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A Transition-Metal Oscillator: Oscillatory Oxidation of Manganese(II) by Periodate in a CSTR[1]

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Abstract: When manganese(II) is oxidized by periodate ion in a flow reactor, periodic oscillation is observed in the pH, the potential of a Pt electrode, and the absorbance over a wide range of visible wavelengths. No bistability is found. Both comparison with the behavior of permanganate oscillators and a model of the present reaction that gives good agreement with the observed oscillation and autocatalytic batch behavior suggest that the oscillations originate from the manganese chemistry. The primary roles of periodate appear to be to generate and to stabilize the higher oxidation states of manganese.

In the overwhelming majority of the known chemical oscillators in which metal ions play a role, they participate either as catalysts (Ce^{4+}, Mn^{2+}, Cu^{2+}, Ag^{+}, Co^{2+}, Fe^{2+} complexes) or in anions (AsO_3^{3-}, MnO_4^-, $Fe(CN)_6^{4-}$). The only exception reported thus far in which the oxidation of a simple metal cation is a central feature of an oscillating chemical reaction is the "minimal permanganate oscillator", the reaction of MnO_4^- and Mn^{2+} (the Guyard reaction) in a flow reactor (CSTR).[2] Even this system is more characteristic of the family of permanganate oscillators, for which it serves as the core, with other nonmetallic reductants[3] replacing the Mn^{2+}.

In this article we demonstrate that the oxidation of Mn^{2+} by periodate in a CSTR is an oscillatory reaction. We further show that the primary contribution of the periodate is to generate and stabilize the higher oxidation states of manganese, that is, the oscillatory behavior arises from the manganese chemistry. Thus the manganese(II)–periodate system is a true transition-metal oscillator. Taken together with the manganese(VII)–reductant oscillators, it begins to suggest how the entire collection of manganese-based oscillatory reactions functions.

The reaction between manganese(II) and periodate is well-known for its utility in both analytical and preparatory chemistry. It affords a qualitative spot test[4] for trace amounts of either Mn(II) or IO_4^-, and it can be used for quantitative determination of Mn(II) by measuring either the light absorbance of the product MnO_4^-[5] or the luminescence of a luminol–periodate–manganese(II) solution.[6] Manganese(II) catalyzes the periodate oxidation of a variety of organic substrates, owing to the formation of reactive higher oxidation states of manganese which are subsequently reduced back to Mn(II) by the substrate.

In spite of the wide range of applicability of the Mn^{2+}–IO_4^- reaction, its kinetics and mechanism have yet to be characterized in detail. Nevertheless, it is known to be autocatalytic, and one may therefore expect interesting behavior under flow conditions.

The recently discovered permanganate oscillators[2,3,7] constitute the first and thus far the only group of transition-metal oscillators. All members of this group consist of permanganate ions as oxidant, a reducing substrate (H_2O_2, ninhydrin, $S_2O_3^{2-}$, S^{2-}, SO_3^{2-}, Mn^{2+}), and phosphate ion as a stabilizer for the key Mn(IV) species. Recent studies[8] have broadened the range of substrates and, more significantly, have succeeded in replacing the stabilizing phosphate species with other oxyanions like AsO_4^{3-} and VO_4^{3-} that have structures and pK values similar to those of phosphate.

The mechanism of the permanganate oscillators is still under study. Permanganate ion itself is consumed immediately after mixing, and $[MnO_4^-]$ does not oscillate. Permanganate is rather a precursor for those species, most likely Mn(II), Mn(III), and/or Mn(IV), though possibly also Mn(V) or Mn(VI), whose concentrations do vary periodically in time, and which are responsible for the observed autocatalysis. The product in these permanganate oscillators is an Mn(IV) species, which may be in a soluble form, especially when it is stabilized by phosphate ions,[9] or in partially hydrolyzed or polymeric form. It can also exist as MnO_2 as either a colloid or a precipitate. This Mn(IV) has been implicated as an autocatalytic species,[10] and the rate of its removal from the reacting mixture is a key parameter in determining whether or not the system can oscillate. Its chemical nature remains an open question.[11]

Of course, the intermediate oxidation states of manganese can be reached not only by reduction of MnO_4^- but also starting from the other extreme, i.e., by oxidation of Mn^{2+} with strong oxidants such as IO_4^-, $S_2O_8^{2-}$, or $P_2O_8^{4-}$. Designing a manganese oscillator from this origin requires finding conditions under which the oxidation is relatively rapid but not complete (i.e., it does not proceed all the way to MnO_4^-) and such that appropriate stabilizers are available for the key manganese species. The search for such conditions starts by varying the pH and initial concentrations to obtain a suitable extent of reaction. We report here the results of our investigation of the periodate oxidation of Mn(II) in a CSTR.

Experimental Section

Materials. Analytical grade $MnSO_4{\cdot}H_2O$ and $NaIO_4$ (both Fisher) were used without further purification. The 0.1 M manganese stock solutions were analyzed by complexometric titration with EDTA and eriochrome black T in ammonia buffer.[12] Periodate stock solutions (0.1 M) were analyzed with an iodometric method.[13] To prevent decomposition, these solutions were stored in amber bottles in a cool, dark place. Under these conditions, a stock solution showed a decrease in $[IO_4^-]$ of 1% per day. Fresh solutions were therefore made every 3 days.

Apparatus and Methods. The batch reaction was monitored by measuring (a) the potential of a Pt electrode vs $Hg|Hg_2SO_4|K_2SO_4$ reference; (b) the pH change (Aldrich combination pH electrode connected to an Orion 501 pH meter); and (c) the visible light absorption using a Varian DM200 UV/VIS spectrophotometer. For detecting low concentrations of intermediates, derivative spectra were taken. We were able

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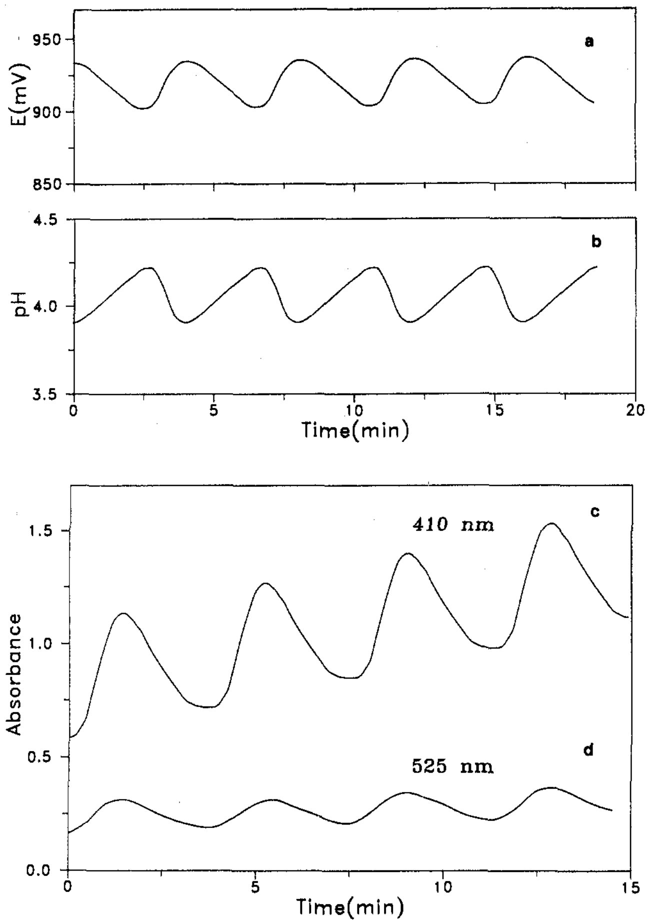

Figure 1. Oscillatory behavior with $[IO_4^-]_0 = 1.5 \times 10^{-3}$ M, $[Mn^{II}]_0 = 1.5 \times 10^{-4}$ M, $k_0 = 0.0227$ s^{-1}, $T = 25$ °C, path length = 4.0 cm: (a) potential of Pt electrode; (b) pH; (c) absorbance at 410 nm; (d) absorbance at 525 nm.

to follow the fast first stage of the reaction by recording spectra at 3-s intervals on a Hewlett-Packard 8452A diode array spectrophotometer equipped with thermostated cell holder and stirrer.

The flow experiments were performed in a thermostated glass reactor of volume 20.5 cm^3 containing Pt, reference, and pH electrodes whose responses were recorded simultaneously on a Linear 1200 double channel recorder. Light absorbance measurements in flow were made in a 34.0-cm^3 plexiglass reactor equipped with a quartz window and placed in the sample compartment of a Perkin-Elmer 552A spectrophotometer. This reactor also permitted simultaneous recording of Pt potential and pH. The flow rate k_0 (reciprocal residence time) could be varied with a Sage 375A peristaltic pump between 0.0011 and 0.0500 s^{-1} with a precision of better than ±1%.

Results

CSTR Experiments. When dilute solutions of Mn(II) and IO_4^- are introduced into the CSTR at 25 °C and with an input concentration ratio $[IO_4^-]_0:[Mn^{II}]_0 \geq 5$, oscillations are observed in the following range of conditions: $[Mn^{II}]_0 = 5 \times 10^{-5}$–$5 \times 10^{-4}$ M, $[IO_4^-]_0 = 1 \times 10^{-3}$–$1 \times 10^{-4}$ M, $k_0 = 2 \times 10^{-3}$–5×10^{-2} s^{-1}. The frequency of oscillation increases monotonically with the input concentrations and the flow rate, while the amplitude reaches a maximum at intermediate values of these parameters. We found no evidence of bistability under any set of experimental conditions.

The oscillatory behavior could be followed in three responses, as illustrated in Figure 1. The Pt potential oscillates with a period of 3–10 min and an amplitude of 10–70 mV about a mean of 900–1000 mV vs SHE. The pH oscillations showed an amplitude of 0.1–0.4 pH units around a mean of pH = 4. Oscillations in light absorbance were found at all wavelengths in the visible range. At several compositions, oscillation between colorless and yellow or between yellow and yellow-brown could be followed visually, but we never observed the pink color characteristic of permanganate. Oscillatory behavior in the CSTR is always accompanied by a small amount of red-brown precipitate that settles on the stirrer, electrodes, and reactor walls. Perhaps because of this precipitate, long runs usually show a slow damping of the oscillatory amplitude.

Table I. Effect of $[KH_2PO_4]$ on Oscillatory Behavior in the Mn^{II}–IO_4^- Reaction in a CSTR[a]

$[IO_4^-]_0$, M	$[Mn^{II}]_0$, M	$[H_2PO_4^-]_0$, M	oscillations[b]	remarks
3.0×10^{-4}	1.5×10^{-4}		no	yellow color, brown precipitate[b]
		1.5×10^{-3}	no	
		3.0×10^{-3}	no	
7.5×10^{-4}	1.5×10^{-4}		no	yellow color
		1.5×10^{-3}	yes	medium (≈25 mV)
1.5×10^{-3}	1.5×10^{-4}		yes	medium (≈30 mV)
		1.5×10^{-3}	yes	medium (≈30 mV)
3.0×10^{-3}	1.5×10^{-4}		yes	medium (≈35 mV)
		1.5×10^{-3}	yes	medium (≈35 mV)
6.0×10^{-3}	1.5×10^{-4}		yes	small (≈10 mV)
		3.0×10^{-3}	yes	large (≈60 mV)
6.0×10^{-3}	3.0×10^{-4}		no	c
		3.0×10^{-3}	yes	medium (≈30 mV)

[a] $k_0 = 0.0227$ s^{-1}. [b] When no oscillations occur, the extent of reaction (estimated from color and precipitate formation) is high. [c] A very weak oscillation of <5 mV amplitude in the Pt potential is observed.

Effects of Added Species on the Oscillatory Behavior. In order to learn more about the oscillatory behavior, we studied the effects of introducing additional species in an oscillatory system with the composition and flow rate shown in Figure 1.

(a) Iodide. Iodide ion is a possible product of the manganese(II)–periodate reaction. We monitored the oscillatory reaction with an iodide-selective electrode both with and without addition of I^- to the input feed. Without added I^-, the iodide concentration in the reactor was very low ($<10^{-6}$ M) and did not oscillate. We conclude that IO_4^- is not reduced to I^- under these conditions. Even very low iodide inputs ($[I^-]_0 = 6 \times 10^{-5}$ M) sharply reduce the amplitude of oscillation, and with $[I^-]_0 = 10^{-4}$ M, the oscillations are completely suppressed with accompanying formation of I_2. This last observation suggests that the Mn(II)–periodate reaction generates iodate, which can react with I^- in the Dushman reaction.

(b) Sulfuric Acid. Addition of H_2SO_4 appears to block or to retard significantly the reaction. With $[H_2SO_4]_0 \geq 10^{-4}$ M, no oscillation, color change, or precipitate are observed.

(c) Sodium Hydroxide. Addition of base also suppresses oscillation, but now apparently because the reaction becomes too rapid. At $[NaOH]_0 = 1 \times 10^{-4}$ M, the oscillations begin but are quickly damped out. When $[NaOH]_0 \geq 2 \times 10^{-4}$ M, we observe a single overshoot–undershoot in both pH and Pt potential after which the solution turns yellow, indicating completion of the reaction.

(d) Buffer. As illustrated in Figure 1b, the pH oscillates between about 3.85 and 4.20. We introduced two buffers, potassium biphthalate (Fisher pH = 4.0 buffer) and acetate–acetic acid (pH 4.05), with pH's in this range to assess the effects of holding $[H^+]$ constant near its oscillatory mean value. Under these conditions, the oscillations in Pt potential are suppressed almost completely, with the amplitude decreasing to less than one-tenth its unbuffered value.

(e) Pyrophosphate Ion as $Na_4P_2O_7$. Pyrophosphate is known to form a stable complex with Mn(III). Introduction of 7.5×10^{-5} M $[P_2O_7^{4-}]_0$ (neutralized to pH 5) completely blocks the oscillation, and no yellow color is seen, even though the pH is high enough (≥4.5) for the reaction to proceed to the nonoscillatory steady state.

(f) Phosphate Ions as KH_2PO_4. The permanganate oscillators function only if $H_2PO_4^-$ is added. The present system in contrast shows oscillations with no added stabilizer. As phosphate binds strongly to Mn(IV) species, we expect that adding $[H_2PO_4^-]$ to the input feed should have a marked effect on the oscillatory behavior of the Mn^{II}–IO_4^- system. In Table I we summarize the result of adding phosphate as we increase the excess of $[IO_4^-]_0$ to $[Mn^{II}]_0$. Several conclusions emerge: (i) At small $R = [IO_4^-]_0/[Mn^{II}]_0$ ratios, the system cannot oscillate with or without

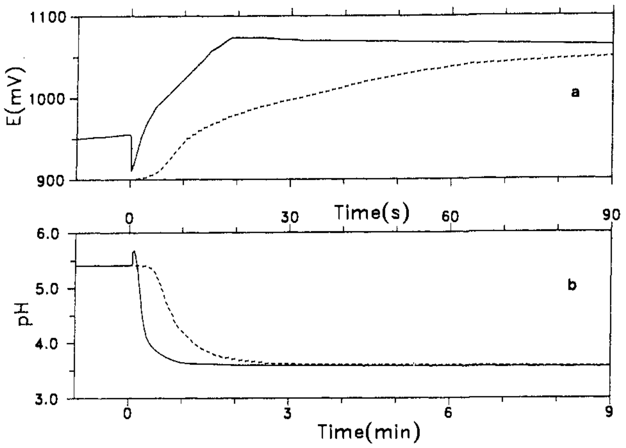

Figure 2. Pt electrode potential (a) and pH (b) in a batch reaction with initial concentrations $[IO_4^-] = 1.5 \times 10^{-3}$ M, $[Mn^{II}] = 1.5 \times 10^{-4}$ M. Reaction was initiated by adding Mn(II) solution to the periodate solution. Time scales are 9 min (solid lines) and 90 s (dashed lines).

added phosphate. (ii) Added phosphate can induce oscillation at compositions where the simple Mn(II)–periodate system is nonoscillatory. (iii) At moderately high excesses (R = 10–20), added $H_2PO_4^-$ has no effect on the oscillatory behavior. (iv) At still higher R, added phosphate significantly enhances the amplitude of oscillation. (v) Despite its ability to act as a buffer, the added phosphate does not suppress the pH oscillations.

We infer from these observations that $H_2PO_4^-$ can contribute to oscillation in two ways: when periodate is in moderate excess, phosphate helps to stabilize Mn(IV), while at high R values it serves to slow the reaction between Mn(II) and IO_4^-. Further arguments in support of these conclusions will be found below.

(g) Arsenate Ion as Na_2HAsO_4. Arsenate can replace $H_2PO_4^-$ as a stabilizer in certain permanganate oscillators,[8] and it interacts with MnO_2 in the same way as PO_4^{3-}.[14] As in the case of phosphate, we observed that addition of arsenate to the feed resulted in oscillatory behavior at some compositions that were nonoscillatory in the absence of a stabilizer.

Batch Experiments. In order to assess the most important component processes in the Mn^{II}–IO_4^- reaction, we studied the reaction under batch conditions over a wide range of concentrations, monitoring pH potential, and light absorbance. Surprisingly, compositions that always resulted in precipitation in a CSTR gave no precipitation in batch even after several weeks. The typical Pt potential and pH traces shown in Figure 2 reveal that the reaction is moderately rapid, autocatalytic (note the dashed curves), and complex.

From the final pH values, we calculated the $[H^+]$ formed in the reaction and used this quantity to assess the stoichiometry of the reaction. The average of 20 runs gave a ratio $\Delta[H^+]/[Mn^{II}]$ of 1.8–1.9, which suggests the following stoichiometry under our experimental conditions:

$$Mn^{2+} + IO_4^- + H_2O \rightarrow (MnO_2)_{soluble} + IO_3^- + 2H^+ \quad (1)$$

Absorption spectra with and without added phosphate were recorded at 3-s intervals. A sequence of such spectra is presented in Figure 3, while Figure 4 shows the absorbance at 340 and 410 nm as a function of time derived from a set of these spectra. The broad absorption from 350 to 650 nm in Figure 3 grows in time, resulting in the final yellow color of the reaction mixture. The yellow color apparently results from the formation of a Mn(IV) species. As indicated in Figure 4, this process is autocatalytic. Addition of $H_2PO_4^-$ shifts the spectrum toward the blue and retards the appearance of the yellow color. These effects suggest that the phosphate inhibits the Mn^{II}–IO_4^- reaction and/or interacts with the yellow product. Under conditions where oscillations occur, no permanganate formation was detected (compare the solid and dashed curves in Figure 3). At much higher reactant concentrations, a few (<2) percent of the total manganese ended up as MnO_4^-, as estimated from the derivative spectra.

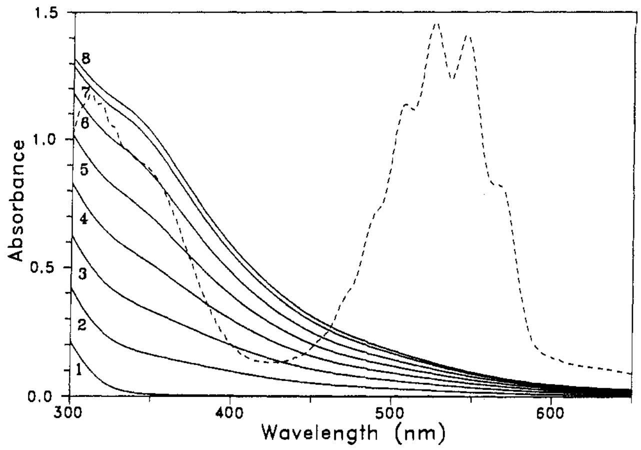

Figure 3. Absorption spectra for a solution of initial composition as in Figure 2 taken at times 3, 12, 21, 30, 39, 48, and 72 s (Nos. 1–8, respectively) after initiation of the reaction. The dashed line shows the spectrum of a 6×10^{-4} M $KMnO_4$ solution in a 1.0 cm path length cell.

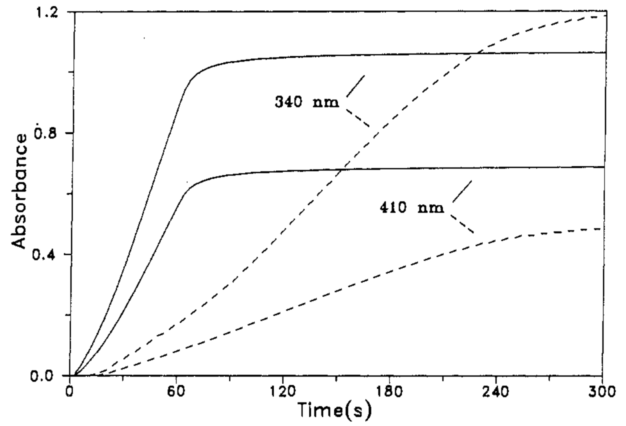

Figure 4. Time evolution of absorption at 340 and 410 nm, characteristic wavelengths for Mn(IV), in a solution of initial composition as in Figure 2 (solid lines). Dashed lines show the absorption when 1.5 M $[H_2PO_4^-]$ is added initially. Curves of similar shape but lower intensity (not shown) are obtained at 525 nm, characteristic for MnO_4^-.

Mechanism

The kinetics and mechanism of the periodate oxidation of Mn(II) have been studied in $HClO_4$ (0.42–3.78 M) by Waterbury et al.[15] and in NH_4OH/NH_4Cl buffer (pH 4.0–9.8) by Tiginyanu et al.[16] The reaction in acid obeys the stoichiometry

$$2Mn^{2+} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5IO_3^- + 6H^+ \quad (2)$$

although the reaction was found to be incomplete, with some of the Mn(II) failing to reach the +7 oxidation state. In near neutral solution, the products are Mn(IV) and Mn(VII) in a ratio that depends upon the pH and the concentration of IO_4^-; the stoichiometry is a mixture of eqs 1 and 2.

Under the conditions where oscillations occur, we may regard eq 1 as the prevailing net stoichiometry. As we have noted above, the form of the product Mn(IV) is ill-defined. It is clear that some of it is soluble and can remain in this state for an extended period of time, yet Mn(IV) can separate out of the solution by precipitation as MnO_2. If the oscillatory instability arises from an autocatalytic process in which Mn(IV) is involved, then this precipitation is extremely important, since it provides a route for removal of the autocatalyst.

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Periodate is a two-electron oxidant. The large number of possible disproportionation reactions allows us to write several autocatalytic cycles involving the different oxidation states of manganese. The absence of bistability suggests that the autocatalysis is quadratic, i.e., first order in the autocatalyst.[17] Our experimental observations suggest that the autocatalytic species is Mn(IV), which is removed by the precipitation process. A crude skeleton model that shows oscillations in all manganese species, some at very low concentrations, and can serve as a general scheme for oscillatory reactions of Mn(II) with two-electron oxidants (represented here by IO_4^-) is

$$Mn^{2+} + IO_4^- \rightarrow Mn^{4+} + IO_3^- \qquad (3)$$

$$Mn^{2+} + Mn^{4+} \rightleftarrows 2Mn^{3+} \qquad (4)$$

$$Mn^{3+} + IO_4^- \rightarrow Mn^{5+} + IO_3^- \qquad (5)$$

$$2Mn^{5+} \rightleftarrows Mn^{4+} + Mn^{6+} \qquad (6)$$

$$Mn^{2+} + Mn^{6+} \rightleftarrows 2Mn^{4+} \qquad (7)$$

$$Mn^{3+} + Mn^{6+} \rightleftarrows Mn^{4+} + Mn^{5+} \qquad (8)$$

$$2Mn^{6+} \rightleftarrows Mn^{7+} + Mn^{5+} \qquad (9)$$

$$Mn^{2+} + Mn^{7+} \rightleftarrows Mn^{4+} + Mn^{5+} \qquad (10)$$

$$Mn^{4+} \rightarrow [MnO_2]_{solid} \qquad (11)$$

To make the model more concrete, we must specify the most likely species in the actual Mn^{II}–IO_4^- system. At pH ≈ 4, Mn(III) and Mn(IV) tend to hydrolyze, while the tetraoxoanions of Mn(V) and Mn(VI) are largely protonated. A full description of the present system would thus include the following species: IO_4^-, IO_3^-, Mn^{2+}, $Mn(OH)^{2+}$, $Mn(OH)_2^{2+}/MnO(OH)^+/MnO_2$, $HMnO_4^{2-}$, $HMnO_4^-$, and MnO_4^-. A somewhat simplified version of the model (12)–(15) yields a preliminary mechanism capable of qualitatively explaining the oscillatory behavior of the manganese(II)–periodate system:

$$Mn^{2+} + IO_4^- + H_2O \xrightarrow{k_1} MnO(OH)^+ + IO_3^- + H^+ \qquad (12)$$

$$Mn^{2+} + MnO(OH)^+ + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2Mn(OH)^{2+} \qquad (13)$$

$$2Mn(OH)^{2+} + IO_4^- + H_2O \xrightarrow{k_3} 2MnO(OH)^+ + IO_3^- + 2H^+ \qquad (14)$$

$$\begin{array}{ccc} MnO(OH)^+ & \xrightarrow{k_4} & [MnO_2]_{colloidal} + H^+ \\ & & \updownarrows \\ & & [MnO_2]_{solid} \end{array} \qquad (15)$$

Addition of steps (12) + (13) + (14) + 2(15) gives the observed stoichiometry of eq 1. Reaction 12 is a relatively slow oxidation of Mn^{2+} to a partially hydrolyzed Mn(IV) species that may be stabilized by periodate. This species is assumed to be the yellow product. The rapid equilibrium of step 13 lies toward the left. Step 14 is a composite process in which manganese intermediates with oxidation states higher than +4 are almost certainly involved.

The autocatalyst $MnO(OH)^+$ is removed from solution in step 15. If this removal occurs on the surface of the precipitate, then the kinetics of this process may be represented by a Langmuir–Hinshelwood type expression of the form

$$-d[MnO(OH)^+]/dt = k_4[MnO(OH)^+]/(1 + r[MnO(OH)^+]) \qquad (16)$$

The rate constant k_4 and the saturation parameter r will depend upon the nature and concentration of the stabilizing species.

Gray and Scott[18] have demonstrated in a set of model calculations that the combination of a quadratic autocatalysis of the sort found in eqs 13 and 14 with Langmuir–Hinshelwood kinetics (eq 16) for removal of the autocatalyst leads to oscillation if the saturation parameter r is large enough.

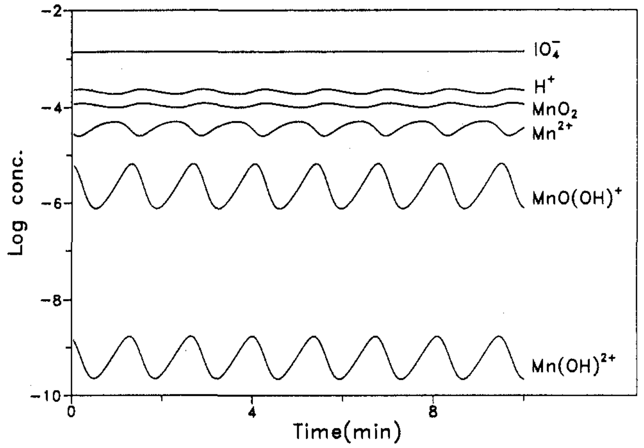

Figure 5. Computer simulation of the oscillatory Mn^{II}–IO_4^- reaction in a CSTR using the mechanism of eqs 12–16. Input concentrations: $[IO_4^-]_0 = 1.5 \times 10^{-3}$ M, $[Mn^{2+}]_0 = 1.5 \times 10^{-4}$ M. Flow rate: $k_0 = 0.01$ s^{-1}. Parameters for simulation: $k_1 = 1$ M^{-1} s^{-1}, $k_2 = 5 \times 10^7$ M^{-2} s^{-1}, $k_{-2} = 1 \times 10^{-6}$ s^{-1}, $k_3 = 1 \times 10^8$ M^{-2} s^{-1}, $k_4 = 5 \times 10^{-1}$ s^{-1}, $r = 7 \times 10^4$ M^{-1}, $[Mn^{III}]_{initial} = [Mn^{IV}]_{initial} = 10^{-10}$ M, $[H^+]_{initial} = 1 \times 10^{-4}$ M.

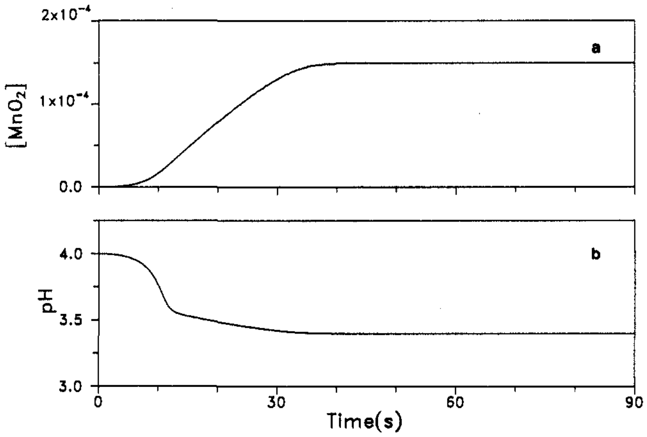

Figure 6. Simulated batch behavior with parameters and initial concentrations as in Figure 5: (a) total $[Mn^{IV}]$ plotted as $[MnO_2]$; (b) pH.

In Figure 5 we show the results of simulating eqs 12–16 with the same input concentrations and flow rate as in Figure 1. Batch simulations are presented in Figure 6. The simulations agree surprisingly well with the experimental results. The periodate concentration is essentially constant. The pH varies by about 0.3 unit around a mean of about 4. If we assume that the yellow color results from $(MnO_2)_{colloidal} + MnO(OH)^+$ and use a molar extinction coefficient for these species of 2000 dm^3 M^{-1} cm^{-1} at 410 nm,[19] then the calculated absorbances are about the same as those in Figure 1c. Like the experiments, the simulations show no bistability, but the calculated oscillation frequency is higher than the observed frequency by about a factor of 3.

As in the experiments, introducing flows of 10^{-4} M H_2SO_4 ($[H^+]_0 = 2 \times 10^{-4}$ M) or NaOH or buffering the pH in the simulations suppresses oscillation. The ability of even small added concentrations of pyrophosphate to suppress both oscillation and the yellow color implies that Mn(III), which forms a very stable $Mn(H_2P_2O_7)_2^-$ complex with pyrophosphate, must play an important role in the oscillatory behavior. The calculated $[Mn^{II}]$ is quite low. However, addition of pyrophosphate should remove $Mn(OH)^{2+}$, shifting equilibrium 13 toward the right, which lowers the concentration of the autocatalytic species $MnO(OH)^+$, and hindering step 14, the second part of the autocatalytic sequence. This view is consistent with the observations of Tinginyanu et al.,[19] who found no autocatalysis in the Mn^{II}–IO_4^- reaction in a pyrophosphate medium at pH 5–8.

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Discussion

The results presented here lead us to conclude that the periodate–Mn(II) oscillator and the permanganate–reductant oscillators form two branches of a single family of manganese-based oscillatory reactions and that elucidation of the mechanism of one branch will contribute greatly to understanding how the other branch works. In both types of reaction, the major end product is Mn(IV), which accelerates its own production. A full description of these reactions requires all oxidation states of manganese from +2 to +7. The contribution of each state to any particular oscillator will depend upon both the pH and whether the partner of the manganese species is a one- or a two-electron reagent.

There do, however, appear to be essential differences between the two types of oscillator. The permanganate–reductant systems[2,3,7] require an auxiliary third component, $H_2PO_4^-$ or HPO_4^{2-}, which is not necessary for the Mn(II)–oxidant reaction. These stabilizing species slow down, regulate, or prevent the flocculation of Mn(IV) species to solid MnO_2. The MnO_4^- oscillators do not exhibit the pH oscillation found in the Mn(II)–periodate system.

It is possible that these differences are not so fundamental as they might seem. We have shown that addition of phosphate does broaden the range of oscillation of the present system. We note that in one recently characterized permanganate oscillator,[8] only two components are necessary, arsenite and permanganate. The arsenate product serves in place of phosphate as the stabilizer for Mn(IV). We suggest that periodate plays an analogous dual role, serving as both oxidant and stabilizer. In support of this view, we offer three pieces of evidence. First, the broad yellow band in the absorption spectrum of the reacted mixture shifts toward lower wavelengths as $[IO_4^-]$ is increased. Second, Jensovsky[20] reports that orthoperiodate can stabilize such anomalous oxidation states as Mn(IV), Co(III), Cu(III), and Ag(III) by complex formation. Finally, Lister et al.[21,22] have prepared and characterized Mn(IV)–periodate complexes by oxidizing $MnSO_4$ with $Na_2H_3IO_6$.

The permanganate oscillators oscillate in buffer and show negligible pH oscillations, perhaps because of the buffering ability of the added phosphate. They are clearly not pH oscillators. The Mn(II)–periodate system in contrast shows measurable oscillations in pH, and buffering strongly suppresses or eliminates the oscillations in Pt potential and absorbance. This system thus meets the criteria for a pH oscillator.[23] However, the amplitude of the pH oscillation is significantly smaller than that of other pH oscillators, and a small Pt potential oscillation does persist even with buffering. Thus the characterization of the $Mn^{II}–IO_4^-$ system as a pH oscillator is marginal.

The simulations presented in Figures 5 and 6 are in good qualitative agreement with experiment. They suggest that we are on the right track. However, none of the rate constants used in those calculations has been measured; all were estimated. We hope that the results presented here, together with the likelihood that understanding this system will lead to further insights into permanganate oscillators and into manganese chemistry of considerable practical importance, will soon lead to further study of the kinetics of the component reactions.

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Silicon and Carbon Solid-State MAS and Liquid-State NMR Study of the Polycondensation of Heteropolysiloxanes

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Abstract: Samples were taken at various stages of the polycondensation between different silicon alkoxides $RSi(OR')_3$ which are reacted together in the preparation of membranes for ultrafiltration and reverse osmosis. ^{29}Si NMR spectra could be interpreted by using empirical increments of the chemical shift, which are characterized for substitutions at the Si atom. It is found that the reaction attains the maximum degree of condensation forming a three-dimensionally infinite siloxane $RSi(OSi\equiv)_3$ backbone, which is, however, partially degraded by thermal treatment (120 °C) leading to $R_2Si(OSi\equiv)_2$ and $Si(OSi\equiv)_4$ groups. The organic part is not affected during these reactions, and side reactions in the early stages of polymerization (e.g. ligand exchange with the solvent) were reversible.

Introduction

Heteropolysiloxanes (HPS) are creating a growing interest in chemistry because of their composite nature,[1,2] made up of an inorganic backbone of siloxane bonds and organic chains which are chemically bound to the backbone and can be used to modify the material properties within a wide range. The early approach was to deposit these compounds on a porous ceramic support in order to obtain a quite dense membrane capable of performing liquid or gas separation. Several requirements must be met by such membranes:[3,4] a few micrometers thickness, absence of

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