New Heterogeneous Chemical Oscillators: Reduction of Manganese Species by Hypophosphite on a Pt Surface

Krisztina Kurin-Csörgei,[†] **Irving R. Epstein,**[*,‡] **and Miklós Orbán**[*,†]

Department of Inorganic and Analytical Chemistry, L. Eötvös University, H-1518 Budapest 112, P.O. Box 32, Hungary, and Department of Chemistry and Volen Center for Complex Systems, MS 015, Brandeis University, Waltham, Massachusetts 02454-9110

Sustained oscillations occur under batch, semibatch, or flow (CSTR) conditions at the surface of a Pt electrode immersed in solutions at pH <2 containing Mn(III), Mn(IV), or Mn(VII) and $H_2PO_2^-$. Additives such as F^- and PO_4^{3-}, which stabilize Mn(III) and Mn(IV) species, lengthen the duration of the batch oscillations. Measurements of the reaction rates of the Mn species with $H_2PO_2^-$, the similarity in the character of the oscillations, and other observations suggest that Mn(III) plays a key role in maintaining the oscillations. This phenomenon, which may be thought of as an open circuit electrochemical oscillation, represents the first example of an electrochemical oscillator based on manganese chemistry.

Introduction

Since Field, Körös, and Noyes' classic study of the mechanism of the Belousov−Zhabotinsky reaction[1] three decades ago, interest in chemical oscillators has focused largely on homogeneous systems. The first examples of chemical oscillation, however, were found in heterogeneous systems,[2,3] and much progress has been made recently in the study of heterogeneous oscillators. In heterogeneous solid−gas and solid−liquid oscillatory chemical systems, the oscillations typically originate from interfacial physical and chemical processes, and it is the state of the surface rather than the composition of the bulk that changes periodically. These oscillators may be divided into two major groups: (i) surface-catalyzed oscillatory oxidations of small inorganic and organic molecules at elevated temperatures[4] and (ii) electrochemical oscillators, in which oxidation or reduction of substances occurs periodically on the surface of externally polarized electrodes in an appropriate supporting electrolyte.[5]

Here we report on a family of heterogeneous oscillators that does not fit exactly into either group. In an aqueous solution containing manganese species of higher oxidation states and sodium hypophosphite, the potential of a Pt vs reference electrode pair oscillates with an amplitude of 300−400 mV without any imposed external current or voltage. Observations described below suggest that no oscillations occur in the bulk of the reaction mixture.

Experimental Section

Materials and Composition. The supporting electrolyte was dilute acid (0.02−1.5 M H_2SO_4, HNO_3, HCl, H_3PO_4, or CH_3COOH). In some experiments, additives, like F^- and PO_4^{3-}, capable of stabilizing Mn(III) and Mn(IV) species were employed as well.

The oxidants (in the concentration range of 5×10^{-5} to 5×10^{-4} M) were Mn(VII) as $KMnO_4$, Mn(IV) as soluble MnO_2,

and Mn(III) as $Mn_2(SO_4)_3$. Stock solutions of 0.02−0.002 M $KMnO_4$ were made by dissolving the commercial reagent $KMnO_4$ (Aldrich, ACS reagent) in distilled water and stored in an amber bottle. New solutions were prepared each day. The stock solution of 4×10^{-4} M soluble Mn(IV) was prepared by mixing 1.6×10^{-4} M $KMnO_4$ with 3.2×10^{-4} M $MnSO_4$ (as $MnSO_4 \cdot H_2O$, Reanal, min 99%, 20% stoichiometric excess to Mn(IV)) in the ratio 1:1.5. The Mn(IV) solution contained 4×10^{-4} M sodium polyphosphate (Aldrich, ACS reagent) as a stabilizer for Mn(IV) against flocculation to solid MnO_2. The conversion of MnO_4^- and Mn^{2+} to Mn(IV) was completed in several days according to the equation:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

The Mn(IV) content of the stock solution was checked spectrophotometrically (λ_{max} = 380 nm, ϵ_{380} = 4680).[6] The Mn(IV) solution, stored in the dark, was stable for several weeks. The stock solution of 4×10^{-3} Mn(III) in 2 M H_2SO_4 was made by dropwise addition of 8×10^{-4} M $KMnO_4$ to a 50-fold excess of $MnSO_4$ in an appropriate amount of H_2SO_4. The conversion took place as:

$$MnO_4^- + 4Mn^{2+} + 8H^+ \rightarrow 5Mn(III) + 4H_2O$$

The excess Mn^{2+} was considered as an inert species with regard to the oscillatory behavior. The Mn(III) content was measured by iodometric titration. The stock solution was stable for about two weeks.

The reductant was $H_2PO_2^-$ as $NaH_2PO_2 \cdot H_2O$ (Sigma). In each experiment, a large (50−100-fold) excess of reductant to oxidant was used.

Apparatus. The experiments were carried out in batch, semibatch, and flow (CSTR) configurations.

The reaction vessel was an undivided thermostated glass beaker of volume 80.0 cm^3 for batch and semibatch experiments, and a reactor of volume 21.5 cm^3 for CSTR runs. Both beaker and reactor were equipped with a Pt vs $Hg/Hg_2SO_4/K_2SO_4$ electrode pair and with a regulated magnetic stirrer. Several

[†] Department of Inorganic and Analytical Chemistry, L. Eötvös University.
[‡] Department of Chemistry and Volen Center for Complex Systems, MS 015, and Brandeis University.
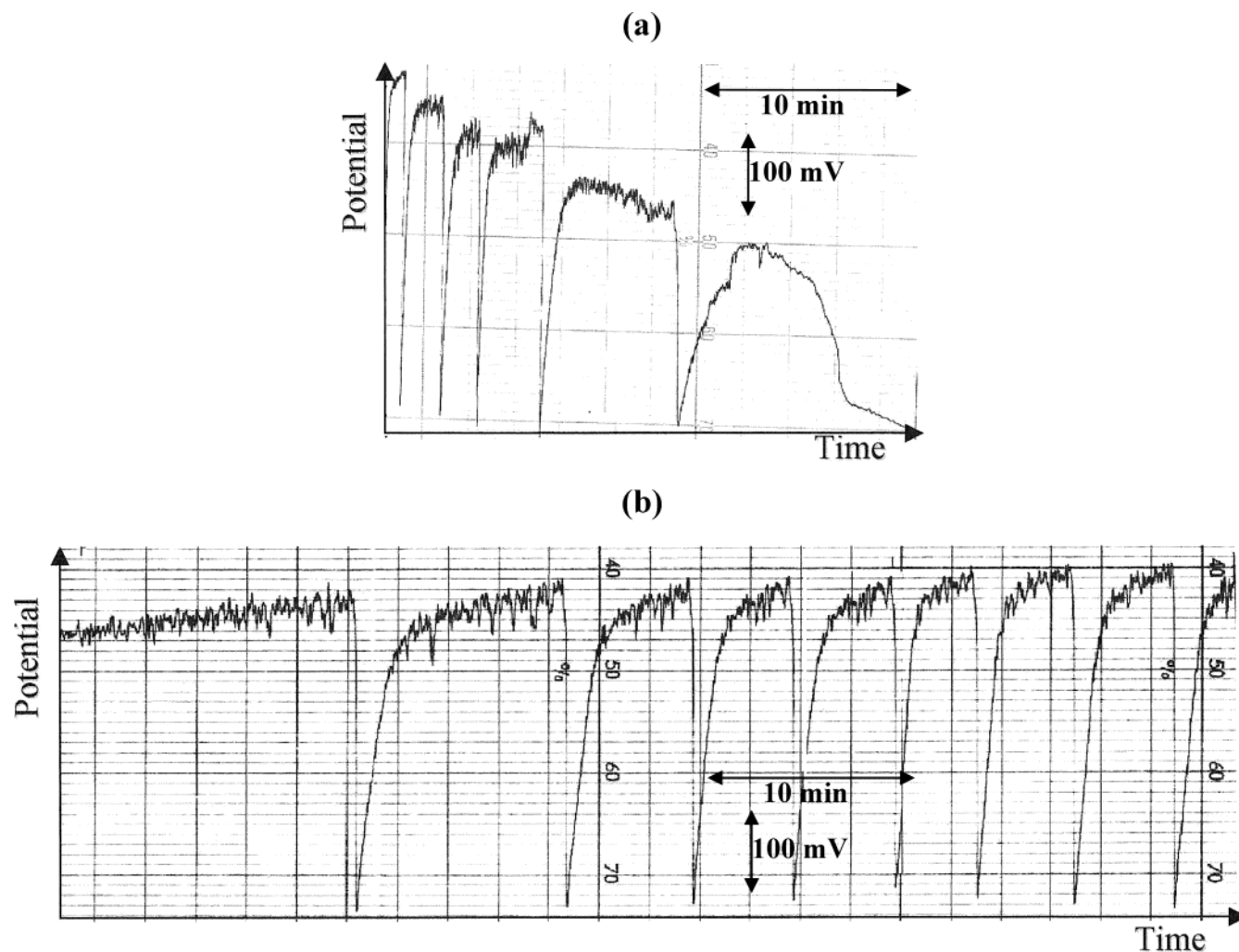
Figure 1. Oscillations in the $MnO_4^- - H_2PO_2^- - H_2SO_4$ system in (a) batch and (b) semibatch conditions. Concentrations: (a) $[KMnO_4] = 1.7 \times 10^{-4}$ M, $[NaH_2PO_2] = 2.2 \times 10^{-2}$ M, $[H_2SO_4] = 6 \times 10^{-1}$ M, (b) $[KMnO_4]_0 = 5 \times 10^{-4}$ M, $[NaH_2PO_2] = 2.2 \times 10^{-2}$ M, $[H_2SO_4] = 6 \times 10^{-1}$ M, $k_0 = 8.2 \times 10^{-4}$ s^{-1}, $V_0 = 33.20$ cm^3, stirring rate: 165 rpm, temperature: 25 °C.

kinds of Pt electrodes were used, including bead and needle types, bright Pt plate electrodes of 25 mm^2 to 8 cm^2 geometric surface area, and a rotating disk-ring electrode assembly with 2 and 25 mm^2 Pt surfaces (Beckman U.S.A.).

Methods. In the batch experiments the supporting electrolyte (acid with or without additives) and $H_2PO_2^-$ were placed in a beaker, and the reaction was initiated by adding all of the oxidant at the same time. In the semibatch arrangement the oxidant was continuously flowed into the reaction mixture, resulting in a total volume that increased in time. In the CSTR, the reagents were pumped into the reactor separately through four inlet tubes. To maintain constant volume in the CSTR, the excess reaction mixture was removed by an outflow tube connected to an aspirator. The potential of the Pt electrode was monitored with a double-channel chart recorder (Kipp & Zonen BD41). In a few cases, the signals of two independent Pt vs reference electrode pairs were simultaneously recorded.

The bulk reaction between MnO_4^-, MnO_2, or $Mn(III)$ and $H_2PO_2^-$ was followed with a diode array spectrophotometer (Agilent 8452). Reaction rates were derived from spectra taken at equal time intervals. The data were evaluated with the ZITA program package.[7]

Results

Dynamics. Under appropriate conditions, as specified in Figures 1−4 and Figure 6 (concentration ratio of oxidant to reductant, identity and concentration of acid, stirring rate, ...), oscillations in the potential of a Pt electrode were observed in the title reactions both in batch and in flow systems. The oscillatory change in the potential was about 350−500 mV during a cycle, and the oscillations occurred within the range of 550 to 1200 mV vs NHE. We have not observed other dynamical phenomena such as multistability, complex oscillations, or chaos to date.

1. Mn(VII)−H₂PO₂⁻−acid system. In H_2SO_4 and HNO_3 solutions (0.5−1.0 M) of the $KMnO_4 - H_2PO_2^- - Pt$ system, only a few (2−5) damped oscillations appear in batch (Figure 1a), but sustained oscillations occur under semibatch (Figure 1b) and CSTR conditions. For example, sustained flow oscillations were obtained with $[KMnO_4] = (1-5) \times 10^{-4}$ M, $[NaH_2PO_2] = 0.005 - 0.02$ M, $[H_2SO_4] = 0.1 - 0.5$ M, (input concentrations are 4 times higher), at flow rates $k_0 = (1.4 - 2.8) \times 10^{-3}$ s^{-1} and stirring rate 200−500 rpm.

Surprisingly, the number of batch oscillations increases significantly if F$^-$ ions are added to the $MnO_4^- - H_2PO_2^- - H_2SO_4$ system (Figure 2a). Even longer-lasting batch oscillations appear if PO_4^{3-} ions are substituted for F$^-$ ions (Figure 2b). These oscillations continue for 1−2 h with an average period of 5−10 min.

In H_3PO_4 solutions (0.1−0.2 M) long-lived batch oscillations, similar to those found in the $H_2SO_4 - PO_4^{3-}$ mixture, were observed.
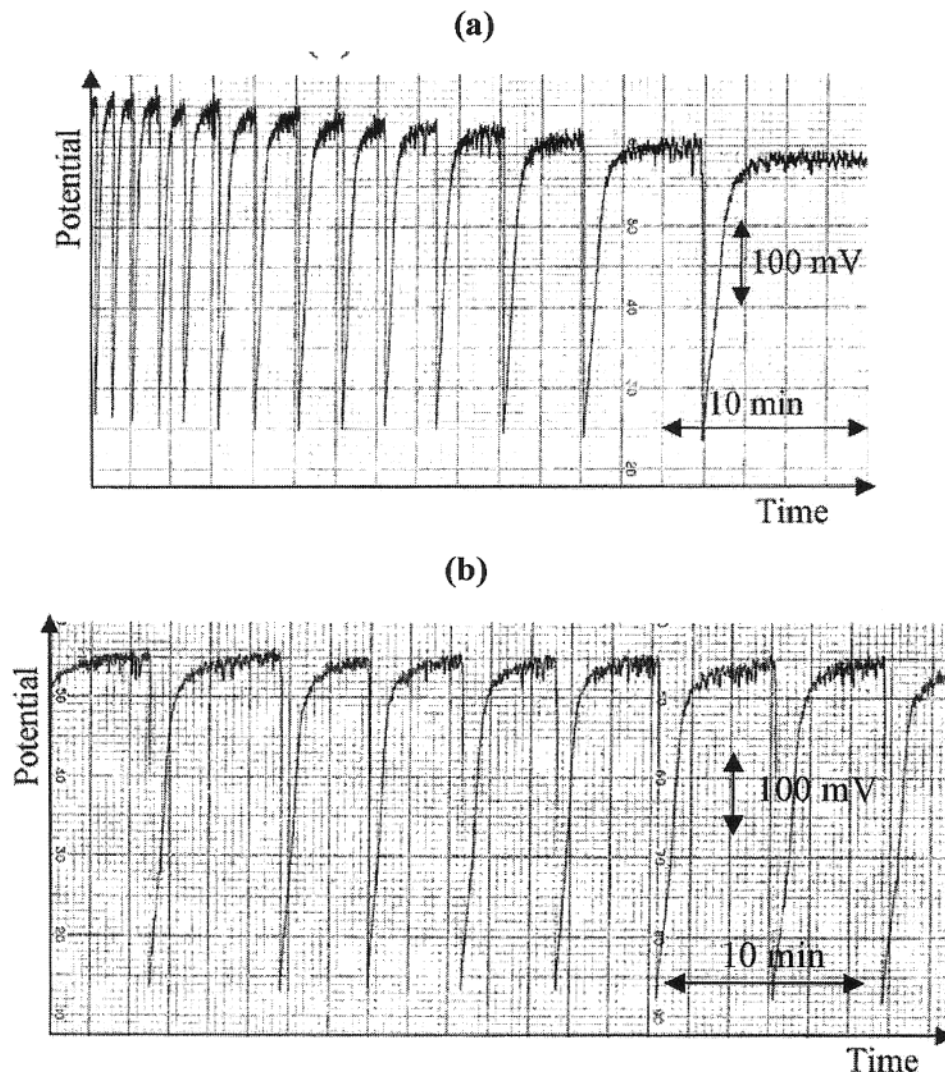
Figure 2. Oscillations in the $MnO_4^- - H_2PO_2^- - H_2SO_4$ batch system with stabilizers: (a) in the presence of F^-; (b) in the presence of PO_4^{3-}. Concentrations: (a) $[KMnO_4] = 1.6 \times 10^{-4}$ M, $[NaH_2PO_2] = 2.2 \times 10^{-2}$ M, $[KF] = 8.3 \times 10^{-3}$ M, $[H_2SO_4] = 2 \times 10^{-1}$ M, stirring rate: 250 rpm. (b) $[KMnO_4] = 5 \times 10^{-4}$ M, $[NaH_2PO_2] = 2.2 \times 10^{-2}$ M, $[H_3PO_4] = 1.05 \times 10^{-1}$ M, stirring rate: 150 rpm, temperature: 25 °C.

In HCl solutions (0.1−0.5 M) no oscillations were found, even in the presence of F^-. In HCl the Pt potential ends up at high values due to the formation of Cl_2 in the reaction between MnO_4^- and HCl.

In CH_3COOH solutions (0.5−1.5 M) oscillations do not occur, even if F^- or PO_4^{3-} are introduced. However, the reduction of MnO_4^- by $H_2PO_2^-$ does occur, resulting in a brownish solution of Mn(IV) and low Pt potential. This and other observations suggest that the pH must be below 2 for oscillatory behavior.

2. Mn(IV)−$H_2PO_2^-$−acid system. With Mn(IV) (in the form of soluble MnO_2 stabilized with polyphosphate), long-lasting batch oscillations, similar to those shown in Figure 2b, were observed (Figure 3). Since this system contains polyphosphate, no additional PO_4^{3-} ions are necessary to induce oscillations. For the acid, either H_2SO_4 or H_3PO_4 can be used.

3. Mn(III)−$H_2PO_2^-$−acid system. Mn(III), in the form of $Mn_2(SO_4)_3$ or $Mn(CH_3COO)_3$, can oxidize $H_2PO_2^-$ in an oscillatory fashion on the surface of a Pt electrode in both batch and flow configurations. The duration of the batch oscillations increased in the presence of F^- or PO_4^{3-}, as observed in the $KMnO_4 - H_2PO_2^- - H_2SO_4 - Pt$ system. A CSTR experiment with Mn(III) is shown in Figure 4, where the close similarity of the oscillations to those obtained with Mn(VII) and Mn(IV) is seen.

The oscillations were observed in a wide range of flow rates ($k_0 = 10^{-4} - 5 \times 10^{-4}$ s^{-1}) and were recorded for about 4 h. The solution mixture in the reactor was colorless throughout this time. The period of oscillation decreases slightly with increasing flow rate without noticeable change in the amplitude.

4. Mn(II)−PbO_2−$H_2PO_2^-$−acid system. Batch oscillations with amplitude and frequency similar to those observed in systems 1−3 were observed when Mn(II) (as $MnSO_4$) and a strong oxidant, solid PbO_2, were mixed with a solution of $H_2PO_2^-$, H_2SO_4, and PO_4^{3-}. The observed oscillations in this system are assumed to result from the rapid oxidation of Mn-(II) by PbO_2 to higher oxidation states followed by a slow reduction by NaH_2PO_2. These oscillations appear to originate from the same processes that occur when higher oxidation states of manganese serve as the initial reagent.

Problems with Reproducibility. Several batch runs were performed using the same composition, the same stirring rate and geometric arrangement of electrodes. It proved quite challenging to achieve reproducibility in the occurrence, induction time, frequency and duration of the oscillatory regime. We offer the following insights into these difficulties:

(i) In systems 1−3 the Pt electrode can reach a steady high potential of about 1.5 V (vs NHE) and then become "poisoned" if either if the ratio of [oxidant] to $[H_2PO_2^-]$ is significantly

New Heterogeneous Chemical Oscillators

J. Phys. Chem. B, Vol. 108, No. 22, 2004 **7355**
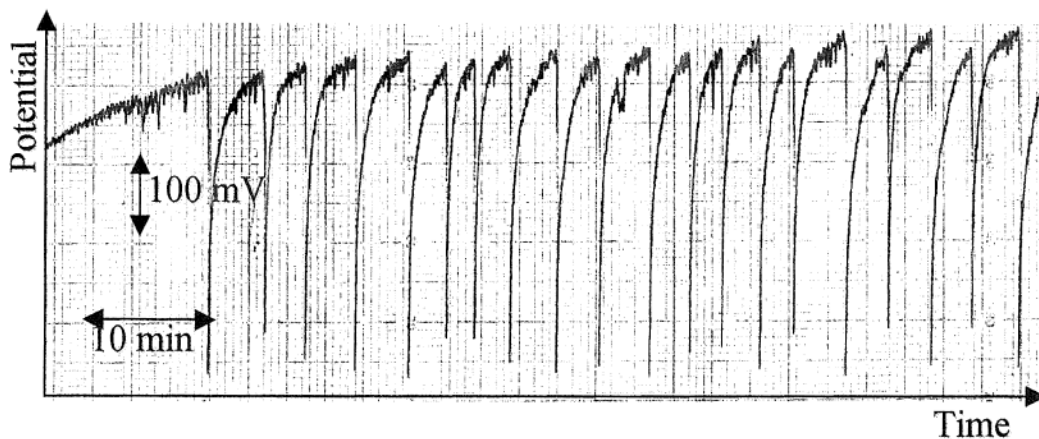
Figure 3. Batch oscillations in the $Mn(IV)-H_2PO_2^- - H_2SO_4$ system. Concentrations: $[Mn(IV)] = 2 \times 10^{-4}$ M, $[NaH_2PO_2] = 2.2 \times 10^{-2}$ M, $[H_2SO_4] = 5 \times 10^{-1}$ M, stirring rate: 300 rpm, temperature: 25 °C.
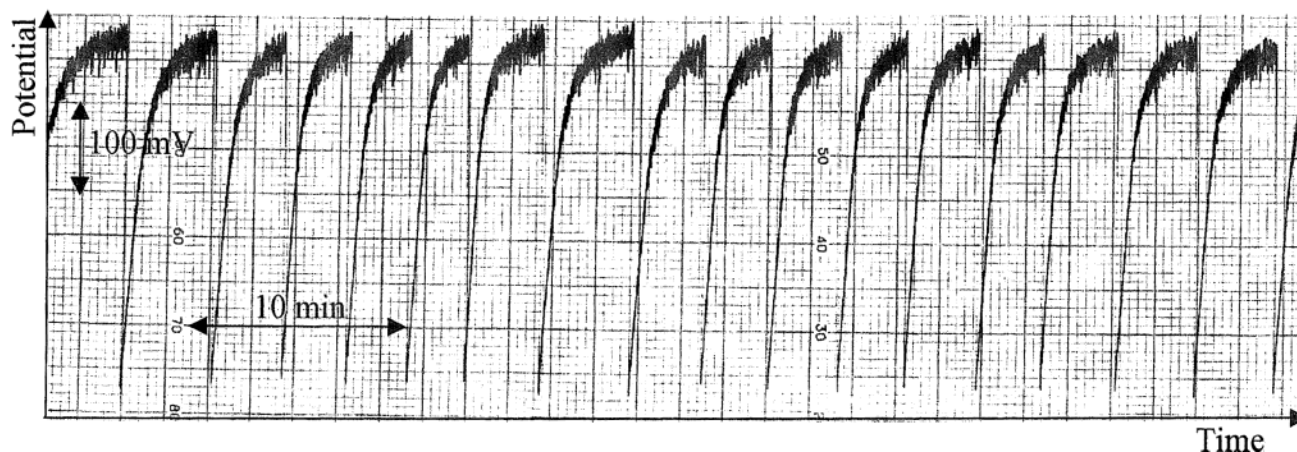
Figure 4. CSTR oscillations in the $Mn(III)-H_2PO_2^- -$acid system. Concentrations: $[Mn(III)]_0 = 2 \times 10^{-5}$ M, $[NaH_2PO_2]_0 = 2.2 \times 10^{-2}$ M, $[H_2SO_4]_0 = 1.2 \times 10^{-2}$ M, $[H_3PO_4]_0 = 6 \times 10^{-2}$ M, stirring rate: 300 rpm, $k_0 = 7 \times 10^{-3}$ s^{-1}, temperature: 25 °C.

higher than that used in the experiments shown in Figures 1−4 or, due to imperfect mixing at initiation, the oxidant is temporarily in local excess around the Pt electrode. Two methods, chemical or mechanical, were found to restore the sensing ability of the Pt electrode. Cleaning the surface of the electrode by either (a) soaking the electrode in a freshly prepared, 1:1 mixture of concentrated H_2SO_4 and concentrated H_2O_2 for an extended period (10 min to overnight) or (b) polishing of the surface of the disk-ring electrodes with a suspension of Al_2O_3 (Gamma Micropolish II, Deagglomerated Alumina, Buehler) ensured reproducible starting conditions in all cases.

(ii) In a number of experiments, an ill-defined induction period precedes the oscillations. During this time the potential of the Pt electrode slowly approaches a maximum value of about 0.9−1.1 V, from which the oscillations start with an abrupt jump.

(iii) Stirring-rate sensitivity of the occurrence and the frequency of oscillations (but not the amplitude) was observed in both batch and flow experiments. Therefore, unless otherwise noted, a constant rate of 300 rpm was maintained in the experiments.

Kinetics. The relative rates of the reactions between the oxidants, $MnO_4^-/MnO_2/Mn(III)$, and the reductant, $H_2PO_2^-$, were determined in order to elucidate the chemical species that are directly involved in the oscillatory process. The decrease in the absorption maximum of $MnO_4^-/MnO_2/Mn(III)$ vs time

was measured using compositions of supporting electrolyte and excess $H_2PO_2^-$ similar to those employed when oscillations were observed ([Mn(III)] was higher due to its low molar absorption, $\epsilon_{480} = 109$). Series of such spectra are shown in Figure 5a, b, and c.

The reactions between MnO_4^- and $H_2PO_2^-$, as well as between Mn(III) and $H_2PO_2^-$, proved to be second order with rate constants of $k = 35$ M^{-1} s^{-1} and $k = 0.07$ M^{-1} s^{-1}, respectively. The reaction between MnO_2 and $H_2PO_2^-$ was found to be autocatalytic, and it cannot be characterized with a single rate constant. The times required for complete reduction of $KMnO_4$, MnO_2, and Mn(III) by $H_2PO_2^-$ at the oscillatory composition are roughly 5 s, 60−120 min (depending on added $[PO_4^{3-}]$), and 25 min, respectively.

Other Observations. (i) No periodic color changes were observed in the bulk of the solution when oscillations appeared in the potential of the Pt electrode. At the start of the reaction the color of the mixture is violet, brown, or pink depending on whether MnO_4^-, Mn(IV), or Mn(III), respectively, serves as oxidant. During the reduction by $H_2PO_2^-$ the color changes gradually: the violet diappears in seconds, but the brown and pink last much longer (20 min to hours). The solution is colorless when the concentration of Mn(III) drops below about 2×10^{-4} M (above this level, red Mn(III) is easily visible) and if all manganese species are reduced to the end product Mn(II). The potential oscillations occur when the solution is brown or pink,
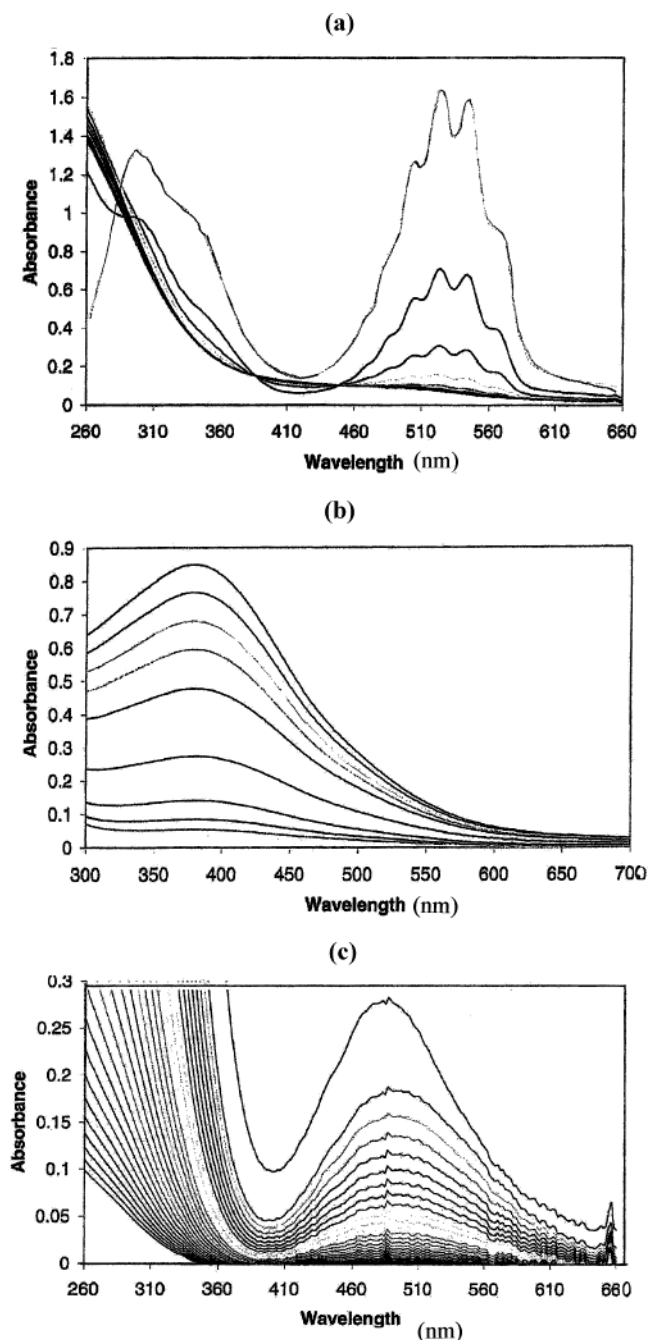
Figure 5. Absorption spectra taken at time intervals (*t*) for the reactions of (a) Mn(VII) and $H_2PO_2^-$ ([KMnO$_4$] = 5 × 10^{-4} M, [NaH$_2$PO$_2$] = 2.2 × 10^{-2} M, [H$_2$SO$_4$] = 2 × 10^{-1} M, [H$_3$PO$_4$] = 2.1 × 10^{-1} M, *t* = 1 s), (b) Mn(IV) and $H_2PO_2^-$ ([Mn(IV)] = 8 × 10^{-5} M, [NaH$_2$PO$_2$] = 2.2 × 10^{-2} M, [H$_2$SO$_4$] = 5 × 10^{-2} M, *t* = 6 min), (c) Mn(III) and $H_2PO_2^-$ ([Mn(III)] = 2.6 × 10^{-3} M, [NaH$_2$PO$_2$] = 2.2 × 10^{-2} M, [H$_2$SO$_4$] = 1.3 M, [H$_3$PO$_4$] = 2 × 10^{-1} M, *t* = 1 min). In all cases, spectrum with the highest absorbance peak represents the initial state, and this peak decreases monotonically with time.

but cycles may be observed in the colorless state as well, both in the CSTR and in batch.

(ii) The electrode geometry (plate, bead, rotating disk) has little effect on the amplitude of batch oscillations. However, the number of batch oscillations was higher on an 8 cm^2 Pt plate than on a small Pt bead, and the bead electrode showed a larger tendency to be pushed by the oxidants to a steady high potential. The rotating disk electrode gave an amplitude similar to that of the Pt plate. When the rotation rate of the disk electrode was increased, the number of oscillations decreased,

and the period and the noise level increased significantly. We therefore abandoned using the rotation rate as a control parameter as is often done in studies of the dynamical behavior of electrochemical oscillators.

Discussion

The $MnO_4^-/MnO_2/Mn(III)-H_2PO_2^-$ systems constitute a family of heterogeneous oscillators: the reaction between higher oxidation state manganese species and hypophosphite ions takes place in a smooth monotonic process in bulk solution (Figure 5) but proceeds in an oscillatory fashion on the surface of a Pt electrode. The essential role of the surface in bringing about oscillatory behavior is established experimentally by our observation of asynchronous oscillations in the solution mixture when the signals of two independent Pt vs reference electrode pairs are simultaneously recorded on a double-channel recorder (Figure 6).

In the systems under study, both physical and chemical processes contribute to the oscillatory behavior. The nonlinearity—an absolute requirement for oscillations to occur in a chemical system—may arise from the oxidation–reduction kinetics and/or from the physical phenomena (adsorption, coverage, transport, film formation/dissolution, ...) that occur at the Pt surface. The pronounced effect of stirring suggests that, at the very least, transport phenomena play a significant role in bringing about oscillations on the Pt electrode.

At this time, we cannot unambiguously identify the feedback mechanism in the chemistry of these oscillators, although we suggest a possible route below. We believe that the underlying chemistry is simple: the key surface reaction occurs between Mn(III) and $H_2PO_2^-$. This statement is supported by both spectrophotometric and dynamical experiments. Bulk spectrophotometric measurements show that when KMnO$_4$ is the starting manganese species, it is rapidly reduced by $H_2PO_2^-$. The KMnO$_4$ color disappears before the oscillations start, implying that KMnO$_4$ does not directly participate in the oscillatory process. The reduction of Mn(IV), formed from KMnO$_4$ or used as initial reagent, requires significantly longer time (up to 2 h), and this reaction serves as a continuous source of Mn(III). The oscillations appear to start as soon as Mn(III) builds up to a critical level. We take Mn(III) to be the major species in bringing about oscillations because it gives rise to oscillatory traces very similar to those of KMnO$_4$ and Mn(IV). When Mn(III) is used as the initial reagent, the oscillations appear after much shorter induction times than in the KMnO$_4$ and Mn(IV) systems. The importance of Mn(III) in these oscillators is also illustrated by the impact of the additives F$^-$ and PO$_4^{3-}$ on the duration of the batch oscillations. These additives form stable complexes with Mn(III) and significantly lengthen the lifetime of Mn(III) in the reaction mixture.

Here we suggest how sustained batch oscillations can be maintained in the Mn(VII)/Mn(IV)/Mn(III)–$H_2PO_2^-$–Pt systems and comment on the role of acids in the oscillatory mechanism. Batch oscillations in a chemical system can occur only if at least one intermediate is continuously supplied by a composite reaction during the overall process. The most obvious choice for this intermediate in the present systems is the "active" form of $H_2PO_2^-$. On the basis of kinetic evidence, Jenkins and Yost[8] proposed that $H_2PO_2^-$ can exist in two tautomeric forms, one reactive, the other inert. An equilibrium catalyzed by H$^+$ is maintained between the two forms, and only a small fraction of the total $H_2PO_2^-$ is in the reactive form. When this reactive hypophosphite is consumed, the excess of inactive $H_2PO_2^-$ acts as a reservoir that regenerates the active species, ensuring steady

New Heterogeneous Chemical Oscillators

J. Phys. Chem. B, Vol. 108, No. 22, 2004 **7357**
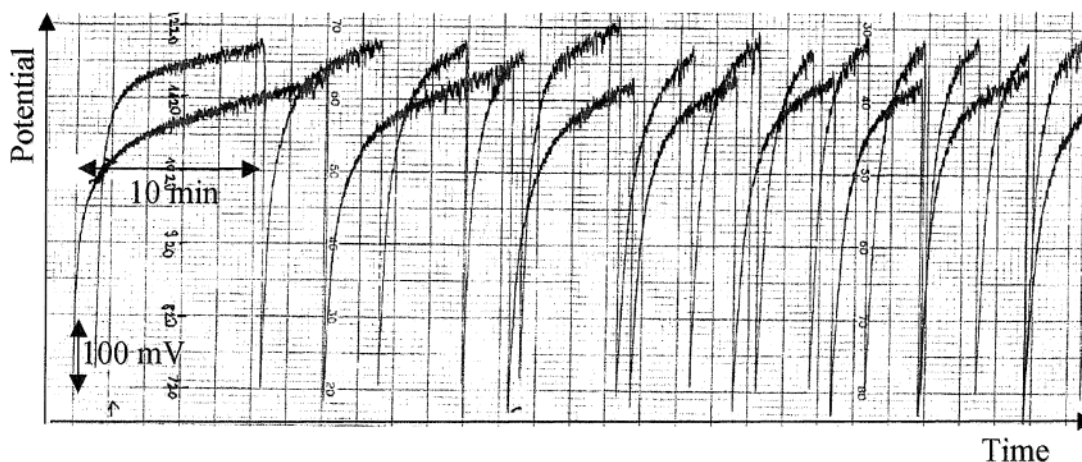
Figure 6. Asynchronous batch oscillations recorded with two Pt vs reference electrode pairs. Concentrations: $[KMnO_4] = 3.6 \times 10^{-4}$ M, $[NaH_2PO_2] = 2.2 \times 10^{-2}$ M, $[H_2SO_4] = 1.4 \times 10^{-2}$ M, $[H_3PO_4] = 1.1 \times 10^{-1}$ M, stirring rate: 300 rpm, temperature: 25 °C.

replenishment of the reagent. Tautomerism of $H_2PO_2^-$ has also been proposed as mechanism for the batch oscillations observed in the homogeneous bromate$-H_2PO_2^-$-dual catalyst$-$acetone system.[9] In addition to this special feature of the hypophosphite, some steps in the reduction of the manganese species must also contribute to the oscillatory behavior observed in the Mn(VII)/Mn(IV)/Mn(III)$-H_2PO_2^-$-Pt systems. To date we have not been able to induce oscillatory Pt responses with reductants other than $H_2PO_2^-$ or with other oxidants (I^-, H_2O_2, AsO_3^{3-}, IO_3^-, BrO_3^-, ClO_2^-, Ce^{4+}).

One, somewhat speculative, explanation for the potential oscillations is as follows. The oscillatory response of the Pt electrode represents a mixed potential, which is determined by the identity and the concentration of the species found in the vicinity of the electrode$-$electrolyte interface. At the start of the experiment the dominant species in the double layer is $H_2PO_2^-$; therefore, the Pt potential assumes a low value. When the manganese species are introduced, Mn(III) diffuses into the double layer, causing the increase in potential seen during the induction period. This potential rise is relatively slow, as Mn(III) must be transported to the surface of Pt and find vacant sites for adsorption. When the ratio of oxidant Mn(III) to reductant $H_2PO_2^-$ at the interface exceeds a critical value, a rapid potential drop occurs as a result of the fast reduction of Mn(III) by the "active" form of $H_2PO_2^-$. The fast drop in potential may arise either from autocatalytic production of the "active" reductant or, more likely, from cooperativity in the reduction process, whereby reducing and releasing Mn(III) from one site increases the accessibility of species bound at neighboring sites to attack by the reductant. This process rapidly depletes both the adsorbed Mn(III) and the "active" $H_2PO_2^-$ at the electrode$-$electrolyte interface. The reductant concentration is slowly restored by the tautomeric equilibrium and transport from the bulk, so that, as fresh Mn(III) arrives from the bulk and readsorbs, another cycle of oscillation can occur. Such a slow buildup and sudden drop in the potential of the Pt electrode have been observed in many electrochemical oscillators under galvanostatic conditions.[10]

In the oscillatory process the surface of Pt serves as a catalyst by speeding up the exchange of electrons between the oxidant Mn(III) and the reductant $H_2PO_2^-$. The complexing agent, PO_4^{3-} or F^-, not only stabilizes Mn(III) but probably facilitates its adsorption by forming an anionic complex. In the catalytic cycle periodic formation and successive reduction of Pt-oxides may also occur, because the voltage at the potential peak is well above the region in which Pt-oxides are formed on the electrode.

The role of acids in bringing about oscillations in the title systems is multifaceted, and both the identity and the concentration of the acid play a role. Hydrogen ion affects the concentrations of several major oscillatory species, promoting the formation of active $H_2PO_2^-$ and preventing the disproportionation of Mn(III) in particular. Long-lasting batch oscillations require the presence of F^- or PO_4^{3-} ions as well, which may account for the fact that in H_2SO_4 and HNO_3 sustained oscillations arise only under CSTR or semibatch conditions, while only in H_3PO_4, which plays a dual role, can sustained batch oscillations be found. In HCl, the manganese species oxidize Cl^- to Cl_2, which poisons the Pt surface. Acetic acid is not strong enough for the system to reach the oscillatory pH range.

Because oscillations in the Mn(VII)/Mn(IV)/Mn(III)$-H_2PO_2^-$ systems do not occur unless the reactions take place in a galvanic cell arrangement, these systems may be viewed as a special kind of electrochemical oscillator, where the current passing through the cell is nearly zero. Because of the lack of any potential- or current-controlled external conditions, such systems are referred to as "open circuit" oscillators in the electrochemical literature, where a number of them are known.[11] What is striking is that in a comprehensive review of electrochemical oscillations,[5] including potentiostatic, galvanostatic, and open-circuit systems, oscillations were reported in a myriad of reactions involving several dozen chemical elements, but none were found to involve manganese. While any mechanistic explanation of these fascinating phenomena must necessarily take into account the physical processes that occur at the electrode surface, it will also be worthwhile to investigate whether the family of *homogeneous* manganese-based oscillating reactions[12] can shed light on the chemical aspects of these fascinating systems.

References and Notes

(1) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649−8664.

(2) Fechner, A. T. *Schweigg. J.* **1828**, *53*, 61−76.

(3) Ostwald, W. *Phys. Z.* **1899**, *8*, 87−88.

(4) Schütz, F.; Henry, B. E.; Schmidt, L. D. *Adv. Catal.* **1993**, *39*, 51−127.

(5) Hudson, J. L.; Tsotsis,T. T. *Chem. Eng. Sci.* **1994**, *49*, 1493−1572.

(6) Horvath, O.; Strohmayer, K. *J. Photochem. Photobiol., A* **1998**, *116,* 69−73.

(7) Peintler, G. *ZITA Version 5.0*; A Comprehensive Program Package for Fitting Parameters of Chemical Reaction Mechanism; JATE: Szeged, Hungary, 1989−1999.

(8) Jenkins, W. A.; Yost, D. M. *J. Inorg. Nucl. Chem.* **1959**, *11,* 297.

(9) Orbán, M.; Kurin-Csörgei, K.; Zhabotinsky, A. M.; Epstein, I. R. *Faraday Discuss.* **2001**, *120*, 11−19.

(10) For example: Keizer, J.; Scherson, D. *J. Phys. Chem.* **1980**, *84*, 2025−2032; Inzelt, G.; Kertész, V. *Electrochim. Acta* **1995**, *40*, 221−225.

(11) For example: Horanyi, G.; Rizmayer, E. M. *J. Electroanal. Chem.* **1983**, *143*, 323−336; Inzelt, G. *J. Electroanal. Chem.* **1993**, *348*, 465−471.

(12) Doona, C. J.; Kustin, K.; Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 7484−7489.