mechanism, it is necessary to know the origin of the chlorine atom, which is a part of vinyl chloride formed. The sources of chlorine atoms could be HCl molecules, ligands of the chloro metal complexes and interstitial chloride ions, arising [20] under mechanical pre-treatment of  $\text{K}_2\text{PdCl}_4$  salt. Reasoning from the hydrochlorination stereoselectivity, the inner sphere chloro ligands participation should be excluded [10]. Relatively, small amounts of the interstitial chloride ions formed under  $\text{K}_2\text{PdCl}_4$  mechanical pre-treatment could not provide the catalytic reaction run. The last conceivable possibility is left: chlorine atom, which is a part of vinyl chloride formed, originates from HCl molecule.

The participation of HCl molecules in the rate-limiting step of the reaction follows from the observation of a noticeable kinetic isotope effect (KIE) when HCl atmosphere is replaced by DCI/HCl mixture. The KIE value for the overall catalytic reaction ( $2.8 \pm 0.4$ ) essentially differs from the value  $\gamma = 6.8 \pm 0.7$  of kinetic isotope effect derived from the ratio of nondeuterated and monodeuterated vinyl chloride yields in the DCI/HCl atmosphere. Therefore, HCl molecules are involved in two different steps of

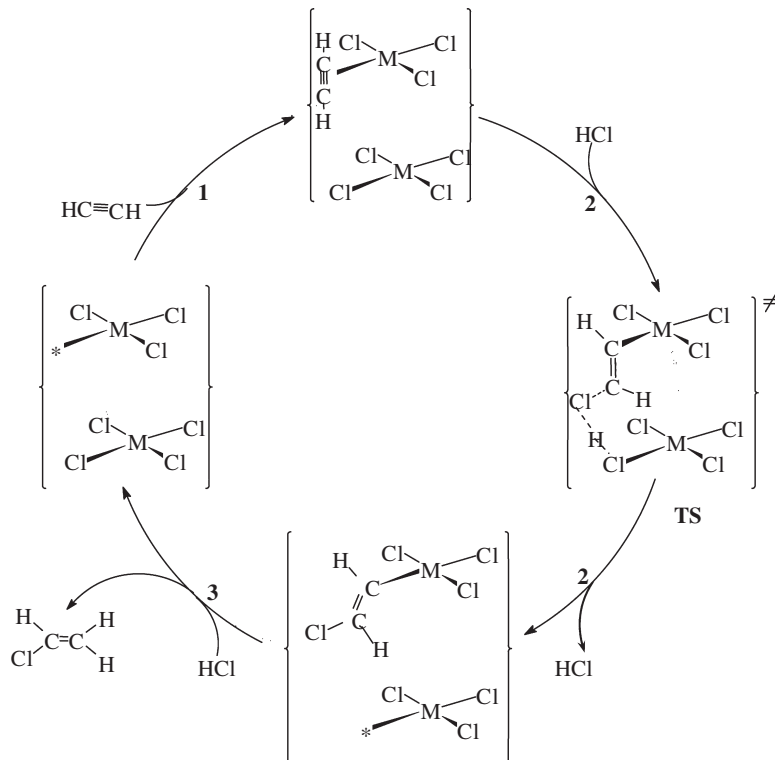


Scheme 2. Mechanism for the reagents adsorption and acetylene catalytic hydrochlorination.





**Scheme 3.** The low-level cell of  $K_2MCl_4$  crystals and the plausible structure of the transition state TE for the acetylene chlorometallation step in the systems 2 ( $M = Pt$ ) and 3 ( $M = Pd$ ).



**Scheme 4.** The stepwise mechanism for catalytic acetylene hydrochlorination in the systems 2 ( $M = Pt$ ) and 3 ( $M = Pd$ ); adjacent metal complexes located on the (100) crystal plane are shown in braces.

the catalytic reaction and one of them is rate-limiting. Hydrogen (deuterium) atom is introduced into the formed vinyl chloride in the faster (i.e., not rate limiting) step. Consequently, the limiting step leads to chlorine atom incorporation into the final product.

We may assume that the rate-limiting step for the overall catalytic reaction is chloropalladation of acetylene, and HCl (DCl) molecules are involved in this transformation. The limiting step of the catalytic acetylene hydrochlorination in closely related system 2 is also acetylene chlorometallation under the action of HCl molecule and the KIE value is  $3.7 \pm 0.4$  [21]. Reasoning from the isomorphism of the crystalline structures and affinity between lattice parameters for  $K_2PdCl_4$  [19] and  $K_2PtCl_4$  [22] crystals, it could be

expected a similarity in the reaction mechanisms as well. The reaction occurs [8] via HCl molecule attack onto  $\pi$ -acetylene complex, located on the (100) crystal plane (Scheme 3). A local positive charge of the crystal lattice defect in the form of monoanion  $[M(\eta^2-C_2H_2)Cl_3]^-$  is favorable to a chlorine atom of polar HCl molecule attack onto  $\pi$ -acetylene complex. The reaction occurs as a concert process in which concurrently with the rupture of  $M-(\eta^2-C_2H_2)$ , H–Cl bonds, and M–Cl bond in the metal complex adjacent to  $\pi$ -acetylene complex the new M–C( $sp^2$ ), C( $sp^2$ )–Cl, and H–Cl bonds are formed (Scheme 3). The distance between metal complexes on the (100) crystal plane  $\sim 4 \text{ \AA}$ , in contrast to  $\sim 7 \text{ \AA}$  on the (001) crystal plane [19,22], and bonds lengths of H–Cl



nyl palladium(II) derivative. Fast protonolysis of the latter species under the action of HCl/DCl yields isotopomers of vinyl chloride and is responsible for the second KIE value.

Such a mechanism for chloropalladation step provides an explanation for high stereoselectivity of catalytic hydrochlorination reaction as well as for a mode of the catalyst's active sites regeneration and excludes extremely unfavorable heterolysis of H–Cl bond with H<sup>+</sup> formation in the absence of solvation.

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