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Kinetics and Mechanism of Decomposition of the β-Chlorovinyl and β-Iodovinyl Complexes of Platinum(IV) in Aqueous Iodide Solutions

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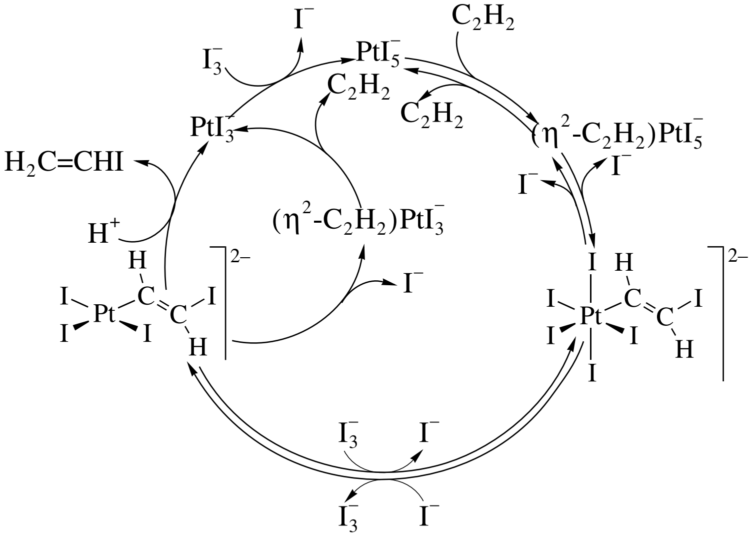
Abstract—It was found that the β-iodovinyl and β-chlorovinyl complexes of platinum(IV) undergo decomposition in acidic aqueous solutions in the presence of NaI (2.5 M) with the simultaneous formation of acetylene and a corresponding vinyl halide RX (X = Cl, I). The kinetics and the composition of products are consistent with a mechanism that includes an equilibrium step of the reduction of the β-halovinyl complexes of Pt(IV) by iodide ions to form corresponding Pt(II) derivatives; the degradation of the above organoplatinum compounds by halogen β-elimination to form acetylene; and a step of the protodemetallation of the σ-vinyl derivatives of Pt(II), which leads to RX. The rate constants of individual steps and the equilibrium constant were estimated.

INTRODUCTION

Previously, it was found that the iodide complexes of Pt(IV) catalyze the hydroiodination of acetylene to vinyl iodide in acidic aqueous solutions at 80°C [1]. Based on kinetic data, reaction scheme (I) was proposed, which includes a sequence of the steps of acetylene iodoplatination with the intermediate formation of a β-iodovinyl complex of Pt(IV) (**1**), the reduction of this complex by iodide ions to a corresponding Pt(II) derivative, and the protolysis of the resulting species with the release of vinyl iodide:



(I)

The formation of the β-iodovinyl complex of Pt(IV) as a result of the reversible iodoplatination of acetylene in aqueous iodide solutions at 40°C was detected by NMR spectroscopy [2]. Recently [3], we prepared the β-chlorovinyl derivative of platinum(IV) $K_2Pt(CH{=}CHCl)Cl_5$ (**2**), an analog of complex **1**. The availability of simple methods for the generation of the above organoplatinum compounds provides an opportunity to independently test scheme (I) and also to compare the reactivities of complexes **1** and **2**. The aim of this work was to study the kinetics and mechanism of decomposition of these species in aqueous iodide solutions.

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EXPERIMENTAL

The reactions were performed in a thermostatted closed reactor filled with a liquid phase by 15–20% with shaking in an argon atmosphere at 59°C, a constant concentration [NaI] = 2.5 mol/l, and a constant ionic strength adjusted with sodium perchlorate ($[HClO_4] + [NaClO_4] = 2.5$ mol/l). The accumulation of acetylene and vinyl halides in a gas phase was monitored by GLC. An LKhM-8MD gas–liquid chromatograph with a flame-ionization detector and a column packed with an SE-30 stationary phase on Inerton NAW was used, which was equipped with a Multikhrom data acquisition system (Ampersand).

Complex **1** was prepared in accordance with the procedure described elsewhere [2]; the residual acetylene was purged with argon, and a small aliquot portion of the resulting solution (10 μl) was added to 2 ml of a thermostatted reaction solution. Complex **2** was prepared in accordance with a published procedure [3] and dissolved in a 2.5 M NaI solution; a small aliquot portion of the resulting solution (10 μl) was used in the reaction as described above. The initial concentrations of the complexes were 10^{-4}–10^{-3} mol/l.

The kinetics of the reactions was studied by monitoring the buildup of gaseous reaction products. The kinetic data were processed using the least-squares technique with a confidence level of 95%. The distribution coefficients of acetylene $\alpha_{C_2H_2} = \dfrac{[C_2H_2]_{gas}}{[C_2H_2]_{solurion}}$ and vinyl halides RX (X = I, Cl) $\alpha_{RX} = \dfrac{[RX]_{gas}}{[RX]_{solurion}}$ between a gas phase and a solution were $\alpha_{C_2H_2} = 2.5 \pm 0.3$, $\alpha_{RCl} = 3.9 \pm 0.4$, and $\alpha_{RI} = 1.2 \pm 0.1$, as measured by a published method [4] at $[HClO_4] = 2.5$ mol/l.[1] The volume ratio between gas and liquid phases in the reactor was 10.6; taking into account the above distribution coefficients, this allowed us to ignore the amount of products remaining in solution.

RESULTS AND DISCUSSION

Reaction scheme (I) suggests that complexes **1** and **2** in acidic aqueous solutions in the presence of an excess of iodide ions[2] decompose with the simultaneous formation of acetylene and a corresponding vinyl halide. Indeed, these reactions were detected (reaction scheme (II); for simplicity, anionic ligands are not shown).

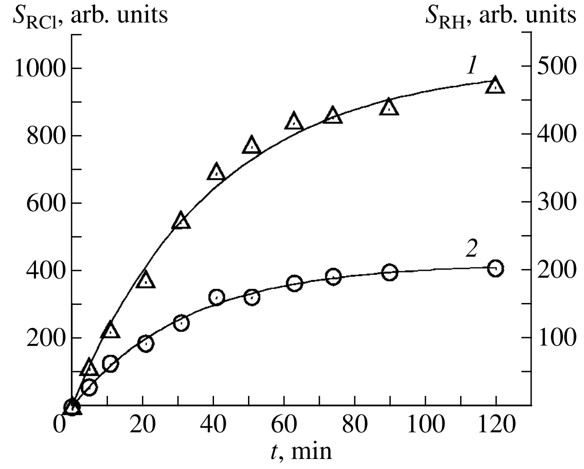
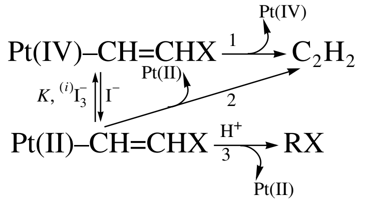


Fig. 1. Typical kinetic curves of the buildup of the decomposition products of complex **2**; $[I_3^-] = 0.0165$ mol/l; $[HClO_4] = 1.25$ mol/l; S is the chromatographic peak area of (*1*) vinyl chloride or (*2*) acetylene; points correspond to experimental data, and lines illustrate calculations by the first-order rate equation $S = S_\infty[1 - \exp(-k^{(2)}t)]$ at (*1*) $k^{(2)} = (4.2 \pm 0.4) \times 10^{-4}$ s^{-1} and $S_{RCl,\infty} = (1010 \pm 43)$ or (*2*) $k^{(2)} = (4.9 \pm 0.4) \times 10^{-4}$ s^{-1} and $S_{RH,\infty} = (213 \pm 12)$.



X=I ($i = 1$), Cl ($i = 2$)

(II)

In the absence of an acid, acetylene was the only decomposition product detected. In acidic solutions, acetylene and a corresponding vinyl halide were formed simultaneously; the buildup of these products corresponds to a first-order rate equation (Fig. 1). As would be expected for parallel reactions, the rate constants of product buildup are equal to each other within the limits of experimental errors and correspond to the apparent rate constant of decomposition of the initial complex. In a qualitative agreement with reaction scheme (II), the apparent rate constants $k^{(i)}$ ($i = 1, 2$) of decomposition of complexes **1** and **2**, respectively, and the ratio $\eta_{RX}/\eta_{C_2H_2}$ between the yields of RX and acetylene increase with concentration of the acid; the addition of iodine resulted in the opposite effect (Tables 1–3).

Quantitatively, in terms of reaction scheme (II), it would be expected that the following relationships will be obeyed for the ratio between product yields and the

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[1] Under these conditions, the distribution coefficients exhibit minimum values because the solubility of the above substrates increases with increasing concentration of the acid [1].

[2] An excess of iodide ions is required for a rapid reaction of the substitution of iodide ligands for chloride ligands in complex **2** (as compared with the characteristic time of the reactions under consideration). For simplicity, henceforth, the b-chlorovinyl complex of Pt(IV) with iodide ligands will also be denoted complex **2**.

Table 1. Dependence of the ratio between the yields of vinyl chloride and acetylene ($\eta_{RI}/\eta_{C_2H_2}$) and the rate constant of consumption of complex **1** ($k^{(1)}$) on the concentrations of $HClO_4$ and I_3^-

$[I_3^-]$, mol/l	$[HClO_4]$, mol/l	$\eta_{RI}/\eta C_2H_2$	$k^{(1)} \times 10^4$, s^{-1}
0.00229	0	0	6.4 ± 0.3
	0.2	0.10 ± 0.03	9.1 ± 0.2
	0.5	0.42 ± 0.01	13.3 ± 0.3
	1.25	1.53 ± 0.03	30.8 ± 0.8
	2	3.82 ± 0.07	50 ± 6
0.00575	0.2	0.10 ± 0.02	10.5 ± 0.5
	0.5	0.35 ± 0.02	12.5 ± 0.6
	1	0.85 ± 0.04	14.6 ± 0.7
	1.5	1.41 ± 0.01	21.00 ± 1.05
	0	0	9.2 ± 0.5
0.0065	0.2	0.09 ± 0.01	8.6 ± 0.2
	0.5	0.32 ± 0.01	12.7 ± 0.5
	1	0.62 ± 0.01	17.0 ± 0.9
0.0129	0	0	7.0 ± 0.1
	0.5	0.16 ± 0.01	9.1 ± 0.3
	1	0.57 ± 0.02	11 ± 3

Table 2. Dependence of the ratio between the yields of vinyl chloride and acetylene ($\eta_{RCl}/\eta_{C_2H_2}$) and the rate constant of consumption of complex **2** ($k^{(2)}$) on the concentration of $HClO_4$

$[HClO_4]$, mol/l	$\eta_{RCl}/\eta_{C_2H_2}$	$k^{(2)} \times 10^4$, s^{-1}
0	0	1.0 ± 0.2
0.25	0.79 ± 0.07	1.3 ± 0.3
0.75	2.6 ± 0.2	3.6 ± 0.2
1.25	4.7 ± 0.5	4.2 ± 0.4
2	13 ± 2	8.9 ± 1.6
2.5	16 ± 4	7 ± 2

Note: $[I_3^-] = 0.0165$ mol/l.

rate constant $k^{(i)}$ of decomposition as a function of $HClO_4$ and I_3^- concentrations:

$$\frac{\eta_{RX}}{\eta_{C_2H_2}} = \frac{k_3^{(i)}[H^+]}{k_2^{(i)} + k_1^{(i)}K^{(i)}[I_3^-]}, \tag{1}$$

$$k^{(i)} = \frac{k_2^{(i)} + k_1^{(i)}K^{(i)}[I_3^-] + k_3^{(i)}[H^+]}{1 + K^{(i)}[I_3^-]}, \tag{2}$$

where $k_j^{(i)}$ are the rate constants of the corresponding steps of reaction scheme (II), and $K^{(i)}$ is the equilibrium constant of an equilibrium between the σ-vinyl derivatives of Pt(II) and Pt(IV) for complexes **1** and **2**.

In accordance with Eq. (1), at a constant concentration of I_3^-, the yield ratio $\eta_{RI}/\eta_{C_2H_2}$ in the case of complex **1** linearly increases with the concentration of $HClO_4$ (Table 1). The slopes of the above functions

$$A = \frac{k_3^{(1)}}{k_2^{(1)} + k_1^{(1)}K^{(1)}[I_3^-]} \tag{3}$$

decrease with the concentration of I_3^-. The parameters $\frac{k_2^{(1)}}{k_3^{(1)}} = (0.7 \pm 0.1)$ mol/l and $\frac{k_1^{(1)}K^{(1)}}{k_3^{(1)}} = 46 \pm 7$ were determined from a linear anamorphosis of Eq. (3) as a function of the concentration of I_3^- (Fig. 2).

Figure 3 demonstrates a linear anamorphosis of function (1) in the case of the decomposition of complex **2**. The parameters $\frac{k_2^{(2)}}{k_3^{(2)}}$ and $\frac{k_1^{(2)}K^{(2)}}{k_3^{(2)}}$ determined from this anamorphosis are 0.08 ± 0.02 and 9.4 ± 0.9 mol/l, respectively. It is reasonable to assume that the equilibrium constants of equilibria between the σ-vinyl derivatives of Pt(II) and Pt(IV) and the rate constants of protolysis for the chlorovinyl and iodovinyl complexes of Pt(II) are close to each other: $k_3^{(1)} = k_3^{(2)}$ and $K^{(1)} = K^{(2)}$. In this case, we obtain the following ratios for the rate constants of halide ion elimination from the β-halovinyl complexes of Pt(IV) and Pt(II): $\frac{k_1^{(1)}}{k_1^{(2)}} = (4.9 \pm 1.2)$ and $\frac{k_2^{(1)}}{k_2^{(2)}} = (8.8 \pm 3.4)$. Evidently, this decrease in reactivity going from β-iodovinyl to β-chlorovinyl derivatives of platinum is a consequence of increasing C–X bond strength in the order X = I, Cl.

On the condition that, in experiments with iodine additives, the equilibrium between the σ-vinyl derivatives of Pt(II) and Pt(IV) is shifted toward the latter species, $K^{(i)}[I_3^-] > 1$. Taking into account the fact that the inequality $\frac{k_2^{(i)}}{k_3^{(i)}} < \left(\frac{k_1^{(i)}K^{(i)}}{k_3^{(i)}}[I_3^-] + [H^+]\right)$ is obeyed for the major portion of experimental conditions, Eq. (2) is rearranged to the form

$$k^{(i)} \approx k_1^{(i)} + \frac{k_3^{(i)}}{K^{(i)}}\frac{[H^+]}{[I_3^-]}, \qquad (4)$$

which is consistent with experimental data (Fig. 4) at $k_1^{(1)} = (7.4 \pm 0.7) \times 10^{-4}\ s^{-1}$, $\frac{k_3^{(1)}}{K^{(1)}} = (4.7 \pm 0.2) \times 10^{-6}\ s^{-1}$, and $k_1^{(2)} = (1.9 \pm 0.6) \times 10^{-4}\ s^{-1}$, $\frac{k_3^{(2)}}{K^{(2)}} = (3.5 \pm 0.5) \times 10^{-6}\ s^{-1}$. Note that the ratios $\frac{k_3^{(i)}}{K^{(i)}}$ for $i = 1$ and 2 are close to each other within the limits of experimental error. This is consistent with the above assumption on the equality between the constants $k_3^{(1)} = k_3^{(2)}$ and $K^{(1)} = K^{(2)}$. The ratio between the rate constants of halide ion elimination from the β-iodovinyl and β-chlorovinyl complexes of Pt(IV) $\frac{k_1^{(1)}}{k_1^{(2)}} = (3.9 \pm 1.6)$, as determined from relationship (4). Within the limits of experimental error, this value is equal to the above value estimated from ratios between the yields of the reaction products.

Table 3. Dependence of the ratio between the yields of vinyl chloride and acetylene ($\eta_{RCl}/\eta_{C_2H_2}$) and the rate constant of consumption of complex **2** ($k^{(2)}$) on the concentration of I_3^-

$[I_3^-]$, mol/l	$\eta_{RCl}/\eta_{C_2H_2}$	$k^{(2)} \times 10^4$, s^{-1}
0	–	31 ± 5
0.00412	12.3 ± 0.4	11.4 ± 0.4
0.00825	7 ± 1	7.6 ± 0.8
0.0165	4.7 ± 0.5	4.2 ± 0.4
0.032	3.3 ± 0.3	3.7 ± 0.6

Note: $[HClO_4] = 1.25$ mol/l.

We use the data in Table 3 for estimating the equilibrium constant $K^{(2)}$ and the rate constant $k_3^{(2)}$ of protolysis of the β-chlorovinyl complex of Pt(II). The treatment of experimental data with the use of Eq. (2) and the above numerical values of $\frac{k_2^{(2)}}{k_3^{(2)}}$ and $\frac{k_1^{(2)}K^{(2)}}{k_3^{(2)}}$ (Fig. 5) gives the following values: $k_3^{(2)} = (2.2 \pm 0.3) \times 10^{-3}\ l\ mol^{-1}\ s^{-1}$ and $K^{(2)} = (400 \pm 100)$ l/mol. Note that the estimated equilibrium constant $K^{(2)}$ for the equilibrium

$$Pt(II){-}CH{=}CHCl + I_3^- \rightleftarrows Pt(IV){-}CH{=}CHCl \qquad (III)$$

is ~30 times lower than the equilibrium constant [4] for the equilibrium

$$Pt(II) + I_3^- \rightleftarrows Pt(IV). \qquad (IV)$$

This decrease of the equilibrium constant can be a consequence of stabilization of the σ-vinyl derivative of

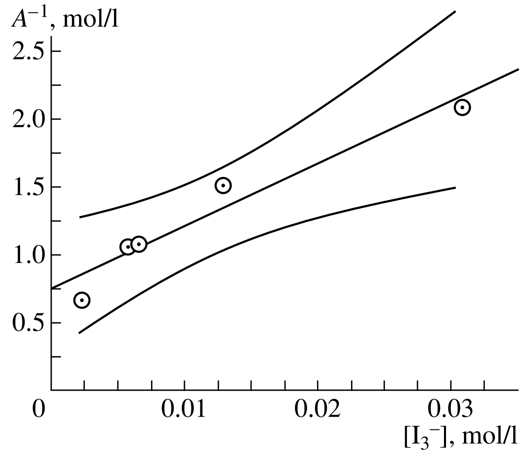

Fig. 2. Linear anamorphosis of Eq. (3) for the reaction of complex **1**; dashed lines indicate a 95% confidence interval.

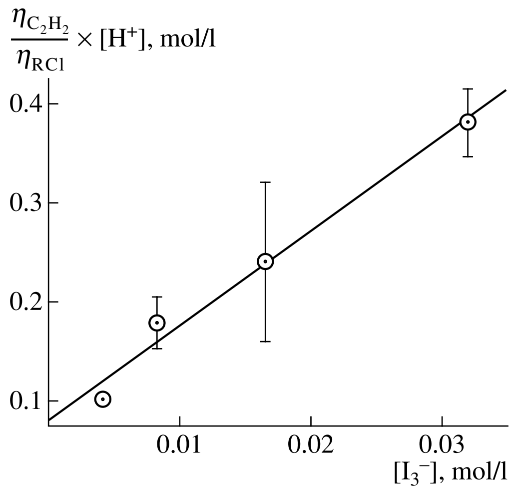

Fig. 3. Linear anamorphosis of Eq. (1) for the decomposition of complex **2**.

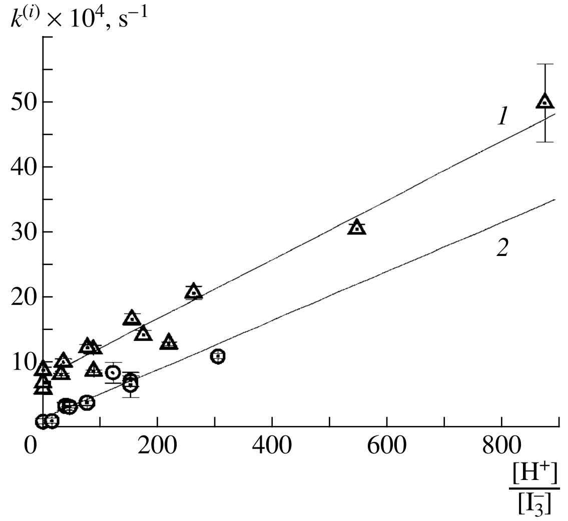

Fig. 4. Dependence of the rate constants of decomposition of the β-halovinyl complexes of Pt(IV) on the parameter $[H^+]/[I_3^-]$ for (*1*) X = I and (*2*) X = Cl.

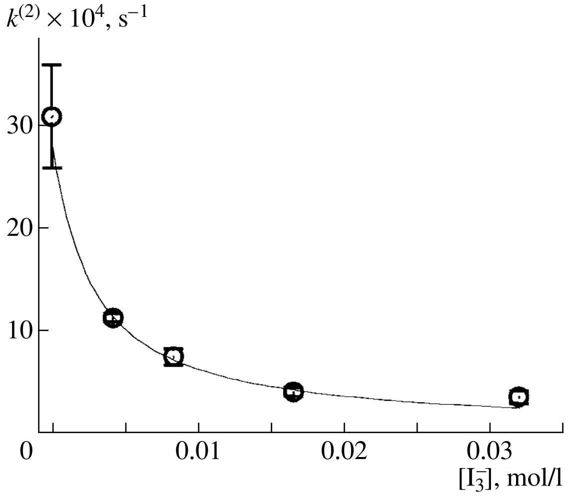

Fig. 5. Dependence of the rate constant of decomposition of the β-chlorovinyl complex of platinum on the concentration of I_3^-. $[HClO_4]$ = 1.25 mol/l. Points correspond to experimental data, and lines illustrate calculations performed by the least-squares techniques with the use of Eq. (2) at $\frac{k_2^{(2)}}{k_3^{(2)}} = 0.08$ mol/l and $\frac{k_1^{(2)}K^{(2)}}{k_3^{(2)}} = 9.4$.

Pt(II) due to the additional coordination of a vinyl ligand to the metal. Such a stabilization of the σ-vinyl derivative of Pt(IV) is improbable because, unlike Pt(II), Pt(IV) compounds do not form stable π complexes [6, 7].

In conclusion, note one more experimental fact. In chloride solutions, unlike iodide solutions, complex **2** at 59°C does not form acetylene and vinyl chloride in detectable amounts. The evident reason for the difference in the reactivities of the chloride and iodide β-chlorovinyl complexes of Pt(IV) consists in the labilizing *trans* effect of iodide ligands. Indeed, β-elimination of the chlorine atom with the formation of acetylene in the decomposition of complex **2** was accompanied by the rupture of not only the carbon–halogen bond but also the Pt–C bond. Evidently, the platinum–carbon bond in a complex containing the iodide ligand in the *trans* position with respect to the σ-vinyl group will be weaker than that in a complex with the *trans* chloride ligand.

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