

KINETIC STUDY OF REDOX REACTION OF Ce^{4+} IONS WITH HYPOPHOSPHITE BY MEANS OF VIBRATING PLATINUM ELECTRODE*

L. TREINDL and J. HATALA

*Department of Physical Chemistry,
Comenius University, 801 00 Bratislava*

Received July 29th, 1976

The kinetics and mechanism of the redox reaction of Ce^{4+} ions with hypophosphite in solutions of perchloric acid were studied by the method of $I-t$ curves at constant potential and cyclic current-potential curves on a vibrating platinum electrode. Analysis of the kinetic, electrochemical, and spectrophotometric data as well as of the results of solubility measurements shows that the redox reaction takes place in six parallel oxidation-reduction steps through intermediate complexes $Ce(H_2PO_2)_n^{4-n}$. Their consecutive complexity constants and individual rate constants were evaluated and on their basis the mechanism of the elementary step of the studied redox reaction is discussed.

The kinetics and mechanism of oxidation of hypophosphorous acid with Ce^{4+} ions in solutions of perchloric acid were studied by Carroll and Thomas¹. They used ^{144}Ce as a radioactive tracer and arrived at a kinetic equation involving concentrations of $Ce(H_2PO_2)_n^{4-n}$ complexes representing intermediate reaction products. By an analysis of the kinetic data they estimated the values of the complexity constants and catalytic coefficients for $n = 1-3$. Mishra and Gupta² studied spectrophotometrically the kinetics of the same reaction in a solution of sulphuric acid. Also according to them the rate-determining step is preceded by an equilibrium of the hypophosphite complex with Ce^{4+} ions. In a solution of sulphuric acid, in addition to this complex also intermediate complexes $Ce(SO_4)(H_3PO_2)^{2+}$ and $Ce(SO_4)_2(H_3PO_2)$ are formed.

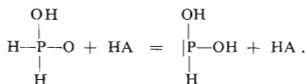
The present work brings results of kinetic measurements of the mentioned reaction obtained by the polarographic method with a vibrating platinum electrode. We showed³ its suitability and advantages in studying oxidations with $Ce(IV)$ with the aid of $I-t$ curves. In the present work we used in the kinetic study of the reaction mechanism besides $I-t$ curves also cyclic $I-E$ curves and we used the vibrating platinum electrode also for solubility measurements of a sparingly soluble salt.

Advantages of vibration electrodes in polarography were reviewed by Harris and Lindsey^{4,5} and its electrochemical applications by Facsko^{6,7}. Polarographic behaviour of the redox system $Ce(IV)-Ce(III)$ in a solution of sulphuric acid was

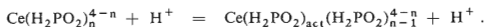
* Part VIII in the series Redox Reactions of Complexes of Cations in Higher Oxidation States; Part VII: Chem. Zvesti, in press.

studied by Desideri⁸ using a "bubbling" smooth electrode. Greef and Aulich⁹ investigated the kinetics of the mentioned redox system in an acid medium using a rotating smooth platinum disc electrode.

Many authors consider the Mitchell's mechanism¹⁰⁻¹³ of the oxidation of hypophosphorous acid, according to which a tautomeric equilibrium between the active and inactive forms of hypophosphorous acid exists in aqueous solutions and this is catalysed by Brönsted acids:



The existence of tautomers of hypophosphorous acid was substantiated¹⁴ by the measurement of the isotopic exchange of tritium between water and undissociated hydrogen of this acid. The isomerization of the inactive to the active form of hypophosphorous acid catalysed by hydrogen ions proceeds through intermediate complexes¹:



However, other authors^{2,15} do not consider the tautomeric equilibrium between both forms as necessary in the explanation of their kinetic investigations.

Since a unique and definitive concept about the oxidation mechanism of hypophosphorous acid with Ce^{4+} ions is lacking, we decided to investigate it by means of a vibrating platinum electrode, spectrophotometry, and solubility measurements of $Ce(IV)$ hypophosphite.

EXPERIMENTAL

An OH-102 type polarograph (Radelkis) served for polarographic kinetic measurements. A platinum electrode with a diameter of 0.5 mm and length of 15 mm was fastened in a glass tube, welded with a copper spiral and coupled with a horizontal vibrator of a frequency of 50 cps. Reactions were carried out in a Kalousek cell with a separated 1M mercurous sulphate reference electrode and a thermostated mantle. The cell temperature was kept constant within $\pm 0.05^\circ C$ by an ultrathermostat (Geräte-Werk Medingen, GFR). The reacting solutions were deaerated and stirred with nitrogen.

Prior to recording the $I-E$ curves, the platinum electrode was ground with a fine emery paper, rinsed, dried, dipped into a solution of $10^{-3} M$ - $Ce(IV)$ in $5M$ - H_2SO_4 , and polarized by a voltage sweep from $+1.3$ to -0.3 V at a rate of 250 mV/min. The electrode was then dipped into the reaction medium or into distilled water in the meantime between individual measurements. The half-wave potential was reproducible with one electrode to ± 10 mV, with several electrodes of the same sort to ± 50 mV.

Spectrophotometric measurements were done on a recording spectrophotometer Specord (Zeiss, Jena) with a time switch.

Chemicals were of reagent grade, water for solutions was redistilled. Ce(IV) solutions were prepared from $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (BDH Chemicals, England) freshly before every series of measurements and were stored in a brown glass bottle. Sodium hypophosphite, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (Lachema, Brno) was factorized by the Bernhart method¹⁶. Ionic strength was adjusted by NaClO_4 . Potentials were measured against 1M mercurous sulphate electrode.

RESULTS

Basic Kinetic Measurements

The half-wave potential of Ce(IV) ions in 5M-HClO₄ was measured as $(+0.905 \pm \pm 0.020)$ V at 20°C. At a concentration of 10^{-3} M hypophosphite the Ce(IV) wave was shifted by 115 mV to more negative potentials and became very steep. The shift of the half-wave potential depends linearly on the logarithm of the concentration of hypophosphite. The slope of the wave increases with the initial concentration of hypophosphite from $n = 0.77$ to 2.02 (n means formal number of exchanged electrons on the assumption of a reversible electrode process). In the course of the redox reaction in the solution the half-wave potential does not shift any more and the wave height decreases with time corresponding to a reaction of the first order. The rate constant was determined from the dependence of the limiting current of Ce(IV) ions at a constant potential of +0.3 V in a solution of 5M-HClO₄, 10^{-3} M-Ce(NO₃)₆²⁻ and 0.05M-NaH₂PO₂ in the temperature interval 17–63°C.

With the use of the Eyring equation the following activation parameters were obtained from the temperature dependence of the rate constant: $\Delta H^\ddagger = 22.7$ kcal/mol = 95.0 kJ/mol, $\Delta S^\ddagger = 5.4$ cal/mol K = 22.6 J/mol K. The rate constant increases with the concentration of hypophosphite in the mentioned medium, reaches a maximum and then decreases (Fig. 1). During investigation of the dependence

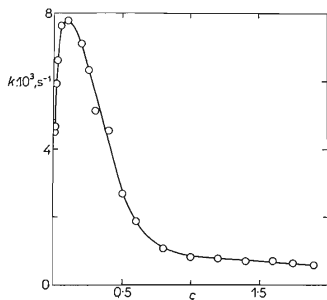


FIG. 1
Dependence of Rate Constant on Hypophosphite Concentration
Initial composition $1 \cdot 10^{-3}$ M- $(\text{NH}_4)_2 \cdot \text{Ce}(\text{NO}_3)_6$ in 5.0M-HClO₄; I 7.0, 20°C.

of the rate constant on the hypophosphite concentration we observed the formation of a white precipitate of Ce(IV) hypophosphite, which dissolved in an excess of hypophosphite solution. The measured rate constant increases linearly with the concentration of H_3O^+ ions at a constant ionic strength I 6.0. With increasing ionic strength and concentration of hydrogen ions the rate constant $k \cdot 10^3, \text{s}^{-1}$ increases as follows (at initial concentrations $1 \cdot 10^{-3}\text{M}-(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and $4 \cdot 10^{-3}\text{M}-\text{NaH}_2\text{PO}_2$ at 40°C):

$I, \text{mol/l}$	1	2	3	4	5	6	7	8
$5\text{M}-\text{H}^+$	—	—	—	—	10.3	17.7	22.3	36.7
$3\text{M}-\text{H}^+$	—	—	5.53	5.80	5.77	5.83	6.08	—
$1\text{M}-\text{H}^+$	1.73	1.87	2.00	2.02	2.08	2.15	—	—

When the reaction kinetics is followed by cyclic current-potential curves at higher hypophosphite concentrations, an anodic-cathodic wave due to the system $\text{Ce(IV)}-\text{Ce(III)}$ is observed whose cathodic portion diminishes during the reaction while the anodic one becomes larger (Fig. 2).

Solubility Measurements

The kinetic behaviour of the reaction system, especially the dependence of the rate constant on the hypophosphite concentration and the shift of the half-wave potential of Ce(IV) ions with increasing hypophosphite concentration suggest a gradual formation of Ce(IV) complexes with hypophosphite as intermediate reaction products. Measurements of the solubility of Ce(IV) hypophosphite as a function of the

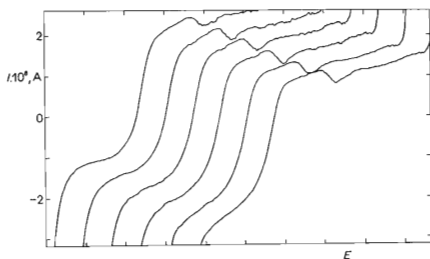


FIG. 2

Dependence of Anodic-Cathodic Wave for $\text{Ce(IV)}-\text{Ce(III)}$ System on Time

$1 \cdot 10^{-3}\text{M}-(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, $1.9\text{M}-\text{H}_3\text{PO}_2$, $5.0\text{M}-\text{HClO}_4$; I 7.0, 20°C ; recorded at 8 min intervals.

concentration of the anion enabled to determine the values of the consecutive complexity constants. The sparingly soluble salt is in a mobile equilibrium with Ce(IV) ions in the solution and its dissolution compensates the loss of Ce(IV) ions during the redox reaction. When the solution is stirred vigorously, the dissolution of the salt is more rapid than the redox process in the solution and thus the solution is kept saturated with Ce(IV) ions. This equilibrium was studied by measuring the limiting current of Ce(IV) ions on the vibrating platinum electrode, which is not influenced by the turbulent streaming of the solution. This limiting current is constant as long as the sparingly soluble salt is in an equilibrium with the saturated solution. As soon as the total amount of Ce(IV) becomes equal to that in a saturated solution, the limiting current begins to decrease exponentially (Fig. 3). The solubility of Ce(IV) hypophosphite, c_r , was determined from the time of the equilibrium t_0 and the rate of the redox reaction. The initial quantity, m , of Ce(IV) is given by

$$m = kc_r t_0 V + c_r V, \quad (1)$$

whence

$$c_r = m/V(k t_0 + 1). \quad (2)$$

The reaction volume V and the value of m were known; the values of k and t_0 were determined from the $I-t$ curves. The obtained dependence of the solubility of Ce(IV) hypophosphite on the concentration of hypophosphite is shown in Fig. 4.

The proportion of individual Ce(IV) complexes in solution was determined from

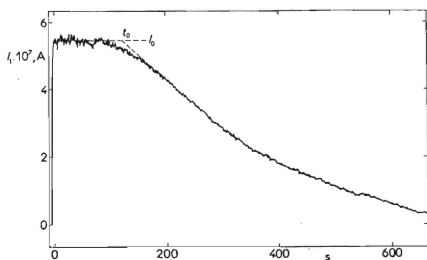


FIG. 3

$I-t$ Curve During Solubility Measurement of Ce(IV) Hypophosphite

$1 \cdot 10^{-3} \text{M} \cdot (\text{NH}_4)_2 \text{Ce}(\text{NO}_3)_6$, $8 \cdot 10^{-2} \text{M} \cdot \text{NaH}_2\text{PO}_2$, $5 \cdot 0 \text{M} \cdot \text{HClO}_4$; $I 7 \cdot 0$, 20°C ; at $0 \cdot 0 \text{V}$ against 1M mercurous sulphate electrode.

the dependence in Fig. 4 by solving five equations for five unknowns in five selected points,

$$\sum_{n=2}^6 SR_n c_L^{n-4} / c_r = 1, \quad (3)$$

where S denotes solubility product of $Ce(IV)$ hypophosphite, R_n apparent stability constant of the complex, and c_L ligand ($H_2PO_2^-$) concentration.

Eq. (3) was derived as follows. The concentration of the saturated $Ce(IV)$ hypophosphite solution can be expressed as

$$c_r = c_A + c_{AL} + \dots + c_{AL_6}, \quad (4)$$

where A denotes Ce^{4+} and L hypophosphite. At a given temperature, ionic strength and concentration of hydrogen ions the constant R_n and the solubility product S are given by

$$R_n = c_{AL_n} / c_A c_L^n, \quad S = c_A c_L^4. \quad (5), (6)$$

The relative proportion of the complex with n ligands is

$$q_n = c_{AL_n} / c_r. \quad (7)$$

If we consider only complexes with $n = 2-6$ whose relative proportion in the solution is higher than 1%, then from Eqs (4)–(6) we obtain (3).

By analysing the mentioned system of five equations we obtain the apparent stability constants R_n and the consecutive complexity constants $K_n = R_n / R_{n-1}$ as follows:

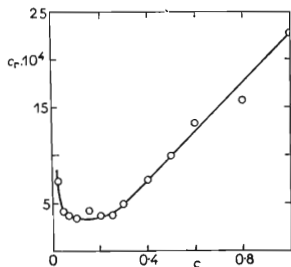


FIG. 4

Dependence of Solubility of $Ce(IV)$ Hypophosphite on Concentration of Hypophosphite

$1 \cdot 10^{-3} M-(NH_4)_2 Ce(NO_3)_6$, $5 \cdot 0 M-HClO_4$;
 $I 7 \cdot 0$, $20^\circ C$.

n	2	3	4	5	6
SR_n	$1.2 \cdot 10^{-7}$	$(7.6 \pm 1.7) \cdot 10^{-6}$	$(2.1 \pm 0.3) \cdot 10^{-4}$	$(6.1 \pm 1.3) \cdot 10^{-4}$	$(1.7 \pm 0.3) \cdot 10^{-3}$
K_n	—	63	27	3.0	3.1

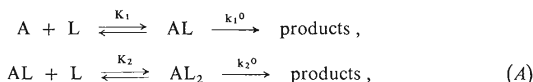
(These data are valid for $1 \cdot 10^{-3}M-(NH_4)_2Ce(NO_3)_6$, concentrations of H_3PO_2 0.025–1M; 5.0M- $HClO_4$, 17.0, 20°C.)

Rate Constants of Individual Redox Reaction Steps

The rate constant k_2^0 of the intramolecular redox reaction of the complex $Ce(H_2PO_2)_2^{2+}$ and the corresponding consecutive complexity constant K_2 were determined from kinetic data. In the region of lower hypophosphite concentrations the reaction rate is given by

$$v = k_1^0[AL] + k_2^0[AL_2]. \quad (8)$$

If we accept the reaction scheme



the equilibrium concentration of the complex $Ce(H_2PO_2)_2^{2+}$ is given as

$$[AL_2] = K_1 K_2 [L]^2 [Ce(IV)] / (1 + K_1 [L] + K_1 K_2 [L]^2), \quad (9)$$

where $[Ce(IV)]$ is the total concentration of Ce(IV) and $[L]$ is the equilibrium concentration of $H_2PO_2^-$ ions. The equilibrium constant¹ is of the order of 10^5 , the hypophosphite concentration is 10^{-4} – $10^{-3}M$, hence $K_1 [L] \gg 1$. Eq. (9) then takes the form

$$[AL_2] = K_2 [L] [Ce(IV)] / (1 + K_2 [L]). \quad (10)$$

In the range of hypophosphite concentrations where the complex AL is present in a negligible proportion with respect to AL_2 , the rate equation (8) takes the form

$$v = k_2^0 K_2 [L] [Ce(IV)] / (1 + K_2 [L]) \quad (11)$$

or

$$k = k_2^0 K_2 [L] / (1 + K_2 [L]), \quad (12)$$

which can be rearranged to

$$1/k = 1/k_2^0 K_2[L] + 1/k_2^0. \quad (13)$$

This equation is in accord with the experimental course in the investigated concentration interval of hypophosphite. An analysis of the linear dependences at 20 and 30°C revealed the values of the rate constant k_2^0 as $2.8 \cdot 10^{-3}$ and $1.1 \cdot 10^{-2} \text{ s}^{-1}$, respectively, whence the corresponding activation parameters were determined as $\Delta H_2^{\ddagger 0} = 24 \text{ kcal/mol}$ ($= 100.44 \text{ kJ/mol}$) and $\Delta S_2^{\ddagger 0} = 18 \text{ cal/mol K}$ ($= 75.3 \text{ J/mol K}$).

The rate constants corresponding to the partial redox steps with $n = 3-6$ were determined from the relative proportion q_n of the complexes and from the experimental rate constant. The overall rate constant for six parallel redox steps is given by

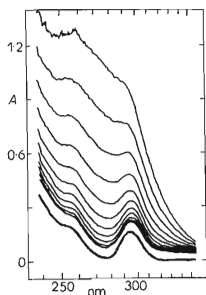
$$k = k_1^0 q_1 + k_2^0 q_2 + \dots + k_6^0 q_6. \quad (14)$$

The values of q_n were determined at different hypophosphite concentrations ranging from 0.025 to 1M. In the interval 1.0–1.9M- $H_2PO_2^-$ the complexes with $n = 1-3$ were present in negligible concentrations against those with $n = 4-6$ (less than 1%). In the range 0.014–0.025M- $H_2PO_2^-$ we determined the relative proportion of complexes with $n = 2-4$ (others constitute less than 1%). The assignment of the rate constants k_3^0 , k_4^0 , and k_5^0 was done numerically on the basis of Eq. (14) by solving a system of equations for each set of experimental values:

n	3	4	5	6
$k_n \cdot 10^3, \text{ s}^{-1}$	6.3 ± 0.7	11 ± 1	1.7 ± 0.3	0.2

FIG. 5
Absorption Maximum of Reaction Product
at λ 297 nm

$2.5 \cdot 10^{-4} \text{ M}-(NH_4)_2Ce(NO_3)_6$, 2M- NaH_2PO_2 , 5M- $HClO_4$; 20°C; in a 2 cm cuvette and recorded at 2 min intervals.



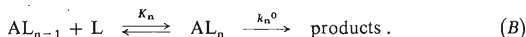
These data refer to an initial solution composition $1 \cdot 10^{-3} \text{M} \cdot (\text{NH}_4)_2 \text{Ce}(\text{NO}_3)_6$ in $5 \cdot 0 \text{M} \cdot \text{HClO}_4$ (I 7.0) at 20°C .

Spectrophotometric Measurements

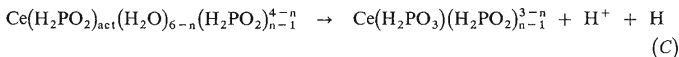
The absorption maximum in the UV region corresponding to Ce(IV) ions in $5 \text{M} \cdot \text{HClO}_4$ is shifted from the original $\lambda_{\text{max}} 276 \text{ nm}$ by the presence of $10^{-3} \text{M} \cdot \text{NaH}_2\text{PO}_2$ to shorter wave lengths, $\lambda_{\text{max}} 264 \text{ nm}$. At higher hypophosphite concentrations (above 0.2M) in the course of the reaction an absorption maximum at $\lambda 297 \text{ nm}$ appears and increases, which corresponds to Ce(III) complexes of the type $\text{Ce}(\text{H}_2\text{PO}_2)_{n-1}(\text{H}_2\text{PO}_3)^{3-n}$ (Fig. 5).

DISCUSSION

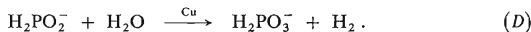
The redox reaction of Ce^{4+} with H_2PO_2^- ions proceeds according to our results in six parallel steps:



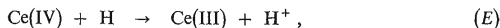
As obvious from the above numerical data, the rate constants increase from k_2^0 to k_4^0 and then abruptly decrease. The most reactive is the intermediate complex $\text{Ce}(\text{H}_2\text{PO}_2)_4$, where there is the highest probability of the occurrence of the active form of the hypophosphite anion and its interaction with a water molecule in the coordination sphere



Hypophosphorous acid can be oxidized by a water molecule on the surface of copper as catalyst¹⁷:



The decrease of the rate constant with 5 or 6 coordinated H_2PO_2^- ligands is then probably caused by lowering the number of coordinated water molecules or even by their absence. The hydrogen atom formed in the step (C) is consumed in the following step:



where Ce(IV) represents an inactive Ce(IV) complex, where no intramolecular reaction proceeds.

TABLE I

Comparison of Initial Rate of Redox Reaction v_0 with Tautomerization Rate v of Hypophosphorous Acid

5.0M- $HClO_4$; 17.0; 20°C.

H_3PO_2 , mol l ⁻¹	$v_0 \cdot 10^6$, mol l ⁻¹ s ^{-1a}	$v \cdot 10^6$, mol l ⁻¹ s ⁻¹
$1.4 \cdot 10^{-2}$	4.48	83
$2.5 \cdot 10^{-2}$	6.60	150
$5 \cdot 10^{-2}$	7.63	300
0.1	7.80	600
0.2	7.10	1 200
0.4	4.52	2 400
0.8	1.07	5 000
1.6	0.68	11 000

As shown in Table I, where the calculated initial reaction rates are compared with the rates of activation (tautomeric rearrangement) of hypophosphorous acid¹⁸, the rate-determining step cannot be an acid-catalyzed rearrangement of the inactive to the active form in the coordination sphere, but rather the step (C). The increase of the rate constant with the concentration of hydrogen ions can be attributed to a shift in the equilibrium in the solution in favour of the active form of hypophosphorous acid and thus to a higher probability of its occurrence in Ce(IV) intermediate complexes.

The increase of both the anodic current and the absorption maximum at λ 297 nm during the reaction is apparently caused by the rising concentration of the Ce(III) complexes, $Ce(H_2PO_2)_{n-1}(H_2PO_3)^{3-n}$, as reaction products in the step (C).

REFERENCES

1. Carroll R. L., Thomas L. B.: *J. Amer. Chem. Soc.* **88**, 1376 (1966).
2. Mishra S. K., Gupta Y. K.: *J. Inorg. Nucl. Chem.* **29**, 1643 (1967).
3. Treindl L., Masaryková S.: *Chem. Zvesti* **28**, 302 (1974).
4. Harris E. D., Lindsay A. J.: *Nature* **162**, 413 (1948).
5. Lindsay A. J.: *J. Phys. Chem.* **56**, 439 (1952).
6. Facsko G.: *Rev. Roum. Chim.* **21**, 191 (1966).
7. Facsko G., Poraicu M.: *Bull. Stiint. Techn. Inst. Politeh. Timisoara, Ser. Chim.* **19**, 247 (1974).
8. Desideri P. G.: *J. Electroanal. Chem.* **2**, 39 (1961).
9. Greef R., Aulich H.: *J. Electroanal. Chem.* **18**, 295 (1968).
10. Mitchell A. D.: *J. Chem. Soc.* **117**, 1322 (1920).

11. Mitchell A. D.: *J. Chem. Soc.* *119*, 1266 (1921).
12. Mitchell A. D.: *J. Chem. Soc.* *121*, 1624 (1922).
13. Mitchell A. D.: *J. Chem. Soc.* *123*, 629 (1923).
14. Jenkins W. A., Yost D., M.: *J. Inorg. Nucl. Chem.* *11*, 297 (1959).
15. Ben-Zvi E.: *J. Phys. Chem.* *67*, 2698 (1963).
16. Bernhart D. N.: *Anal. Chem.* *26*, 1798 (1954).
17. Luniachkas A. M., Gianutene I. K., Zhitkiavichiute I. I.: *Liet. TSR Mokslu Akad. Darb., Ser. B*, 2, 3 (1974).
18. Griffith R. O., McKeown A., Taylor R. P.: *Trans. Faraday Soc.* *36*, 752 (1940).

Translated by K. Micka.