The influence of ionic medium on the kinetics of ligand replacement in the $PtdienH_2O^{2+}$ complex in an aqueous solution

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The influence of the ion background ($NaClO_4$, $LiClO_4$, and $HClO_4$) on the kinetics of the reaction $PtdienH_2O^{2+} + X^- \longrightarrow PtdienX^+ + H_2O$ (X = Cl, Br, I, SCN, and N_3) was studied at 25 °C by spectrophotometry. Changes in the rate constant with increase in the ionic strength are described by the Debye—Hückel and Gosh—Bjerrum equations. The reaction $PtdienCl^+ + H_2O \longrightarrow PtdienH_2O^{2+} + Cl^-$ was studied by potentiometry, and its rate constant was established to depend weakly on variations of the medium.

Key words: salt effect, effect of medium, platinum(II) complexes, diethylenetriamine.

The kinetics of the reactions of $PtdienH_2O^{2+}$ (dien is diethylenetriamine, $NH_2CH_2CH_2NHCH_2CH_2NH_2$) with X^- anions, where X = Cl, Br, I, SCN, NO_2, and pyridine, in aqueous solution has been studied previously[1] at a low ionic strength (<0.01 mol L^{-1}) and $C_X \gg C_{Pt}$ by conductometry.

$$PtdienH_2O^{2+} + X^- \rightleftharpoons PtdienX^+ + H_2O \qquad (1)$$

The authors concluded[1] that two mechanisms take place for square platinum(II) complexes: normal replacement of the ligands (second-order reaction) and replacement limited by the escape of H_2O from the coordination sphere of platinum(II) (first-order reaction). The following values have been previously[2] obtained for the equilibrium constants of reaction (1): $\log K = 3.4$ (X = Cl) and 4.0 (X = Br) at the ionic strength of 0.32 mol L^{-1}. Based on these data, the authors of the later work[3] have shown that the conclusion[1] about two mechanisms is insufficiently substantiated, since the reversibility of the reaction studied was not taken into account in processing the data. In addition, the effect of the ionic strength was not taken into account in Ref. 1. Since the data on the kinetics of reaction (1) are important for understanding the mechanism of reactions of replacement of ligands in the coordination sphere of Pt^{II}, in this work, we studied the dependence of the rate constant of this reaction on the ionic strength.

Experimental

$(PtdienNO_3)NO_3$ was synthesized by the known procedure[4] but at somewhat higher pH (~5) to accelerate the process.[5] Chloroplatinic acid (analytically pure grade) and diethylenetriamine (Merck) were used. The content of platinum in the samples was determined by gravimetry (reducing of platinum(II) to platinum(0) with hydrazine) and spectrophotometrically after platinum(II) was oxidized to platinum(IV) and the latter was transformed into H_2PtCl_6. The initial solution contained a minor quantity of NO_3^- ions ($\leq 10^{-2}$ mol L^{-1}), which was estimated from the spectra (using the known spectra of $PtdienBr^+$ and NO_3^-) and on the basis of the starting concentrations of the reagents used in the synthesis of the complexes. The background salts ($NaClO_4$, $LiClO_4$) were obtained from perchloric acid (reagent grade) and sodium and lithium carbonates (specially pure grade). In addition, sodium and potassium chloride, bromide, iodide, thiocyanate, and azide (not worse than reagent grade) were used. It is important for X = N_3 that starting solutions of the background salts should not contain noticeable amounts of the acid. In the other cases, no effect of pH on the kinetics (at pH < 5) was observed. Kinetic experiments were carried out at $C_{Pt} = (0.5-2) \cdot 10^{-3}$ mol L^{-1}, $C_X = (0.5-15) \cdot 10^{-3}$ mol L^{-1}. No formation of the fluoride complex $PtdienF^+$ was observed even at $[F^-] = 0.1$ mol L^{-1}.

Reaction (1) was studied by spectrophotometry at 25.0 °C. Optical densities of solutions (*D*) were measured on a Specord instrument in the region $\nu = (30-36) \cdot 10^3$ cm^{-1}.

Kinetic experiments for reactions of formation and aquation of $PtdienCl^+$ were carried out by the potentiometric method using AgCl of Ag electrodes calibrated by solutions with known concentrations of HCl or $AgClO_4$, respectively, and with the required ionic strengths. A V7-23 voltmeter was used for measuring electrodriving forces of the corresponding systems. The error of measuring edf was not greater than 0.3 mV. Measurements were carried out 3—5 min after mixing reagents. For example, when aquation of $PtdienCl^+$ was studied, an equilibrium solution containing $PtdienH_2O^{2+}$, $PtdienCl^+$, and Cl^- in the known concentrations ($C_{Ag} > C_{Cl}$) was added to a solution of $AgClO_4$. During aquation, the Cl^- ions released are bound by Ag^+ ions to form $AgCl_s$. The value $[PtdienCl^+] = C_{Cl} - C_{Ag} + [Ag^+]$ was calculated from edf-chains with the silver electrode. The kinetics of establishment of the potential restricted the lower limit of C_{Ag} by the value $\sim 5 \cdot 10^{-4}$ mol L^{-1}.

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Results and Discussion

The study of reaction (1) at low [X$^-$] values and at small conversion depths when [PtdienX$^+$] is low showed that the contribution of the direct first-order reaction to the observed rate of formation of PtdienX$^+$ is insignificant (Fig. 1). Taking into account the level of possible random and systematic errors, this contribution can be estimated to be at least fivefold lower than that previously found.[1] This fact and the published data[3,6] make it possible to reject the model proposed previously[1] and analyze the data with account for the reversibility of the reaction. In this case, the expression of the reaction rate has the form

$$d[MH_2O^{2+}]/d\tau = k_{-1}[MX^+] - k_1[MH_2O^{2+}][X^-], \quad (2)$$

where M = Ptdien. Although the standard analytical solution of the differential equation (2) and plotting the dependences of [MH$_2$O^{2+}] on τ are possible, processing of these dependences to obtain the rate constants and their confident intervals is rather difficult. Direct numerical differentiation of d[MH$_2$O^{2+}]/dτ followed by the calculation of the constants for these systems is not an exact procedure. Therefore, we used a method including the term-by-term numerical integration of Eq. (2). All equilibrium concentrations in the right part of Eq. (2) can be calculated from the equation of balance and observed values of the optical density. Therefore, at a sufficient density of experimental values, this integration can be performed almost without a decrease in accuracy. After the integration, Eq. (2) takes the form

$$\Delta \ln[MH_2O^{2+}] = k_{-1}A_1 - k_1A_2, \quad (3)$$

where $A_1 = \int([MX^+]/[MH_2O^{2+}])d\tau$, $A_2 = \int[X^-]d\tau$, integration is performed from τ_1 to τ_i, $\Delta \ln[MH_2O^{2+}] = \ln([MH_2O^{2+}]\tau_i/[MH_2O^{2+}]\tau_1)$, $[MX^+] = (D(\tau_i) - D(0))/l\Delta\varepsilon$, where $\Delta\varepsilon$ is the difference between the extinction coefficients of MH$_2$O^{2+} and MX$^+$; l is the optical path length of the cell, $[MH_2O^{2+}] = C_M - [MX^+]$, and $[X^-] = C_X - [MX^+]$. The further processing of these data (a set of $\Delta\ln[MH_2O^{2+}]$, A_1 and A_2 for different τ_i) and the estimation of k_{-1} and k_1 can be carried out by standard linear methods (including linear weighed LSM). The k_{-1} and k_1 values obtained can be used as the first approximation for further processing by nonlinear methods. The k_{-1} values have, as a rule, significant dispersion, but their values are close to those obtained from the equilibrium constants ($K = k_1/k_{-1}$), calculated at $\tau \to \infty$ from the data on D_∞, C_M, and C_X. Under conditions of the most kinetic experiments, the accuracy of determination of the K values is low. The k_1 values determined previously[1] and found by us coincide well for the corresponding values of ionic strength (I), except those for X = SCN for which our values are noticeably higher. The dependence of logk_1 on I in the region of low and moderate ionic strengths for X = Cl in aqueous and water-ethanol (58 vol.%) media are presented in Fig. 2. The changes in logk_1 observed are described by the Debye—Hückel equation

$$\log k_1(I) = \log k_1(0) + A\Delta z^2 I^{1/2}/(1 + BI^{1/2}) + b_{DH}I,$$
$$\Delta z^2 = 4, \quad (4)$$

which is quite consistent with the common concept that these processes occur *via* the formation of the ion (diffusion) pair,[7] and almost all the description of the salt effect on k_1 is reduced to a standard thermodynamic problem of description of the effect of a medium on the equilibrium constant of formation of this pair. Despite sharp differences in k_1 in the region of low I for water and water-ethanol mixtures, at I ~ 1 mol L^{-1} the k_1 values for the given X are close for different concentrations of alcohol: the effect of a medium caused by

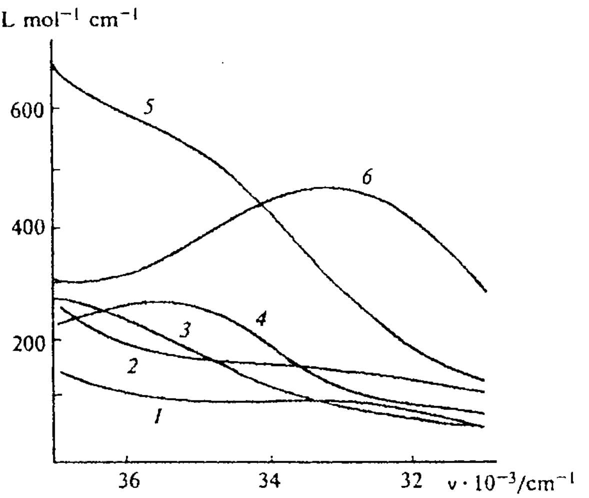

Fig. 1. Spectra of forms of PtdienX$^+$ in an aqueous solution: X = H$_2$O (*1*), SCN (*2*), Cl (*3*), Br (*4*), N$_3$ (*5*), and I (*6*): C_X = 0.1—0.01 mol L^{-1}, C_{Pt} = (0.5—2)·10^{-3} mol L^{-1}. Kinetic measurements for X = I were performed at ν = 33000 cm^{-1}; for other X, at 36000 cm^{-1}.

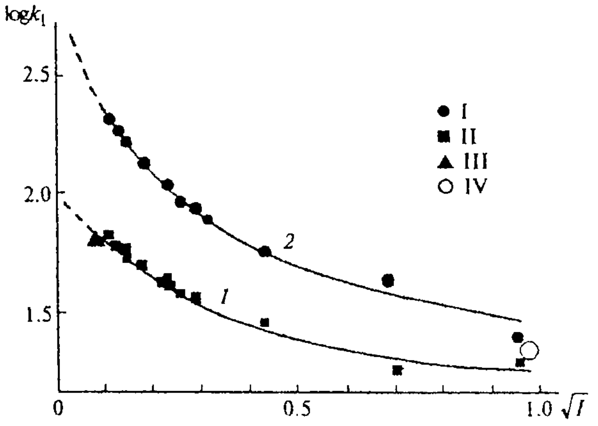

Fig. 2. Dependences of logk_1 on $\sqrt{I}$ (X = Cl; τ/min) in the region of low and moderate ionic strengths created by NaClO$_4$: *1*, aqueous solution; *2*, water-ethanol solution (58 vol.% ethanol); I and II, our data; III, Ref. 1; IV, 1 mol L^{-1} LiClO$_4$ in 58% ethanol.

replacement of a solvent decreases as the ionic strength increases. This is related to the fact that although at I = 0 the k_1 value increases as the dielectric constant (D) decreases, but the slope ($d\log k_1/d(I^{1/2})$) increases simultaneously in modulus. For 58% alcohol and water, the ratio of these slopes was 2—2.5 (theoretical value 2.33). Some measurements for X = Cl were performed at 35 °C to elucidate the effect of the salt background on the temperature dependence of the rate constant. The difference in $\log k_1$ at two temperatures for the system indicated is almost independent (within errors) of the ionic strength. Estimation of the activation energy from these data gives the value of 14 kcal mol^{-1}. The use of Eq. (4) for describing the dependences of $\log k_1$ on I shows that the standard deviations of approximation s are close to the independently estimated experimental errors of determination of k_1. Therefore, there it makes no sense to use more complex equations (with a greater number of estimated parameters) than Eq. (4). Due to the high correlation of estimates of B and $\log k_1(0)$, the B value can be estimated only approximately (Table 1). Nevertheless, the value obtained (1.4—1.5) is close to the B value that is usually used for taking into account the effect of the ionic strength (1.5,[8] 1.6[7]). Therefore, to estimate $\log k_1(0)$ and b_{DH}, the results were processed by LSM at the constant values B = 1.5 for water and B = 2.0 for 58% ethanol ($B_{et}/B_{aq} = (D_{et}/D_{aq})^{1/2} = 1.33$). In addition to the Debye—Hückel equation, the Gosh—Bjerrum equation can be used for the description of the dependence of the rate constant on the ionic strength[9]

$$\log k_1(I) = \log k_1(0) + a\Delta z^2 I^{1/3} + b_{GB}I. \qquad (5)$$

The $\log k_1(0)$ values obtained from the same experimental data by models (4) and (5) differ noticeably. Standard deviations of approximation s by Eqs. (5) and (4) differ insignificantly up to ionic strengths I = 6—7. The parameters of models (4) and (5) are presented in Table 1.

Table 1. Parameters of models (4) and (5) for media created by $MeClO_4$ (25 °C)

X (Me)	$\log k_1(0)$*	b*	s*	$\log k_1(0)$**	b**	s**
Cl (Na)	1.97(1)	0.081(3)	0.03	2.02(1)	0.210(4)	0.05
(H)	1.97(1)	0.13(2)	0.05	2.02(1)	0.25(2)	0.05
(Na, 58% ethanol)	2.86(2)	0.10(5)	0.05	2.83(2)	0.36(7)	0.05
Br (Na)	2.85(3)	0.00(2)	0.07	2.96(4)	0.15(1)	0.08
(H)	2.85(3)	0.10(3)	0.08	2.96(4)	0.25(3)	0.08
I (Na)	3.77(7)	0.01(2)	0.09	3.88(9)	0.16(3)	0.01
SCN (Na)	3.60(9)	0.03(2)	0.12	3.72(9)	0.17(2)	0.15
N_3 (Na)	1.98(2)	0.054(4)	0.03	2.10(4)	0.20(1)	0.08

Note. The following values were used in the calculations for aqueous solutions: B = 1.5, A = 0.51, $a\Delta z^2$ = 1.04; for 58% ethanol, B = 2.0, A = 1.19, $a\Delta z^2$ = 1.84. Experimental values B = 1.4—1.5 and $a\Delta z^2$ = 0.96+0.06 (water), $a\Delta z^2$ = 1.6+0.2 (58% alcohol). The values in parentheses are the standard deviation expressed in units of the least significant digit, *i.e.*, 1.97(1)±0.01. * The values were calculated by the Debye—Hückel equation. ** The values were calculated by the Gosh—Bjerrum equation.

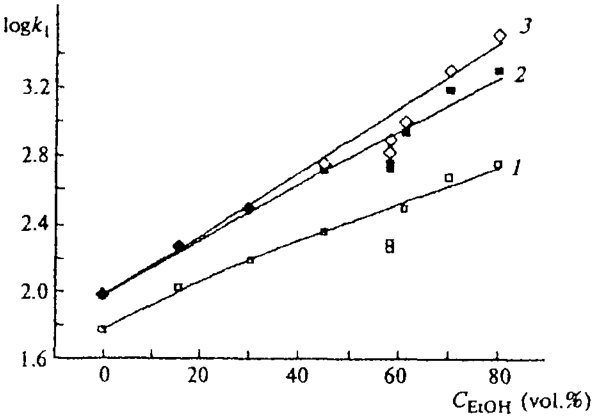

Fig. 3. Dependences of $\log k_1$ on the content of ethanol (vol.%): *1*, experimental values obtained at $I \approx 0.01$ mol L^{-1}; *2*, after introduction of corrections by Eq. (4); *3*, by Eq. (5).

The dependence of the experimental values of $\log k_1$ determined at the low (10^{-2} mol L^{-1}) ionic strength on the content of ethanol is presented in Fig. 3. Despite the fact that the ionic strength is low, corrections to its change, which affect (increase) the slope of the dependence of $\log k_1(C_{al})$ on the alcohol content, should be introduced to isolate correctly the effect of the influence of the organic component of the solvent. Although in model (4) parameter A is inversely proportional to $(D)^{3/2}$, and in model (5) parameter a is inversely proportional to D (see Fig. 3), these corrections do not differ strongly for both models (see Fig. 3).

Since the aquation of $PtdienCl^+$ was also studied in the presence of silver(I), it was necessary to elucidate whether the kinetics of the reaction depends on the concentration of Ag^+ ions. Our data (Fig. 4) show that the rate constant (k_1) of this reaction is independent of $[Ag^+]$ and is satisfactorily described by the equation

$$d\ln[MCl^+]/d\tau = -k_{-1}, \qquad (6)$$

in which the k_{-1} values agree with those obtained from other data. This implies that, first, Ag^+ does not participate in the limiting stage of hydrolysis of the Pt—Cl bond and, second, the inverse reaction is the limiting stage in process (2). Taking into account the level of systematic and random errors, we can assert that under our experimental conditions, the contribution of other possible processes to the aquation of MCl^+, in particular, second-order reactions involving Ag^+, is <15%. The value of the slope at τ = 0 (see Fig. 4) corresponds to the $[MCl^+]$ value in the initial equilibrium solution calculated from the spectra, which is evidence for the absence of considerable systematic distortions in potentiometric measurements. The k_{-1} value for MCl^+ depends slightly on the ionic strength: it is equal to

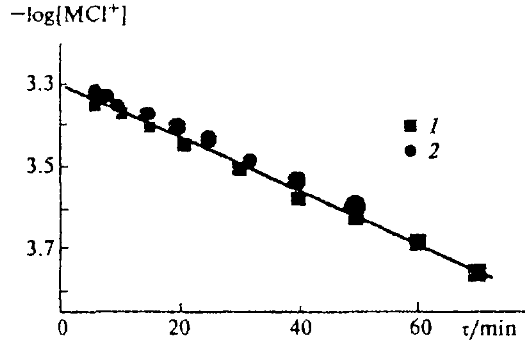

Fig. 4. Dependences of $\log[MCl^+]$ on τ during aquation (3, 6): C_{Pt} = $1.06 \cdot 10^{-3}$ mol L^{-1}, C_{Cl} = $7.06 \cdot 10^{-4}$ mol L^{-1}, I = 1.0 ($NaClO_4$); C_{Ag} = $1.41 \cdot 10^{-3}$ (*1*) and $0.72 \cdot 10^{-3}$ (*2*) mol L^{-1}.

$(1.00 \pm 0.05) \cdot 10^{-2}$ and $(1.2 \pm 0.1) \cdot 10^{-2}$ min^{-1} for 1.0 and 5.0 *M* solutions of $NaClO_4$, respectively, and $(1.20 \pm 0.06) \cdot 10^{-2}$ min^{-1} for a 1.0 *M* solution of $LiClO_4$ in 58% ethanol. Therefore, the $\log K(2)$ value for X = Cl is equal to 3.20 (I = 1.0) and 4.00 (I = 0). These values almost coincide with those obtained previously[10] for $Pt(NH_3)_3Cl^+$, but the k_1 and k_{-1} values for $Pt(NH_3)_3Cl^+$ are lower by ~5 times. For $PtdienBr^+$, the k_{-1} value is only a little lower ($7.8 \cdot 10^{-3}$ min^{-1} at I = 0.32[2]) than that for $PtdienCl^+$.

It follows from the data obtained that the change in $\log K(2)$ with the ionic strength is almost the same as that for $\log k_1$. Thus, we can conclude that the ion pair, whose monomolecular transformation into products is almost independent of the ionic strength, is formed in reaction (1) as an intermediate form.

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