

# Kinetic Study of the Reduction of Thallium(III) Ions by Hypophosphites

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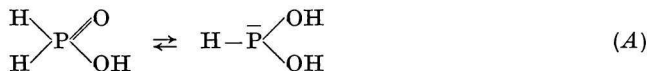
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The kinetics of thallium(III) reduction by hypophosphites has been followed on the basis of time dependence of limiting diffusion current of trivalent thallium by using either a rotating platinum electrode or a dropping mercury electrode. It has been demonstrated that the reaction is one of the first order with respect to the concentration of Tl(III) ions. The temperature dependence of rate constant has been used for the determination of activation parameters  $\Delta H^\ddagger = 20.5 \text{ kcal mole}^{-1}$  and  $\Delta S^\ddagger = -2.2 \text{ cal deg}^{-1} \text{ mole}^{-1}$ . The dependence of the observed rate constant on the concentration of Tl(III) ions is interpreted by an autocatalytic character of reaction. The results obtained by means of both electrodes are discussed and a probable reaction mechanism is proposed.

It is a great deal of papers [1–11] which have pursued the kinetics and mechanism of hypophosphorous acid oxidation. Some authors [1–7, 11] have discussed the oxidation of hypophosphorous acid to phosphorous acid on assumption that a tautomeric rearrangement of the inactive to active form of hypophosphorous acid according to the following scheme precedes the proper oxidation



Thus they have been allowed to discuss the oxidation of hypophosphorous acid to phosphorous acid on the basis of the rate equation according to *Mitchell* [1–4]. The assumption of tautomeric mechanism has not been proved unambiguously though it is supported by the study of tritium exchange between  $\text{H}_3\text{PO}_2$  and  $\text{T}_2\text{O}$  [12]. Several cations such as  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ , and  $\text{Ce}^{4+}$  have been used up to now as oxidizing agents in kinetic studies of the hypophosphorous acid oxidation [1–9].

As to the kinetic study of Tl(III) ion reduction, the principal problem consists in the question whether this process proceeds as one- or two-electron transfer. The views of authors [13–23] are not uniform in this respect. Some of them suppose a one-electron transfer and the existence of short-lived Tl(II) whereas the others assume a two-electron transfer.

From the point of view of these problems we approach to the study of hypophosphite oxidation by Tl(III) ions which has not been described yet.

## Experimental

Kinetic measurements were performed by recording the time dependence of the limiting diffusion current of Tl(III) ions at the potential of  $-0.05$  V against a normal calomel electrode. The Kalousek vessel was used as an electrolytic vessel and was dipped into Hoeppler ultrathermostat during measurements. The normal calomel electrode filled with 1 N solution of sodium chloride was employed as a reference electrode. Either the dropping mercury electrode modified according to *Smoleř* with the flow-rate  $m = 1.84$  mg s $^{-1}$  and the height of mercury column  $h = 78$  cm or rotating platinum electrode was used as an indication electrode. A platinum wire of 0.5 mm diameter and 5 mm length sealed in a glass tube filled with mercury was used as a rotating platinum electrode. The electrode thus constructed was fitted in a rotation stirrer, M 22 Radiometer. Experiments were carried out at a constant number of revolutions per minute (600 rev./min.). In case of the dropping mercury electrode, polarographic currents were recorded by a polarograph of Radelkis Co, type OH-102. When the rotating platinum electrode was used the currents were amplified before hand by means of a photoelectric amplifier WF 70, Zomp (Poland) the outlet of which was connected to a recorder with dotted record, Regula, type Z 31 m A6 (Nová Paka, ĀSSR).

Thallium(III) chloride was prepared by oxidizing thallium(I) chloride with gaseous chlor. Sodium hypophosphite, puriss., was recrystallized. All other chemicals were analytical grade.

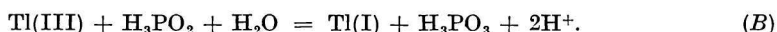
The rate constants which occur in particular relationships are an average of four independent measurements accurate to  $\pm 6\%$ .

## Experimental Results

The kinetics of Tl(III) ion reduction in the presence of excess hypophosphites was always followed in a solution of 2 M-HClO $_4$ . On the basis of limiting diffusion current the reaction order with respect to Tl(III) ion concentration was found to be  $n = 1$ . The rate constants were determined by using the kinetic equation for the first order reaction (Fig. 1). Activation parameters were determined on the basis of the temperature dependence of reaction rate (Fig. 2) by means of Eyring equation. Activation enthalpy  $\Delta H^\ddagger = 20.5 \pm 2.6$  kcal mole $^{-1}$  and activation entropy  $\Delta S^\ddagger = -2.2 \pm 0.7$  cal deg $^{-1}$  mole $^{-1}$  were calculated by the method of least squares.

The measured rate constant does not change with concentration of perchloric acid within the concentration range 1–4 M at constant ionic strength  $\mu = 4$  (NaClO $_4$ ). The rate constant does not change with increasing ionic strength in the interval from  $\mu = 1$  to  $\mu = 4$  at constant perchloric acid concentration too. But the rate constant increases linearly with hypophosphite concentration (Fig. 3). The dropping mercury electrode having been used, the slope of this relationship is approximately twice as great as in case of the rotating platinum electrode. The rate constant also depends on the concentration of Tl(III) ions (Fig. 4). Near the beginning, it rises almost linearly and reaches a limiting value at higher concentrations. The limiting values of rate constants are greater in case the dropping mercury electrode and not the rotating platinum electrode has been employed.

After the completion of reaction all products have been quantitatively determined in solution in accordance with the stoichiometric equation



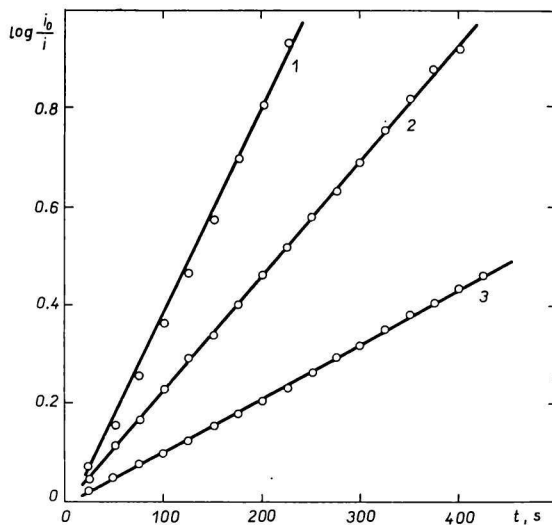


Fig. 1. Proof of the first order reaction for the reduction of Tl(III) ions by hypophosphites.

2 M-HClO<sub>4</sub>, 6 × 10<sup>-2</sup> M-NaH<sub>2</sub>PO<sub>2</sub>.

1. 4 × 10<sup>-3</sup> M-TlCl<sub>3</sub>; 2. 1 × 10<sup>-3</sup> M-TlCl<sub>3</sub>; 3. 2 × 10<sup>-4</sup> M-TlCl<sub>3</sub>.

Temperature 24.8°C.

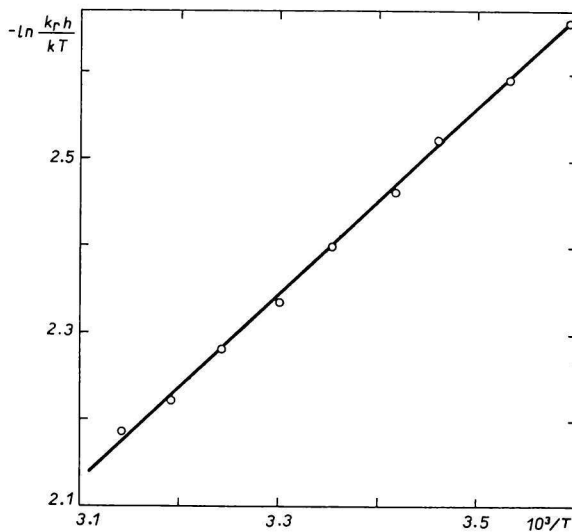


Fig. 2. Temperature dependence of rate constant.

2 M-HClO<sub>4</sub>, 2 × 10<sup>-2</sup> M-NaH<sub>2</sub>PO<sub>2</sub>, 10<sup>-3</sup> M-TlCl<sub>3</sub>.

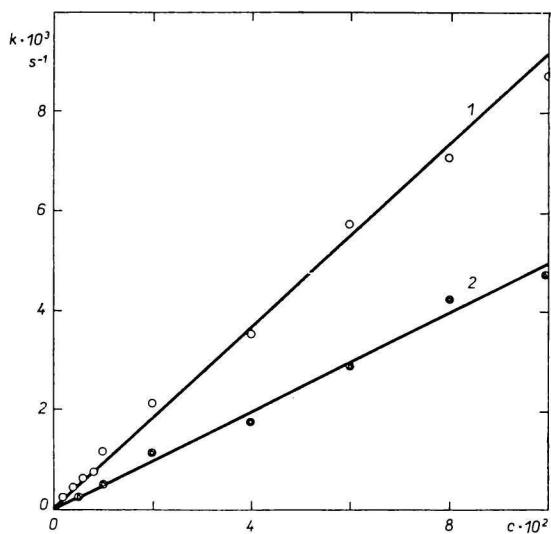


Fig. 3. Variation of rate constant with the concentration of hypophosphites.  $2 \text{ M-HClO}_4$ ,  $5 \times 10^{-4} \text{ M-TlCl}_3$ . Temperature  $24.8^\circ\text{C}$ .  
 1. by means of dropping mercury electrode; 2. by means of rotating platinum electrode.

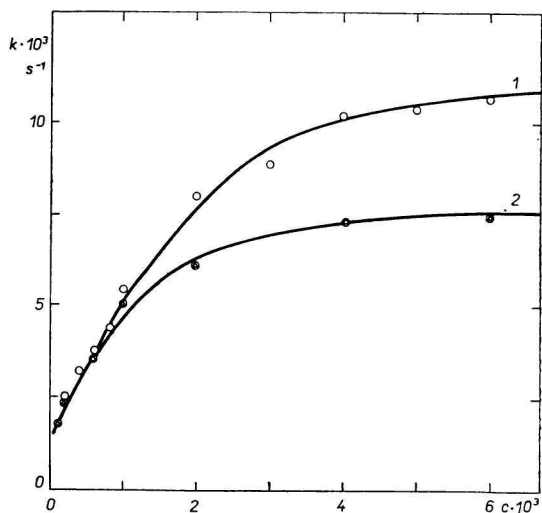
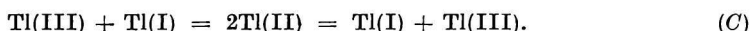


Fig. 4. Variation of rate constant with the concentration of Tl(III) ions.  $2 \text{ M-HClO}_4$ ,  $5 \times 10^{-2} \text{ M-NaH}_2\text{PO}_2$ . Temperature  $24.8^\circ\text{C}$ .  
 1. by means of dropping mercury electrode; 2. by means of rotating platinum electrode.

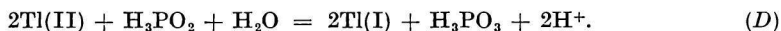
## Discussion

It has been found on the basis of time dependence of limiting diffusion current of Tl(III) ions by both half life and differential methods that the reaction order with respect to the Tl(III) concentration is equal to one *i.e.*  $n = 1$ . This result is also confirmed by a linear relationship between  $\log i_0/i$  and time which holds during two half life periods of reaction at least (Fig. 1). The dependence of the measured rate constant on the Tl(III) concentration seems to be in contradiction with these results. This dependence, however, indicates an autocatalytic character of the redox reaction studied. Likewise, *Krishna* and *Sinha* [30] have observed a dependence of first order reaction rate constant on the concentration of oxidizing agent for the oxidation of Tl<sup>+</sup> ions by Ce(IV) ions.

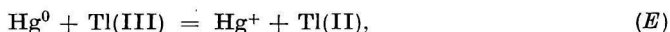
The oxidation of hypophosphorous acid by Tl(III) ions proceeds according to stoichiometric equation (B). Provided hypophosphites are present in excess, the competitive reaction of Tl(III) ions with phosphorous acid must not be assumed. The autocatalytic character may be due to a consecutive competitive reaction of phosphorous acid with Tl(II) ions which should be considered as an intermediate of the reaction (C) involving electron transfer



The question concerning the existence of Tl(II) ions is not solved completely yet [13–29]. The formation of Tl(II) is supposed for the oxidation of V(III) and Fe(II) by *Daugherty* [13] and *Higginson* [14], respectively, as well as for the electro-reduction of Tl(III) ions [28, 29]. On the other hand, the two-electron transfer is assumed in case of the bromide oxidation by Tl(III) ions in chloride solutions [18] and in melts [19] as well as for the elucidation of kinetics of V(II) ion [24] and Hg(I) ion [25] oxidation. According to [17], Tl(II) ions formed in the course of radiolysis oxidize selectively ethylenediamine and glycine before their disproportionation. On this basis we assume too that Tl(II) ions as an intermediate of reaction (C) react with hypophosphorous acid as follows



The essentially greater values of rate constants obtained by means of a dropping mercury electrode in comparison to the values obtained with a rotating platinum electrode are not the sum of reaction rates of reactions involving the reduction of Tl(III) ions by hypophosphites and mercury. The last reaction runs in given medium with reaction rate about  $10^{-7} \text{ s}^{-1}$  what is approximately 0.1% of the measured rate constant corresponding to the reaction of Tl(III) ions with hypophosphites. This fact can be explained by the catalytic effect of Hg atoms. The prove of their existence in aqueous solutions ( $10^{-7} \text{ M}$  at 20°C) is to be presented by the measurements of metallic mercury solubility in water [31]. This catalysis may be due to the reaction



which may be followed by the reaction (D). The existence of reaction (E) is confirmed by the formation of Hg<sub>2</sub>Cl<sub>2</sub> precipitate in reaction system with a dropping mercury electrode.

## References

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