Inner- and outer-sphere reductive elimination during decomposition of the platinum(IV) β-ammonioethyl complex in aqueous solutions

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The β-ammonioethyl complex of platinum (IV), $KPt(CH_2CH_2NH_3)Cl_5$, undergoes two types of transformations in aqueous chloride solutions, *i.e.*, inner- and outer-sphere reductive elimination, depending on the pH of the medium. In acidic solutions outer-sphere decomposition, which consists of an S_N2 attack by the chloride ion of the α-carbon atom of the complex anion [*trans*-$Pt(CH_2CH_2NH_3)Cl_4(H_2O)]^-$ (or at the complex with a vacant coordination site in the *trans*-position relative to the $-CH_2CH_2NH_3$ group; these two variants are kinetically indistinguishable) occurs to yield β-chloroaminoethane and $PtCl_4^{2-}$. In alkaline solutions decomposition occurs after deprotonation of the ammonium group of the starting complex as an intramolecular nucleophilic attack of the amino group at the α-carbon atom in [*trans*-$Pt(CH_2CH_2NH_2)Cl_4(H_2O)]^-$ (or in the complex with a vacant coordination site in the *trans*-position relative to the β-aminoethyl group). In this case aziridine (Az) and $PtCl_4^{2-}$ are the primary products. Aziridine is coordinated with the unreacted starting complex to give a compound that is stable with respect to reductive elimination. Cyclometallation of the latter species gives the uncharged complex $\overline{Pt(CH_2CH_2N}H_2)(Az)Cl_3$ insoluble in water.

Key words: reductive elimination; nucleophilic substitution; platinum (IV); alkyl complexes; mechanism.

The ammonioethyl complex of platinum (IV), $KPt(CH_2CH_2NH_3)Cl_5$ (**1a**), is formed[1] in the oxidative addition of aziridine (Az) to the tetrachloride complex of platinum (II). When heated in acidic aqueous solutions, complex **1a** undergoes the inner-sphere reductive elimination[2–5] typical of platinum (IV) monoalkyl derivatives.

$$RPt^{IV} + Cl^- \rightarrow RCl + Pt^{II} \qquad (1)$$

The specific nature of the β-ammonioethyl complex manifests itself in deprotonation of the ammonium group. The emergence of the nucleophilic center (the NH_2 group) causes[5] inner-sphere reductive elimination resulting in regeneration of aziridine due to the attack of the "free" NH_2 group at the α-carbon atom of the σ-alkyl complex. As far as we know, this reaction is the first example of this kind* of reductive elimination for d^6-complexes. The purpose of the present work has been to study in detail the peculiarities of the decomposition of complexes **1a**.

Results and Discussion

Reductive elimination in alkaline solutions. Alkalizing an aqueous solution of complex **1a** (1.09 mmol) with potassium carbonate (1.09 mmol) for 3 days affords 98 mg of a yellow crystalline product insoluble in water. Its elemental composition is close to that of the complex $\overline{Pt(CH_2CH_2N}H_2)(Az)Cl_3$ (**1b**). Found (%): C, 11.9; H, 3.2; N, 6.8; Pt, 51.1. $C_4H_{11}Cl_3N_2Pt$. Calculated (%): C, 12.36; H, 2.85; N, 7.21; Pt, 50.20. The IR spectrum of the product (a pellet with KBr, ν/cm^{-1}) exhibits bands at 3269 s, 3190 vs (NH), 3000 vs, 2913 m, 2844 w (OH) as well as bands at 1230 vs and 877 vs which have been assigned[7] to platinum (IV)-coordinated aziridine. The ^{1}H NMR spectrum of compound **1b** was recorded by dissolving it in D_2O acidified with DCl. It exhibits signals for the starting complex **1a**, δ: 3.95 (t, J_{HH} = 5.82 Hz, $^2J_{^{195}Pt-^1H}$ = 85 Hz, α-H); 2.68 (t, β-H) and the signal for protonated aziridine: 2.71 (s). According to atomic emission spectroscopy, complex **1b** does not contain potassium.

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* The inner-sphere reductive elimination reactions $M^n\!\!<^{X}_{Y} \longrightarrow M^{n-2} + XY$ are normally regarded[6] to be a result of a three-centered concerted process during which the X and Y groups in the transition state are still partly bonded with the central atom.

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The pathway from complex **1a** to complex **1b** involves the formation of several intermediate species which can be detected by ^{1}H NMR spectroscopy. Within 30 min after partial neutralization of a solution of complex **1a** (0.2 mmol in 1 mL of D_2O) by the addition of 0.1 mmol of K_2CO_3, at least five groups of signals, in addition to those of the starting complex, can be recorded. The following group of signals increase with time, δ: 3.55 (t, J_{HH} = 6.82 Hz, $^2J_{^{195}Pt-^1H}$ = 75.4 Hz); 3.00 (t); 2.27—2.20 (m). These signals coincide with the ^{1}H NMR spectrum of a D_2O solution of a mixture of the starting complex and equimolar amounts of Az and K_2CO_3. This allows one to assign the latter group of signals to a compound having the structure [*trans*-$Pt(CH_2CH_2NH_2)AzCl_4]^-$ (**1c**). Product **1c** is practically the only one which can be detected in the ^{1}H NMR spectrum when a twofold excess of K_2CO_3 is added to a solution of complex **1a** and the reaction mixture is kept for 4 h. After the precipitate of compound **1b** accumulated during this reaction is separated and the filtrate is acidified with DCl as well as upon dissolving compound **1b** in a D_2O—DCl mixture, the ^{1}H NMR spectrum displays the signals of the starting complex and protonated aziridine. The latter confirms the above-presented composition of complex **1b**, which is obviously able to give **1a** and AzH^+ upon acidification.

The above-noted complex character of the ^{1}H NMR spectrum makes it possible to suggest that the solution obtained after the partial neutralization of **1a** contains, along with complexes **1a** and **1c**, several other species, which incorporate a $NH_2CH_2CH_2$— and/or $NH_3{}^+CH_2CH_2$— group bonded with platinum.* Taking this fact into account, we may present a possible scheme of the **1a**→**1c**→**1b** transformation as the following combination of steps.

$$\underset{\mathbf{1a}}{[Pt(CH_2CH_2NH_3)Cl_5]^-} + OH^- \rightleftharpoons [Pt(CH_2CH_2NH_2)Cl_5]^{2-} + H_2O \quad (2)$$

$$[Pt(CH_2CH_2NH_2)Cl_5]^{2-} + H_2O \rightleftharpoons [trans\text{-}Pt(CH_2CH_2NH_2)Cl_4H_2O]^- + Cl \quad (3)$$

$$[trans\text{-}Pt(CH_2CH_2NH_2)Cl_4(H_2O)]^- + OH^- \rightleftharpoons [trans\text{-}Pt(CH_2CH_2NH_2)Cl_4OH]^{2-} + H_2O \quad (4)$$

$$2[trans\text{-}Pt(CH_2CH_2NH_2)Cl_4(H_2O)]^- \rightleftharpoons [trans\text{-}Pt(CH_2CH_2NH_2)Cl_4(\mu\text{-}NH_2CH_2CH_2)PtCl_4(H_2O)]^{2-} + H_2O \quad (5)$$

$$[trans\text{-}Pt(CH_2CH_2NH_2)Cl_4(H_2O)]^- \longrightarrow AzH^+ + PtCl_4{}^{2-} + H_2O \quad (6)$$

$$AzH^+ + OH^- \rightleftharpoons Az + H_2O \quad (7)$$

$$[trans\text{-}Pt(CH_2CH_2NH_2)Cl_4(H_2O)]^- + Az \rightleftharpoons \underset{\mathbf{1c}}{[trans\text{-}Pt(CH_2CH_2NH_2)Cl_4Az]^-} + H_2 \quad (8)$$

$$[trans\text{-}Pt(CH_2CH_2NH_2)Cl_4Az]^- \longrightarrow \underset{\mathbf{1b}}{Pt(CH_2CH_2NH_2)(Az)Cl_3} + Cl^- \quad (9)$$

Reactions (2)—(4) are the reversible steps of deprotonation, hydration, and acid-type dissociation of the hydrated ligand, respectively.

Due to the speed of the establishment of the acid-base equilibrium (4), [*trans*-$Pt(CH_2CH_2NH_2)Cl_4(H_2O)]^-$ and [*trans*-$Pt(CH_2CH_2NH_2)Cl_4(OH)]^{2-}$ should have a common signal in the ^{1}H NMR spectrum. Step (5) is included in the scheme on the basis of the known ability of amines to form stable complexes with platinum (IV); the rate of this reaction should be relatively high,* due to the strong *trans*-effect of the alkyl radical. Step (6) is the key reaction of the inner-sphere reductive elimination of AzH^+, which is converted into Az in the alkaline medium (step (7)), and then forms complex **1c** (step (8)). Inner-sphere substitution of amine for the chloride ligand in **1c** affords the water-insoluble neutral compound **1b** (step (9)).

An analog of the β-ammoniumethyl complex, the platinum (IV) σ-acetonyl complex $[Pt(CH_2COCH_3)Cl_5]^{2-}$, does not decompose with a noticeable rate in weakly alkaline solutions at 30 °C. Taking this into account, together with the fact that the reactivity of the latter complex in inner-sphere S_N2 reductive elimination is considerably higher than that of complex **1a** (see below), we did not include reactions of outer-sphere decomposition of **1a** under the action of Cl^- and OH^- in Eqs. (2)—(9).

Let us now consider the kinetics of reductive elimination. The reactions were carried out in buffer solutions with fixed pH values; the decrease in the optical density (D) at the absorption maximum (λ = 260 nm) at low initial concentrations of complex **1a** ($[\mathbf{1a}]_0$ = 10^{-4}—10^{-5} M) was measured. In terms of Eqs. (2)—(9), one should expect that under given conditions, when equilibrium (5) is shifted to the right, the rate of the decrease in D would obey a first-order equation. This is valid only for the initial rates; the $(dD/d\tau)_{\tau\to 0}$ values depend linearly on $[\mathbf{1a}]_0$ (Fig. 1). In the course of the

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* The presence of a Pt—C bond in these species can be inferred from the presence of platinum satellites in the ^{1}H NMR spectra.

* The formation of binuclear complexes through the reaction of the "free" amino group of the β-aminoethyl complex with Pt^{II} evolved in step (6) is less probable due to the inertness of the latter. As shown below, under the conditions considered this reaction can really be ignored.

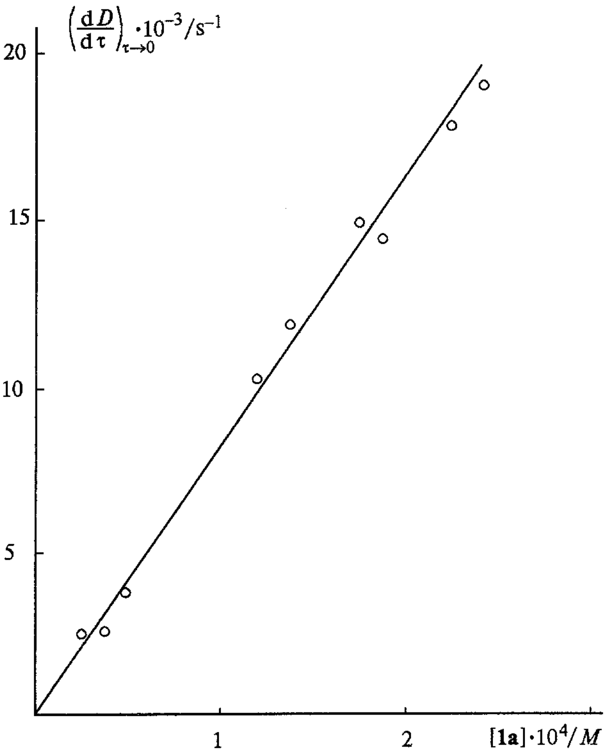


Fig. 1 The dependence of $(dD/d\tau)_{\tau\to 0}$ on the concentration of the starting complex. pH = 7.9, 30 °C, the values for the $(dD/d\tau)_{\tau\to 0}$ parameter are referred to an optical distance of 1 cm.

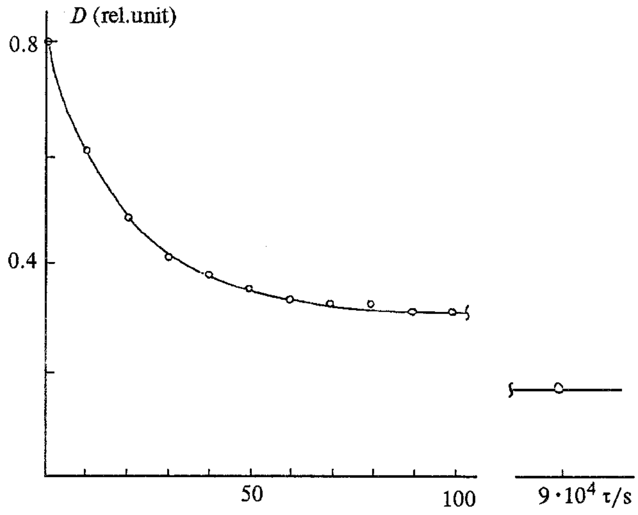


Fig. 2. The typical decomposition kinetics of complex **1a** in alkaline solutions. pH = 8.3, 30 °C, [NaCl] = 3.0 *M*.

reaction decomposition of the complex decelerates (Fig. 2). As shown below, this is associated with the fact that the aziridine evolved in reaction (6) inhibits reductive elimination. Coordination of the "free" amino group of the platinum (IV) β-aminoethyl complex with the platinum (II) evolved in reaction (6) would have resulted in similar deceleration of reductive elimination. However, a separate run (Table 1) has shown that additions of platinum (II) in amounts comparable with those of the starting complex **1a** do not noticeably affect the decomposition kinetics of **1a**.

At a constant concentration of Cl^- ($[Cl^-] = 3.0$ *M*), the dependence of the rate constant $k = -(d\ln D/d\tau)_{\tau\to 0}$ on pH (Table 2) looks like a titration curve. Therefore, it is actually the deprotonated form of the platinum(IV) β-ammonioethyl complex that undergoes reductive elimination (step (6)). The pK_a value for aminoethylplatinum estimated from the kinetic data ($pK_a \approx 8.2$) is close to the corresponding values[8] for β-bromoaminoethane ($pK_a \approx 8.5$) and β-fluoroaminoethane ($pK_a \approx 8.8$).

Table 1. The pH dependence of the rate constant of decomposition of complex **1a**

pH	$k\cdot 10^3/s^{-1}$
5.6	0.17±0.01
6.0	0.80±0.03
7.0	1.7±0.1
7.5	2.0±0.1
8.0	6.3±0.3
8.3	25.9±0.6
8.8	42.0±1.7

Note. [NaCl] = 3.0 *M*, 30 °C.

At a constant ionic strength ($[NaCl] + [NaClO_4] = 3.0$ *M*) and fixed pH (pH = 5.6) decomposition of the complex according to the accepted scheme (see reactions (2)—(3), (6)) decelerates, as the concentration of Cl^- increases (see Table 1). The kinetic equation for the change in $[Cl^-]$ has the following form (the linear anamorphosis is given in Fig. 3).

$$k = k_6/(1 + K_{Cl}[Cl^-]). \qquad (10)$$

Here and from this point on, k_i is the rate constant for the i-th step of the above-presented scheme and $K_{Cl} = k_{-3}/k_3$ is the (−3) equilibrium constant. At pH = 5.6, K_{Cl} and k_6 are equal to 0.73±0.11 M^{-1} and $(5.36\pm 0.14)\cdot 10^{-4}$ s^{-1}, respectively.

When $[Cl^-]$ is 3.0 *M* and $[Az]_0 \gg [RPt^{IV}]$, where $[Az]_0$ is the concentration of aziridine added, the k values satisfy Eq. (11) over the whole concentration

Table 2. The dependence of the rate constant of decomposition of complex **1a** on the concentration of Cl^-

$[Cl^-]/M$	$k\cdot 10^4/s^{-1}$
0	5.4±0.1
1.0	3.0±0.2
2.0	2.1±0.1
3.0	1.7±0.1
3.0*	1.6±0.6

Note. pH = 5.6, 30 °C, $[NaCl] + [NaClO_4] = 3.0$ *M*.
* In the presence of $2\cdot 10^{-4}$ *M* K_2PtCl_4.

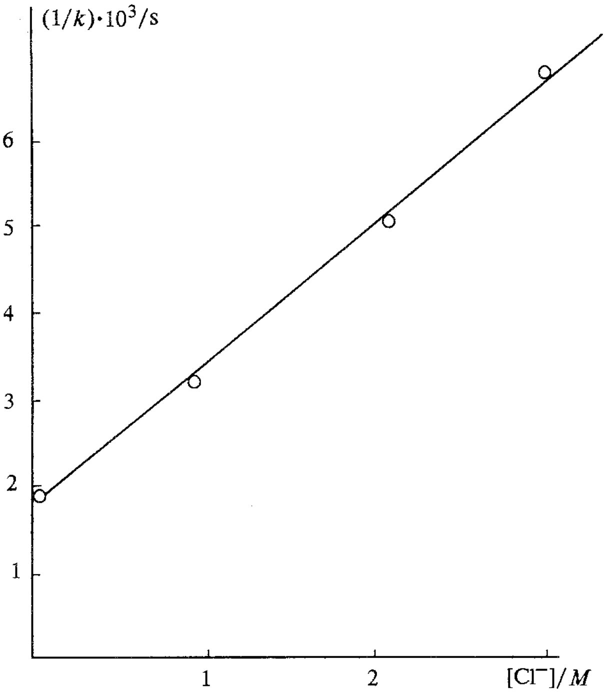
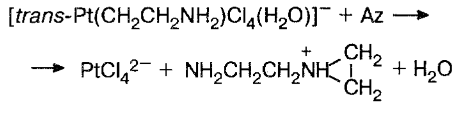


Fig. 3. The dependence of the rate constant for the inner-sphere decomposition of complex **1a** on the concentration of Cl^-. The linear anamorphosis for Eq. (10). pH = 5.6, 30 °C, $[NaCl] + [NaClO_4] = 3.0$ *M*.

region studied (Table 3) (the linear anamorphosis is given in Fig. 4):

$$k \approx (k_6 + k_{Az}[Az]_0/K_{Az}[Az]_0. \qquad (11)$$

$k_{Az}/K_{Az} = (1.4\pm0.2)\cdot10^{-4}$ s^{-1} and $k_6/K_{Az} = (2.3\pm0.2)\cdot10^{-7}$ *M* s^{-1}. Provided that equilibrium (8) is shifted to the right in the concentration range studied, dependence (11) is in agreement with Eqs. (2)—(9) supplemented with a reaction whose stoichiometry, in analogy with other known[2—4] reactions of outer-sphere reductive elimination, may be represented by Eq. (12).



$$[trans\text{-}Pt(CH_2CH_2NH_2)Cl_4(H_2O)]^- + Az \longrightarrow PtCl_4^{2-} + NH_2CH_2CH_2\overset{+}{N}H\!\left\langle\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right. + H_2O \qquad (12)$$

k_{Az} in Eq. (11) is the rate constant of reaction (12) and K_{Az} is the equilibrium constant for reaction (8).

This interpretation of the effect of Az on the decomposition rate of complex **1a** is independently confirmed by the data (Table 4) on the effect of another heterocyclic amine, imidazole (Im). When [Im] varies, the first-order rate constants of the decomposition of RPt^{IV} ($[RPt^{IV}] << [Im]$) obey an equation similar to (11) at $k_{Im}/K_{Im} = (2.8 \pm 0.3)\cdot10^{-5}$ s^{-1} and $k_6/K_{Im} = (4.62\pm0.04)\cdot10^{-7}$ *M* s^{-1} (the linear anamorphosis is given in Fig. 4), where k_{Im} and K_{Im} are the rate and equilibrium constants of the reactions, which are similar to (12) and (8), respectively, but involve imidazole.

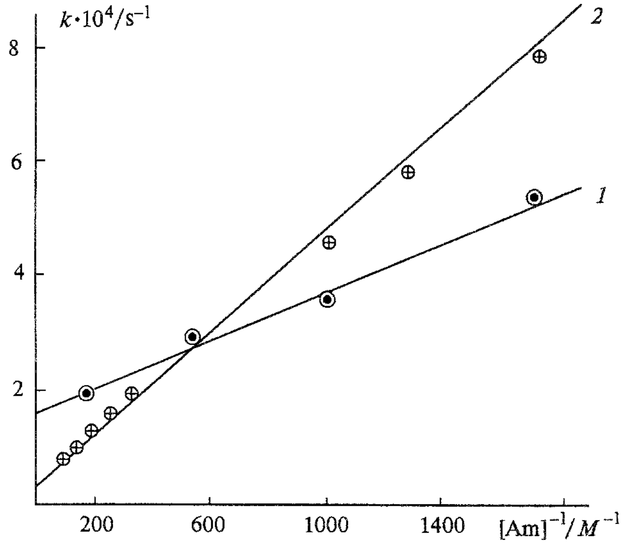


Fig. 4. The dependence of the rate constant for the inner-sphere decomposition of complex **1a** on the concentration of amines (Am) added: Az(*1*), Im(*2*). The linear anamorphosis for Eq. (11). pH = 8.3, 30 °C, [NaCl] = 3.0 *M*.

It should be noted as well that the above-mentioned deceleration of decomposition of complex **1a** in alkaline solutions can be described satisfactorily in terms of a scheme that includes reactions (2)—(4) and (6)—(8) with the assumption that equilibrium (8) is established

Table 3. The dependence of the rate constant of decomposition of complex **1a** on the concentration of aziridine $[Az]_0$ added

$[Az]_0\cdot10^3/M$	$k\cdot10^4/s^{-1}$
0.6	5.26±0.01
1.0	3.56±0.01
2.0	2.78±0.02
4.0	1.86±0.01
8.0	1.76±0.02

Note. pH = 8.3, 30 °C, [NaCl] = 3.0 *M*.

Table 4. The dependence of the rate constant of decomposition of complex **1a** on the concentration of imidazole $[Im]_0$ added

$[Im]_0\cdot10^3/M$	$k\cdot10^4/s^{-1}$
0.6	8.07±0.14
0.8	5.99±0.10
1.0	4.72±0.09
2.0	2.74±0.02
3.0	1.88±0.01
4.0	1.45±0.01
5.0	1.20±0.01
6.0	1.02±0.01
8.0	0.86±0.01
10.0	0.71±0.01

Note. pH = 8.3, 30 °C, [NaCl] = 3.0 *M*.

quickly and is almost completely shifted to the right under the conditions of the kinetic experiments. Assuming that the time dependence of optical density (*D*) flattens out (see Fig. 2), when the reaction is practically arrested due to the conversion of unreacted RPt(IV) into the inactive complex *trans*-$RPt^{IV}Az$ (reaction (8)), we obtain the following equation,

$$\ln(D_\tau - D_\infty) = -2k_6\tau + \text{const}, \qquad (13)$$

where D_τ and D_∞ are *D* values at instant τ and at the "plateau", respectively. Processing the experimental data (Fig. 5) according to Eq. (13) gives k_6 values which coincide to within the experimental error with those obtained by the method of initial rates. For example, for the conditions outlined in the Fig. 5 caption, this method yields values for k_6 equal to $(5.5\pm0.1)\cdot10^{-4}$ and $(2.5\pm0.1)\cdot10^{-2}$ s^{-1} for pH 5.6 and 8.3, respectively (*cf.* the values $(5.4\pm0.1)\cdot10^{-4}$ and $(2.59\pm0.06)\cdot10^{-2}$ s^{-1} are obtained from initial rates).

Decomposition of complex 1a in acidic chloride solution affords the only organic product, β-chloroaminoethane (reaction (1)). At $[Cl^-] >> [RPt^{IV}]$ and at constant ionic strength, $[HCl] + [HClO_4] = 3.0$ *M*, this reaction follows first-order kinetics with respect to the organometallic substrate; the $k = d(\ln[RPt^{IV}])/d\tau$ *vs* $[Cl^-]$ (Table 5) dependence satisfies the normal[2—4] equation for reaction (1):

$$k = k_1[Cl^-]/(1 + K_{Cl}[Cl^-]), \qquad (14)$$

where K_{Cl} was defined above, and k_1 is the rate constant of the reaction, which consists of an S_N2 attack of Cl^- at the α-carbon atom in the complex [*trans*-$PtRCl_4(H_2O)]^-$ (see Refs. 2—4). k_1 and K_{Cl} for Eq. (14) at various temperatures are given below.

	T/°C		
Parameter	80.5	88	94
$k_1\cdot10^{-3}$ /L mol^{-1} s^{-1}	0.50±0.01	0.99±0.02	1.98±0.04
K_{Cl}/M^{-1}	1.4±0.3	1.16±0.02	1.33±0.03

The decomposition rate of the platinum (IV) β-ammonioethyl complex in acidic media is lower than the rates of analogous reactions of σ-acetonyl[3] and methyl[2] derivatives by two and three orders of magnitude, respectively. The K_{Cl} values for these organometallic compounds are of the same order of magnitude and depend slightly on the temperature (*cf.* Refs. 2, 3). Therefore, the difference in the stability of these compounds is associated with the variation of k_1. Table 6 presents the activation parameters for reaction (1) of the platinum (IV) β-ammonioethyl complex. A comparison of these values with the data for methyl[2] and acetonyl[3] derivatives indicates that the activation energies of reaction (1) coincide within the experimental error, and the difference between the reactivities of RPt^{IV} complexes in the R = CH_3, CH_2COCH_3, and $CH_2CH_2NH_3^+$ series is

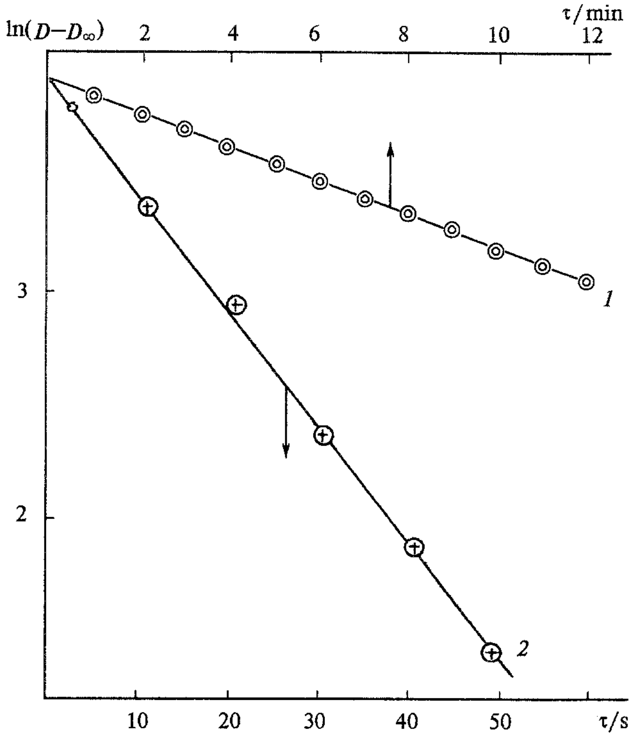


Fig. 5. An example of the processing of the experimental data on the kinetics of the inner-sphere decomposition of complex **1a** according to Eq. (13): pH = 5.6, 30 °C (*1*); pH = 8.3, 30 °C, [NaCl] = 3.0 *M* (*2*).

Table 5. The dependence of the pseudo first-order rate constant of the consumption of complex **1a** in acidic chloride solutions on the concentration of Cl^-

$[Cl^-]/M$	$k\cdot10^4/s^{-1}$		
	80.5 °C	88 °C	94 °C
0.2	0.80±0.01	1.59±1.15	3.03±0.08
0.3	1.00±0.02	2.25±0.02	4.32±0.04
0.5	—	2.98±0.02	5.8±0.2
0.8	—	—	7.7±0.2
1.0	1.98±0.02	4.50±0.06	8.26±0.08
2.0	2.53±0.02	6.05±0.07	11.5±0.4
2.5	—	6.6±0.1	—
3.0	3.22±0.09	7.1±0.1	12.0±0.3

Note. $[HCl] + [HClO_4] = 3.0$ *M.*

Table 6. Activation parameters of decomposition of complexes RPt^{IV} in acidic aqueous solutions under the action of Cl^-

R	A/M^{-1} s^{-1}	$(E_a/R)\cdot10^3$
CH_3*	$1.2\cdot10^{17}$	14.6±0.4
CH_2COCH_3**	$3.2\cdot10^{15}$	14.3±0.6
$CH_2CH_2NH_3$	$2.1\cdot10^{13}$	13.6±2.1

Note. $[HCl] + [HClO_4] = 3.0$ *M.* * See Ref. 2. **See Ref. 3.

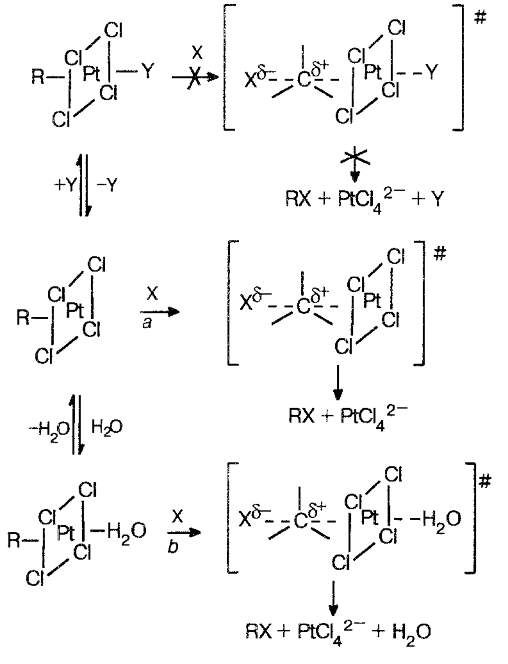
caused for the most part by the distinction between the preexponential factors: these values decrease on going from the methyl to the β-ammonioethyl derivatives by 4 orders of magnitude, which is probably due to the increase in steric hindrance to S_N2 substitution over this series.

Thus, the platinum (IV) β-ammonioethyl complex undergoes two types of transformations, inner- or outer-sphere reductive elimination, depending on the reaction conditions. In acidic solutions, where outer-sphere decomposition occurs, complex **1a** is much more stable than its analog, the σ-acetonyl complex of platinum (IV). In alkaline solutions, when the ammonium group is deprotonated, complex **1a** decomposes by the inner-sphere mechanism. Under these conditions complex **1a** is much more reactive than the σ-acetonyl derivative, which cannot undergo the inner-sphere reductive elimination under consideration. Taking into account that the outer-sphere reaction occurs according to an S_N2 mechanism,[2—4] one may reasonably presume that the inner-sphere reaction is also an S_N2 process, *i.e.*, the mechanism of Pt—C bond cleavage is identical for both types of processes.

The form of Eqs. (10), (12), and (14) indicates that both reaction pairs involve only those complexes which do not contain a chloride ligand or an amino group in the *trans*-position with respect to the alkyl group (Scheme 1, X is an "external" or "internal", *i.e.*, incorporated into R, nucleophile; Y = Cl^-, Im, Az, *etc.*). In aqueous chloride solutions two possibilities remain: the reductive elimination may involve either those species with a coordination vacancy in the *trans*-position (path *a*) or those containing a water molecule as the *trans* ligand (path *b*).

These two pathways are kinetically indistinguishable and lead to type (10), (12), or (14) kinetic equations depending on the nature of X and Y.

Scheme 1



Experimental

The β-ammonioethyl complex of platinum(IV) was prepared by the known procedure.[1] Salts of "high purity" (NaCl) and "chemically pure" (K_2CO_3 and $NaClO_4$) grades as well as "chemically pure" HCl and $HClO_4$ were used without additional purification. Aziridine was purified by distillation and imidazole was recrystallized from benzene. Phosphate and borate buffers were prepared by the previously described procedure.[9]

Kinetics was measured on the basis of the decrease in optical density (a Specord UV-VIS spectrophotometer) of the solution (λ = 260 nm). In the case of acidic chloride solutions the results were processes according to the kinetic equation

$$\ln(D_\tau - D_\infty) = k\tau + \text{const},$$

where $D\tau$ and D_∞ are the optical density of a solution at instant τ and after 6—8 periods of the half-conversion of **1a**, respectively. To calculate the rate constants *k* of decomposition of complex **1a** in alkaline solutions, the experimental data were approximated using STATGRAPHICS software, version 3.0, by a polynomial of the form

$$D_\tau = A_0 + A_1\tau + A_2\tau^2 + A_3\tau^3 + \ldots + A_n\tau^n.$$

An example of this approximation for pH = 8.0, [NaCl] = 3.0 *M*, 30 °C with $n = 5$, $A_0 = 1.06$, $A_1 = -6.66 \cdot 10^{-3}\ s^{-1}$, $A_2 = 1.83 \cdot 10^{-4}\ s^{-2}$, $A_3 = -3.11 \cdot 10^{-6}\ s^{-3}$, $A_4 = 2.58 \cdot 10^{-8}\ s^{-4}$, $A_5 = -8.05 \cdot 10^{-11}\ s^{-5}$ is given below.

	τ/c							
	0	20	30	40	60	80	100	120
D_{exp}	1.06	0.98	0.96	0.94	0.92	0.90	0.88	0.86
D_{calc}	1.06	0.979	0.959	0.944	0.918	0.896	0.884	0.861

The *k* values were determined from the equation $k = A_1/A_0$.

NMR spectra were recorded on Varian-Gemini-200 (200 MHz) and Bruker CXP-400 (400 MHz) spectrometers. DSS was used as the internal standard. The formation of β-chloroaminoethane in the decomposition of complex **1a** under the action of Cl^- in acidic aqueous solutions was confirmed by comparing the ^1H NMR spectrum of the product of this reaction (δ(α-CH_2) 3.47 (t); δ(β-CH_2) 3.93 (t)) with that of the product of the opening of the aziridine ring in a DCl—D_2O solution.

IR spectra were recorded on a Specord IR-75 spectrophotometer. Atomic emission spectra were recorded on an LMA-1 spectrometer.

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