

Kinetic study of the redox reaction of the Ce(IV) ions with hypophosphites in a solution of sulfuric acid*

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Received 8 February 1977

Accepted for publication 17 November 1978

Dedicated to Professor S. Stankoviánsky on his 70th birthday

The results of kinetic study of the redox reaction of the Ce(IV) ions with hypophosphites in a solution of sulfuric acid are described. On the basis of these results, the probable reaction mechanism is discussed. In particular, the dependence of the measured rate constant on concentration of hypophosphites is analyzed and the consecutive constants of complexity of the sulfate-hypophosphite cerium(IV) complexes and individual rate constants corresponding to particular intramolecular redox steps are evaluated by the iteration method.

Описываются результаты кинетического изучения окислительно-восстановительной реакции ионов Ce(IV) с гипофосфитами в растворах серной кислоты, на основании которых обсуждается возможный механизм реакции. Особенное внимание уделяется зависимости найденной константы скорости от концентрации гипофосфитов. Методом итераций получены константы ступенчатого комплексообразования сульфато-гипофосфитных комплексов церия(IV) и индивидуальные константы скорости отдельных внутримолекулярных степеней окисления.

The kinetics and mechanism of redox reaction of the Ce(IV) ions with hypophosphites in solutions of perchloric acid were studied by *Carroll and Thomas* [1]. *Mishra and Gupta* [2] were concerned with kinetic study of the same reaction in solutions of sulfuric acid and used spectrophotometry for this purpose. Because of inconsistency in interpretation of the reaction mechanism, we described [3] the results of kinetic study of this reaction obtained by the use of Pt-vibrating electrode, spectrophotometry, and solubility measurements of cerium(IV)

* Part IX of the series "Redox Reactions of Complexes with Cations in Higher Oxidation States". For Part VIII see *Collect. Czech. Chem. Commun.* **42**, 2332 (1977).

hypophosphite in solutions of perchloric acid. This paper is concerned with the influence of sulfuric acid medium on the above-mentioned mechanism and kinetics.

Experimental

The working procedure of kinetic polarographic measurements by means of Pt-vibrating electrode was described in [3].

All chemicals used were anal. grade. The solutions of the Ce(IV) ions were prepared from ammonium cerium(IV) sulfate (BDH Chemicals LTP Poole, England) or cerium(IV) sulfate (Lachema, Brno) by dissolving them in sulfuric acid (Merck, Darmstadt) or in a mixture of sulfuric acid and perchloric acid (Laboratorchemie, VEB, Apolda). The ionic strength was adjusted by a suitable addition of sodium perchlorate (Lachema, Brno). The solutions of sodium hypophosphite were standardized by the *Bernhart* method [4]. Each series of measurements was carried out with fresh solutions and the stock solutions of the Ce(IV) ions were kept in dark bottles.

The numerical analysis of the relationships measured was performed on a computer Siemens 4004/150 in the Institute of Computing Technique of the Komenský University in Bratislava.

Results

In solutions of 1 M sulfuric acid, the Ce(IV) ions give on a Pt-vibrating electrode a well-developed polarographic wave corresponding to electroreduction of Ce(IV) to the Ce(III) ions, the half-wave potential against a 1 M mercurousulfate being +0.27 V. On addition of sodium hypophosphite, the polarographic wave splits in two waves and the magnitude of cathodic limiting currents exponentially decreases with time (Fig. 1). The new

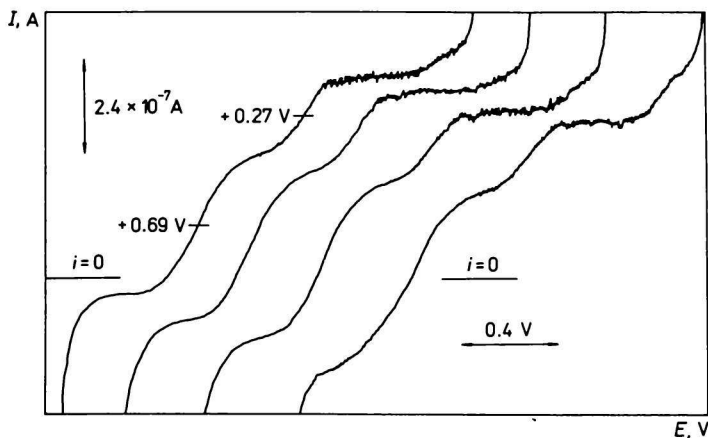


Fig. 1. Dependence of polarographic waves of the hypophosphite cerium(IV) complexes on time.
 10^{-3} M-Ce(SO₄)₂, 10^{-3} M-NaH₂PO₂, 1 M-H₂SO₄, temperature 40°C.
 Individual curves were successively recorded in 9 min intervals.

wave formed with a half-wave potential of +0.69 V against the same reference electrode evidently corresponds to a one-electron reduction of the sulfate-hypophosphite cerium(IV) complexes.

Table 1 gives the values of the ratio of the new wave to total limiting current of the Ce(IV) ions in cathodic region as a function of sulfuric acid concentration, sodium hypophosphite concentration, and temperature. The value of this ratio increases with concentration of hypophosphites and with temperature whereas it decreases with increasing concentration of sulfuric acid. The total cathodic limiting diffusion current of the Ce(IV) ions decreases with time according to the kinetic law of first-order reactions.

We observed changes in absorption spectrum in the region 230–260 nm (Fig. 2) in mixtures of sulfuric acid and perchloric acid solutions. These changes were observable at

Table 1

Variation of the ratio of limiting current of the hypophosphite cerium(IV) complexes and total limiting current of the cerium(IV) ions with NaH_2PO_2 concentration

H_2SO_4 , mol l ⁻¹	NaH_2PO_2 , mol l ⁻¹ $c \cdot 10^3$	t , °C	L
1.0	0.5	40	0.33 ± 0.02
1.0	1.0	40	0.31 ± 0.02
1.0	2.5	40	0.38 ± 0.02
1.0	10.0	40	0.47 ± 0.02
0.05	1.0	40	0.86 ± 0.04
0.11	1.0	40	0.71 ± 0.02
0.21	1.0	40	0.58 ± 0.03
0.51	1.0	40	0.51 ± 0.04
0.75	1.0	40	0.45 ± 0.04
1.0	1.0	40	0.31 ± 0.02
1.0	1.0	15	0.19 ± 0.01
1.0	1.0	20	0.22 ± 0.01
1.0	1.0	40	0.31 ± 0.02
1.0	1.0	45	0.36 ± 0.03

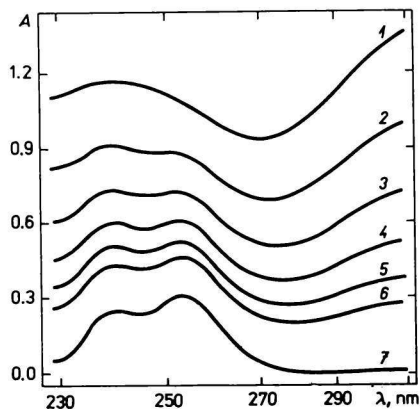


Fig. 2. Time dependence of absorption spectrum of the hypophosphite cerium(IV) complexes.

5×10^{-4} M-Ce(SO₄)₂, 5×10^{-3} M-NaH₂PO₂,
10⁻¹ M-H₂SO₄, 1 M-HClO₄, temperature
30°C.

Curves 1–6 were successively recorded in 10.5 min intervals whereas curve 7 was recorded after 9 h.

lower sulfuric acid concentrations. We did not succeed in recording the e.s.r. spectrum of eventual intermediary radicals by using the flow method.

The reduction of the Ce(IV) ions, present in excess in sulfuric acid solutions, by hypophosphites is a first-order reaction with respect to concentration of the Ce(IV) ions in the time interval of three reaction half-times. Table 2 supplies the values of rate constants (s^{-1}) for several temperatures. On the basis of temperature dependence of the rate constant in 1 M solution of sulfuric acid, the activation energy was evaluated by means of the Arrhenius equation. Thus it was found $E = 75.2 \pm 0.2 \text{ kJ mol}^{-1}$ for 10^{-3} M concentration of sodium hypophosphite and $E = 97.2 \pm 0.2 \text{ kJ mol}^{-1}$ for 0.5 M concentration of sodium hypophosphite.

Table 2

 Influence of temperature on the value of rate constant 1.0 M- H_2SO_4 , $10^{-3} \text{ M-Ce}(\text{SO}_4)_2$

NaH_2PO_2 , mol l^{-1}	t , $^\circ\text{C}$	$k \cdot 10^4$, s^{-1}
10^{-3}	15	0.144
10^{-3}	20	0.201
10^{-3}	30	0.617
10^{-3}	40	1.62
10^{-3}	45	2.58
5×10^{-1}	30	31.2
5×10^{-1}	35	51.5
5×10^{-1}	40	92
5×10^{-1}	45	190
5×10^{-1}	50	322

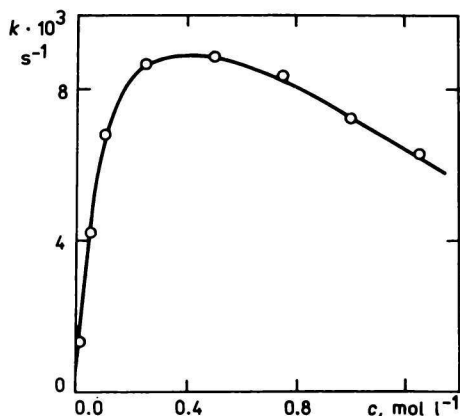


Fig. 3. Variation of the experimental rate constant with hypophosphite concentration. $10^{-3} \text{ M-Ce}(\text{SO}_4)_2$, 1 M- H_2SO_4 , temperature 40°C .

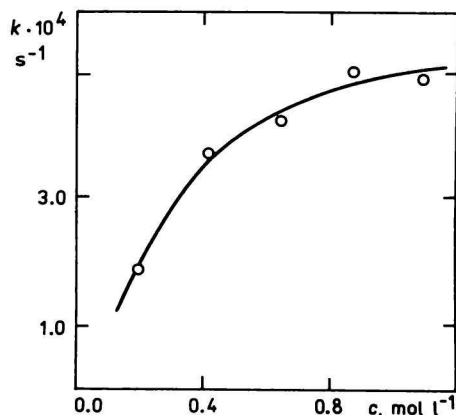


Fig. 4. Variation of the experimental rate constant with concentration of the H_3O^+ ions. $10^{-3} \text{ M-Ce}(\text{SO}_4)_2$, $2 \times 10^{-3} \text{ M-NaH}_2\text{PO}_2$, $10^{-1} \text{ M-H}_2\text{SO}_4$, $I = 1.0 \text{ M}$, temperature 40°C .

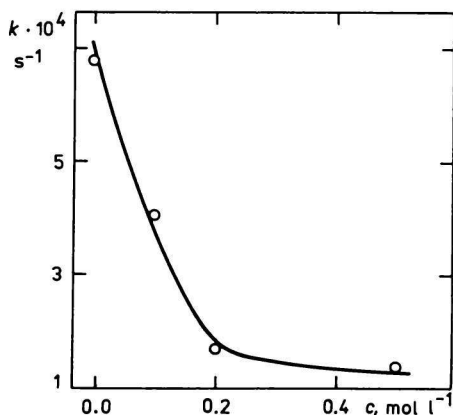


Fig. 5. Variation of the experimental rate constant with concentration of the sulfate ions. 10^{-3} M- $(NH_4)_2Ce(NO_3)_6$, 10^{-3} M- NaH_2PO_2 , $I = 1.0$ M, temperature $40^\circ C$.

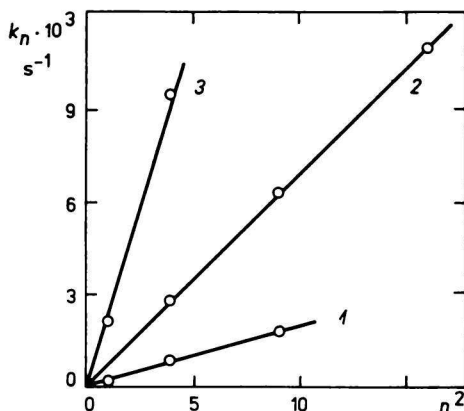


Fig. 6. Individual rate constants as a function of squared number of the coordinated hypophosphite ions.

1. Measurements of Carroll and Thomas [1]; 2. our results obtained with the solution of 5 M- $HClO_4$ [3]; 3. results of this study.

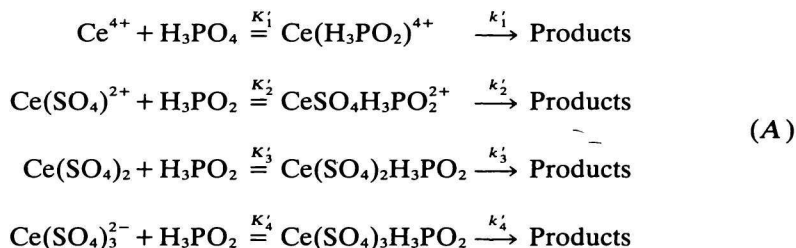
The value of rate constant increases nonlinearly with concentration of hypophosphites at constant ionic strength and constant concentration of the H_3O^+ ions. In this way, it reaches a maximum and afterwards it decreases (Fig. 3). In sulfuric acid solutions, the value of rate constant increases nonlinearly with concentration of the H_3O^+ ions and tends towards maximum (Fig. 4). The value of rate constant decreases nonlinearly with increasing concentration of the sulfate ions at constant ionic strength (Fig. 5).

Discussion

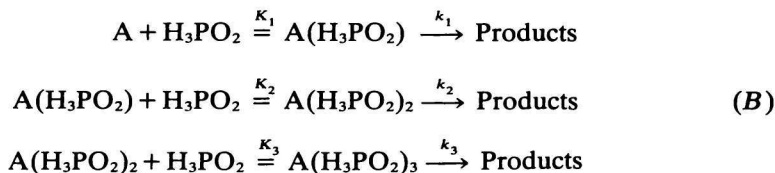
The above results of kinetic study of the redox reaction of sodium hypophosphite with cerium(IV) sulfate in solutions of sulfuric acid complement the kinetics and mechanism of this reaction in solutions of perchloric acid which were described in [3]. As obvious from Fig. 1 and Table 1, an equilibrium between the sulfate-hypophosphite cerium(IV) complexes ($E_{1/2} = +0.69$ V) and sulfate cerium(IV) complexes ($E_{1/2} = +0.27$ V) must exist in solutions of sulfuric acid. The intramolecular redox transformation of the sulfate-hypophosphite cerium(IV) complexes is likely to be a slow and rate-determining step in the whole reaction. Since the cerium(IV) complexes are generally sensitive to substitution, the establishment of equilibria proceeds very rapidly. The equilibrium shifts in favour of the sulfate-hypophosphite complexes with increasing concentration of hypophosphites and with temperature. An increase in sulfuric acid concentration shifts the equilibrium in opposite sense, which results in a decrease in the observed rate constant. The dependence of rate constant on hypophosphite concentration

has an analogous character as observed in perchloric acid solutions [3], but the position of maximum is different. The maximum of this relationship is at the 0.4 M concentration of hypophosphites in the medium of 1 M sulfuric acid while it is already at the 0.1 M concentration of hypophosphites in the medium of 5 M perchloric acid. This observation also indicates an inhibitory effect of sulfate ions or a competition of the sulfate cerium(IV) complexes with the sulfate-hypophosphite complexes.

The spectral measurements are in harmony with this idea. Other experimental results are also, in general, consistent with the reaction mechanism suggested by *Mishra and Gupta* [2] according to which the hypophosphite complexes are formed in four parallel steps



It results from the dependence of rate constant on hypophosphite concentration at 1 M sulfuric acid concentration (Fig. 3) that the sulfate-hypophosphite cerium(IV) complexes with increasing number of the coordinated H_3PO_2 molecules consecutively arise in the medium of sulfuric acid, too. By analyzing this graphical relationship in three intervals of hypophosphite concentration by the procedure according to *Carroll and Thomas* [1], we obtained the individual rate constants for the redox reactions inside the coordination sphere and the consecutive constants of complexity according to the following reaction scheme



In the solution of 1 M sulfuric acid at 40°C, the symbol A stands for the prevailing aqua-sulfate cerium(IV) complex. The equilibria corresponding to the equilibrium constants K_1 , K_2 , and K_3 are established in much shorter time than needed for the individual redox steps corresponding to the rate constants k_1 , k_2 , and k_3 to proceed.

In the calculations according to *Carroll and Thomas* [1], a correction of the equilibrium hypophosphorous acid concentration with respect to its degree of coordination in the Ce(IV) complexes was carried out. The correction was

performed with each group of constants and for each hypophosphorous acid concentration by iteration according to the following formula

$$L = L_0 - A_0 \frac{\sum_{j=1}^3 \left(j \prod_{i=1}^j K_i L^j \right)}{1 + \sum_{j=1}^3 \left(L^j \prod_{i=1}^j K_i \right)} \quad (1)$$

where L_0 is the analytical concentration of hypophosphorous acid, A_0 stands for concentration of the Ce(IV) ions, and L is the concentration of the noncoordinated hypophosphorous acid molecules. The arithmetic mean of the determined and in the preceding step inserted value was used in each iteration step. For positive values of the constant of complexity, the procedure converges in the interval $0-L_0$.

For the first complex, the values were obtained from the relationship between rate constant and hypophosphite concentration in the interval 10^{-3} — 7.5×10^{-3} M- H_3PO_2 . In the first approximation, the constant of stability was $K_1 = 58.9$ and the individual rate constant was $k_1 = 2.8 \times 10^{-3} \text{ s}^{-1}$. The values for the complex $\text{A}(\text{H}_3\text{PO}_2)_2$ were estimated in the concentration interval 2.5×10^{-2} — 10^{-1} M- H_3PO_2 . If we take into account that the course of reaction through the first intermediary complex falls to 3% in this interval, we obtain the values $K_2 = 28.1$ and $k_2 = 8.2 \times 10^{-3} \text{ s}^{-1}$. Afterwards, we obtained the optimum values of the constants K_1 , K_2 , k_1 , and k_2 for the above concentration intervals. These values express the dependence of rate constant on hypophosphite concentration accurate to $\pm 4\%$ (Table 3). The values of K_3 and k_3 could be only appraised for the concentration interval 0.5—1.25 M- H_3PO_2 in which the value of the measured rate constant decreases with increasing hypophosphite concentration.

As obvious from Fig. 6, the first two values of individual rate constants which were obtained in this work are a linear function of squared number of the coordinated hypophosphite ions. The situation is similar in the medium of 5 M perchloric acid [3] as well as in the system studied by Carroll and Thomas [1]. For the region of low or medium hypophosphite concentrations, this relationship may

Table 3

Consecutive constants of complexity and individual rate constants of intermediary complexes
1 M- H_2SO_4 , 10^{-3} M-Ce(SO_4)₂, 10^{-3} —1.25 M- NaH_2PO_2 , temperature 40°C

n	K , l mol ⁻¹	$k \cdot 10^3$, s ⁻¹
1	276 ± 28	2.14 ± 0.22
2	14.3 ± 1.5	9.45 ± 0.95
3	0.25 ± 0.08	< 3.5

be expressed by the equation $k_n = qn^2$ where k_n is an individual rate constant, q is a parameter dependent on medium and temperature, and n denotes the number of the hypophosphite molecules coordinated to a Ce(IV) ion in the intermediary complex.

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Translated by R. Domanský