KINETICS AND MECHANISM OF A REDOX REACTION OF Ce^{4+} IONS WITH HYDROXYLAMINE*

Ľ.TREINDL and A.VILUDOVÁ

Institute of Physical Chemistry, Comenius University,
801 00 Bratislava

Kinetics and mechanism of a redox reaction of Ce^{4+} ions with hydroxylamine hydrogen sulphate in $1-5M$ sulphuric acid solutions has been investigated. From the kinetic measurements the rate equation

$$-d[Ce^{4+}]/dt = k[Ce^{4+}]\,[NH_3^+OH]\,[H_3O^+]/[HSO_4^-]^2$$

was derived, which is consistent with the reaction mechanism suggested according to which intra-molecular redox reaction of intermediate complex $CeSO_4 . NH_2OH^{2\pm}$ is the slowest rate determining step. Likewise shift of the absorption maximum of Ce^{4+} ions by 14 nm in presence of hydroxylamine gives evidence of the kinetics through the intermediate complex. From the point of view of the mechanism suggested, also other phenomena like effect of ionic strength, kinetic isotope effect of solvent, *etc.* are discussed.

A great attention has been up to now paid to the study of kinetics and mechanism of hydroxyl-amine redox reactions. Several authors[1-4] studied oxidation of hydroxylamine by Co^{3+} ions. Authors[1-3] studied its kinetics and stoichiometry which is dependent upon ratio of concentrations of the reactants. A sixfold excess of hydroxylamine provides a quantitative oxidation to nitrogen. In the sixfold excess of Co^{3+} ions hydroxylamine is oxidized to nitrate, six Co^{3+} ions being spent at the same time. Similarly as in[4], indirect dependence of the rate of reaction upon concentration of H_3O^+ ions was observed, on the basis of which a conclusion could be made that the $CoOH^{2+}$ ion is the reacting particle. Jindal and coworkers[5] examined kinetics of oxidation of hydroxylamine by cyanoferrate ions. Hlasivcová and Novák[6] investigated redox reaction of hydroxylamine with $Cr_2O_7^{2-}$ ions. Excess of dichromate leads to nitrate as the oxidation product of hydroxylamine, whereas in excess of hydroxylamine, dinitrogen oxide results as a product of reduction. Oxidation of hydroxylamine by vanadium (V)[7] proceeds mostly to nitrogen and to some part also to dinitro-gen oxide, vanadium (V) being reduced to vanadium(IV). Catalytic effect of Cu^{2+} ions on the reaction of hydroxylamine with U^{4+} ions[8], and kinetics of oxidation of hydroxylamine by Ag^{2+} ions[9] have been further studied.

Two papers[10-11] describe oxidation of hydroxylamine by Ce^{4+} ions, where hydroxylamine hydrochloride was employed for the kinetic studies, effect of the present Cl^- ions on equilibrium of Ce^{4+} ions as well as on the rate of their reduction being not taken into account. Paper[10] primarily deals with the study of the reaction

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stoichiometry; the dependence of the stoichiometric ratio upon concentration of sulphuric acid is here examined and only basic kinetic data of the reaction under study are given. Paper[11] presents kinetics of the given reaction in a more detail, however, it cannot be regarded as a final study, particularly because of the mentioned presence of Cl^- ions in the solution. When discussing the reaction mechanism, formation of the intermediate complex only is considered in the latter paper.

For this reason and other critical comments, it was necessary to study again the redox reaction quoted and, on the basis of new observations, to add to a deeper understanding of the reaction mechanism.

EXPERIMENTAL

Kinetics of oxidation of hydroxylamine hydrogen sulphate by Ce^{4+} ions was followed mainly polarographically using time dependences of the limiting diffusion current of Ce^{4+} ions at a potential of -0.4 V against potential of $1 M$ mercurous sulphate electrode. As indicator electrode the dropping mercury electrode of the following capillary constants was employed: time of drop of 2.9 s in distilled water and mercury flow-rate of 1.8 mg . s^{-1}; height of the mercury column in a currentless state was 50 cm. The reaction solution was always placed in a thermostated Kalousek cell with a separated $1 M$ mercurous sulphate electrode. Tempering of the cell with the solution was provided by an ultrathermostat with a precision within $\pm 0.05°C$.

Spectrophotometric measurements were made with use of spectrophotometer "Specord UV-VIS Carl Zeiss, Jena. Gas-chromatographic analysis of the reaction mixture was performed on a „Perkin-Elmer" apparatus, model F11, involving thermal conductivity detector.

All the reagents used were A. R. grade. Redistilled water or D_2O (99·86%, Institute for Utilization and Research of Radioisotopes, Prague) was used to prepare the solutions. For kinetic measurements, freshly prepared hydroxylamine hydrogen sulphate solution was always employed. The ionic strength (I) was adjusted by a suitable amount of sodium perchlorate. When needed, the hydrogen ion concentration was adjusted by increasing concentration of perchloric acid, while sodium perchlorate kept the ionic strength and concentration of ClO_4^- ions constant.

The rate constant (s^{-1}) was determined with a precision of $\pm 3\%$ as tangent of linear dependence $-\ln i/i_0 = f(t)$, where i_0 is the limiting diffusion current at the beginning of the reaction and i is the limiting current at the given time of the reaction. The points of the dependence given are average of four independent measurements.

RESULTS

The studied reaction of oxidation of hydroxylamine by Ce^{4+} ions in 0.5 to $5 M$ sulphuric acid solutions obeys the following stoichiometric equation:

$$16\ Ce(SO_4)_2 + 4\ NH_3^+OH + 3\ H_2O = 8\ Ce_2(SO_4)_3 + N_2O + 2\ HNO_3 + \\ + 8\ H_2SO_4 + 4\ H^+. \tag{A}$$
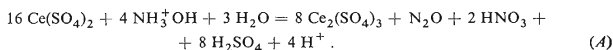
Stoichiometric ratio $C_{Ce^{4+}} : C_{NH_2OH} = 4 : 1$ was determined by polarometric titration which was based on measuring the limiting current of Ce^{4+} ions always at the time, when the hydroxylamine added has already been oxidized.

The rate equation of the reaction studied could be formulated on the basis of the determination of partial orders of reaction. We used differential and integral methods to determine order of the reaction as being equal to unity, with respect to the concentration of Ce^{4+} ions. The rate constant k_{exp} (s^{-1}) is a linear function of the hydroxylamine concentration. The rate equation could be in a first approximation defined:

$$-d\,[Ce(IV)]/dt = k_2[Ce(IV)]\,[NH_3^+OH]\,,\qquad(1)$$

where k_2 is the rate constant of the second order $(1\,mol^{-1}\,s^{-1})$. On the basis of the temperature dependence of the rate constant, activation parameters $\Delta H^{\neq} = 13\cdot8 \pm \pm\,0\cdot4\,kcal\,mol^{-1}$ and $\Delta S^{\neq} = -18\,cal\,K^{-1}\,mol^{-1}$ were determined using the Eyring equation. The dependence of the rate constant upon ionic strength of the electrolyte could be examined in the region of higher ionic strengths only with respect to possible hydrolysis of Ce^{4+} ions in diluted sulphuric acid solutions. With the increasing ionic strength, value of the rate constant is being exponentially diminished (Fig. 1). To elucidate the effect quoted, we measured temperature dependences of the rate constant for a minimum and maximum values of the ionic strength and we calculated parameters of activation (for $I = 1\cdot4$, $\Delta H^{\neq} = 9\cdot8\,kcal\,mol^{-1}$ and $\Delta S^{\neq} = -29\,cal\,K^{-1}$, mol^{-1}, for $I = 3\cdot0$, $\Delta H^{\neq} = 13\cdot2\,kcal\,mol^{-1}$ and $\Delta S^{\neq} = -20\,cal\,K^{-1}\,mol^{-1}$).
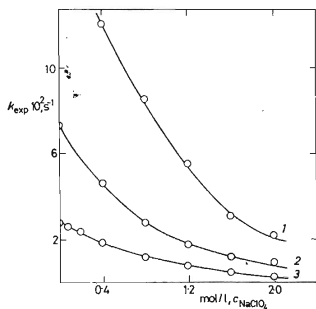
FIG. 1

Dependence of Rate Constant upon Ionic Strength ($NaClO_4$)

$4\,.\,10^{-3}$M-$NH_2OH\,.\,H_2SO_4$, $4\,.\,10^{-3}$M--$Ce(SO_4)_2$, 1 1M-H_2SO_4, 2 2M-H_2SO_4, 3 3M-H_2SO_4.
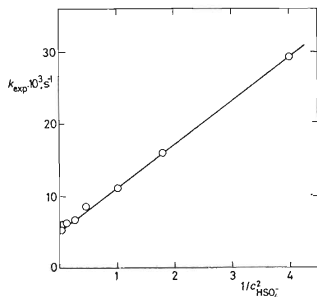
FIG. 2

Analysis of Dependence $k_{exp} = f([HSO_4^-])$

$4\,.\,10^{-3}$M-$NH_2OH\,.\,H_2SO_4$, $4\,.\,10^{-3}$M--$Ce(SO_4)_2$, $I = 5\cdot0$, $t = 25°C$.

The rate constant obtained from the experiments increases linearly with the rising concentration of hydrogen ions according to relation $k_{exp} = k + k'[H_3O]^+$. The experimental rate constant decreases nonlinearly with the increasing concentration of sulphate ions for constant values of the ionic strength and concentration of H_3O^+ ions, and is a linear function of reciprocal value of the square of sulphate ions concentration (Fig. 2). To make clearer nature of the given dependence, we measured temperature dependences of the rate constant at the minimum and maximum concentration of sulphate ions; by means of the Eyring equation the parameters of activation were calculated (for $C_{HSO_4^-} = 0.5$ mol 1^{-1}, $\Delta H^* = 14.2$ kcal mol^{-1} and $\Delta S^* = -18$ cal K^{-1} mol^{-1}; for $C_{HSO_4^-} = 5.0$ mol 1^{-1}, $\Delta H^* = 16.2$ kcal mol^{-1} and $\Delta S^* = -13$ cal K^{-1} mol^{-1}).
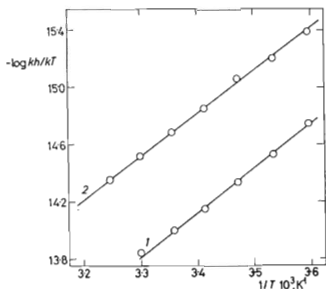
FIG. 3

Temperature Dependences of Rate Constant in Ordinary and Heavy Waters

$4 . 10^{-3}$M-NH$_2$OH . H$_2$SO$_4$, $4 . 10^{-3}$M-Ce(SO$_4$)$_2$, 3M-H$_2$SO$_4$ 1 in H$_2$O, 2 in D$_2$O.

In order to elucidate the reaction mechanism, the kinetic solvent isotope effect can be employed. Because of the ratio $k_{H_2O} : k_{D_2O}$ being as a rule dependent on temperature, it is more suitable to express it as $\delta \Delta H^* = \Delta H^{\ddagger}_{D_2O} - \Delta H^{\ddagger}_{H_2O}$ and $\delta \Delta S^* = \Delta S^{\ddagger}_{D_2O} - \Delta S^{\ddagger}_{H_2O}$ (ref.[12]). From the temperature dependence of the rate constants in ordinary and heavy waters (Fig. 3) the activation parameters, or values $\delta \Delta H^*$ and $\delta \Delta S^*$, were calculated; for $4 \cdot 10^{-3}$M-NH$_2$OH . H$_2$SO$_4$, $4 . 10^{-3}$M-Ce(SO$_4$)$_2$, 3M-H$_2$SO$_4$ in H$_2$O: $\Delta H^* = 13.8$ kcal mol^{-1} and $\Delta S^* = -18$ cal K^{-1} mol^{-1}, in D$_2$O: $\Delta H^* = 13.8$ kcal mol^{-1} and $\Delta S^* = -21$ cal K^{-1} mol^{-1}.

The absorption maximum of Ce(IV) ions in a 3M-H$_2$SO$_4$ solution in presence of hydroxylamine is shifted by 14 nm (from original value λ_{max} 320 nm to value λ'_{max} 306 nm). The maximum decreases in the course of the reaction, the λ_{max} value does not change any more.
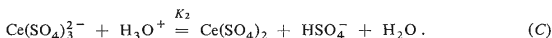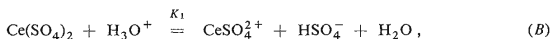
Presence of N$_2$O was detected in the reaction mixture by gas-chromatography.

DISCUSSION

The experimental rate equation of the given reaction may be defined, in accordance with the established partial orders with respect to concentration of both reactants, hydrogen, and sulphate ions, in the following way:

$$-\mathrm{d}[Ce^{4+}]/\mathrm{d}t = k[Ce^{4+}] [NH_3^+OH] [H_3O^+]/[HSO_4^-]^2 . \tag{2}$$

The dissociation constant K_d of the hydroxylamine ion is according to Briegleb[13] equal to $1 \cdot 09 . 10^{-6}$. In the concentration region of $1-5M\text{-}H_2SO_4$, protonated hydroxylamine strongly prevails in the solution so that the change in hydrogen ion concentration will result only in a very low percentage increase of the protonized form. Character of the catalytic effect of H_3O^+ ions will rather rest upon their influence on ionic equilibria of Ce(IV) complexes. The Ce^{4+} ions are in the sulphuric acid solution present in the form of sulphate complexes $CeSO_4^{2+}$, $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$ (ref.[14]) and according to other authors[15] likewise as $HCe(SO_4)_3^-$ and $H_3Ce(SO_4)_4^-$. The concentration of hydrogen ions affects according to ref.[14] equilibria of sulphate complexes in the following way:

$$Ce(SO_4)_2 + H_3O^+ \overset{K_1}{=} CeSO_4^{2+} + HSO_4^- + H_2O , \tag{B}$$

$$Ce(SO_4)_3^{2-} + H_3O^+ \overset{K_2}{=} Ce(SO_4)_2 + HSO_4^- + H_2O . \tag{C}$$

The reaction mechanism given below which involves successive formation of Ce(IV) complexes[14] and regards intramolecular redox reaction of intermediate complex of Ce(IV) with hydroxylamine as a slow and rate determining step, corresponds best to our experimental results. Its formation is confirmed also by a shift of the absorption maximum of Ce^{4+} ions in presence of hydroxylamine by 14 nm towards shorter wave lengths. Summary concentration of Ce^{4+} ions in the given solution is expressed by relationship:

$$[Ce(IV)] = [CeSO_4^{2+}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{2-}] . \tag{3}$$

When considering effect of concentration of hydrogen ions in accordance with equations (B) and (C), we can express summary concentration of Ce^{4+} ions by

$$[Ce^{4+}] = [CeSO_4^{2+}] \frac{K_1 K_2 [H_3O^+]^2 + K_2 [HSO_4^-][H_3O] + [HSO_4^-]^2}{K_1 K_2 [H_3O^+]^2} . \tag{4}$$

For a slow rate determining step, relation

$$v = k[CeSO_4NH_2OH^{2+}] , \tag{5}$$

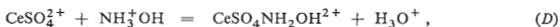holds, where $[CeSO_4NH_2OH^{2+}]$ is the equilibrium concentration of intermediate in accordance with equation:

$$CeSO_4^{2+} + NH_3^+OH \overset{K}{=} CeSO_4NH_2OH^{2+} + H_3O^+ \,. \qquad (6)$$
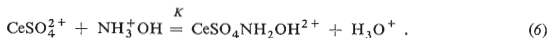
From equations (4), (5), and (6) we obtain:

$$k_{exp} = \frac{kKK_1K_2[NH_3^+OH][H_3O^+]}{K_1K_2[H_3O^+]^2 + K_2[HSO_4^-] + [HSO_4^-]^2} \,. \qquad (7)$$

If K_1 and $K_2 \ll 1$,

$$k_{exp} = \frac{kKK_1K_2[NH_3^+OH][H_3O^+]}{[HSO_4^-]^2} \,. \qquad (8)$$

Rate equation (8) resulting from the reaction mechanism suggested is in good agreement with that achieved experimentally. The redox reaction of Ce^{4+} ions with hydroxylamine proceeds then in the given media probably according to the following scheme:

$$CeSO_4^{2+} + NH_3^+OH = CeSO_4NH_2OH^{2+} + H_3O^+ \,, \qquad (D)$$

$$CeSO_4NH_2OH^{2+} \rightarrow CeSO_4^+ + NH_2O\cdot + H_3O^+ \,, \qquad (E)$$

$$NH_2O\cdot + Ce^{4+} \rightarrow Ce^{3+} + HNO + H_3O^+ \,, \qquad (F)$$

$$2\,HNO \rightarrow N_2O + H_2O \qquad (G)$$

and simultaneously

$$HNO + 4\,Ce^{4+} + 2\,H_2O \rightarrow NO_3^- + 4\,Ce^{3+} + 5\,H_3O^+ \,. \qquad (H)$$
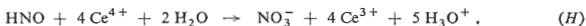
The idea that the $CeSO_4^{2+}$ ion is the reacting particle of Ce(IV) follows from the dependence of experimental rate constant upon concentration of sulphate ions and is in accordance with findings of other authors[16]. The given scheme of the reaction mechanism is consistent also with the stoichiometry determined. Results of the temperature dependence of the kinetic solvent isotope effect and appropriate parameters of activation likewise correspond to the reaction mechanism suggested. The fact that activation enthalpy values are equal in ordinary as well as heavy waters gives evidence of the fact that the H_2O molecule, or OH^- ion does not function as a bridge of the electron transfer[17]. The kinetic solvent isotope effect consists in this case in the change of entropy of activation. The entropy of activation in D_2O is by three entropy units more negative than in H_2O. This difference may be explained by

a stronger structure of heavy water (solvatation shell of reactants as well as activated complex) under equal conditions.

The change in parameters of activation with the increasing concentration of HSO_4^- ions implies effect of temperature on values of equilibrium constants K, K_1, and K_2. Likewise effect of the ionic strength upon value of the rate constant measured will probably imply primary and secondary salt effect. It will be possible to evaluate the given dependences quantitatively not until the thermodynamic quantities ΔH° and ΔS° corresponding to equilibrium constants K, K_1, and K_2 are known.

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