

## KINETICS OF OXIDATION OF HYPOPHOSPHITOPENTAMMINE-CHROMIUM(III) ION WITH PERIODATE

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The kinetics of oxidation of hypophosphitopentamminechromium(III) ion with periodate was investigated as a function of the temperature, ionic strength, and concentration of perchloric acid. The reaction rate decreased with increasing ionic strength and concentration of perchloric acid. The redox reaction proper involving transfer of an oxygen atom is preceded by dissociation of hydrogen from the coordinated hypophosphite. The reactivity of the latter is compared with that of the free hypophosphite.

The kinetics of oxidation of polyatomic ligands coordinated in transition metal complexes is interesting from several points of view. In studying these reactions in solution, deviations from the electrostatic theory were often found related mainly to the values of activation parameters<sup>1-3</sup>. Differences in the reactivity of free and coordinated substrates were found in several cases<sup>4-6</sup>, sometimes, however, the kinetic parameters are only little different<sup>7,8</sup>. Oxidation of the hypophosphite ion in the coordination sphere of Cr(III) ion was not studied hitherto. Our aim was to obtain basic kinetic data about oxidation of hypophosphitopentamminechromium(III) ion with periodate, which would enable, among others, to compare the reactivity of the free with that of the coordinated hypophosphite.

### EXPERIMENTAL

Trihydrate of hypophosphitopentamminechromium(III) perchlorate was prepared according to the literature<sup>9</sup>. The content of Cr was calculated according to the formula  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_2] \cdot (\text{ClO}_4)_2 \cdot 3 \text{H}_2\text{O}$  (455.1) as 11.43%, found 11.5%. The absorption spectrum of the solution of the complex salt with maxima (molar absorption coefficients) at 370 nm ( $37.8 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) and 504.5 nm ( $54.5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) agrees with that described in the cited work<sup>9</sup> within the range of experimental errors. Sodium perchlorate (Fluka, Basel) was of reagent grade as other chemicals, which were from Lachema, Brno. Absorption spectra of the complex were recorded on a recording spectrophotometer SF-8 (LOMO, Leningrad, USSR). The reaction proceeded in the presence of an excess of the complex, since at an equimolar ratio of the reactants or at an excess of periodate the oxidation leads to Cr(VI). With regard to the fact that periodate ions show an intense band in the UV region with a maximum at 225 nm ( $10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) and the complex does not absorb in this region, the reaction course was followed by measuring the decrease of the absorbancy of periodate. The reaction was started by mixing tempered solutions of the

reactants, which were immediately placed into the tempered cuvette of a Specord UV-VIS type spectrophotometer (Carl Zeiss, Jena). The temperature of the solution was accurate to within  $\pm 0.1$  K. The spectrophotometer was connected with a time switch ZG-1 (Thalheim, GDR) which enabled recording of a limited part of the spectrum at selected intervals. The rate constants were evaluated by the Guggenheim's method<sup>10</sup> and the relative error did not exceed  $\pm 4\%$ .

## RESULTS AND DISCUSSION

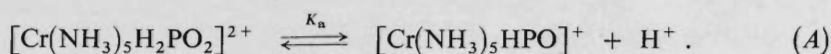
The values of the rate constants for oxidation of  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_2]^{2+}$  ions with periodate at various temperatures, concentrations of  $\text{HClO}_4$  and ionic strengths are given in Table I. From experimental data the following rate equation can be derived:

$$-d[\text{IO}_4^-]/dt = k[\text{IO}_4^-]_0 [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_2^{2+}]_0, \quad (1)$$

where the subscript zero refers to total concentrations. With respect to the excess of the complex salt, its concentration is involved in the experimental rate constant, i.e.,  $k_{\text{exp}} = k[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_2^{2+}]_0$ . Besides oxidation of the complex, oxidation of the free hypophosphite with periodate was also studied and the rate constants are given in Table II.

The influence of ionic strength on the rate of oxidation of the complex was studied in the interval from 0.0608 to 0.3608 mol/dm<sup>3</sup> at 336.7 K. The dependence of  $\log k_{\text{exp}} = f[\sqrt{I}/(1 + \sqrt{I})]$  was linear with a slope of  $-1.99$  close to the theoretical value of  $-2.16$  corresponding to a reaction between oppositely charged ions with a product of charge numbers  $z_A z_B = -2$ . This agrees with the finding that the undissociated form of the complex ion with a charge of  $+2$  prevails in the given medium (Table I).

It follows from the data in Table I that the rate-determining step is preceded by the equilibrium



In a study of the oxidation of hypophosphite with peroxodisulphate<sup>11</sup> it was found that the  $\text{H}_2\text{PO}_2^-$  ion can split off another hydrogen ion and the equilibrium constant of this reaction is  $\text{p}K_{\text{II}} \approx 9$  at 313 K. It is known from a considerable amount of work about the kinetics of reactions of coordination compounds in solution that the coordination of a ligand enhances the ability to split off hydrogen. The total concentration of the complex in (1) can then be expressed as

$$[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_2^{2+}]_0 = [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_2^{2+}] + [\text{Cr}(\text{NH}_3)_5\text{HPO}^+] \quad (2)$$

$$[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_2^{2+}]_0 = [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_2^{2+}] (1 + K_a/[\text{H}^+]). \quad (3)$$

Assuming that the rate of oxidation of the dissociated form is  $v_D = k_D[\text{Cr}(\text{NH}_3)_5 \cdot \text{HPO}_2^+][\text{IO}_4^-]_0$ , we can write

$$k_{\text{exp}} = k_D K_a / ([\text{H}^+] + K_a), \quad (4)$$

$$1/k_{\text{exp}} = [\text{H}^+] / k_D K_a + 1/k_D. \quad (5)$$

TABLE I

Dependence of rate constant for oxidation of hypophosphitopentamminechromium(III) ion with periodate on temperature, concentration of perchloric acid and ionic strength.  $3.56 \cdot 10^{-3} \text{M}$   $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_2]^{2+}$ ,  $2 \cdot 10^{-4} \text{M-KIO}_4$

T K	$I$ $\text{mol dm}^{-3}$	$c_{\text{HClO}_4}$ $\text{mol dm}^{-3}$	$k \cdot 10^2$ $\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$
308.7	0.0608	0.050	1.72
314.3	0.0608	0.050	2.20
319.9	0.0608	0.050	3.24
324.4	0.0608	0.050	3.78
329.0	0.0608	0.050	5.02
329.0	0.1108	0.001	20.6
329.0	0.1108	0.003	15.6
329.0	0.1108	0.005	11.1
329.0	0.1108	0.007	9.08
329.0	0.1108	0.010	7.18
329.0	0.1108	0.300	5.60
329.0	0.1108	0.050	4.42
329.0	0.1108	0.100	3.71
333.8	0.0608	0.050	6.23
336.7	0.0608	0.050	7.69
336.7	0.0908	0.050	6.62
336.7	0.1208	0.050	5.58
336.7	0.2108	0.050	4.33
336.7	0.3608	0.050	3.45

TABLE II

Dependence of rate constant for oxidation of hypophosphite ions with periodate on temperature.  $4 \cdot 10^{-3} \text{M-NaH}_2\text{PO}_2$ ,  $2 \cdot 10^{-4} \text{M-KIO}_4$ ,  $0.05 \text{M-HClO}_4$

T, K	303.3	314.6	323.6
$k \cdot 10^2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	1.62	4.57	10.6

Hence, the reciprocal value of the experimental rate constant should be linearly dependent on the acid concentration, which is indeed the case in the concentration interval 0.001–0.01 mol/dm<sup>3</sup> HClO<sub>4</sub> (Fig. 1). The slope of the straight line gave the dissociation constant of reaction (A),  $K_a = 4.7 \cdot 10^{-3}$  mol, and from the intersection with the ordinate we obtained the rate constant of oxidation of the dissociated form,  $k_D = 0.212$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. At higher acid concentrations, the dependence  $1/k_{\text{exp}} = f([\text{H}^+])$  is not linear, probably owing to the participation of the undissociated form of the ligand (Scheme A) in the reaction. In such a case, Eq. (4) has to be replaced by

$$k_{\text{exp}} = (k_D K_a + k_a [\text{H}^+]) / ([\text{H}^+] + K_a). \quad (6)$$

The rate constant  $k_a$  corresponding to the oxidation of the complex  $[\text{Cr}(\text{NH}_3)_5 \cdot \text{H}_2\text{PO}_2]^{2+}$  was determined from the latter equation to give  $k_a = 2.96 \cdot 10^{-2}$  mol<sup>-1</sup> . s<sup>-1</sup> dm<sup>3</sup>.

TABLE III

Thermodynamic activation parameters for oxidation of hypophosphitopentamminechromium(III) ion (I) and free hypophosphite ion (II) with periodate

Reaction	$E_A$ kJ mol <sup>-1</sup>	$S^\ddagger$ J mol <sup>-1</sup> K <sup>-1</sup>	$A$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	$P$
I	45.4	-140.4	$8.16 \cdot 10^5$	$1.31 \cdot 10^{-4}$
II	75.2	-39.8	$1.47 \cdot 10^{11}$	$2.37 \cdot 10$

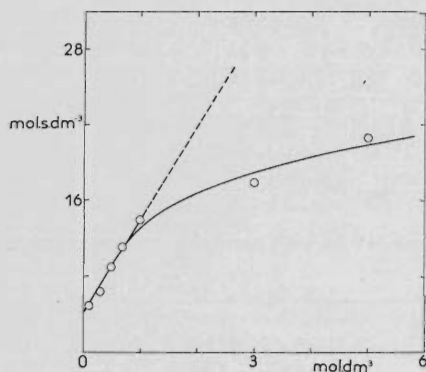


FIG. 1

Dependence of reciprocal value of experimental rate constant ( $1/k$ ) for oxidation of hypophosphitopentamminechromium(III) ion with periodate on concentration of perchloric acid ( $c_{\text{HClO}_4}$ ).  $3.56 \cdot 10^{-3}$  M  $[\text{Cr}(\text{NH}_3)_5 \text{H}_2\text{PO}_2]^{2+}$ ,  $2 \cdot 10^{-4}$  M-KIO<sub>4</sub>;  $T = 329$  K,  $I = 0.1108$  mol/dm<sup>3</sup>

The thermodynamic activation parameters of coordinated and free hypophosphite ions are given in Table III. The activation energy  $E_A$  and the preexponential term  $A$  were calculated from the Arrhenius equation, the activation entropy from the Eyring equation, the sterical factor  $P$  by dividing the preexponential term with the frequency factor, which was set equal to  $6.2 \cdot 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , a value typical for solutions<sup>12</sup>. The activation energy for the oxidation of the coordinated hypophosphite ion is close to that for the oxidation of other polyatomic ligands in Co(III) and Cr(III) complexes where an oxygen atom is transferred from the oxidation agent to the ligand<sup>4,7,13</sup>, although the value of  $E_A$  for the studied reaction is obviously an apparent activation energy involving the temperature dependence of the constants  $k_a$ ,  $k_D$ , and  $K_A$ . The large difference between the activation energies for oxidation of the coordinated and free hypophosphite is notable. A similar difference was observed in oxidation of the free and bound azide ions<sup>4</sup>, whereas in the oxidation of free and bound thiocyanate ions in the complex  $[\text{Cr}(\text{NH}_3)_5\text{NCS}]^{2+}$  the corresponding values are 48.9 and 47.2 kJ/mol, *i.e.*, practically equal within the range of experimental errors<sup>7,8</sup>. The found values of the steric factor and activation entropy are at variance with the simple electrostatic theory of ionic reactions according to which  $\Delta S^\ddagger > 0$  and  $P > 1$  for reactions between oppositely charged ions<sup>14</sup>. A similar disagreement with the theory was found in oxidation of other coordination bound polyatomic ligands<sup>1-3,7,14,15</sup>. In contrast, the oxidation of free hypophosphite ions with periodate has a negative activation entropy in accord with the theory but the steric factor is larger than one although this reaction involves equally charged ions. This is obviously in relation to the fact that the rate-determining step in the oxidation of hypophosphite is the formation of a tautomeric equilibrium under formation of a reactive form with a free electron pair on the P atom<sup>16,17</sup>.

Measurements of the rate of the reaction between  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_2]^{2+}$  and periodate at various concentrations of perchloric acid showed that the dissociated form of the complex ion is more reactive than the undissociated one. This can be attributed to an increase of the electron density on the P atom after splitting off of hydrogen. An O atom is bound to the free electron pair of the P atom to give a phosphitopentamminechromium(III) ion and an iodate ion; the oxidation proceeds without breaking the central ion-ligand bond.

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