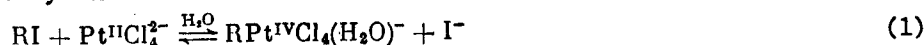


INTERMEDIATE FORMATION OF AN ETHYL COMPLEX  
OF PLATINUM(IV) IN THE  $\text{EtI-PtCl}_4^{2-}\text{-H}_2\text{O}$  SYSTEMV. V. Zamashchikov, E. S. Rudakov,  
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Methyl [1], acetyl [2], and carboxymethyl [3] complexes of platinum(IV) ( $\text{R} = \text{Me}$ ,  $\text{CH}_2\text{COMe}$ ,  $\text{CH}_2\text{COOH}$ ) are obtained by the reaction\*



In an aqueous solution containing  $\text{Cl}^-$  ions, these complexes slowly convert into the corresponding chloride and hydroxyl derivatives of the organic ligand R [1, 4, 5].

A reaction of  $\text{PtCl}_4^{2-}$  with ethyl iodide is also known [6], but the complex formed ( $\text{R} = \text{Et}$ ) is relatively unstable, and its existence is concluded mainly from observation of ethyl chloride and ethanol as the products of its reaction with nucleophiles. It was therefore important to study in detail the properties of the  $\sigma$ -ethyl complex of platinum(IV) obtained by reaction (1). In the present work, the PMR spectrum parameters of this complex were determined, and the kinetics of its formation and dissociation in solution were studied.

When ethyl iodide is added to a solution of  $\text{K}_2\text{PtCl}_4$  in  $\text{D}_2\text{O}$ , the accumulation of ethyl chloride (PMR spectrum: quadruplet at  $\delta 3.62$ , triplet at  $\delta 1.45$  ppm), ethanol ( $\delta 3.69$ ,  $1.20$  ppm), and an intermediate product, an ethyl complex of platinum ( $\delta 4.11$ ,  $0.54$  ppm), is observed. To assign the last signal, we carried out reaction (1) with ethyl iodide  $\text{CD}_3\text{CH}_2\text{I}$  deuterated in the methyl group, so that platinum satellites could be observed in the PMR spectrum, with an integral intensity close to 34%. This value corresponds to the natural content of the  $^{195}\text{Pt}$  isotope. The spin-spin splitting constant is equal to  $^2J_{195\text{Pt}-\text{C}(\text{H})_2} = 86.4$  Hz. The platinum satellites of the  $\beta$ -proton signals of  $\text{EtPt}^{\text{IV}}$  ( $^3J_{195\text{Pt}-\text{C}(\text{H})_3} = 18$  Hz) were observed when the reaction was carried out in a  $\text{CD}_3\text{OD}$  medium.<sup>†</sup>

Comparison of the parameters of the PMR spectra of the ethyl and other  $\sigma$ -organic derivatives of platinum(IV), obtained by reaction (1) and by oxidation of Zeiss's salt solutions by molecular chlorine [7] (Table 1) shows that the values of  $^2J_{195\text{Pt}-\text{C}(\text{H})_2}$  increase in the series  $\text{MePt}^{\text{IV}} < \text{EtPt}^{\text{IV}} \approx \text{OHCH}_2\text{CH}_2\text{Pt}^{\text{IV}} \approx \text{ClCH}_2\text{CH}_2\text{Pt}^{\text{IV}} < \text{MeCOCH}_2\text{Pt}^{\text{IV}} \approx \text{HOOCCH}_2\text{Pt}^{\text{IV}}$ , symbatically with increase in the chemical shifts.

We shall now consider the paths of decomposition of the ethyl complex of platinum(IV). After some time, the concentration of ethylplatinum(IV) passes through a maximum (Table 2). Ethanol and ethyl chloride accumulate in parallel, and also form after the disappearance of ethyl iodide in the system, which proves the intermediate role of ethylplatinum(IV). This should lead, in particular, to an S-shaped dependence of the concentration of  $\text{EtCl}$  and  $\text{EtOH}$  on time. This effect is sharply observed (Fig. 1) when the more sensitive GLC method is used to monitor the accumulation of ethyl chloride in the gaseous phase of an agitated closed reactor.

In 0.15 M solution of  $\text{K}_2\text{PtCl}_4$  at  $\sim 20^\circ\text{C}$ , the kinetics of change in the concentration of ethyl iodide, ethylplatinum(IV), ethanol, and ethyl chloride, taking into account the conditions  $[\text{EtI}] \ll [\text{Pt(II)}]$  correspond (see Table 2) to the equations [see scheme (2)]  $d[\text{RI}]/d\tau = -k_1[\text{RI}]$ ;  $d[\text{RPt(IV)}]/d\tau = k_1[\text{RI}] - (k_2 + k_3)[\text{RPt(IV)}]$ ;  $d[\text{ROH}]/d\tau = k_2[\text{RPt(IV)}]$ ;  $d[\text{RCl}]/d\tau = k_3[\text{RPt(IV)}]$  at  $k_1 = 1.67 \cdot 10^{-4}$ ,  $k_2 = 4.1 \cdot 10^{-5}$ , and  $k_3 = 2.0 \cdot 10^{-5} \text{ sec}^{-1}$ .

\*The iodide ions formed are bound by an excess of platinum(IV).

<sup>†</sup>Under these conditions, the stationary concentration of  $\text{EtPt}^{\text{IV}}$  is higher than that in the aqueous solutions, as the result of increase in the rate of reaction (1) due to higher solubility of ethyl iodide in methanol.

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TABLE 1. Parameters of PMR Spectra of Alkyl Complexes of Platinum(IV) and Their Analogs

| Complex*   | $\delta_{H_{\alpha}}$ , ppm | ${}^2J_{195Pt-C-1H}$ , Hz | $\delta(H_{\beta})$ , ppm | ${}^3J_{195Pt-C-C-1H}$ , Hz |
|--|-----------------------------|---------------------------|---------------------------|-----------------------------|
| CH <sub>3</sub> Pt <sup>IV</sup> [1]                   | 3.07                        | 77.2                      | —                         | —                           |
| CH <sub>3</sub> CH <sub>2</sub> Pt <sup>IV</sup>       | 4.44                        | 86.4                      | 0.54                      | 18                          |
| ClCH <sub>2</sub> CH <sub>2</sub> Pt <sup>IV</sup> [7] | 4.11                        | 82.0                      | 3.92                      | —                           |
| OHCH <sub>2</sub> CH <sub>2</sub> Pt <sup>IV</sup> [7] | 3.99                        | 85.0                      | 3.48                      | —                           |
| HOCH <sub>2</sub> Pt <sup>IV</sup> [3]                 | 4.39                        | 98.4                      | —                         | —                           |
| CH <sub>3</sub> COCH <sub>2</sub> Pt <sup>IV</sup> [2] | 4.69                        | 98.4                      | 2.23†                     | —                           |

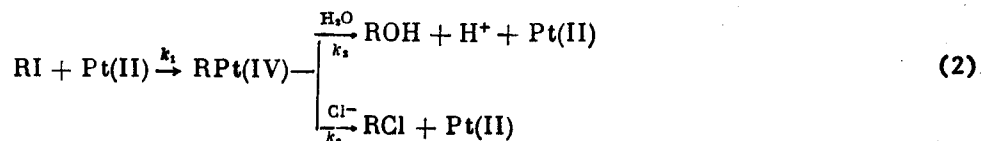
\*The data for the methyl complex [5] show that in aqueous solutions under PMR measurement conditions, the complexes are present in the form of an equilibrium mixture of two particles  $RPt^{IV}Cl_3^{2-}$  and  $RPt^{IV}Cl_2(H_2O)^-$ .

† $\delta(H_{\gamma})$ .

TABLE 2. Time-Dependent Change in Concentrations ( $M \cdot 10^2$ ) of Ethyl Iodide, Ethylplatinum(IV), Ethanol, and Ethyl Chloride in Reaction of Ethyl Iodide with  $K_2PtCl_4$ \*

| $\tau$ , min | [EtI] |       | [EtPt <sup>IV</sup> ] |       | [EtOH] |       | [EtCl] |       |
|--------------|-------|-------|-----------------------|-------|--------|-------|--------|-------|
|              | exp.  | calc. | exp.                  | calc. | exp.   | calc. | exp.   | calc. |
| 20           | 1.55  | 1.56  | 0.37                  | 0.34  | 0.28   | 0.44  | —      | —     |
| 40           | 1.28  | 1.27  | 0.61                  | 0.58  | 0.44   | 0.49  | —      | —     |
| 61           | 0.97  | 1.03  | 0.73                  | 0.77  | 0.50   | 0.50  | —      | —     |
| 79           | 0.86  | 0.86  | 0.86                  | 0.88  | 0.54   | 0.54  | 0.28   | 0.25  |
| 103          | 0.68  | 0.67  | 0.98                  | 0.98  | 0.65   | 0.59  | 0.30   | 0.28  |
| 126          | 0.53  | 0.54  | 1.04                  | 1.04  | 0.70   | 0.65  | 0.34   | 0.31  |
| 150          | 0.42  | 0.42  | 1.03                  | 1.06  | 0.81   | 0.71  | 0.36   | 0.34  |
| 185          | 0.30  | 0.30  | 1.00                  | 1.05  | 0.87   | 0.80  | 0.42   | 0.38  |
| 233          | 0.18  | 0.19  | 0.94                  | 0.98  | 0.97   | 0.92  | 0.42   | 0.44  |
| 260          | —     | —     | 0.90                  | 0.93  | 1.00   | 0.98  | 0.45   | 0.47  |
| 285          | —     | —     | 0.86                  | 0.88  | 1.01   | 1.04  | 0.48   | 0.49  |
| 306          | —     | —     | 0.83                  | 0.83  | 1.07   | 1.08  | 0.50   | 0.51  |
| 330          | —     | —     | 0.82                  | 0.78  | 1.09   | 1.13  | 0.49   | 0.54  |
| 367          | —     | —     | 0.75                  | 0.70  | 1.15   | 1.20  | 0.54   | 0.57  |
| 417          | —     | —     | 0.70                  | 0.80  | 1.23   | 1.28  | 0.59   | 0.61  |

\* $[K_2PtCl_4] = 0.15$  M, D<sub>2</sub>O, Bruker SXP-4-100 NMR spectrometer, internal standard — acetone, scanning time (400 scannings) — 13.3 min; the calculated values of the concentrations were found by using scheme (2).



R = Et.

The values of  $k_2$  and  $k_3$  were found from the condition of a minimum sum of squares of deviations of the experimentally determined EtPt(IV) concentration and the calculated concentration according to scheme (2), taking into account the ratios of yields of EtOH and EtCl. The yield of ethyl chloride in 0.15 M solution of  $K_2PtCl_4$  is  $32 \pm 4\%$  and decreases to  $17 \pm 3\%$  when the initial concentration of  $K_2PtCl_4$  is decreased to 0.05 M. This agrees with the data for the methyl complex [4], as its rate of dissociation to methyl chloride decreases with decrease in  $Cl^-$  concentration. The yield of ethanol in 0.05 M solution of  $K_2PtCl_4$  is  $75 \pm 6\%$ . We should note that under conditions similar to those shown above, the dissociation of methylplatinum(IV) gives mainly methyl chloride; the yield of methanol does not exceed 14% [5]. This can be explained by the known fact that the rate of hydrolysis increases [8] and the rate of  $S_N2$  substitution decreases on transition from R = Me to R = Et, for example, on transition from MeCl to EtCl [9].

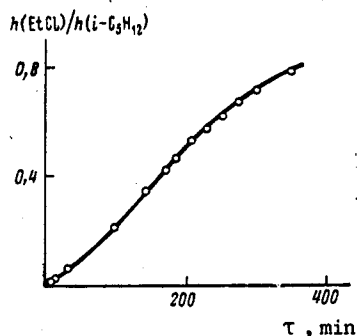


Fig. 1. Time-dependent change in relative concentration of ethyl chloride in gaseous phase in closed agitated reactor;  $h(\text{EtCl})/h(i\text{-C}_5\text{H}_{12})$  is ratio of heights of chromatographic peaks of ethyl chloride and isopentane, used as internal standard;  $[\text{EtI}] \ll [\text{K}_2\text{PtCl}_4] = 0.1 \text{ M}$ , aqueous solution,  $298^\circ\text{K}$ .

In general, from the available data [1-3, 4, 7], a stability series of the alkyl complexes of platinum(IV) and their analogs with respect to reductive elimination:  $\text{Pt}^{\text{IV}}\text{CH}_2\text{COOH} > \text{Pt}^{\text{IV}}\text{CH}_2\text{COMe} \approx \text{Pt}^{\text{IV}}\text{CH}_2\text{CH}_2\text{Cl} \approx \text{Pt}^{\text{IV}}\text{CH}_2\text{CH}_2\text{OH} \gg \text{Pt}^{\text{IV}}\text{Me} \gg \text{Pt}^{\text{IV}}\text{Et}$ , can be constructed. The introduction of electron-acceptor substituents and decrease in the steric accessibility of the  $\alpha$ -carbon atom lead to increase in the stability of the complex in this series.

Since in the ethyl complex there are  $\beta$ -hydrogen atoms, the presence of a still another path of the dissociation of the complex could be expected, namely, via the  $\beta$ -elimination. This reaction probably proceeds in the case of the hexyl complex of platinum(IV), formed by reaction (1) with iodoheptane [10], or in the reaction of hexane with  $\text{PtCl}_6^{2-}$  [10, 11]. The observations [12, 13] on dehydrogenation in the oxidation of alkanes indicate that  $\beta$ -elimination can be a very general reaction of alkyl complexes of platinum. However, the data in Table 2 show that under the conditions that we studied, dehydrogenation proceeds only to an inappreciable extent (the sum of  $\text{EtCl}$ ,  $\text{EtOH}$ , and  $\text{EtPt}^{\text{IV}}$  is close to 100%). In fact, at  $298^\circ\text{K}$  in a 0.05 M solution of  $\text{K}_2\text{PtCl}_4$ , the ethylene complex of platinum(II) is formed in a yield of about 1% only (based on  $\text{EtI}$ ; isolated and identified in the form of an adduct with  $\text{Py}$ ). With increase in temperature, the yield of Zeisse's salt decreases. The formation of Zeisse's salt under our conditions cannot be explained by the known reaction [14] of platinum(II) with ethanol, formed as the result of hydrolysis of ethylplatinum(IV). At  $298^\circ\text{K}$  in a 0.1 M solution of  $\text{K}_2\text{PtCl}_4$ , the rate of accumulation of the  $\pi$ -complex in the reaction of platinum(II) with  $\text{EtI}$  is 4-5 times higher than the rate of formation of Zeisse's salt in the reaction of  $\text{Pt}(\text{II})$  with ethanol at an initial concentration 10 times the initial concentration of  $\text{EtI}$ , and hence the concentration of ethanol formed in the system studied.

The small fraction of  $\beta$ -elimination in the dissociation of ethyl-complex of platinum(IV) may probably be due to the absence under our experimental conditions of coordinational vacancies in  $\text{EtPt}(\text{IV})$  in the cis position with respect to the alkyl group, which are necessary [15] for the elimination to proceed. It is not excluded that  $\beta$ -elimination proceeds more readily in the alkyl complexes of platinum(II), the first intermediates in the oxidation of alkanes in the  $\text{Pt}(\text{II})$ - $\text{Pt}(\text{IV})$  system. This, in particular, may be the reason for the relatively high yields of the dehydrogenation products in the oxidation of cyclohexane.

#### EXPERIMENTAL

The PMR spectra were recorded on Bruker SXP-4-100 (90 MHz) and Bruker WM-250 (250 MHz) spectrometers, using DSS (the Na salt of 2,2-dimethyl-2-silapentane-5-sulfonic acid) or acetone as internal standards.

The experiments were carried out directly in PMR ampules at  $\sim 20^\circ\text{C}$ .  $\text{K}_2\text{PtCl}_4$  was added to a saturated solution of  $\text{EtI}$  in  $\text{D}_2\text{O}$ , and the PMR spectra of the reaction mixture were recorded at given periods of time.

The yields of the ethylene complex of platinum was determined by displacing ethylene from the coordination sphere of platinum by adding a large excess of thiocyanate ions to the reaction products, followed by GLC analysis of the ethylene liberated.

Identification of Ethylene Complex of Platinum(II). A saturated solution of  $K_2PtCl_4$  and EtI (excess in the form of a separate phase) in  $H_2O$  was stirred for 4 h at  $\sim 20^\circ C$ . The solvent was distilled in vacuo at  $\sim 20^\circ C$ . The residue was extracted by chloroform, and the extract was shaken with an aqueous solution of pyridine (0.03 ml in 10 ml of  $H_2O$ ). The chloroform solution was dried over  $Na_2SO_4$ , the solvent was evaporated in vacuo, and the residue was chromatographed on silica gel plates (eluent -  $CHCl_3$ ). Yield,  $\sim 1\%$  (based on Pt) of complex  $(CH_2=CH_2)PtCl_2C_5H_4N$ , identified by comparison with a sample synthesized by the reaction of  $PtCl_6^{2-}$  with ethylene in acetone with irradiation by light [16, 17].

#### CONCLUSIONS

1. In the reaction of potassium tetrachloroplatonate with ethyl iodide in an aqueous solution at room temperature, the ethyl complex of platinum(IV) is formed, which is characterized by PMR spectra.

2. In aqueous solutions containing chloride ions, the ethyl complex of platinum(IV) decomposes to form ethanol, ethyl chloride and an ethylene complex of platinum(II).

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