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Catalytic hydrochlorination of acetylene by gaseous HCl on the surface of mechanically pre-activated K_2PtCl_6 salt

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Abstract

Acetylene undergoes hydrochlorination by gaseous HCl in the absence of a solvent during mechanical treatment of K_2PtCl_6 powder. Acetylene consumption and vinyl chloride formation do not stop when mechanical treatment is interrupted. In the DCl atmosphere, *trans*-D-vinyl chloride is formed. It was assumed that the catalytic reaction proceeds on the active sites, which are K_2PtCl_6 lattice defects in the form of topologically bound couple $PtCl_4^{2-}$–$PtCl_5^{-}$ generated by mechanical pre-activation of K_2PtCl_6 salt under acetylene. Reaction begins with acetylene chloroplatination by a coordinatively unsaturated Pt(IV) complex producing intermediate formation of β-chlorovinyl Pt(IV) derivative. The complementary reduction of this intermediate by Pt(II) yielding the corresponding Pt(II) organometallic derivative and protonolysis of the latter species result in vinyl chloride formation and regeneration of active site of the catalyst.
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Keywords: Hydrochlorination; Protonolysis; Lattice defects

1. Introduction

Acetylene hydrochlorination is used in vinyl chloride manufacture and hazardous $HgCl_2$ supported on activated carbon is a commercial catalyst [1]. The high toxicity of the catalyst forces out the search for nonmercuric catalytic systems. Complexes of various transition metals are known to catalyze acetylene hydrochlorination under homogeneous conditions: Cu[I] [1], Au[III] [2], Pt[II] [3,4], Pd[II] [5,6] and Rh[III] [7]. Platinum and palladium complexes possess high activity but are too unstable. Under heterogeneous conditions, complexes of platinum(II) and gold(III) [8,9] when used on activated carbon display activity, Au catalyst is better; and the highest activity was found [10] for supported liquid-phase rhodium(III) catalyst on activated carbon. However, these heterogeneous reactions require high temperature (170–180 °C).

Metal complex catalysis for acetylene hydrocarbon transformation involves, as a rule, the intermediate formation of organometallic species with a metal–carbon σ-bond [11]. Actually, the selectivity and efficiency of catalytic systems are often controlled by the facility of formation and consequent transformations of intermediates. One of the routes for formation of organometallic σ-bonded intermediates consists of a nucleophilic attack by inner- or outersphere nucleophiles onto an intermediate alkyne π-complex. If the coordinated acetylene is attacked by an external nucleophile, the *trans* addition of the latter and metal to the triple bond takes place, otherwise a product of *cis*-addition is formed. In any case, an intermediate acetylene π-complex formation is absolutely necessary for further activation of a triple C–C bond.

It is well known that platinum(IV) complexes with simple inorganic ligands do not form stable π-complexes with unsaturated species [12], and this was perhaps the reason for the fact that Pt^{4+} has been considered as inert toward alkynes. We have found that iodo Pt(IV) complexes in acidic aqueous or methanol solutions catalyze acetylene hydroiodination

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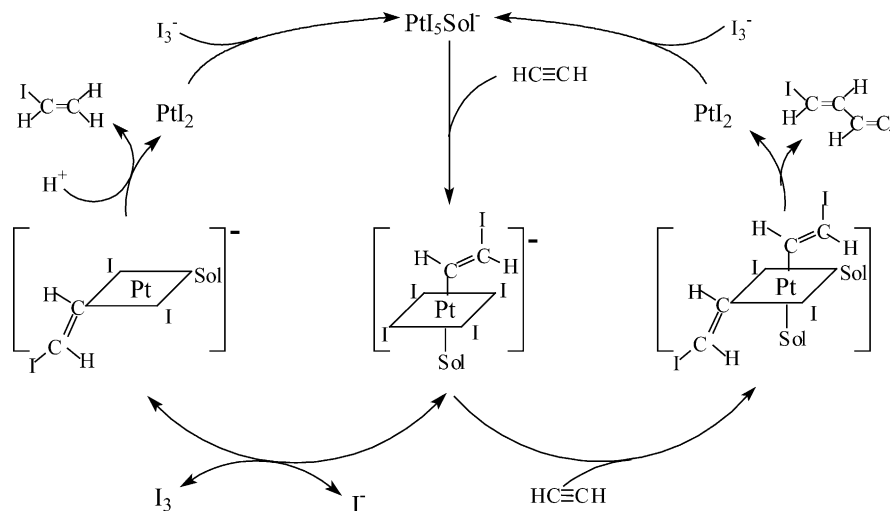
Scheme 1.

into vinyl iodide [13]. In the absence of an acid but in the presence of iodine iodo platinum(IV) complexes catalyze acetylene dimerization, which is accompanied by addition of iodine to give (*E,E*)-1,4-diiodobutadiene-1,3 [14]. The reactions involve the iodoplatination step with the intermediate β-iodovinyl platinum(IV) complex formation [15]. In the case of acetylene catalytic hydroiodination the reduction of the intermediate by iodide ions to the appropriate derivative of platinum(II) and subsequent protonolysis of the latter species lead to vinyl iodide formation. In the absence of an acid the intermediate monovinyl platinum(IV) complex is trapped by another acetylene molecule yielding a divinyl derivative. Decomposition of the latter organoplatinum compound via reductive elimination step gives the diiodobutadiene as the final product (Scheme 1).

Chloroplatinate complexes under similar conditions are inert. Iodo platinum(IV) complexes are more labile than chloro ones because of the stronger *trans*-effect of iodide ligands, and this is perhaps the reason for a difference in the activities of chloro and iodo complexes. Recently, we have found [16] that mechanical disintegration of K_2PtCl_6 solid salt in a vibrational mill results in appearance and accumulation of coordinatively unsaturated Pt(IV) complexes as structural defects on the surface of the solid:

$$[PtCl_6]^{2-} \xrightarrow{\text{mechanical activation}} [PtCl_5^*]^- + Cl^-, \qquad (1)$$

where $[PtCl_5^*]^-$ is a coordinatively unsaturated complex. If the lack of activity toward acetylene is associated with the absence of vacancies in the coordination sphere of chloro Pt(IV) complexes, then K_2PtCl_6 should be active under conditions of mechanical treatment.

We have experimentally tested this hypothesis, and this article reports the results.

2. Experimental

The reactions were carried out in a closed vibratory reactor containing grinding bodies made of glass. A vibratory micromill MMVE-0.005 was used with specific power intensity ca. $15\,W\,kg^{-1}$. Acetylene consumption and products 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 relative concentrations of acetylene (RH) and vinyl chloride (R′Cl) were determined as the ratios of the chromatographic peak areas for these compounds, $S(RX)$, to the area of the methane peak, $S(CH_4)$, which was used as an internal standard: $\phi(RX) = S(RX)/S(CH_4)$. The K_2PtCl_6 (0.3 g) or K_2PtBr_6 (0.3 g) powders were pre-ground for 1 h before a run—the period that was necessary for reaching the limit of the specific surface area. Then, the mixture of acetylene, methane (internal standard) and HCl was fed into the reactor via a rubber seal.

The platinum salts K_2PtX_6, K_2PtX_4 (X = Cl, Br) were prepared according to standard techniques [17] and were recrystallized before use.

Deuterium chloride was received by the reaction of NaCl and D_2SO_4. The liberated gaseous HCl/DCl mixture was consequently blown through IR gas cuvette (with windows made from NaCl) and the reactor charged with catalyst. The reactor filled up with HCl/DCl mixture was used for monitoring the acetylene hydrochlorination kinetics. DCl content in the DCl/HCl mixture was estimated as the ratio of areas under IR bands of DCl and HCl in the IR spectrum. The FTIR Perkin-Elmer Spectrum BX instrument was used.

^{1}H NMR measurements were performed in CD_3OD solutions using a Varian GEMINI instrument operating at 200 MHz. The residual acetylene and formed vinyl chloride were removed from the reactor by evacuation and/or blow-through with dry air before the extraction of
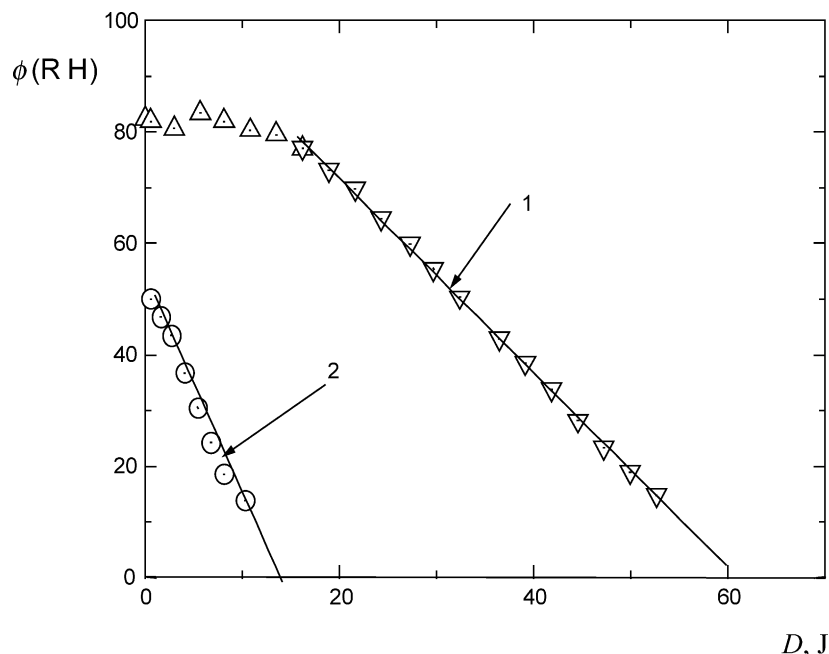
Fig. 1. Typical kinetic dependencies of acetylene consumption on the energy supplied during continuous mechanical treatment. Curve 1: without a K_2PtCl_4 additive and curve 2: with 10 mol% K_2PtCl_4 additive.

β-chlorovinyl platinum(IV) complex. The organoplatinum derivative formed on the platinum salt surface was extracted with CD_3OD.

To carry out chemical tests on the presence of β-chlorovinyl platinum(IV) complex, the latter was extracted with methanol as described above. The extract was dried in an air current without heating. Dry residue was dissolved in 3 ml of water. The aliquot (0.2 ml) of the solution obtained was added to the closed and temperature-controlled reactor containing 2 ml of aqueous solution of NaI (2.5 M)–$HClO_4$ (0.25–2.5 M)–I_2 (0–0.0366 M) at 60 °C. The kinetics of the organoplatinum(IV) derivative decomposition was derived from vinyl chloride and acetylene accumulation controlled by GLC.

Samples for investigation by means of X-ray photoelectron spectroscopy were prepared as described in [18]. Spectra were excited by Mg Kα ($h\nu = 1253.6$ eV) irradiation. The peak of C 1s (285.0 eV) was used for calibration of the spectra. Relative atomic concentrations were determined from the ratio of measured integral intensities of the X-ray photoelectron lines using Scofield's data on the cross sections of Mg Kα irradiation absorption [19].

3. Results

3.1. Reactions performed under continuous mechanical treatment

Under the conditions of vibratory comminution, K_2PtCl_6 causes acetylene hydrochlorination by gaseous HCl in the absence of a solvent. During mechanical treatment of a Pt(II) salt, K_2PtCl_4, no noticeable acetylene consumption was detected under analogous conditions, and vinyl chloride was not formed.[1]

A plot of the amount of acetylene consumed during K_2PtCl_6 treatment versus dose of energy consumed has two portions (Fig. 1, curve 1). In the beginning of the reaction, an induction period is observed. Then, acetylene consumption follows the zero-order rate law with respect to acetylene. The addition of K_2PtCl_4 to K_2PtCl_6 substantially shortens the induction period. This is suggestive of Pt(II) accumulation during the induction period because of K_2PtCl_6 reduction by acetylene.

Indeed, a noticeable reduction of Pt(IV) into Pt(II) was detected by X-ray photoelectron spectroscopy in the surface layers of K_2PtCl_6 solid salt mechanically treated under acetylene or propylene[2] (Table 1). If K_2PtCl_6 powder was mechanically treated in air this effect was not observed. A significant decrease of the element content ratio Cl/Pt in the surface layers of solid was also registered (Table 1).

Thus, one could draw the conclusion that disintegration of K_2PtCl_6 in the presence of unsaturated hydrocarbons mentioned above results in reduction of Pt(IV) into Pt(II) as well as in the formation of coordinatively unsaturated complexes on the surface.

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[1] Note that the situation is different in aqueous solutions: Pt(II) chloride complexes catalyze acetylene hydrochlorination, whereas Pt(IV) complexes do not show any catalytic activity [1].

[2] Platinum(II) was also detected in the surface layers of K_2PtCl_6 samples aged for long time in air. Only freshly recrystallized samples were free from admixtures of Pt^{2+} on the surface.

Table 1
Position of photoelectron peaks (eV) and ratio of elements content (atomic units) on the surface of K_2PtCl_6 samples after mechanical treatment in the atmosphere of different gases
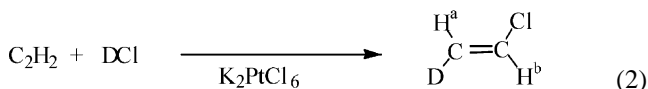
Sample	Pt $4f_{7/2}$ (Pt^{4+})	Pt $4f_{7/2}$ (Pt^{2+})	K $2p_{3/2}$	Cl 2p	K/Pt	Cl/Pt
K_2PtCl_6, ground in the propylene atmosphere	75.2 (26)	72.5 (74)	293.1	198.8	1.3	3.0
K_2PtCl_6, ground in the acetylene atmosphere	75.2 (34)	72.8 (66)	293.1	198.9	1.6	3.8
K_2PtCl_6 (recrystallized)	75.7 (98)	–	293.6	199.3	2.0	Was not measured
K_2PtCl_4	–	73.2	293.0	199.6	Was not measured	Was not measured

Calibration is based on the C 1s peak (285.0 eV). The percentages of the appropriate platinum states are given in parentheses.

3.2. Reactions on the surface of pre-activated K_2PtCl_6 in the absence of continuous mechanical treatment (the post-effect reactions)

Acetylene consumption and vinyl chloride formation still proceed when mechanical treatment is stopped. For active catalyst formation a preliminary mechanical treatment of K_2PtCl_6 in acetylene, ethylene or propylene atmosphere for an hour is necessary. The platinum salt pre-activated in atmosphere of other reductive gases—dihydrogen, carbon oxide, or iso-butane—does not demonstrate any appreciable activity. Platinum(II) salt, K_2PtCl_4 partially oxidized by chlorine under conditions of mechanical treatment is inactive, too.

Vinyl chloride formed in the atmosphere of DCl has a *trans*-configuration.[3]

$$C_2H_2 + DCl \xrightarrow{K_2PtCl_6} \begin{array}{c} H^a \\ C \\ D \end{array} = \begin{array}{c} Cl \\ C \\ H^b \end{array} \qquad (2)$$

Vinyl chloride and vinyl bromide (yield ratio is ≈6:1, respectively) are formed in parallel in the course of acetylene reaction on the surface of bromo platinum catalyst[4] in the presence of gaseous HCl under conditions of large excess of C_2H_2 with respect to HCl.

The first-order rate law describes acetylene uptake in the post-effect reaction in the atmosphere of HCl. The yield of vinyl chloride based on the amount of acetylene consumed in the reaction is close to 100%. No noticeable decrease in catalyst activity is observed after realization of eight turnover numbers based on bulk catalyst or 1700 based on platinum located on the surface of the catalyst.[5]

3.2.1. Estimation of turnover frequency value (TOF)

The values of rate constants for acetylene consumption from gaseous phase of the closed reactor $k_{eff} = -d(\ln \varphi(RH))/dt$ under conditions of approximately 20- and 3-fold excess of HCl with respect to acetylene, coincide within the range of experimental errors. This can be

a consequence of HCl molecules nonparticipation in the rate-limiting step of the reaction otherwise the alteration of HCl concentration on the catalyst surface under these conditions should be neglected. The latter is possible, for example, in the case of ultimate Langmuir's or multilayer surface filling with HCl molecules.

The participation of HCl molecules in the rate-limiting step of the reaction was proved by observation of a noticeable kinetic isotope effect when HCl atmosphere is replaced on DCl/HCl mixture. The rate constants values for acetylene consumption in the atmosphere of HCl and DCl/HCl mixture[6] were $k_{eff}^{HCl} = (3.4 \pm 0.2) \times 10^4 \, s^{-1}$ and $k_{eff}^{DCl/HCl} = (2.5 \pm 0.2) \times 10^4 \, s^{-1}$, respectively. The value $k_{eff}^{DCl} = 1.8 \times 10^{-4} \, s^{-1}$ of rate constant for acetylene consumption in DCl atmosphere was calculated from the Eq. [20], $k_{eff}^{DCl} = (k_{eff}^{DCl/HCl} - k_{eff}^{HCl}\chi)/(1 - \chi)$, where χ is mole fraction of HCl in the DCl/HCl mixture. Hence, the kinetic isotope effect value $k_{eff}^{HCl}/k_{eff}^{DCl} = 1.9$ is appreciable and this fact proves the participation of HCl molecules in the rate-determining step of the reaction.

The implementation of the first-order rate law for acetylene consumption in the heterogeneous reaction (2), obviously, means that acetylene is adsorbed according to Henry's equation:

$$[RH]_{ads} = K \times P(RH), \qquad (3)$$

where $[RH]_{ads}$ is the surface concentration of acetylene, K the constant of adsorption equilibrium, and $P(RH)$ is the partial pressure of acetylene. Indeed, in this case the total amount of acetylene in the reactor, $N(RH)$, can be presented by the equation:

$$N(RH) = \frac{V_g P(RH)}{RT} + S_{sp} \times m \times K \times P(RH), \qquad (4)$$

where V_g is the volume of gaseous phase of the reactor, S_{sp} and m are, respectively, the specific surface and mass of the catalyst. After differentiation of the Eq. (4) on time, we receive:

$$\frac{dN(RH)}{dt} = \frac{V_g}{RT}\frac{dP(RH)}{dt}\left(1 + \frac{1}{\alpha\lambda}\right), \qquad (5)$$

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[3] ^{1}H NMR in CDCl$_3$ solution, δ (ppm): 5.52 (H^a), 6.31 (H^b); J(H^{a}H^b) = 14.75, J(H^{b}D) = 1.03 Hz.

[4] The bromo platinum catalyst was formed by grinding of K_2PtBr_6 salt in the acetylene atmosphere for an hour.

[5] Specific surface area of the catalyst was 3 m^2/g.

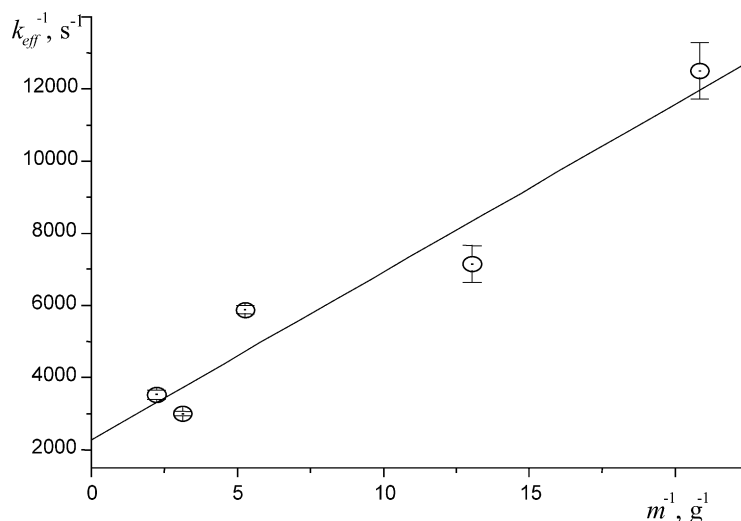[6] The estimated from IR spectrum content of DCl in the DCl/HCl mixture was ca. 58%.

Fig. 2. The dependence of k_{eff} on the mass of the catalyst. The linear anamorphosis of Eq. (8).

where $\alpha = (RT \times K)^{-1}$, $\lambda = V_g/S_{sp} \times m$. The $N(RH)$ value decreases in time in the course of the reaction, i.e.:

$$\frac{dN(RH)}{dt} = -k \times S_{sp} \times m \times [RH]_{ads}, \qquad (6)$$

where k is the first-order rate constant. Equating the right sides of Eqs. (5) and (6) and taking into account dependence (3) we arrive at desired first-order rate law for acetylene consumption from gaseous phase of the reactor:

$$\frac{dP(RH)}{dt} = -\frac{k}{1+\alpha\lambda} P(RH), \qquad (7)$$

From Eq. (7) it follows that experimentally determined value k_{eff} and the first-order rate constant k are bound by relation:

$$k_{eff} = \frac{k}{1+\alpha\lambda}, \qquad (8)$$

Eq. (8) satisfies experimental dependency of k_{eff} on the catalyst mass at $k = (4.4 \pm 1.5) \times 10^{-4}\,s^{-1}$ and $K = (1.2 \pm 0.6) \times 10^{-8}\,mol\,m^{-2}\,Pa^{-1}$ (Fig. 2).

Let us use k and K values obtained above for TOF magnitude estimation. The number N_{Pt} of platinum atoms located on $1\,m^2$ of catalyst surface could be estimated from the lattice parameter for K_2PtCl_6, $\alpha = 9.78 \times 10^{-10}\,m$ [21]: $N_{Pt} = 2(1/a^2)/N_a \approx 3.5 \times 10^{-6}\,mole\,m^{-2}$, where N_a is Avogadro number, factor 2 was introduced because one unit cell contains two platinum atoms. Hence, the TOF value is equal to ca. $0.2\,mol\,C_2H_2\,(mol\,Pt)^{-1}\,s^{-1}$ in the case when the surface is covered by a monolayer (or multilayer) of HCl molecules (see above) and the partial pressure of acetylene is 1 atm.

3.2.2. Intermediate formation of β-chlorovinyl platinum(IV) complex Pt^{IV}–CH=CHCl

By analogy with catalytic acetylene hydroiodination in an aqueous solution (Scheme 1), heterogeneous acetylene hydrochlorination may be considered to proceed via a β-halovinyl Pt(IV) derivative. Indeed, the formation of β-chlorovinyl platinum(IV) complex, Pt^{IV}–CH=CHCl, under these conditions was confirmed by ^1H NMR and chemical tests.

The reaction was stopped by reactor evacuation and/or blow-through with dry air. The complex was extracted with methanol, and the extract was dried in an air current without heating. The dry residue was dissolved in CD$_3$OD. The ^1H NMR spectrum contains two doublets at $\delta = 6.51$ and 5.69 ppm, $J(HH) = 12.3\,Hz$, accompanied by platinum satellites, $^2J(^{195}Pt-^1H) = 72.5$) and $^3J(^{195}Pt-^1H) = 28.2\,Hz$, respectively.

$^{13}C\{^1H\}$ (CD$_3$OD): $\delta = 114.5$ (singlet with ^{195}Pt satellites, $J(^{195}Pt-^{13}C) = 45.7\,Hz$), 96.6 (singlet with ^{195}Pt satellites, $J(^{195}Pt-^{13}C) = 749.6\,Hz$).

The essential difference in the $J(Pt-C)$ values confirms the σ-mode for Pt–C bond, and $J(HH)$ value large enough indicates the *trans*-(anti)-addition of platinum and chlorine atoms to acetylene triple bond.

The formation of β-chlorovinyl platinum(IV) complex was confirmed by chemical tests as well. The analogous β-iodovinyl platinum(IV) complex decomposes in aqueous solutions of NaI yielding acetylene [22] and—in the presence of an acid—vinyl iodide [3]. Routes for β-chlorovinyl platinum(IV) complex decomposition under similar conditions should be obviously the same. Indeed, addition of the catalyst extract to NaI (2.5 M)–HClO$_4$ (0.25–2.5 M)–I$_2$ (0–0.0366 M) aqueous solution at 60 °C results in release of vinyl chloride (R′Cl) and acetylene (RH). Kinetics of the products accumulation follows the first-order equation. The values of rate constant for the organoplatinum derivative (RPt(IV)) decomposition, $k_{dec} = -d(\ln[RPt(IV)])/dt$, and the ratio of the product yields, $\eta(RH)/\eta(R'Cl)$, at varying acid and iodine concentrations and fixed ionic strength 5 M, supported by addition of NaClO$_4$, are presented below:
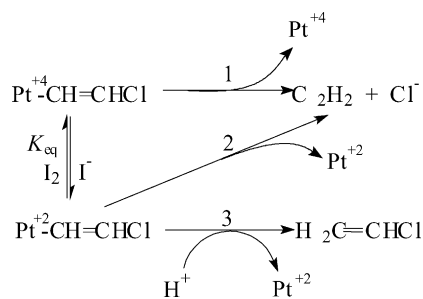
Scheme 2.

[I$_2$] (mol l^{-1})	[H$^+$] (mol l^{-1})	k_{dec} ($\times 10^{-4}$, s^{-1})	$\eta(RH)/\eta(R'Cl)$
0.0061	0.5	4.5 ± 0.3	1.3 ± 0.3
0.0366	0.5	3.0 ± 0.3	2.6 ± 0.5
0.0122	0.25	4.8 ± 0.2	2.2 ± 0.4
0.0122	2.5	15.0 ± 0.8	0.044 ± 0.006

The yield ratio of acetylene and vinyl chloride increases with increase in the iodine concentration and/or with decrease in the acid concentration. The values of rate constants of the reaction increase with increase in the acid concentration and with decrease in the iodine concentration. Qualitatively the results obtained are in agreement with those that could be expected for β-chlorovinyl Pt(IV) derivative (cf. [13]). Taking into account the strong *trans*-influence of iodide ligands, it is possible to assume that substitution of chloride ligands by iodide proceeds much faster than decomposition of the β-chlorovinyl Pt(IV) complex into acetylene and vinyl chloride. Reversible reduction of the β-chlorovinyl Pt(IV) compound by iodide ions into corresponding derivative of platinum(II) characteristic for platinum(IV) iodide complexes [23], and protonolysis of the latter yields vinyl chloride. β-Elimination of chloride ion from the organoplatinum derivatives leads to acetylene formation (Scheme 2, inorganic auxiliary ligands are omitted).

Competition of protonolysis and oxidation by iodine of the intermediate β-chlorovinyl Pt(II) complex explains the decrease in the yield of vinyl chloride and in the rate of organoplatinum derivative decomposition with decrease in acid concentration and/or increase in iodine concentration.

4. Discussion

Let us consider a plausible nature of the active sites of the catalyst carrying out the post-effect reaction. The following experimental facts seem to be important:

- The hydrochlorination does not proceed at a noticeable rate on the surface of K$_2$PtCl$_4$ or K$_2$PtCl$_6$ salts pre-activated in air or other "inert" gases (see above).
- The Pt^{3+} species formed [6] by mechanical treatment of K$_2$PtCl$_6$ salt are located on the surface of intergranular

borders which is inaccessible for adsorption from the gaseous phase [16], and therefore they could not be responsible for the heterogeneous hydrochlorination reaction.

- The hydrochlorination proceeds very slowly on the surface of pre-activated in air of K$_2$PtCl$_6$ and K$_2$PtCl$_4$ (10 mol%) salts mixture.
- To form the active catalyst preliminary grinding of platinum(IV) salts in atmosphere of "active" gases—acetylene, ethylene, or propylene—is necessary. Such a treatment leads to the formation of coordinatively unsaturated platinum complexes and, in the contrast to pre-activation in atmosphere of "inert" gases, to the partial reduction of Pt^{4+} into Pt^{2+} on the catalyst surface.

Consequently, a simultaneous presence of platinum complexes in the both oxidation states +2 and +4 on the catalyst surface is necessary for carrying out of the reaction. One could assume that the catalytic reaction proceeds on the active sites, which are K$_2$PtCl$_6$ lattice defects in the form of Pt^{2+} dopant in the K$_2$PtCl$_6$ matrix.

The regularities observed can be rationalized in the framework of Scheme 3. Just as for catalytic acetylene hydroiodination the key intermediate of heterogeneous acetylene hydrochlorination is β-halogenovinyl, namely β-chlorovinyl Pt(IV) derivative, presumably formed in the step of acetylene chloroplatination by coordinatively unsaturated Pt(IV) complexes (step 1). Note that σ-organic derivatives of Pt(IV) do not undergo protodemetalation at a noticeable rate. This reaction requires preliminary reduction of organoplatinum(IV) into corresponding Pt(II) derivative (cf. [13]). Thus, vinyl chloride is probably formed on the active site of the catalyst (such an active site is shown in brackets), and the role of platinum(II) complexes consists in complementary reduction [24] of β-chlorovinyl Pt(IV) complex into the corresponding Pt(II) derivative. Taking into account that the solid phase does not contain free chloride ions, one may consider that the stoichiometric consequence of such a reaction must be the formation of a coordinatively unsaturated Pt(IV) complex in addition to the platinum(II) organometallic compound. The protonolysis of β-chlorovinyl Pt(II) derivative under the action of HCl (step 3) yields vinyl chloride and recovers the active site of catalyst, a topologically bound couple [PtCl$_4$]$^{2-}$ − [PtCl$_5^*$]$^-$.

Let us consider the probable mechanism for acetylene chloroplatination step. The following experimental facts seem to be essential. Firstly, the solid K$_2$PtCl$_6$-gaseous HCl system under discussion does not contain external nucleophiles in amounts comparable with the quantity of the vinyl chloride formed. Nevertheless the only product with *trans*-configuration is formed. Secondly, vinyl chloride is the main product of the reaction on the surface of bromo platinum catalyst under conditions of C$_2$H$_2$ large excess with respect to HCl. Hence, chlorine atom, which is a part of vinyl chloride formed, originates from HCl molecule. We may assume that the reaction proceeds as a concert
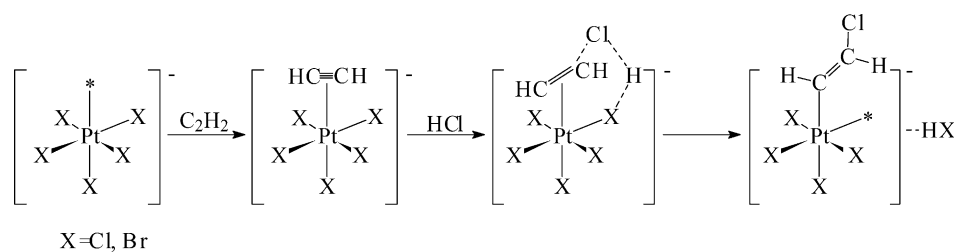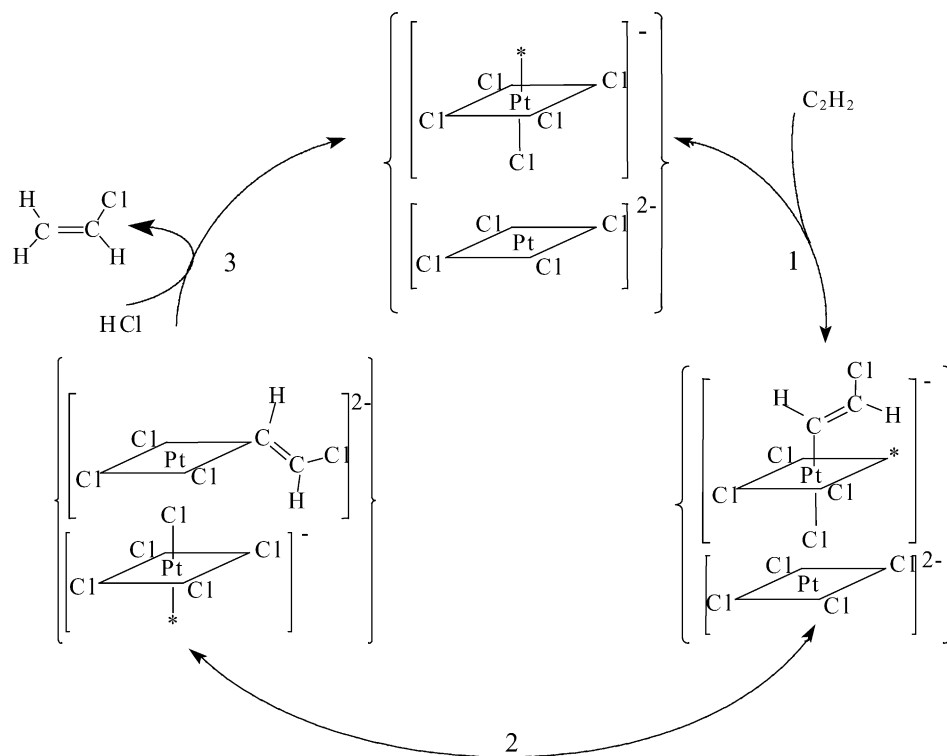
Scheme 3.

Scheme 4.

process via six-membered transition state (Scheme 4). The value for kinetic isotope effect does not contradict to the assumption of non-linear structure of transition state [20]. Such a mechanism excludes extremely unfavorable heterolysis of H–Cl bond with H^+ formation in the absence of solvation and explains the high stereoselectivity of the reaction.

The organoplatinum compound formed according to such a mechanism (Scheme 4) contains coordination vacancy, and, hence, serves as a charged defect of K_2PtX_6 crystalline lattice, which is able to specifically adsorb HX polar molecules. Electrostatically bound to active sites of the catalyst HX molecules can be partially consumed in the protonolysis of the organometallic platinum(II) derivative (Scheme 3, step 3) or take part in the next halogenoplatination step yielding the appropriate β-halogenovinyl derivative of platinum(IV). The last reaction may be responsible for the minor vinyl bromide formation on the surface of bromo platinum catalyst in HCl presence.

It is remarkable that such a mode for treatment of solids essentially broaden capabilities of heterogeneous catalysis: the mechanical treatment of initially inert toward acetylene K_2PtCl_6 salt results in formation of the active catalyst for acetylene hydrochlorination.

Acknowledgements

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