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Formation and Decomposition of the Methylplatinum(IV) Complex in the Mechanically Activated K_2PtCl_4 Powder–MeI Vapor System

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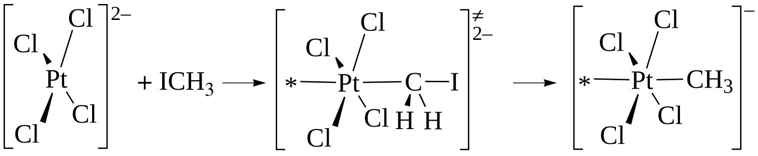
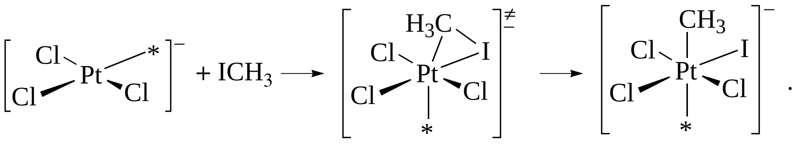
Abstract—Mechanical treatment of the K_2PtCl_4 solid salt in a vibrating mill results in Pt–Cl bond heterolysis to form coordinatively unsaturated Pt(II) complexes. At room temperature, the freshly treated K_2PtCl_4 salt absorbs methyl bromide and evolves methyl chloride to the gas phase. The reaction mechanism involves the following sequence of steps: the oxidative addition of methyl iodide to Pt(II) with the intermediate formation of Pt(IV) methyl complexes and the decomposition of the latter due to intramolecular reductive elimination with methyl chloride formation. The first step of the reaction of MeI with the preactivated surface of the K_2PtCl_4 salt is assisted by active sites, which are regenerated in each act of the chemical transformation of MeI into MeCl involving in the chain substitution of halogen in methyl iodide. The coordinatively unsaturated surface platinum complexes can act as such active sites. Due to their effective positive charge, they can provide electrophilic assistance to nucleophilic substitution. Chain termination is probably due to the coordination of the complex with a coordination vacancy and an interstitial chloride ion to the inactive K_2PtCl_4 complex.

INTRODUCTION

In aqueous solutions, the $[PtCl_4]^{2-}$ anion, similar to chloride ions, is a metal-centered nucleophile, which reacts with methyl iodide to form the Pt(IV) methyl complex (MePt(IV)) [1–3]. This oxidative addition can occur via either the S_N2 mechanism (reaction (I), transition state model **A**) [2, 3] or the mechanism of concerted three-center addition in which the coordinatively unsaturated Pt(II) complex simultaneously acts as a nucleophile attacking the carbon atom and an electrophile binding the leaving group [4] (reaction (II), transition state model **B**)


(I)

A


(II)

B

The decomposition of MePt(II) due to reductive elimination with chloride ions yields methyl chloride. Evidently, reductive elimination, which is the reverse of oxidative addition, can either occur as S_N2 nucleophilic substitution (Cl^- is the attacking nucleophile and $[PtCl_4]^{2-}$ is the leaving group) or as intramolecular transformation via a three-center mechanism. Decomposition via the S_N2 mechanism was established [3, 5–7] for reactions in aqueous solutions. The three-center mechanism of reductive elimination probably occurs during the thermolysis of the $Cs_2PtMeCl_5$ solid salt at 270°C in the absence of a solvent [8].

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It is known that the grinding of powders under impact loading destroys the crystal structure of the near-surface layer, due to which the physicochemical properties of powders change and their reactivity substantially increases [9–12]. After mechanical activation, the solid KCl salt demonstrates reactivity in the heterogeneous nucleophilic substitution of halogen in RI vapor (R = Me, Et, Pr) [13–17]. The driving force of the reaction is the stabilization of the leaving group (iodide ion) by structural defects of the KCl lattice, which are anionic vacancies. These structural defects are generated during the preliminary mechanical treatment of the salt and bear an effective positive charge facilitating the binding of a leaving group. The stoichiometric consequence of the elementary act of the chemical transformation of RI into RCl is the generation of a new anionic vacancy instead of the former one and the appearance of the foreign iodide ion in the anionic KCl sublattice. The decay of the active site, that is, anionic vacancy, occurs because of electron transfer to the latter from the foreign iodide ion to form the *F*-site.

We can assume that the mechanical treatment of the K_2PtCl_4 powder as well as K_2PtCl_6 [18] also results in the appearance of the coordinatively unsaturated platinum complexes on the salt surface

$$[PtCl_4]^{2-} \xrightarrow{\text{mechanical treatment}} [PtCl_3^*]^- + Cl^-. \qquad \text{(III)}$$

The point defect of the lattice in the form of the single-charge $[PtCl_3^*]^-$ anion bears an effective positive charge and, similar to the anionic vacancies on the surface of the mechanically treated KCl salt, can stabilize the leaving group (iodide ion) in the reaction with methyl iodide facilitating the nucleophilic attack of the carbon atom by Pt(II) to form the Pt(IV) methyl complex. In addition to these processes, the methylation of such coordinatively unsaturated complexes according to the three-center mechanism (II) can be expected.

The purpose of this work is to study the influence of mechanical activation on the reaction of the K_2PtCl_4 solid salt with methyl iodide vapor.

EXPERIMENTAL

Weighted salt samples (0.3 g) were subjected to mechanical treatment for 60 min in an MMVE-0.005 vibrating micromill in air.[1] The working frequency and amplitude of vibrations of the vibrating reactor were $f = 50$ Hz and $h_0 = 5.5$ mm, respectively, which corresponded to a specific rating of ≈15 W/kg. A glass 17.37-ml vibrating reactor containing glass grinding balls was hermetically closed with a rubber gasket.

After mechanical treatment, chromatographically pure ethylene (70 ml) was bubbled through the reactor if necessary.

The K_2PtX_4 salts (X = Cl, Br) were prepared using a standard procedure [19] and preliminarily dried for 3 days in a desiccator at 12–140°C. An increase in the duration of drying had no noticeable effect on the kinetics of the reactions. All procedures were carried out in a dry box.

2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO) was used as a paramagnetic probe. An aliquot (0.6 ml) of a solution of the nitroxyl radical (2×10^{-3} mol/l) in hexane was injected with a syringe through a rubber gasket into the vibrating reactor filled with the mechanically activated platinum salt, after which the solvent was evaporated in an argon flow.

The carbonyl complexes and Zeise salt ($K[PtCl_3(C_2H_4)]$) were prepared as follows. An atmosphere of CO or ethylene was created in a closed reactor containing the mechanically activated K_2PtCl_4 solid salt. After 30 min, the unreacted gas was removed by evacuation and/or in a dry air flow.

IR spectra were recorded using a SPECORD-IR75 in KBr pellets.

A liquid substrate (1–10 μl) was injected into the reactor through the rubber gasket with a microsyringe after the mechanical treatment of the salt. The consumption of methyl iodide and the accumulation of methyl chloride in the gas phase of the reactor were monitored by GLC using an LKhM-8MD chromatograph with a flame-ionization detector and a 3-m column packed with the 5% SE-30 stationary phase on Chromaton NAW. Samples were taken from the gas phase of the reactor through the rubber gasket using a dosing syringe with a fixed volume. The reaction was carried out at room temperature.

The number of moles of MeX in the gas phase of the reactor (m_g(MeX)) and the partial pressure of MeX (P(MeX)) were determined as described in [14]. The number of moles of MeX adsorbed at room temperature on the K_2PtCl_4 surface (m_{ads}(MeX), μmol/g) was determined from the difference between the amount of the substance in the gas phase of the reactor after the complete desorption of MeX when the K_2PtCl_4 surface was poisoned with water additives and m_g(MeX). Water (its amount was sufficient for the poisoning of the salt surface, cessation of the reaction, and entire desorption of methyl halide to the gas phase of the reactor[2] (20 μl) was injected with a syringe through the rubber gasket while preserving the containment of the reactor. The specific surface area of the salt surface determined by the BET method from argon desorption was equal to 3.1 m^2/g. The surface concentration of MeX, C_{ads}(MeX), (mol/m^2) was determined from the ratio of the m_{ads}(MeX) value to the surface area of the salt surface.

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[1] Independent experiments showed that the reaction also occurred in argon.

[2] An increase in the amount of water added to the reactor did not substantially change the m_{ads}(MeX) value.

^{1}H NMR spectra were recorded in methanol-d_4 using a Varian GEMINI instrument with a working frequency of 200 MHz. The extraction of Zeise's salt or methyl complexes of Pt(IV) from the sample surface was preceded by evacuation and/or dry air bubbling through the reactor until methyl iodide and methyl chloride completely disappeared from the gas phase above the solid salt surface (GLC monitoring). For the quantitative determination of the Pt(IV) methyl complex and Zeise's salt on the sample surface, extraction was performed by a fixed volume of CD_3OD containing a known amount of sodium acetate, whose signal intensity was used as an internal standard.

To perform chemical tests for the presence of the Pt(IV) methyl complex, we used the known reaction of decomposition of the latter in acidic aqueous solutions containing a chloride ion with methyl chloride formation [3–5] in ~100% yield. With this purpose, MePt(IV) was extracted with CH_3OH as described above. The extract was dried in an air flow without heating. The dry residue was dissolved in distilled water (3 ml). An aliquot (0.2 ml) of the resulting solution was added to the closed reactor, which was shaken and whose temperature was maintained constant, containing an aqueous solution (2 ml) of a mixture of $HClO_4$ (0.5 M), NaCl (2.5 M), and $NaClO_4$ (2.0 M) at 41°C. Under these conditions, $K_2PtMeCl_5$ undergoes reductive elimination to evolve MeCl to the gas phase [3–5]. The kinetics of decomposition of the Pt(IV) methyl complex was monitored by GLC by methyl chloride accumulation. The concentration of the complex in the extract was determined using the preliminarily obtained calibrating plot of the amount of the added methyl complex synthesized according to [8] vs. the surface area of the chromatographic peak of MeCl formed after the complete decomposition of $Cs_2PtMeCl_5$. Note that the pseudo-first-order rate constants of the decomposition of the complex obtained in the heterogeneous reaction, $(8.8 \pm 0.5) \times 10^{-4}$ s^{-1}, coincide with those of the decomposition of $Cs_2PtMeCl_5$ obtained by the method described in [8], $(8.8 \pm 0.7) \times 10^{-4}$ s^{-1}.

ESR spectra were recorded in an SE/X-2544 radiospectrometer with a working frequency of 9.4 GHz using the Mn(II)/MgO system as a standard.

X-ray structure studies were carried out with a DRON-UM1 diffractometer using CuK_α irradiation and the Ni filter.

RESULTS

Mechanically active transformations in the coordination sphere of the K_2PtCl_4 complexes. The mechanochemical treatment of the solid K_2PtCl_4 salt, unlike K_2PtCl_6 [18], did not result in the homolytic cleavage of the Pt–Cl bond: we failed to detect the formation of any paramagnetic species. In this case, the Pt–Cl bond is heterolyzed to form the coordinatively unsaturated Pt(II) complexes (reaction (III)). The following experimental facts confirm the formation of Lewis acid sites (LAS), viz., species of coordination vacancies ($[PtCl_3^*]^-$).

1. Adsorption of TEMPO on the mechanically activated Pt(II) salt surface indicates the presence of LAS. When TEMPO (1.7 μmol/g) is supported, the ESR spectrum contains the only signal corresponding to the radicals with hindered rotational mobility. In this case, the A'_{zz} parameter is 32.2 Oe. An increase in the amount of the introduced radical broadens the ESR lines, probably due to the exchange interaction. Unlike the ESR spectra of TEMPO on the mechanically treated K_2PtCl_6 salt, the signal belonging to the radicals with a higher rotational mobility is not observed in the case of K_2PtCl_4. This fact does not allow us to use this method for the estimation of the limiting amount of LAS formed by the mechanical treatment of K_2PtCl_4.

2. The freshly treated salt absorbs carbon oxide from the gas phase to form the platinum carbonyl complex $[PtCl_3(CO)]^-$. The IR spectrum of the latter in a KBr pellet contains a band of the stretching vibration of the coordinated carbonyl group,[3] ν(CO) 2115 cm^{-1}.

3. The consumption of ethylene from the gas phase by the freshly treated salt leads to the formation of Zeise's salt, whose anion is the ethylene π complex $[PtCl_3(C_2H_4)]^-$. The formation of this product was detected by ^{1}H NMR.[4] According to the estimate from the ^{1}H NMR data, ~5 μmol of Zeise's salt per gram of treated $K_2[PtCl_4]$ are formed. When the mechanically treated $K_2[PtCl_4]$ salt is kept for six months at room temperature, the coordinatively unsaturated complexes almost completely relax: the salt surface remains virtually unchanged, but ethylene is not noticeably absorbed on this sample with Zeise's salt formation.

Adsorption isotherms of MeI and MeCl on the mechanically treated K_2PtCl_4 surface. The data on MeI and MeCl (MeX) adsorption on the mechanically activated K_2PtCl_4 surface are presented in Table 1. As can be seen, the surface concentration of the adsorbed substrates C_{ads}(MeX) monotonically increases with an increase in the partial pressure of methyl halide vapor P(MeX), which can be described by curves with saturation. The plot of C_{ads}(MeX) vs. P(MeX) with saturation corresponds to the Langmuir equation

$$C_{ads}(\mathrm{MeX}) = \frac{C_{max}(\mathrm{MeX})K_{ads}(\mathrm{MeX})P(\mathrm{MeX})}{1 + K_{ads}(\mathrm{MeX})P(\mathrm{MeX})}, \quad (1)$$

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[3] For terminal carbonyls ν(CO) usually lies between 2125 and 1850 cm^{-1}, that is, differs from ν(CO) for free CO, which is 2143 cm^{-1} [20].

[4] After unreacted ethylene was thoroughly removed from the reactor, the product was extracted by deuteriomethanol. The spectrum of the extract corresponds to that of Zeise's salt (δ = 4.20 ppm, $J(^{195}Pt–^1H)$ = 56.0 Hz).

Table 1. Surface concentration of the substrates adsorbed on the mechanically activated K_2PtCl_4 surface (C_{ads}(MeX)) as a function of the partial pressure of methyl halide vapor (P(MeX))

P(MeCl), Pa	C_{ads}(MeCl), μmol/m^2	P(MeI), Pa	C_{ads}(MeI), μmol/m^2
0.10	0.35	0.34	4.50
0.71	2.30	0.89	10.10
1.04	1.18	1.28	7.06
1.75	3.21	1.90	11.33
2.22	2.44	4.14	15.70
2.46	3.00	5.34	18.70
4.43	4.60	5.70	16.09
–	–	13.03	20.19
–	–	16.46	20.77

Table 2. Parameters of the Langmuir equation for MeX adsorption on the activated K_2PtCl_4 and KCl surfaces [14]

MeX	K_{ads}(MeX) ×10^3, Pa^{-1}		C_{max}(MeX), μmol/m^2	
	K_2PtCl_4	KCl	K_2PtCl_4	KCl
MeI	0.06 ± 0.02	0.9 ± 0.2	21 ± 1	21 ± 3
MeCl	0.08 ± 0.03	9 ± 3	5.0 ± 0.8	1.6 ± 0.1

where C_{max} is the maximum surface concentration of MeX in the adsorption layer, and K_{ads}(MeX) is the adsorption equilibrium constant for MeX. The corresponding linearized plots are presented in Fig. 1.

The parameters of MeX adsorption on the activated K_2PtCl_4 surface determined from the linear plots of Eq. (1) and, for comparison, those for the activated KCl surface are presented in Table 2. The C_{max} parameters (monolayer capacity) for MeI on the K_2PtCl_4 and KCl surfaces coincide, which evidently corresponds to the almost complete coverage of the salt surface with the adsorbed substrate (cf. [14]).

As in the case of adsorption on the mechanically treated KCl salt, the C_{max} parameter for MeCl is lower than that for MeI, and the adsorption equilibrium constants on the K_2PtCl_4 surface for MeCl are somewhat higher than the corresponding value for MeI. By analogy to [14], we can assume that MeCl formed in the reaction is adsorbed on the surface region in the vicinity of the active site, which induced this reaction. In this case, the maximum surface concentration of MeCl, C_{max}(MeCl), should be determined to a great extent by the concentration of active sites on the surface. In the framework of this assumption, the higher K_{ads} value for methyl chloride compared to that for methyl iodide can be a consequence of a higher adsorption heat due to the specific interaction of the reaction product with the surface region in the vicinity of the active site resulting in the transformation of MeI into MeCl.

Kinetics of methyl chloride accumulation. At room temperature, the freshly treated K_2PtCl_4 salt absorbs methyl iodide with methyl chloride evolution to the gas phase.[5]

$$CH_3I + K_2PtCl_4 \longrightarrow CH_3Cl + K_2PtCl_3I. \qquad (IV)$$

The addition of water vapor to the reactor substantially retards the reaction, and the presence of 1 μl of water inhibits it completely. After the treated salt was allowed to stay for six months at room temperature, its active sites resulting in reaction (IV) were almost completely deactivated: the specific surface area of the salt remained virtually unchanged, but methyl iodide consumption and methyl chloride evolution on the this surface did not occur at a noticeable rate.

In the case of the maximal coverage of the surface with the substrate and the large initial amount of methyl iodide, the curve of methyl chloride formation (taking into account the salt adsorbed on the surface) consists of three regions (Fig. 2). In the beginning of the reaction, MeCl evolution accelerates and then the product is accumulated for 4 to 5 h at a constant rate. The yield of methyl chloride calculated per unreacted substrate in the second region is close to 100%. If the reaction is carried out for a longer time, the evolution of methyl chloride slows down and ceases after approximately a day reaching the limit $m_{max}(MeCl) \approx 83$ μmol/g.

Let us compare the maximal amount of methyl chloride formed in the reaction with 1 g of the activated salt, $N_{max}(MeCl) = N_A m_{max}(MeCl) \approx 5.0 \times 10^{19}$ molecule/g (N_A is Avogadro's number), and the amount of the complex anions on the surface of 1 g of the salt, $N_{sp}(Pt) = N(Pt)S_{sp} \approx 1.5 \times 10^{19}$ ion/g, where $N(Pt) \approx 5 \times 10^{18}$ ion/m^2 is the number of the Pt complex ions per 1 m^2 of the K_2PtCl_4 surface.[6] Taking into account that the $[PtCl_4]^{2-}$ complex ion contains four chloride ligands, we obtain that the N_{max}(MeCl) value is comparable with the amount of chlorine atoms on the surface of platinum complexes.

Taking into account that the system does not contain free chloride ions in an amount comparable with that of methyl chloride formed[7] and the profile of the evolution of the product, we can conclude that MeCl is formed due to the intramolecular decomposition of the intermediate Pt(IV) methyl complex.

$$A + CH_3I + [PtCl_4]^{2-} \xrightarrow{k_1} A \cdot I^- + [Pt(CH_3)Cl_4^*]^-, \quad (V)$$

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[5] A similar reaction with methyl bromide formation occurs on the freshly treated platinum bromide salt, K_2PtBr_4.

[6] The value of $N(Pt) \approx 5 \times 10^{18}$ particle/m^2 was estimated from the lattice parameters of K_2PtCl_4, $a = b \approx 7 \times 10^{-10}$ m, $c = 4.13 \times 10^{-10}$ m [21].

[7] According to Eq. (III), the amount of free interstitial chloride ions in the system is equal to $[A]_0$, where $[A]_0 = 5$ μmol/g is the initial concentration of the coordinatively unsaturated particles generated by the mechanical treatment.

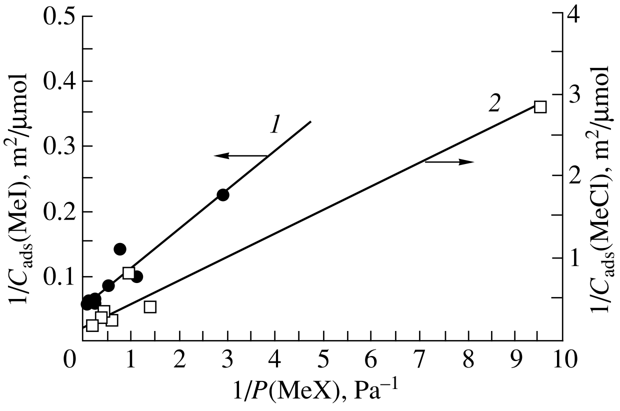

Fig. 1. Linear plots of the Langmuir isotherm for the adsorption of (*1*) methyl iodide and (*2*) methyl chloride formed on the mechanically activated K_2PtCl_4 surface.

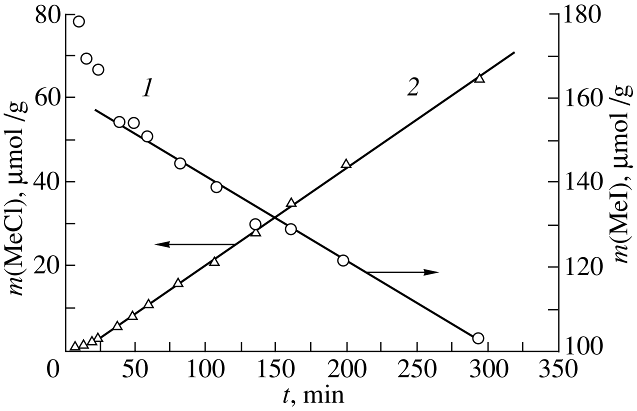

Fig. 2. Kinetics of (*1*) MeI consumption and (*2*) MeCl accumulation in the reaction of MeI with the activated K_2PtCl_4 salt in excess MeI.

$$[Pt(CH_3)Cl_4^*]^- \xrightarrow{k_2} [PtCl_3^*]^- + CH_3Cl, \qquad \text{(VI)}$$

where A is the surface active site inducing the reaction. In fact, in the framework of reactions (V) and (VI), provided that a change in the concentration of the active sites and adsorbed substrate on the K_2PtCl_4 surface[8] during the first 3–5 h of the reaction can be neglected, we obtain the following equation for a change in the total amount of methyl chloride m(MeCl) in time:

$$m(\mathrm{MeCl}) = k_1 C_{\max}(\mathrm{MeI})[\mathrm{A}]S_{\mathrm{sp}}t + \frac{k_1 C_{\max}(\mathrm{MeI})[\mathrm{A}]}{k_2}S_{\mathrm{sp}}(\exp(-k_2 t) - 1). \qquad (2)$$

In this approximation, $1/k_2$ is the characteristic time for attaining the stationary concentration of the intermediate Pt(IV) methyl complex. After this stationary concentration was achieved, methyl chloride is linearly accumulated, which agrees with the experimental plot of m(MeCl) vs. time (Fig. 2) at $k_1C_{\max}(\mathrm{MeI})[\mathrm{A}]S_{\mathrm{sp}} = (3.9 \pm 0.1) \times 10^{-3}$ μmol g^{-1} s^{-1}.

Formation of the intermediate Pt(IV) methyl complex. In fact, the formation of the Pt(IV) methyl complex under these conditions was confirmed by ^{1}H NMR and chemical tests [1, 7]. The MePt(IV) complex was extracted with methanol after unreacted methyl iodide was removed from the reactor by evacuation and/or purging with dry air. The ^{1}H NMR spectrum of the extract in CD_3OD coincides with that of the methyl complexes obtained in [1, 3] under homogeneous conditions: two signals are observed, namely, a singlet at $\delta = 3.09$ ppm accompanied with satellites $^2J(^{195}\mathrm{Pt}–^1\mathrm{H}) = 78.6$ Hz and a singlet at $\delta = 3.20$ ppm with satellites $^2J(^{195}\mathrm{Pt}–^1\mathrm{H}) = 79.7$ Hz. The ratio of the intensities of these satellites (≈2 : 1) remains unchanged with time. The signal in the higher field is assigned to the $[Pt(CH_3)Cl_5]^{2-}$ complex and/or *trans*-$[Pt(CH_3)Cl_4S]^-$ ($S=CD_3OD$ or D_2O), and that in the lower field is assigned to the complex containing the iodide ligand in the equatorial plane (see [3]). The kinetics of changes in the amount of MePt(IV) agrees with the assumption that this complex is intermediately involved in reaction (IV) (Fig. 3). With the above assumptions, reactions (V) and (VI) lead to the following equation for the change in the amount of the intermediate product with time:

$$m(\mathrm{MePt(IV)}) = \left(\frac{k_1 C_{\max}(\mathrm{MeI})[\mathrm{A}]}{k_2}S_{\mathrm{sp}}(1 - \exp(-k_2 t))\right), \qquad (3)$$

which agrees with the experimental plot at $k_2 = (8 \pm 4) \times 10^{-4}$ s^{-1} and $\frac{k_1 C_{\max}(\mathrm{MeI})[\mathrm{A}]}{k_2}S_{\mathrm{sp}} = (7 \pm 1)$ μmol/g. The parameter determined from these data, $k_1C_{\max}(\mathrm{MeI})[\mathrm{A}]S_{\mathrm{sp}} = (5.6 \pm 3.6) \times 10^{-3}$ μmol g^{-1} s^{-1}, coincides within the experimental error with the value obtained independently using Eq. (2). Then, taking into account $C_{\max}(\mathrm{MeI}) = 21 \pm 1$ μmol/m^2 and the specific surface area $S_{\mathrm{sp}} = 3.2$ m^2/g, we obtain the estimate $k_1[\mathrm{A}] = 8 \times 10^{-5}$ s^{-1}.

Reactions in an ethylene atmosphere. The coordinatively unsaturated Pt(II) complexes generated on the surface due to the mechanical treatment of the K_2PtCl_4 powder efficiently absorb ethylene from the gas phase and are transformed into Zeise's salt anion

$$[PtCl_3^*]^- + C_2H_4 \longrightarrow [\eta^2\text{-}(C_2H_4)PtCl_3]^-. \qquad \text{(VII)}$$

It is known that the oxidative addition of methyl iodide to the Pt(II) π-ethylene complex $[Pt(\eta\text{-}C_2H_4)Cl_3]^-$ in an aqueous solution is accompanied by ethylene elimination from the coordination sphere of platinum [22]. It

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[8] At the limiting surface coverage with the substrate the surface concentration of the latter remains unchanged and equal to $C_{ads}(\mathrm{MeI}) = C_{\max}(\mathrm{MeI})$ at a considerable change in the methyl iodide pressure in the gas phase.

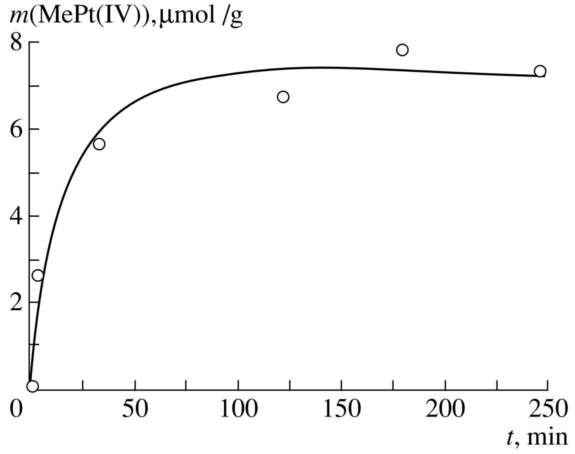

Fig. 3. Kinetics of the accumulation of the Pt(IV) methyl complex in the reaction of MeI with the activated K_2PtCl_4 salt.

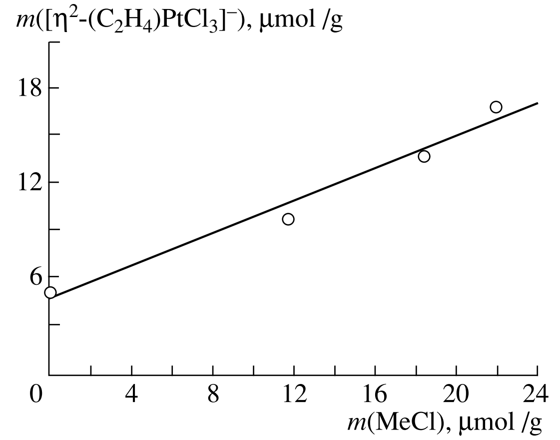

Fig. 4. Amount of Zeise's salt as a function of the amount of evolved MeCl in the reaction of MeI with the activated K_2PtCl_4 salt in ethylene.

was of interest to elucidate the influence of ethylene coordination to the $[PtCl_3^*]^-$ complexes on the heterogeneous reaction with methyl iodide.

In an ethylene atmosphere, reaction (IV) is approximately twice as slow, but the patterns of substrate consumption and product formation are similar to those described above. In this case, methyl chloride accumulation is accompanied by ethylene consumption with the formation of Zeise's salt: the amount of Zeise's salt formed linearly increases with an increase in the amount of the evolved methyl chloride (Fig. 4). The intercept on the ordinate axis on the plot of $m([\eta^2\text{-}(C_2H_4)PtCl_3]^-)$ vs. $m(MeCl)$ coincides within experimental errors with the amount of Zeise's salt formed when ethylene is absorbed by the freshly treated K_2PtCl_4. The slope of this straight line is 0.51 ± 0.05.

In this case, we did not detect the Pt(IV) methyl complex containing the iodide ligand in the equatorial plane in the ^1H NMR spectrum of the methanol (CD_3OD) extract; only $[Pt(CH_3)Cl_5]^{2-}$ and/or *trans*-$[Pt(CH_3)Cl_4S]^-$ (S=CD_3OD or D_2O) complexes were observed.

X-ray structure study. The iodide ions formed in reaction (IV) can enter the coordination sphere of platinum or form the KI phase. This should be manifested in the diffraction pattern as either a change in the lattice parameters[9] of K_2PtCl_4 or the appearance of new signals assigned to the KI phase. For X-ray structure studies we used polycrystalline samples of the mechanically treated K_2PtCl_4 salt before the reaction with methyl iodide (sample **1**) and the same samples after the reaction with MeI in air (sample **2**) and ethylene (sample **3**). The diffraction pattern of sample **1** completely corresponds to the published data [23] for the single-phase K_2PtCl_4 salt. The diffraction pattern of sample **2** exhibits shifts of diffraction maxima corresponding to the parameter $a = b$ (the initial structure has a tetragonal system, space group $P4/mmm$) toward a decrease in the angle, that is, an increase in the lattice parameter (Fig. 5). It is seen from Fig. 5 that the doublets [111] and [210], [101] and [200], and [211] and [220] discernible in sample **1** almost look like singlets for sample **2**. In all presented doublets, the line with the greater Miller index for the parameter *a* is shifted. For the doublet [200] this shift estimated from the distance between the centers of diffraction maxima reaches 0.2 Å. This shift indicates that the parameter *a* increases in the near-surface layers, which can be explained by the inclusion of iodine atoms in the coordination sphere of the metal complex. At the same time, the position of lines related to the parameter *c* remained unchanged, which is probably due to the inclusion of an iodide ion in the coordination sphere of platinum complexes arranged in the crystallographic planes (*h*, *k*, 0). After the samples were allowed to stay at room temperature for three months, the structure of sample **2** relaxed to the initial state **1**. This is evidently related to the thermodynamic instability of state **2**.

Sample **3** does not exhibit these effects, and its diffraction pattern is close to that for sample **1**, but the integral intensities of several X-ray maxima are redistributed. Unfortunately, despite this fact, it is impossible to detect the appearance of the KI phase, because all X-ray reflections of KI coincide with those of the basic K_2PtCl_4 structure. To resolve this situation, we carried out an experiment using the platinum bromide salt, K_2PtBr_4. In this case, the reflections [100], [220], [222], and [331] corresponding to the KI phase [23] were detected and did not coincide with the reflections of K_2PtBr_4.

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[9] The ion radius of the iodide ion is much greater than that of the chloride ion.

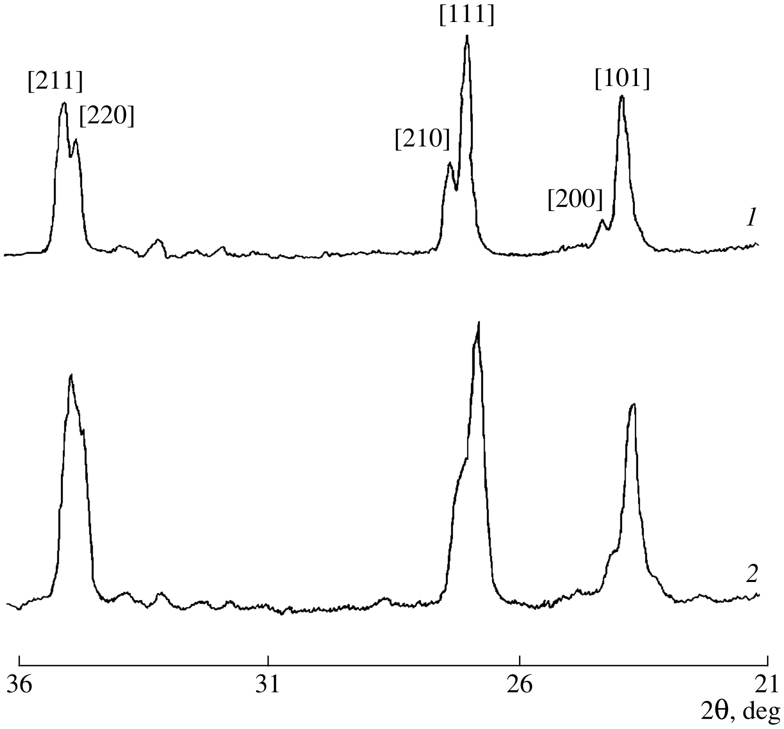
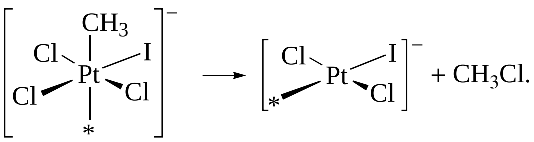


Fig. 5. X-ray patterns of the mechanically treated K_2PtCl_4 salt (*1*) before and (*2*) after the reaction with methyl iodide in air.

DISCUSSION

Let us consider possible mechanisms of the reaction. Provided that the coordinatively unsaturated $[\mathrm{PtCl}_3^*]^-$ complexes are active sites, we assume two routes of the reaction. The first route is the three-center oxidative addition of methyl iodide followed by the reductive elimination of methyl chloride (reactions (II) and (VIII)).



(VIII)

The stoichiometric consequence of reaction (II) is the formation of the Pt(IV) methyl complex with a coordination vacancy. The decomposition of the latter with the formation of methyl chloride (reaction (VIII)) should yield a mixed chloride–iodide coordinatively unsaturated complex. In this case, no migration over the reaction site surface occurs, and the amount of methyl chloride formed should not exceed $3[A]_0$, where $[A]_0 = 5$ μmol/g is the initial concentration of coordinatively unsaturated species generated by the mechanical treatment. In our case, a much greater amount of methyl chloride is evolved and, hence, the considered route cannot be the main one.

The second route is oxidative addition via the S_N2 mechanism with the electrophilic assistance by the coordinatively unsaturated complexes followed by the reductive elimination of methyl chloride (reactions (V) and (VI), where $A = [\mathrm{PtCl}_3^*]^-$).

A similar electrophilic assistance by the Pt(II) aqueous–chloride complexes [24] and mercury(II) salts [25] to the oxidative addition of methyl iodide to the Pt(II) tetrachloride complexes was found for reactions in aqueous solutions. The stoichiometric consequence of reaction (V) is the formation of the Pt(IV) methyl complex with the $[\mathrm{Pt(CH_3)Cl}_4^*]^-$ coordination vacancy and the $[\mathrm{PtCl}_3^*]^- \cdot \mathrm{I}^-$ ion pair and/or the mixed chloride–iodide $[\mathrm{PtCl_3I}]^{2-}$ complex. The latter were detected by XRD. Intramolecular reductive elimination (reaction (VI)) yields methyl chloride and results in the regeneration of the complex with the coordination vacancy. In this case, the active sites on salt surface are mobile. Chain termination can also occur due to the recombination of the coordinatively unsaturated complex and interstitial chloride ion formed in reaction (III)

$$[\mathrm{PtCl}_3^*]^- + \mathrm{Cl}^- \longrightarrow [\mathrm{PtCl}_4]^{2-}. \qquad \text{(IX)}$$

Taking into account that the point defects, including the interstitial chloride ions, are localized predominantly on the salt surface [26], we arrive at a reasonable explanation for the fact that the reaction is restricted by approximately one monolayer of the platinum salt. This chain mechanism suggests the surface concentrations of the active states A are constant in time at the initial moments of the reaction (see above) when quadratic chain termination can be neglected and that the amount of evolved methyl chloride is relatively large. Note that, according to mechanism involving reactions (V) and (VI), methyl chloride is formed in the vicinity of the electrophilic site, a complex with the coordination vacancy. This fact can be the reason for the higher adsorption equilibrium constant of MeCl: due to the electrostatic interaction, the adsorption heat of methyl chloride on the $[PtCl_3^*]^-$ complex bearing a positive charge can evidently be higher than the adsorption heat on the electroneutral surface regions.

The NMR signals from the methyl complexes with and without the iodide ligand in the equatorial plane are detected for methanol extracts of the methyl complex. Assuming that, at the moment of extraction, the iodide ligand does not enter the coordination sphere of the $[Pt(CH_3)Cl_4]^-$ complex[10] and excluding a similar secondary reaction in the solid phase due to the hindered mobility, we have to assume that the methyl complex containing the iodide ligand in the equatorial plane is formed by the three-center mechanism (II) and/or due to the methylation of the mixed platinum(II) chloride–iodide complex. According to reactions (V) and (VI), the $[PtCl_3^*]^-$ and $[PtCl_3I]^{2-}$ complexes formed in the chemical transformation of MeI into MeCl can be localized only near each other. This fact makes the methylation of the last particle sterically possible in the next act of chain propagation. It is likely that the presence of the iodide ligand in the coordination sphere enhances the nucleophilicity of the Pt(II) complex, which additionally favors this reaction.

Mechanism (V)–(VI) also allows us to explain the effects observed for reaction (IV) in ethylene. If reaction (VII) occurs rather rapidly, it results in the efficient decay of the coordinatively unsaturated complexes and, hence, prevents the formation of the mixed chloride–iodide complex in reaction (V).[11] Since Zeise's salt anion is still a positively charged structural defect, it can stabilize the leaving group to form the $[\eta^2\text{-}(C_2H_4)PtCl_3]^- \cdot I^-$ ion pair and, correspondingly, electrophilically assist the S_N2 methylation of the $[PtCl_4]^{2-}$ anion. The decomposition of the methyl complex formed in reaction (VI) results in the regeneration of the coordinatively unsaturated Pt(II) complex, which yields Zeise's salt anion in reaction (VII). This fact explains the linear plot of $m([\eta^2\text{-}(C_2H_4)PtCl_3]^-)$ vs. $m(MeCl)$ (Fig. 4). The slope of the straight line of this plot differs from zero and can be a consequence of the competition of reaction (VII) and reactions (V) and (X) for the iodide ion entering the coordination sphere of platinum

$$[PtCl_3^*]^- \cdot I^- \longrightarrow [PtCl_3I]^{2-}. \qquad (X)$$

The formation of the KI phase in the reaction with methyl iodide in ethylene is likely explained by the relaxation of the $[\eta^2\text{-}(C_2H_4)PtCl_3]^- \cdot I^-$ defect in the reaction

$$K_2[Pt(\eta^2\text{-}C_2H_4)Cl_3] \cdot I \longrightarrow KPt(\eta^2\text{-}C_2H_4)Cl_3 + KI. \qquad (XI)$$

According to numerous published data [27–30], intramolecular reductive elimination from Pt(IV) complexes occurs through a pentacoordinated intermediate. Such a pentacoordinated Pt(IV) methyl complex with a vacancy in the *trans* position to the methyl group should form in the reactions under consideration. This fact most likely explains the instability of the pentacoordinated $[Pt(CH_3)Cl_4^*]^-$ derivative, unlike the stable hexacoordinated $[Pt(CH_3)Cl_5]^{2-}$ complex in the form of the solid $K_2Pt(CH_3)Cl_5$ salt. Additional stabilization of $[Pt(CH_3)Cl_4^*]^-$ by the crystalline field of the basic structure can be another reason for the difference between the reactivities of $[Pt(CH_3)Cl_4^*]^-$ in the K_2PtCl_4 matrix and $[Pt(CH_3)Cl_5]^{2-}$ in the $K_2Pt(CH_3)Cl_5$ matrix.

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[10] Since no evolution of the spectra in time is observed, this process occurs either very rapidly or very slowly.

[11] In this case, the formation of the mixed chloride–iodide complex should be accompanied by the displacement of ethylene from the coordination sphere, and this contradicts the experiment.

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