Sustained and Damped Oscillations in the Permanganate-Hydroxylamine Reaction in a **Continuous-Flow Stirred Tank Reactor**

Arpád Nagy, Anna Olexová, and Ľudovít Treindl*

Department of Physical Chemistry, Comenius University, 842 15 Bratislava, Czechoslovakia (Received: November 21, 1990; In Final Form: March 11, 1991)

The reaction system MnO_4 - $NH_2OH-H_3PO_4$ in a CSTR exhibits sustained and damped oscillations, if MnO_4 -ions are at a stoichiometric ratio or in an excess. The design of this permanganate chemical oscillator is based on the phase diagrams in the $[NH_2OH]_0-k_0$ and $[H_3PO_4]_0-k_0$ planes. An interaction of solvated $Mn(IV)_{sol}$ ions, which are in equilibrium with $(MnO_2)_{col}$ stabilized by the presence of $H_2PO_4^-$ ions, with manganese species mostly in higher oxidation states seems to be the core of our permanganate oscillator with hydoxylamine.

Introduction

Although transition metals play a major role in enzyme-catalyzed reactions, chemical oscillators based on the transition-metal chemistry are rare. The first chemical oscillator of this kind has been reported only in 1986.¹ The first permanganate oscillator, the $KMnO_4-H_2O_2-H_3PO_4$ reaction in a continuous-flow stirred tank reactor (CSTR),¹ was soon followed by the report of oscillatory reactions of the system KMnO₄-ninhydrin-H₃PO₄² and the KMnO₄-KNO₂-formic acid-methanol system.³ The design of the first permanganate oscillator including a kinetic tristability was described in this Journal.⁴ In the meantine Orban and Epstein^{5,6} found the Guyard⁷ reaction in a CSTR to be a "minimal permanganate oscillator" which might serve as a core from which other oscillating permanganate reactions could be generated. Recently, we succeeded in finding conditions under which chemical oscillations of manganese can be based on the Mn²⁺ ion oxidation by periodates in a CSTR.⁸ However, it is not proved so far that the oscillatory behavior of the above-mentioned permanganate oscillatory systems have a common route.

Therefore, we tried to find even more permanganate oscillators, from which the following one, based on the oxidation of hydroxylamine by MnO_4^{-} ions, is the topic of this paper. We believe that only by designing permanganate oscillators in a whole series would we be able to formulate their skeleton mechanism.

Experimental Section

Materials. Stock solutions were prepared from commercially available KMnO₄ (P.A., Lachema, Brno), NH₂OH·¹/₂H₂SO₄ (p.a., Lachema, Brno), and H₃PO₄ (p.a., Lachema, Brno). A stock solution of KMnO4 was prepared by the procedure of Kolthoff et al.⁹ Hydroxylamine solutions were prepared daily. The NH₂OH content was determined by titrating with a standardized solution of $KMnO_4$. The concentration of H_3PO_4 was checked by alkalimetry. Dilutions were made with twice-distilled water.

Apparatus. We used a glass CSTR¹⁰ (26 mL) with a mantle connected to a TB 150 ultrathermostat (Medingen) and monitored the oscillatory reaction polarographically by means of a static Pt electrode in a flowing, well-stirred solution. The polarographic current at a potential of 0.0 V against the potential of a 1 M Hg/Hg_2SO_4 electrode in the absence of a supporting electrolyte results mostly from the electroreduction of MnO_4^- ions. The measured current is limited by the convective diffusion of electroactive species. The experiments were performed with a stirring

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frequency of 2700 min⁻¹ by means of a mixing propeller. The flow of solution through the CSTR was driven by a peristaltic pump, Type 2-15 ZALIMP, (Poland). No air gap was present between the surface of the solution and the reaction cap.

Methods. Reactant solutions were added through three independent tubes into the CSTR. The data of concentrations correspond to the values that would be reached by the input species in the reactor if no reaction were to occur. The polarographic measurements were made by using a polarograph of Type LP 7 Laboratorni Přistroje, n.p. (Czechoslovakia).

In a closed system the reaction was followed spectrophotometrically by using a spectrophotometer of type SPECORD M 40, Zeiss, Jena (Germany), with a thermostated 1-cm quartz cuvette.

For the flow experiments, the reactor was filled at the highest available pump speed. After a steady state was attained, the flow rate was lowered and a new steady or oscillatory state was established. The procedure was continued until the system passed discontinually to another set of steady or oscillatory states which have the form of sustained or damped oscillations. The flow rate was increased stepwise until the system attained its initial state and so completed the hysteresis loop. The same procedure was used when the kinetic bistability was studied. When the entire range of flow rates had been probed for one set of input concentrations, the sequence was repeated for a new feed composition. The data measured in this way were used for the construction of the corresponding phase diagram.

Results and Discussion

The reduction of MnO_4^- ions by hydroxylamine in a solution of phosphoric acid proceeds autocatalytically (Figure 1). The course of the autocatalytic reaction and its inflection time prolongs with an increasing concentration of $H_2PO_4^-$ ions (Figure 2).

When we follow the reaction system KMnO₄-NH₂OH-H₃PO₄ in a CSTR at a stoichiometric ratio or in an excess of MnO₄⁻ ions, we observe its oscillatory behavior as sustained or damped oscillations in the dependence from the k_0 value (Figure 3). As is seen in this figure, the "reversible" transition from damped to sustained oscillations is possible. The design of the permanganate chemical oscillator with hydroxylamine is characterized by the phase diagrams in Figures 4 and 5. In both the figures it is seen that the region of the kinetic bistability touches the region of sustained oscillations only in a narrow interval of NH₂OH or H_3PO_4 concentrations. The wide region of damped oscillations in the neighborhood of the region of sustained oscillations suggests a Hopf bifurcation on the borderline separating the two regions. Fortunately, quite a big region of sustained oscillations, which are well reproducible, is not disturbed by MnO₂ precipitation.

The permanganate oxidation of hydroxylamine is a complex reaction consisting of a number of component reactions. In dilute solutions of phosphoric acid under given conditions the following stoichiometric equation corresponds to the net reaction

$$2MnO_4^- + 3NH_3OH^+ \rightarrow 2MnO_2 + 3NOH + 4H_2O + H^+$$
 (1)

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Figure 1. Measured absorbance-time curves in a closed permanganatehydroxylamine system: $[MnO_4^-]_0 = 4.5 \times 10^{-5} \text{ M}, [H_3PO_4]_0 = 2 \times 10^{-3} \text{ M}, [NH_2OH]_0 = 10^{-5} \text{ M} (1), 2 \times 10^{-5} \text{ M} (2), 3 \times 10^{-5} \text{ M} (3), 4 \times 10^{-5} \text{ M} (4), 5 \times 10^{-5} \text{ M} (5), 6 \times 10^{-5} \text{ M} (6).$ $\lambda = 525 \text{ nm}, T = 15 \text{ °C}.$



Figure 2. Influence of the H₃PO₄ concentration on absorbance-time curves: $[MnO_4^{-}]_0 = 4.5 \times 10^{-5} \text{ M}$, $[NH_2OH]_0 = 3 \times 10^{-5} \text{ M}$, $[H_3PO_4]_0 = 5 \times 10^{-4} \text{ M}$ (1), 10^{-3} M (2), $2 \times 10^{-3} \text{ M}$ (3). $\lambda = 525 \text{ nm}$ (solid lines), 418 nm (dotted lines), T = 15 °C.



Figure 3. "Reversible" transition from damped to sustained oscillations: $[MnO_4^-]_0 = 4.5 \times 10^{-5} \text{ M}, [NH_2OH]_0 = 4 \times 10^{-5} \text{ M}, [H_3PO_4]_0 = 1.75 \times 10^{-3} \text{ M}, T = 30 \text{ °C}.$ Arrows indicate points of transition.

where the species NOH is not stable and in a dimerization leads to the N_2O production:

$$2NOH \rightarrow N_2O + H_2O \tag{2}$$

The final products of the hydroxylamine reduction of MnO_4^- ions are colloidal particles of MnO_2 stabilized by $H_2PO_4^-$ ions.¹¹ Since phosphoric acid is a necessary component also of this permanganate oscillator, we assume the colloidal MnO_2 to be a



Figure 4. Phase diagram in the $[NH_2OH]_0-k_0$ plane. $[MnO_4^-]_0 = 4.5 \times 10^{-5} M$, $[H_3PO_4]_0 = 2 \times 10^{-3} M$. T = 30 °C. OSS = oxidized steady state, RSS = reduced steady state; \diamond , bistability, \diamond , sustained oscillations, \heartsuit , transition to reduced steady state through damped oscillations.



Figure 5. Phase diagram in the $[H_3PO_4]_0-k_0$ plane. $[MnO_4^-]_0 = 4.5 \times 10^{-5} \text{ M}$, $[NH_2OH]_0 = 4 \times 10^{-5} \text{ M}$. T = 30 °C. OSS = oxidized steady state, RSS = reduced steady state; \diamond , bistability, \diamond , sustained oscillations, \heartsuit , transition to reduced steady state through damped oscillations.

reservoir of $Mn(IV)_{sol}$ ions that can interact with other manganese species. This interaction of solvated $Mn(IV)_{sol}$ ions with manganese species mostly in higher oxidation states seems to be the core of permanganate oscillators of our type^{1,2,4,13} rather than the Guyard reaction.^{4,5,12} Our assumption is supported also by the fact that the oscillations in the KMnO₄-NH₂OH-H₃PO₄ system occur only at a stoichiometric ratio or in an excess of MnO₄⁻ ions. Although the successive reaction between Mn(IV)_{sol} and NH₂OH as follows

$$Mn(IV)_{sol} + NH_3OH^+ \rightarrow Mn(II) + NOH + 3H^+$$
 (3)

cannot be excluded, the steady-state concentration of Mn(II) ions at insufficient concentrations of NH_2OH will be probably very low, in order to start the Guyard reaction.

Further detailed study of the elementary steps of the permanganate oxidation of hydroxylamine in the presence of phosphoric acid both in a closed system and in a CSTR will be the project of our laboratory.

Registry No. MnO₄, 14333-13-2; NH₂OH, 7803-49-8; H₃PO₄, 7664-38-2.

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