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Abstract

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ON THE OXIDATION OF A SERIES OF PLATINITES BY SODIUM VANADATE

It is known that, up to the present time, studies on the influence of various addends on the rates of oxidation reactions of complex compounds of divalent platinum have been very few and have been only qualitative in character, whereas establishing regularities in the kinetics of oxidation–reduction processes involving platinum complexes is of undoubted interest both theoretically (questions of the mutual influence of atoms in the molecule) and from the standpoint of practical applicability in various fields of chemistry and chemical technology (catalysis, the preparation of pure metals, and analytical purposes). The question of obtaining quantitative characteristics of the rates of oxidation reactions of platinites was prepared by investigations of the schools of I. I. Chernyaev and A. A. Grinberg, which provided fairly complete information on the nature of the reaction products and on the thermodynamics of oxidation processes ([1]-[4]).

In the present work the results are set forth of investigations of the oxidation reactions of a series of platinites by sodium vanadate, with the aim of elucidating the influence of ligands on the oxidation rates of platinites; some considerations are also expressed concerning the mechanism of these reactions. The use of a single oxidizing agent for a series of similar complexes makes it possible to determine the specific features of the influence of ligands on the oxidation rate of the central atom. The slow rate of oxidation of platinites, the one-electron nature of the process, and the well-known value of the free energy of the system VO_2^+/VO_2 make sodium vanadate a very convenient oxidizing reagent ([5]). The reducing agents used were: K_2PtBr_4, K_2PtCl_4, $[Pt(NH_3)_4]SO_4$.

Study of the dependence of the oxidation rate on different initial concentrations of platinites and vanadate made it possible to determine the order with respect to each of the substances; it proved to be equal to unity both with respect to vanadate and to platinum. The overall order of the reaction, determined by Wilkinson' s method ([6]) and by the method of H. M. Emanuel and D. K. Knorre ([7]) at equal initial concentrations of the reagents (in equiv/l), is equal to two;

thus, on the basis of these experiments, the mechanism of platinum oxidation may be represented as proceeding through the stage of formation of trivalent platinum, followed by rapid oxidation to tetravalent platinum, according to the following reaction scheme:

$$Pt^{II} + VO_2^+ \xrightarrow{\text{slow}} Pt^{III} + VO_2$$

$$Pt^{III} + VO_2^+ \xrightarrow{\text{fast}} Pt^{IV} + VO_2$$

The rate constants, calculated from the second-order equation and retaining a constant value at different concentrations of the reagents, are presented in Table 1.

The data of Table 1 show that the increase in the oxidation rate occurs in the series $Br > Cl > NH_3$, i.e., the influence of addends on the oxidation rate is highly specific. In this connection it was of interest to determine quantities associated with the energetics of the transition state. From the temperature dependence of the rate constants of the reactions, the ener-

gies of activation, enthalpies and entropies of activation (the values of these quantities are given in Table 1).

From the data of Table 1 it is evident that, despite the increase in the activation energy on going from NH_3 to Br^-, the reaction rate increases, apparently owing to a considerable change in the entropy of activation. If one proceeds from the

Table 1

Results of experiments on the oxidation of a series of platinites by sodium vanadate

Complex	Concentration of (Cl^-), mol/l	T, °C	Initial concentration, mol/l: Pt^{II}	Initial concentration, mol/l: $VO_2^{\bullet}$	Rate constant, $mol/l^{-1} \cdot sec^{-1}$	Activation energy, $E_a^{\ddagger}$, cal/mol	Activation enthalpy, $\Delta H^{\ddagger}$, cal/mol	Activation entropy, $\Delta S^{\ddagger}$, e.u.
K_2PtBr_4		16.5	$1.1 \cdot 10^{-3}$	$4.95 \cdot 10^{-3}$				
K_2PtBr_4		16.5	$1.1 \cdot 10^{-3}$	$1.03 \cdot 10^{-2}$	$(1.8 \pm 0.2) \cdot 10^{-2}$	20900	20300	+5.62
K_2PtBr_4			$1.1 \cdot 10^{-3}$	$7.2 \cdot 10^{-3}$				

Complex	Concentration of (Cl^-), mol/l	T, °C	Initial concentration, mol/l: Pt^{II}	Initial concentration, mol/l: $VO_2^{\bullet}$	Rate constant, $mol/l^{-1} \cdot sec^{-1}$	Activation energy, $E_a^{\ddagger}$, cal/mol	Activation enthalpy, $\Delta H^{\ddagger}$, cal/mol	Activation entropy, $\Delta S^{\ddagger}$, e.u.
K_2PtBr_4		20	$1.1 \cdot 10^{-3}$	$4.95 \cdot 10^{-3}$	$(2.8 \pm 0.2) \cdot 10^{-2}$			
K_2PtBr_4		25	$1.1 \cdot 10^{-3}$	$4.95 \cdot 10^{-3}$	$(4.6 \pm 0.5) \cdot 10^{-2}$			
K_2PtBr_4		30	$1.1 \cdot 10^{-3}$	$4.95 \cdot 10^{-3}$	$(7.5 \pm 0.8) \cdot 10^{-2}$			
K_2PtBr_4		25	$2.53 \cdot 10^{-3}$	$1.013 \cdot 10^{-2}$				
K_2PtBr_4			$3.56 \cdot 10^{-3}$	$1.013 \cdot 10^{-2}$				
K_2PtBr_4			$5.065 \cdot 10^{-3}$	$1.013 \cdot 10^{-2}$	$(6.9 \pm 0.3) \cdot 10^{-2}$			
K_2PtBr_4			$5.065 \cdot 10^{-3}$	$5.015 \cdot 10^{-3}$				
K_2PtBr_4			$5.065 \cdot 10^{-3}$	$2.02 \cdot 10^{-2}$				
K_2PtCl_4		30	$5.065 \cdot 10^{-3}$	$1.013 \cdot 10^{-2}$	$(9.4 \pm 0.2) \cdot 10^{-3}$	15200	14800	−17.2
K_2PtCl_4		35	$5.065 \cdot 10^{-3}$	$1.013 \cdot 10^{-3}$	$(1.4 \pm 0.2) \cdot 10^{-2}$			
K_2PtCl_4		40	$5.065 \cdot 10^{-3}$	$1.013 \cdot 10^{-3}$	$(2.2 \pm 0.1) \cdot 10^{-2}$			
K_2PtCl_4	10^{-1}	25	$5 \cdot 10^{-3}$	$1.035 \cdot 10^{-2}$	$(3.7 \pm 0.3) \cdot 10^{-2}$			
K_2PtCl_4	10^{-2}	25	$5 \cdot 10^{-3}$	$1.035 \cdot 10^{-2}$				
$[Pt(NH_3)_4]SO_4$		40	$5.015 \cdot 10^{-3}$	$1.03 \cdot 10^{-2}$				
$[Pt(NH_3)_4]SO_4$			$3.65 \cdot 10^{-3}$	$1.03 \cdot 10^{-2}$				

Complex	Concentration of (Cl^-), mol/l	T, °C	Initial concentration, mol/l: Pt^{II}	Initial concentration, mol/l: $VO_2^{\bullet}$	Rate constant, $mol/l^{-1} \cdot sec^{-1}$	Activation energy, $E_a^{\ddagger}$, cal/mol	Activation enthalpy, $\Delta H^{\ddagger}$, cal/mol	Activation entropy, $\Delta S^{\ddagger}$, e.u.
$[Pt(NH_3)_4]SO_4$			$2.57 \cdot 10^{-3}$	$1.03 \cdot 10^{-2}$	$(3.6 \pm 0.1) \cdot 10^{-3}$			
$[Pt(NH_3)_4]SO_4$			$5.015 \cdot 10^{-3}$	$2.06 \cdot 10^{-3}$				
$[Pt(NH_3)_4]SO_4$		50	$5.015 \cdot 10^{-3}$	$1.03 \cdot 10^{-2}$	$(5.8 \pm 0.3) \cdot 10^{-3}$			
$[Pt(NH_3)_4]SO_4$		60	$5.015 \cdot 10^{-3}$	$1.03 \cdot 10^{-2}$	$(8.5 \pm 0.4) \cdot 10^{-3}$	8400	8300	−41.3
$[Pt(NH_3)_4]SO_4$		65	$5.015 \cdot 10^{-3}$	$1.03 \cdot 10^{-2}$	$(1.03 \pm 0.4) \cdot 10^{-2}$			
$[Pt(NH_3)_4]SO_4$		40	$5.065 \cdot 10^{-3}$	$1.03 \cdot 10^{-2}$	$(2.25 \pm 0.1) \cdot 10^{-2}$			

assumption that the change in the entropy factor is connected to a considerable extent with the influence of the charge of the activated complex on the rearrangement of the hydration sphere, then such a regularity is quite explicable. Indeed, in the case of Reiset' s first-base sulfate the charge of the activated complex in the first stage of the reaction is +3, whereas in the case of $PtCl_4^{2-}$ and $PtBr_4^{2-}$ the charge is −1:

$$[Pt(NH_3)_4^{2+} \cdot VO_2^+]^{3+} \qquad [PtCl_4^{2-} \cdot VO_2^+]^-.$$

In addition, the fact of considerable hydration of the initial platinite may create substantial steric hindrances for active collisions of the reactants. From the standpoint of the electron-transfer theory developed by Libby ([8]), the stabilizing influence of the hydration sphere can be understood as due to the introduction of small negative ions. Indeed, experiments carried out with additions of Cl^- ions showed a considerable increase in the oxidation rate (the reaction order did not change in this case). The results of the experiments are presented in Table 1. The fact of acceleration of the reaction can be explained by the incorporation of chlorine ions into the hydration sphere of the platinite, as a result of which electron transfer through a Taube-type bridged complex is facilitated. The

indicated regularities were also noted for other oxidizing agents, such as $KMnO_4$, Cl^{IV}, $KClO_3$.

Establishing the fact of a higher oxidation rate of $PtBr_4^{2-}$ and $PtCl_4^{2-}$ in comparison with $Pt(NH_3)_4^{2+}$ does not contradict the results of the investigations of A. A. Grinberg and N. I. Kats on determining the structure of isomers ([9]), since even earlier ([10]) the possibility of oxidizing $Pt(NH_3)_4^{2+}$ by chloroplatinate, which has a high oxidizing ability, had been demonstrated; therefore, taking into account the fact that the titration curve is an equilibrium curve, the first jump in potential indeed corresponds to the oxidation of $Pt(NH_3)_4^{2+}$.

Experimental Part

The investigations were carried out by the sampling method. The reagents were prepared according to known procedures. It should be noted that acidity has a very strong effect on the reaction rate; therefore all experiments were conducted at a constant acidity equal to 2.89 mol/l with respect to sulfuric acid. Ice water was used as the solution that inhibited the reaction. The influence of the water temperature and of dilution ensured practically instantaneous inhibition of the reaction, as was established by special experiments. The unreacted vanadate was titrated with barium diphenylsulfonate as the indicator. The error in determining the rate constant in all experiments did not exceed 8% (in the case of K_2PtBr_4, up to 10%, since the titration error is somewhat higher owing to the coloration of the bromoplatinite solution).

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Note: Figure translations are in progress. See original paper for figures.