

## Processes in $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ –Solvent Systems. Part I: Alcohol Solutions

N. V. Klimova<sup>a,\*</sup>, A. G. Ivanov<sup>a</sup>, A. V. Lebedev<sup>a</sup>, and Academician P. A. Storozhenko<sup>a</sup>

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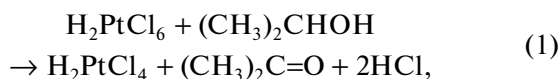
**Abstract**—Transformation of  $\text{H}_2\text{PtCl}_6$  over time under the action of 2-octanol has been studied by NMR, IR spectroscopy, GLC, and GC/MS. It has been found for the first time that the alcohol in a  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ –2-octanol solution is hydrochlorinated to give 2-chlorooctane. Dehydrated platinum chlorides catalyze the elimination of methyl groups in trimethylchlorosilane and hexamethyldisiloxane, which leads to the formation of polydimethylsiloxanes. It has been assumed that the resulting  $\pi$ -complex of  $\text{H}_2\text{PtCl}_4$  with octene-1 is not stable in a hydrochloric medium and rapidly decomposes to release chloroalkyl.

**Keywords:** platinum chlorides, Speier’s catalyst,  $\pi$ -complex, hydrochlorination, NMR spectra, Reduction in alcohol media, 2-chlorooctane

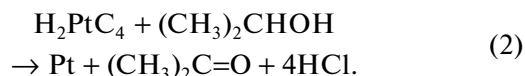
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Alcoholic solutions of chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) are among the widely used catalysts in the production of organosilicon monomers and polymers in the addition reactions of olefins and oligomers with multiple bonds, respectively, to  $-\text{SiH}$  groups. As a result of studying the hydrosilylation reaction at sufficiently low temperatures, it has been found [1] that chloroplatinic acid in isopropyl alcohol (Speier’s catalyst, SpC) is extremely active in this reaction. Also, platinum black, platinized carbon, and potassium chloroplatinite  $\text{K}_2\text{PtCl}_4$  proved to be highly efficient [1].

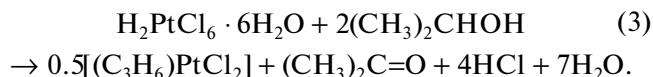
Summarizing numerous publications, it can be stated that compounds of platinum in different oxidation states exhibit catalytic properties in SpC. At the same time, it seems that there is no clear understanding of the mechanism of formation of Pt(II) complexes, in particular, from  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and alcohols, since the works often contain conflicting and even mutually exclusive data. For example, it has been hypothesized in [2–4] that the Pt(II) propylene complex is not formed in the composition of SpC, and Pt(IV) is successively reduced to Pt(0) by reactions (1) and (2):



<sup>a</sup> State Scientific Center of the Russian Federation  
“State Research Institute for Chemistry and Technology  
of Organoelement Compounds”, Moscow, 105118 Russia  
\*e-mail: nk20160412@gmail.com

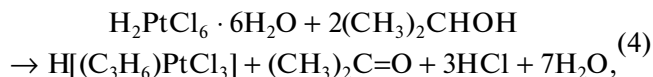


On the other hand, it has been stated in [5–11] that Pt(II) is coordinated to olefins formed by dehydration of alcohols (3):



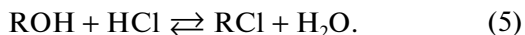
Early studies used anhydrous  $\text{PtCl}_4$  [12], platinum chloride salts with dry alcohols [13, 14], and anhydrous  $\text{Na}_2\text{PtCl}_6$ , which was then dissolved in alcohol [15]. In our opinion, dehydration led to the creation of favorable conditions for the intermediate formation of olefins by alcohol dehydration. However, in the SpC medium, chloroplatinic acid already contains 6 moles of water, which can hinder the reaction of alcohol dehydration, since it is known [16] that it proceeds under rather severe conditions in the presence of strong water-removing agents, such as concentrated sulfuric acid.

There are also significant disagreements on the stability of  $\pi$ -complexes of platinum chlorides with olefins. For example, it has been concluded in [5] that the chloride ion released in a chemical transformation according to equation (4),



stabilizes the anionic complex  $\text{H}[(\text{C}_3\text{H}_6)\text{PtCl}_3]$ , while in [8] it has been stated that  $[(\text{C}_3\text{H}_6)\text{PtCl}_3]^-$  decomposes with the release of propylene under the action of chloride ions at room temperature.

At the same time, there are studies that have shown that Pt(II) forms complexes with alcohols [17, 18], ketones [19, 20], and water [21]. Surprisingly, but none of the researchers paid attention to the fact that water can be formed during the exchange reaction between alcohol and hydrogen chloride, which is widely used in the production of chloroalkyls [22]:



In exchange reactions (5), Lewis acids—metal chlorides (for example,  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ , etc.)—are mainly used as a catalyst. It is quite possible that platinum chloride compounds can act as a catalyst in the above system.

Since, as noted above, the relevance of expanding knowledge about the composition and transformations of the SpC over time and under various conditions is obvious, to refine the above characteristics of SpC, in this work we have studied the behavior of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in an excess of 2-octanol. The choice of 2-octanol is due to the rather high boiling point of octene-1, which makes it easy to identify it when it is formed by alcohol dehydration both in the composition of the complex and in the free state.

## EXPERIMENTAL

The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were recorded on Bruker AM-360 and AVANCE 600 spectrometers. All chemical shifts were expressed in ppm relative to TMS. The solvent was  $\text{CDCl}_3$ .

GLC analysis was carried out on a Kristall 2000 chromatograph; 1 m  $\times$  3 mm column filled with 5% SE-30 on Chromaton N–AW HMDS as a stationary phase; carrier gas, helium; detector, katharometer.

The molecular weight and structure of the compounds were determined on an Agilent 7890A triple quadrupole GC/MS mass spectrometer with an Agilent 240 ion trap unit.

The IR spectra were recorded on a Specord M-80 IR Fourier spectrophotometer.

**Reaction of chloroplatinic acid hexahydrate with octanol-2.**  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (1 g, 0.0019 mol) was dissolved in 20 mL (0.1259 mol) of 2-octanol. The solution was stirred for 10 min at room temperature, then stirred at 100°C until the precipitation of platinum began and the solution became completely clear. Samples for analysis were taken after 1, 3, 7, 10, and 13 h. The weight of the isolated product was 16.9 g. The product composition: 0.11 g (0.00056 mol) (0.65%) of colloidal platinum(0), 0.43 g (0.0013 mol) (2.55%) of  $\text{H}_2\text{PtCl}_4$ , 16.1 g (0.1238 mol) (95.44%) of 2-octanol, 0.23 g (0.0018 mol) (1.36%) of 2-octanone, and trace amounts of 2-chlorooctane.

**Reaction of chloroplatinic acid hexahydrate with ethanol and 1-octene.** Crystalline  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (0.5 g, 0.00097 mol) was mixed with 0.045 g (0.00097 mol) of

ethanol and 0.11 g (0.00097 mol) of 1-octene and stirred at 75°C for 6 h. Final composition of the reaction mixture: 0.3 g (0.00089 mol) of  $\text{H}_2\text{PtCl}_4$ , 0.08 g (0.00054 mol) of 2-chlorooctane, and trace amounts of 1-octene.

**Reaction of chloroplatinic acid with trimethylchlorosilane and 2-octanol.**  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (0.62 g, 0.0012 mol) was mixed with 1.56 g (0.0144 mol) of  $(\text{CH}_3)_3\text{SiCl}$  and stirred for 1 h at room temperature. Then, 0.31 g (0.0024 mol) of 2-octanol was added, and the mixture was stirred at 100°C for 8 h. The following products were identified in the final reaction mixture:  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ ,  $(\text{CH}_3)_3\text{SiCl}$ ,  $(\text{CH}_3)_3\text{SiO}[(\text{CH}_3)_2\text{SiO}]_n\text{Si}(\text{CH}_3)_3$ , platinum(II) and platinum(0) compounds, 2-octanol, 2-octanone, and 2-chlorooctane.

**Reaction of chloroplatinic acid with trimethylchlorosilane, 1-octene, and 2-octanol.**  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (2 g, 0.0039 mol) was mixed with 5.03 g (0.0463 mol) of  $(\text{CH}_3)_3\text{SiCl}$  and stirred for 1 h at room temperature. Then, 8.5 mL (0.0542 mol) of 1-octene was added, and the mixture was stirred at 75°C for 6.5 h. Next, 0.61 mL (0.0039 mol) of 2-octanol was added, and stirring was continued at 75°C for 9 h until colloidal platinum(0) appeared, which was decanted, washed 3 times with acetone, and calcined at 250°C for 1 h. Dry colloidal platinum(0) (0.22 g, 0.0011 mol) was isolated in 28.9% yield.

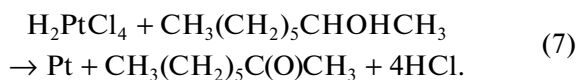
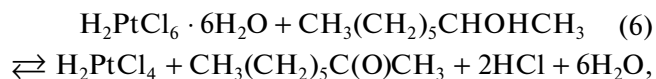
## RESULTS AND DISCUSSION

To accelerate chemical processes in the selected  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ –2-octanol system, the mixture was subjected to thermal treatment. The initial solution was analyzed by  $^1\text{H}$  NMR spectroscopy and the spectrum was compared with that of reference 2-octanol [23]. Along with the signals of the 2-octanol protons, a new signal was observed at  $\delta = 2.72$  ppm, corresponding to the protons of hydrate water of chloroplatinic acid.

After stirring at 100°C for 1 h, no changes were observed in the  $^1\text{H}$  NMR spectrum of the reaction mixture, and an absorption band at 1712  $\text{cm}^{-1}$  appeared in the IR spectrum, which corresponded to the stretching vibrations of the C=O bond ( $\nu_{\text{C=O}}$ ) in 2-octanone. An increase in the intensity of the  $\nu_{\text{C=O}}$  band in the IR spectra of the samples taken after 3 and 7 h indicated that the content of 2-octanone was growing. The results of the analysis of the solution by GLC after 13 h, when some of the platinum precipitated in the form of fine platinum black, showed that the content of 2-octanone increased to 2 wt %, while the content of 2-octanol decreased by 6%. The formation of 2-octanone was also confirmed by NMR: the  $^{13}\text{C}$  NMR spectrum showed a signal at  $\delta = 208.9$  ppm, characteristic of the C=O bond; the  $^1\text{H}$  NMR spectrum showed the resonances of  $\text{CH}_3$  and  $\text{CH}_2$  protons at the carbonyl group ( $\delta = 2.37$  and 2.08 ppm, respec-

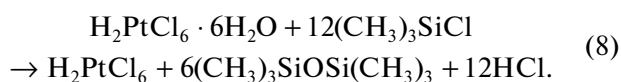
tively). The  $^1\text{H}$  NMR spectrum of the product also showed a signal from the  $\text{CHCl}$  group of the alkyl chloride in the form of a sextet at 3.97 ppm, which confirmed the formation of 2-chlorooctane. The presence of 2-octanone and 2-chlorooctane in the reaction products was demonstrated by GC/MS.

It follows from the research results that no formation of 1-octene and 2-octene by the dehydration reaction of 2-octanol under the action of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  is observed; the products are 2-octane (reactions (6), (7)) and 2-chlorooctane yielded by exchange reaction (5) of 2-octanol with hydrogen chloride.



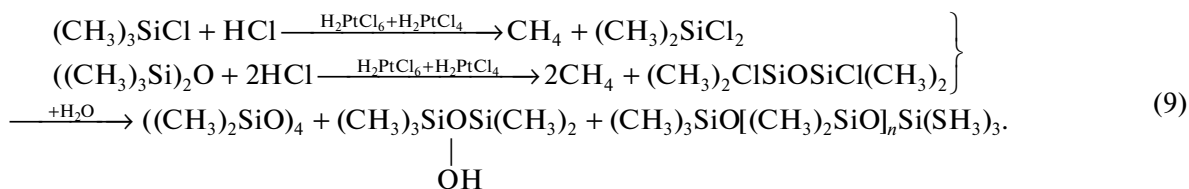
Using GLC data, the amount of the resulting 2-octanone was determined and then it was calculated that Pt(IV) was 100% reduced to Pt(II) and about 30% was further reduced to Pt(0). The same result was obtained in the gravimetric study of precipitated colloidal Pt(0).

In the next experiment,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  was treated with  $(\text{CH}_3)_3\text{SiCl}$  for its dehydration according to reaction (8). To accurately exclude the presence of water in the system, a small excess of  $(\text{CH}_3)_3\text{SiCl}$  was taken, which does not affect the processes under study.



The resulting mixture of  $\text{H}_2\text{PtCl}_6$  and hexamethyldisiloxane was stirred in 2-octanol at  $100^\circ\text{C}$  for 8 h. 2-Octanone was obtained similarly to reaction (6), which has been confirmed by the  $^{13}\text{C}$  NMR spectrum, which shows a signal from the carbonyl group at 211.89 ppm, while no resonances of  $\text{C}=\text{C}$  groups are observed in the range 114–139 ppm. Therefore, even in a partially dehydrated  $\text{H}_2\text{PtCl}_6$ –2-octanol system, the reaction of alcohol dehydration to form octenes does not occur.

When  $\text{H}_2\text{PtCl}_6$  treated with trimethylchlorosilane was mixed with 1-octene at  $75^\circ\text{C}$  for 6.5 h, the  $^1\text{H}$  NMR spectrum of the reaction mixture showed a signal at  $\delta = 4.03$  ppm, arising from the corresponding  $-\text{CHCl}$  group, and signals at  $\delta = 4.99$  and 5.86 ppm from 1-octene traces. After stirring this mixture with the addition of 2-octanol at  $75^\circ\text{C}$  for 9 h, the mixture contained trace amounts of 1-octene and 2-chlorooctane (the  $-\text{CClH}$  signal at  $\delta = 58.0$  ppm in the  $^{13}\text{C}$  NMR spectrum). The  $^{29}\text{Si}$  NMR spectrum showed signals at  $-19.5$ ,  $-21.2$ ,  $-21.8$ , and  $-22.5$  ppm arising from  $-\text{Si}(\text{CH}_3)_2\text{O}-$  dimethylsiloxy units. These units could only be a result of the elimination of one of the methyl substituents in trimethylchlorosilane, which was taken in excess, or hexamethyldisiloxane formed during reaction (8). Hence, the following transformations (9) took place in this system:



In the experiment on the preparation of the  $\pi$ -complex of Pt(II) with 1-octene,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  was mixed with ethanol and 1-octene combined in the 1 : 1 : 1 molar ratio. The ratio of the components was taken in such a way that the amount of ethanol did not exceed that required for Pt(IV) reduction to Pt(II) by analogy with reaction (1), and Pt(II), in turn, formed a  $\pi$ -complex with 1-octene. No precipitation of Pt(0) was observed during the reaction. The  $^{13}\text{C}$  NMR study of the reaction products has shown that the  $\text{C}=\text{C}$  bond is almost completely hydrochlorinated to give the  $\text{C}-\text{Cl}$  bond, which is confirmed by the presence of a new signal at  $\delta = 63.35$  ppm in the spectrum. There is no resonance signal of the  $-\text{CH}_2-\text{OH}$  group at 3.7 ppm in the  $^1\text{H}$  NMR spectrum, which indicates that ethanol is completely consumed for the reduction of Pt(IV) to Pt(II) by analogy with reaction (1) with the

only difference that acetaldehyde is formed instead of acetone.

## CONCLUSIONS

(1) Based on the analysis of literature data describing the behavior of platinum chlorides in alcohol media, it can be stated that platinum compounds in different oxidation states have catalytic activity in them.

(2) It has been determined that Pt(IV) in  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  under the action of an excess of 2-octanol at  $100^\circ\text{C}$  is completely reduced to Pt(II), which is then reduced by 30% to Pt(0) within 13 h due to the oxidation of the alcohol to 2-octanone.

(3) It has been shown for the first time that in the  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ –2-octanol system, 2-chlorooctane is

formed through the exchange reaction between 2-octanol and hydrogen chloride.

(4) It has been proven that both hydrated and dehydrated  $\text{H}_2\text{PtCl}_6$  and  $\text{H}_2\text{PtCl}_4$  do not cause the formation of 1-octene and 2-octene by dehydration of 2-octanol.

(5) It has been demonstrated that even  $\text{H}_2\text{PtCl}_6$  dehydrated with trimethylchlorosilane catalyzes the formation of 2-chlorooctane by hydrochlorination of 1-octene.

(6) It has been found that a dehydrated mixture of  $\text{H}_2\text{PtCl}_6$  and  $\text{H}_2\text{PtCl}_4$  catalyzes the elimination of methyl groups from trimethylchlorosilane and hexamethyldisiloxane to form polydimethylsiloxanes.

(7) It has been assumed that the resulting  $\pi$ -complex of  $\text{H}_2\text{PtCl}_4$  with 1-octene is not stable in hydrochloric acid medium and rapidly decomposes with the release of chloroalkyl.

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#### CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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