INFLUENCE OF THE NATURE OF THE LOWER FREE ORBITAL OF PLATINUM(IV) BIPYRIDYL COMPLEXES ON THE KINETICS AND THE MECHANISM OF ELECTRON TRANSFER PROCESSES IN WHICH THEY PARTICIPATE

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The kinetics of outer-sphere electron transfer reactions with the participation of $[PtEn_xbipy_{2-x}Cl_2]^{2*}$ complexes (x = 0-2) have been studied. The formal potential and the internal barrier of self-exchange reactions with the electron $Pt(IV) \neq Pt(III)$ have been estimated. A correlation has been shown to exist between the parameters of outer-sphere and intramolecular electron transfer.

Electron transfer reactions with the participation of transition metal complexes, which lead to the formation of highly reactive complexes with an "unusual" degree of oxidation of the metal, are attracting great interest. This offers the possibility of the practical use of such reactions in a wide range of catalytic reactions [1] and for the development of theoretical models [2], which make it possible to study the influence of the electron structure of complexes on the reaction kinetics.

It has been shown in [3, 4] that outer-sphere electron transfer (OET) reactions with the participation of Pt(IV) amine halide complexes possess high internal barriers (ΔG_{Pt}^{\neq}) in the self-exchange reactions with an electron Pt(IV) \neq Pt(III). It is assumed in [3, 4] that this is caused by significant changes in the equilibrium distances between the metal-halogen nuclei in the transfer of an electron to the σ -antibonding d-orbitals of platinum. On the other hand, the investigation of the luminescence properties of the complexes $[PtEn_2Cl_2]^{2^*}$, $[PtEnbipyCl_2]^{2^*}$, and $[Ptbipy_2Cl_2]^{2^*}$ shows [5, 6] that the replacement of ethylenediamine (En) by the heterocyclic amine 2,2'-bipyridyl (bipy), which contains free low-energy π^* antibonding orbitals, leads to a change in the nature of the lower free orbital of the complex: $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$. This makes it possible to study on these complexes the influence of the nature of the lower free orbital on the kinetics and the mechanism of electron transfer processes.

The platinum complexes and the electron donors (Table 1) were synthesized by the procedures given in [4-7]. The rate constants k_q of the bimolecular OET reactions were determined with a relative error of $\leq 15\%$ [4] from the quenching of the luminescence of the donors, or by pulse photolysis of Cr(III) complexes in the presence of an irreversible electron donor (EDTA).

RESULTS AND DISCUSSION

The investigation of the kinetics of the reactions of electron donors with platinum complexes as function of their concentrations showed that the formation of the Pt(III) complexes was the limiting stage of the reaction

$$D + Pt (IV) \stackrel{k_{-d}}{\underset{k_{d}}{\Rightarrow}} D \dots Pt (IV) \stackrel{k_{-c}}{\underset{k_{d}}{\Rightarrow}} D^{+} \dots Pt (III) \stackrel{k_{-d}}{\longrightarrow} D^{+} + Pt (III) \rightarrow Pt (II).$$
(1)

The observed rate constant (Table 1) does not depend on the rate of the secondary reactions of the Pt(III) complexes; it is determined by the ratio of the rate constants of the elementary processes:

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Donor	$-\frac{E(D/D^+)}{V}$	[PIEn,Cl,]2+		[PtEnbipyCl _s] ²⁺		[Ptbipy,Cl,]2+	
		$k_q \cdot 10^{-7}$, mole.sec	∆ <i>c</i> ≠, eV	$k_q \cdot 10^{-7}$, mole.se	∆G≠, eq eV	$k_q \cdot 10^{-7}$. mole sec	∆G≠. c eV
[Osbipy _s] ²⁺ *	1,02	200	0,13				_
[Rubipy ₃] ^{2+*}	0,86	130	0,15	29 0	0,13	380	0.12
[Irbipy ₂ Cl ₂] ^{2+*}	0,51	13,0	0,23	125	0,18	150	0.18
[Cr(4,4'(CH ₃) ₂ bipy) ₃] ²⁺	0,45	-	_	16,0	0,24	30,0	0,23
[Crbipy _s] ²⁺	0,26	2,00	0,26	6,0	0,26	18,0	0,24
[Cr(5 Clphen) ₃] ²⁺	0,18	—	—	3,0	0,28	11,0	0,25

TABLE 1. Rate Constants and Changes in the Free Activation Energy of OET Reactions of Pt(IV) Complexes

*Donor in electron-excited state.

$$k_{q} = k_{d} \left[1 + \frac{k_{-d}}{k_{e}} \left(1 + \frac{k_{-c}}{k_{-d}} \right) \right]^{-1}.$$
 (2)

It is known [4] that for a large number of platinum complexes and of reducing agents used in the present work $k'_{-d} \gg k_{-e}$. In the adiabatic approximation this permits us to calculate the change in the free activation energy ΔG^{\neq} of the OET process

$$\Delta G^{\neq} = RT \ln \left[\left(\frac{1}{k_q} - \frac{1}{k_d} \right) \frac{kT}{h} K_0 \right]$$
(3)

and to use for the estimation of the parameters E(Pt(IV)/Pt(III)) and ΔG^{τ}_{Pt} , which characterize the single-electron reduction of the Pt(IV) complexes, the equation

$$A \cong \Delta G^{\neq} - E \left(D^{+}/D \right) - \Delta W = \frac{(\Delta G_{\text{Pl}}^{\neq} + \Delta G_{\text{D}}^{\neq})^{2}}{4\Delta G^{\neq}} - E \left(\text{Pt} \left(\text{IV} \right)/\text{Pt} \left(\text{III} \right) \right), \tag{4}$$

where kT/h is the universal frequency factor; K_0 is the equilibrium constant of the formation and diffusion separation of the D...Pt(IV) complex; $E(D^*/D)$ and E(Pt(IV)/Pt(III)) are the formal redox potentials of the electron donor and acceptor; ΔW is the difference between the work of connecting (bringing together) and separating the reactants and reaction products; $\Delta G_D^{\neq} = (0.22 \pm 0.04) \text{ eV } [4]$ is the internal barrier of self-exchange reactions with the donor electron. The values of k_d , K_0 , and ΔW at the experimental conditions were calculated by the procedures given in [4]. The experimental data for the investigated complexes (Fig. 1) are in good agreement with the results obtained from Eq. (4). The value of ΔG_{Pt}^{\neq} [4] is a parameter for the energy of reorganization of the inner sphere ΔG_{is}^{\neq} and the outer sphere ΔG_{OS}^{\neq} of the complex in the electron transfer process

$$\Delta G_{\rm Pl}^{\pm} = \Delta G_{is}^{\pm} + \Delta G_{os}^{\pm} , \qquad (5)$$

$$\Delta G_{os}^{\neq} = \frac{1}{4R} \left(\frac{1}{D} - \frac{1}{D_s} \right), \tag{6}$$

where R is the sum of the radii of the Pt(IV) and Pt(III) complexes [8]; D and D_S are the optical and the statistical permeability of the solvent.

The analysis of the obtained values of E(Pt(IV)/Pt(III)) and ΔG_{is}^{\neq} shows (Table 2) that the introduction of the bipyridyl ligand into the inner sphere of the complex has practically no influence on the redox potential and leads to a significant decrease of ΔG_{is}^{\neq} . The value of ΔG_{is}^{\neq} is determined by a change in the electron transfer process of the equilibrium distance between the nuclei and of the force constants of the metal-ligand bonds; it depends strongly on the nature of the molecular orbitals of the complex that take part in the redox process (redox orbitals [9]). A comparison of the obtained values for ΔG_{is}^{\neq} (Table 2) with $\Delta G_{is}^{\neq} = 0.45$ eV (in the outersphere electron transfer to the σ -antibonding redox orbitals of $[Pt(NH_3)_4Cl_2]^{2+}$ [4]) as well as with $\Delta G_{is}^{\neq} \approx 0.1$ eV (in the reduction of bipyridyl complexes of Os(II), Ru(II), and Ir(III), accompanied by electron transfer to the π^* -antibonding orbitals of the ligand [4]), shows that the decrease of ΔG_{is}^{\neq} in the order $[PtEn_2Cl_2]^{2+} \gg$ $[PtEnbipyCl_2] \approx [Ptbipy_2Cl_2]^{2+}$ is caused by a change in the nature of the redox orbitals of the complexes $\sigma^* \rightarrow \pi^*$. The increased value of ΔG_{is}^{\neq} , observed for the bipyridyl complexes of Pt(IV) in comparison with the bipyridyl complexes with "pure" π^* -redox orbitals is probably due to the partial participation of the σ^* -orbitals of the metal because of their similarity from an energy standpoint.

Complex	E (Pt (IV)/Pt (III))	∆c _{pt} , eV	∆ <i>G</i> [≠] , eV	<i>E</i> ⁰⁻⁰ .eV	Φ,eV
[PtEn ₂ Cl ₂] ²⁺ [PtEnbipyCl ₂] ²⁺ [Ptbipy ₂ Cl ₂] ²⁺ 44 9, 9,	0,0 0,1 0,1	0,7 0,5 0,4	0,4 0,2 0,2	2,8 2,8 2,7	0,4 0,4 0,1
	A 1,00-		2		
	0,75- 0,50-				
	225-	6 1,	/ <u>\</u>		

TABLE 2. Thermodynamic and Kinetic Parameters of Outersphere and Intramolecular Electron Transfer of Pt(IV) Complexes

Fig. 1. Kinetics of OET reactions with the participation of $[PtEnbipyCl_2]^{2*}$ ions (curve 1) and $[Ptbipy_2Cl_2]^{2*}$ ions (curve 2) according to Eq. (4).

This conclusion is in agreement with the results of the investigation of intramolecular electron transfer processes which lead to the formation of lower electron-excited states (EES) of the complexes. It was established in [5, 6] that the replacement of ethylenediamine with bipyridyl in the inner sphere of the complexes leads to a change in the orbital nature of the lower EES: $(d-d^*) \rightarrow (\pi-\pi^*)$. A comparison of the parameters that characterize the outer-sphere and intramolecular electron transfer in Pt(IV) complexes shows that the thermodynamic as well as the kinetic characteristics of these processes correlate. Thus, it follows from Table 2 that negligible changes in E(Pt(IV)/Pt(III)) for the investigated complexes are in good agreement with the similar energy required for the pure electron transfer (E^{0-0}) between the EES and the ground state of the complex; the decrease in ΔG_{is}^{\neq} correlates with a decrease in the Stokes shift (Φ) of the luminescence and absorption bands. As already mentioned in [5], this permits us to consider the Pt(IV) complexes in the lower EES as a model for the Pt(III) complexes and to use the spectroscopic parameters of the lower EES in order to describe the structure and properties of the highly reactive Pt(III) complexes as function of the ligand environment.

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