mode is the most intriguing. The observed frequencies and relative intensities agree quite well with those calculated at the MP2/6-31G* level, except that almost all the frequencies are overestimated, as usual. However, the extremely flat energy profile computed for the twisting motion apparently has its minimum at the wrong position, 38° instead of 0° twist.

This could simply be due to the approximate nature of the calculation. For instance, inadequacies in the evaluation of correlation energy might vary with the dihedral angle and the resulting extent of π-conjugation. However, it is perhaps more likely that the problem lies elsewhere: the experiments are performed in condensed phase, and the calculations are performed for an isolated molecule and neglect the energy of solvation. The experimental result is independent of the exact nature of the solid environment and probably reflects the intrinsic preferences of the molecule in a compact and polarizable medium, rather than the packing preferences of the matrix material. Perhaps the planar molecule is sufficiently more polarizable and its van der Waals stabilization sufficiently greater to move the shallow minimum in the potential energy surface to 0° dihedral angle.

Two other possibilities to reconcile the results of the calculations with the experimental findings have occurred to us, but neither is very appealing. The first would be to postulate that the molecule tunnels rapidly on the IR time scale between the two mirror-symmetry related gauche forms corresponding to the computed dihedral angles of +38° and −38°. The second possibility is that the torsional barrier is so small that already the lowest vibrational level lies above it. This is unlikely, since the calculated value of $h\nu/2$ for this mode is only 90 cm^{-1}, while the calculated barrier height is 319 cm^{-1}.

Either way, the computed potential energy minimum could still be at 35–40° yet the IR spectrum of the molecule would effectively correspond to a C_{2v} overall symmetry. In both cases, the molecules would have to be packed very inefficiently and be accommodated in quite large cavities in the matrix in order to permit large-amplitude motions. This strikes us as unlikely, given that the results are the same in seven different matrix environments.

We conclude that a correct reproduction of the quite inescapable experimental finding, a planar or nearly planar *s-cis*-1,3-butadiene in a variety of matrix environments, remains as an interesting challenge for structural theory.

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Registry No. 1,3-Butadiene, 106-99-0.

The Minimal Permanganate Oscillator and Some Derivatives: Oscillatory Oxidation of $S_2O_3^{2-}$, SO_3^{2-}, and S^{2-} by Permanganate in a CSTR[1]

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Abstract: Oscillatory behavior is reported in the permanganate oxidation of several species in the presence of KH_2PO_4 in a stirred tank reactor. With Mn^{2+} as the reductant and NaOH added to maintain the proper pH, the resulting system is the "minimal permanganate oscillator," which serves as a core from which other oscillating permanganate reactions can be generated. In one example, discussed in detail, the manganous ion and NaOH are replaced by thiosulfate ion and H_2SO_4, respectively. Other permanganate oscillators contain sulfite or sulfide ions as the reductant. The phosphate serves both as a stabilizer of soluble Mn(IV) and as a pH buffer.

Oscillatory behavior is found in a wide range of enzyme-catalyzed reactions, and transition metals play a major role in the functioning of the enzymes involved in these processes. In view of this fact and the multiplicity of oxidation states available to many transition metals, compounds of these elements seem ideal candidates to serve as starting points for new chemical oscillators. It is therefore surprising that the first chemical oscillator based on transition-metal chemistry has only recently been reported. This system, the $KMnO_4$–H_2O_2–H_3PO_4 reaction in a flow reactor (CSTR), was discovered by Nagy and Treindl.[2] It was soon followed by reports of two more permanganate oscillators, the $KMnO_4$–ninhydrin–H_3PO_4[3] and the $KMnO_4$–KNO_2–formic acid–methanol[4] systems.

In a recent communication,[5] we presented initial results on a new and simpler permanganate oscillator, the Guyard[6] reaction of Mn^{2+}, MnO_4^-, and phosphate at near neutral pH in a CSTR. We referred to this system as the "minimal permanganate oscillator". A minimal oscillator in a family of oscillatory reactions may be defined[7] as that oscillator containing components that are found in all members of the family as reactants or are generated during the reaction, and from which no component can be removed without destroying the ability of the system to oscillate. Since all permanganate–substrate reactions lead to manganese(II), and the phosphate is essential for oscillation, the Mn^{2+}–MnO_4^-–phosphate system is the minimal member of the family of MnO_4^-–reductant–phosphate oscillators, of which the first two examples[2,3] contain hydrogen peroxide and ninhydrin as the reductant.

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Table I. States Observed in the $KMnO_4$–$MnSO_4$–KH_2PO_4–NaOH Flow System as a Function of Input $[KH_2PO_4]_0$[a]

$[KH_2PO_4]_0$, M	state[b]	flow rate, s^{-1}	amplitude, mV	period, min	pH
7.5×10^{-4}	SS	all			8.0
1.25×10^{-3}	OS	0.019	65	5	7.2
		0.015	40	8	7.0
		0.0085	20	15	6.9
1.5×10^{-3}	OS	0.048	45	1.1	7.0
		0.019	62	6	7.0
		0.015	53	9.5	7.0
		0.0085	36	14	7.0
2.25×10^{-3}	OS	0.019	75	6	6.6
		0.015	85	9	6.6
		0.0105	78	20	6.5
3.0×10^{-3}	SS	0.019			
	OS	0.0105	85	15	6.2

[a] Fixed concentrations: $[KMnO_4]_0 = 9 \times 10^{-5}$ M, $[MnSO_4]_0 = 2.5 \times 10^{-4}$ M, $[NaOH]_0 = 1 \times 10^{-3}$ M. $T = 25$ °C. [b] SS = steady state; OS = oscillatory state.

If one can identify a minimal oscillator, it is often straightforward to use that system as a core for building additional members of the family. For example, the BrO_3^-–Br^-–Mn^{2+} "minimal bromate oscillator[8]" gives rise to a variety of inorganic bromate oscillators[9] in which bromide ion is replaced by reducing agents that generate Br^- from bromate. Similarly, many oscillators containing chlorite and iodine-containing species[10] can be constructed from the minimal ClO_2^-–I^- system.[11]

We report here further details of the minimal permanganate oscillator. We then show how it has been used to fabricate three new permanganate oscillators: the reduction of permanganate by sulfite, thiosulfate, and sulfide ions in the presence of $H_2PO_4^-$ in a CSTR. The thiosulfate system is analyzed in some detail, while the other two systems are discussed more briefly as illustrations of the insights gained in studying the minimal and the thiosulfate oscillators.

Experimental Section

Materials. All chemicals used ($KMnO_4$, $MnSO_4 \cdot 4H_2O$, $Na_2S_2O_3 \cdot 5H_2O$, Na_2SO_3 anhydrous, $Na_2S \cdot 9H_2O$, KH_2PO_4) were of analytical grade (Fisher), and no further purification was made. Stock solutions were prepared in deionized water, and the concentrations were checked by conventional titrimetric methods. The 10^{-1} M $KMnO_4$, $MnSO_4$, $Na_2S_2O_3$, and KH_2PO_4 stock solutions could be stored for about 10 days without measurable change in their concentrations. The experiments utilized 10^{-5}–10^{-3} M solutions, which were always freshly diluted from the stock solutions prior to use. In preparing the Na_2SO_3 and Na_2S solutions, precautions were taken to avoid air oxidation. In those cases the deionized water was first purged with argon for 10–15 min, and care was taken to exclude air when the solution was prepared, stored, diluted, and introduced into the reactor.

Methods. The permanganate oxidations of Mn^{2+} and $S_2O_3^{2-}$ were studied under both batch and flow conditions. With the substrates SO_3^{2-} and S^{2-}, only CSTR measurements were performed. In the batch experiments, the potential of a Pt electrode (vs Hg|Hg_2SO_4, K_2SO_4 reference electrode), the pH (Aldrich combination calomel–pH electrode connected to an Orion SA 720 pH meter), and the light absorbance of the reactants, intermediates, and products at the appropriate wavelengths (Perkin-Elmer 552 UV/VIS spectrophotometer) were recorded.

The CSTR experiments were carried out in a thermostated glass reactor of volume 20.5 cm^3 equipped with a variable speed magnetic stirrer and Pt, reference, and combined glass electrodes, so that the redox potential and pH could be simultaneously monitored with a double channel recorder (Linear 1200). Another reactor (volume 34.0 cm^3) made of plastic, equipped with quartz windows, magnetic stirrer, and Pt and reference electrodes, was placed in one of the compartments of the spectrophotometer, and the light absorbance and Pt potential were simultaneously recorded. The reactor in the spectrophotometer had a path length of approximately 4.0 cm. A four-channel peristaltic pump (Sage 375A) drove the solutions into the reactor, which was vigorously mixed. No air gap was allowed to form between the top of the solution and the reactor cap. The flow rate (reciprocal residence time, k_0) could be varied from 0.00109 to 0.0500 s^{-1} with an accuracy of ±0.5%.

Table II. States Observed in the $KMnO_4$–$MnSO_4$–KH_2PO_4–NaOH Flow System as a Function of Input $[NaOH]_0$[a]

$[NaOH]_0$, M	state[b]	flow rate, s^{-1}	amplitude, mV	period, min	pH
2.5×10^{-4}	SS	all			5.0
5×10^{-4}	SS	0.019			
	OS	0.015	60	13	6.1
1×10^{-3}	OS	0.048	45	1.1	7.0
		0.019	62	6	7.0
		0.015	53	9.5	7.0
		0.0085	36	14	7.0
2×10^{-3}	SS	all			10.8

[a] Fixed concentrations: $[KMnO_4]_0 = 9 \times 10^{-5}$ M, $[MnSO_4]_0 = 2.5 \times 10^{-4}$ M, $[KH_2PO_4]_0 = 1.5 \times 10^{-3}$ M. $T = 25$ °C. [b] SS = steady state; OS = oscillatory state.

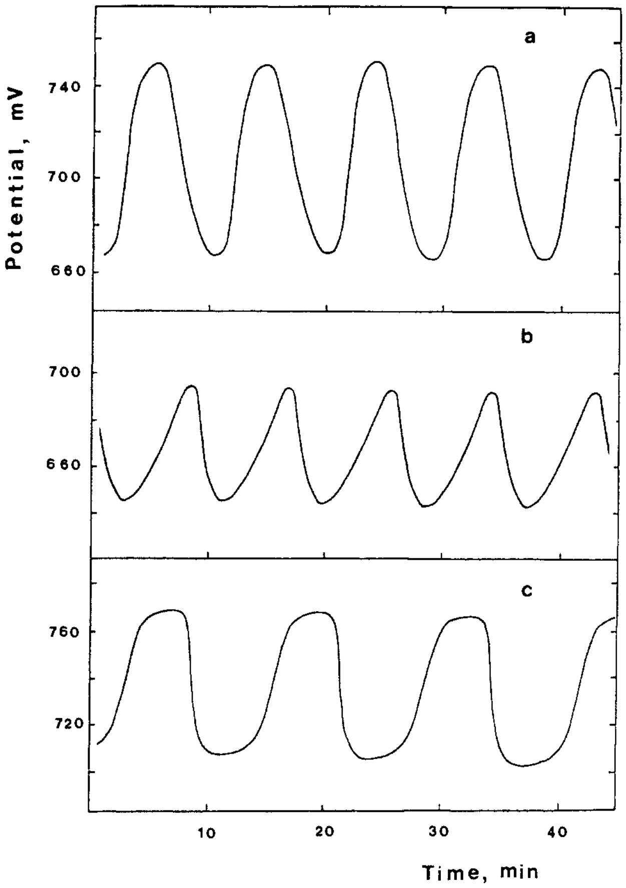

Figure 1. Oscillatory Pt electrode potential traces. Fixed constraints: $[KMnO_4]_0 = 9 \times 10^{-5}$ M, $[MnSO_4]_0 = 2.5 \times 10^{-4}$ M, $k_0 = 0.015$ s^{-1}, $T = 25$ °C; (a) $[KH_2PO_4]_0 = 2.25 \times 10^{-3}$ M, $[NaOH]_0 = 1 \times 10^{-3}$ M; (b) $[KH_2PO_4]_0 = 1.5 \times 10^{-3}$ M, $[NaOH]_0 = 1 \times 10^{-3}$ M; and (c) $[KH_2PO_4]_0 = 1.5 \times 10^{-3}$ M, $[NaOH]_0 = 5 \times 10^{-4}$ M.

Results

$KMnO_4$–$MnSO_4$–KH_2PO_4–NaOH (Minimal) System. A summary of the behavior of the minimal manganese oscillator, including a phase diagram in the $[KMnO_4]_0$–$[MnSO_4]_0$ plane showing the oscillatory domain at fixed inputs $[KH_2PO_4]_0$ and $[NaOH]_0$, was presented in ref 5. Here we give additional details, especially those of relevance to constructing further permanganate oscillators.

Oscillation occurs only when the ratio $[KMnO_4]_0$:$[MnSO_4]_0$ is close to 4:1. The input concentrations of the other two constituents, $[KH_2PO_4]_0$ and $[NaOH]_0$, must also be kept within narrow limits. In Tables I and II we list the state of the system

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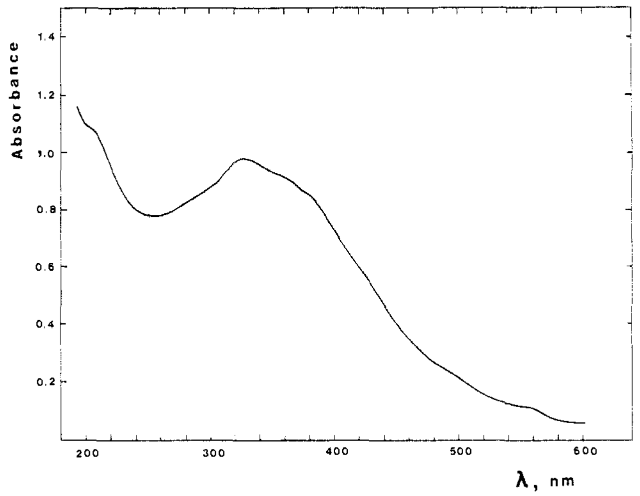

Figure 2. UV/vis spectra of a reaction mixture with $[KMnO_4]_0 = 4 \times 10^{-5}$ M, $[MnSO_4]_0 = 1.25 \times 10^{-4}$ M, $[NaOH]_0 = 1 \times 10^{-4}$ M, $[KH_2PO_4]_0 = 1.5 \times 10^{-3}$ M. Path length $l = 1.00$ cm.

when $[KH_2PO_4]_0$ or $[NaOH]_0$ is varied at fixed input concentrations of the other reagents. Typical oscillatory Pt potential traces at three of the compositions in Tables I and II are shown in Figure 1.

During the oscillations in Pt potential, the pH remains constant at a value between 6 and 7, which depends on the input concentrations. The oscillatory reaction mixture is always brownish-yellow, and visible brown MnO_2 precipitation accompanies the oscillation. Because of this precipitation, we did not perform flow experiments in the spectrophotometer on the oscillating minimal system, though we were able to follow the oscillations in the $KMnO_4$–$Na_2S_2O_3$ reaction where there is a little or no precipitation (see below). We did, however, take absorption spectra of the batch reaction while simultaneously recording the pH and the Pt potential in an effort to determine the origin and nature of the brownish-yellow color. Figure 2 depicts the spectrum of an oscillatory composition taken 15 min after mixing the reagents.

The evolution of the yellow color together with the potential of the Pt electrode are shown in Figure 3. The potential trace shows two maxima, which coincide with rapid color changes, first from pink to yellow and then to tobacco yellow. In another run, in which we recorded the absorbance at 530 nm, where $KMnO_4$ has a characteristic absorption peak, we observed the immediate and complete disappearance of the permanganate. During the reaction the pH hardly changed, owing to the buffering effect of KH_2PO_4; the starting pH of 6.90 decreased only to 6.75. When the KH_2PO_4 was omitted, we found a considerable decrease in pH, from 7.00 to 3.95, as a result of production of H^+ in the $KMnO_4$–$MnSO_4$ reaction. Initial pH's of 10, 7, and 4.8 gave very fast, moderately fast, and sluggish reactions, respectively, which is characteristic for the Guyard reaction

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

Somewhat surprisingly, we found no evidence of bistability in the minimal permanganate system. Because of the fine precipitation of MnO_2, which settles on the walls of the reactor and on the electrodes, the threshold value of the flow rate at which oscillations start or stop and the amplitude of oscillations may differ slightly when the flow rate is first increased and then decreased. However, careful observation suggests that this narrow range of hysteresis does not represent genuine bistability, but is rather a consequence of the above heterogeneity.

$KMnO_4$–Red–KH_2PO_4–H_2SO_4 Systems (Red = $S_2O_3^{2-}$, SO_3^{2-}, S^{2-}). Since the $KMnO_4$–$MnSO_4$ reaction oscillates in the presence of appropriate amounts of KH_2PO_4 and NaOH, one might expect to be able to construct other oscillators by substituting for the input of manganous ion reducing agents that generate Mn(II) in reaction with $KMnO_4$. So far we have found three substrates, $S_2O_3^{2-}$, SO_3^{2-}, and S^{2-}, that react in an oscillatory fashion with MnO_4^-. The input solutions of SO_3^{2-} and S^{2-} are quite alkaline, and their

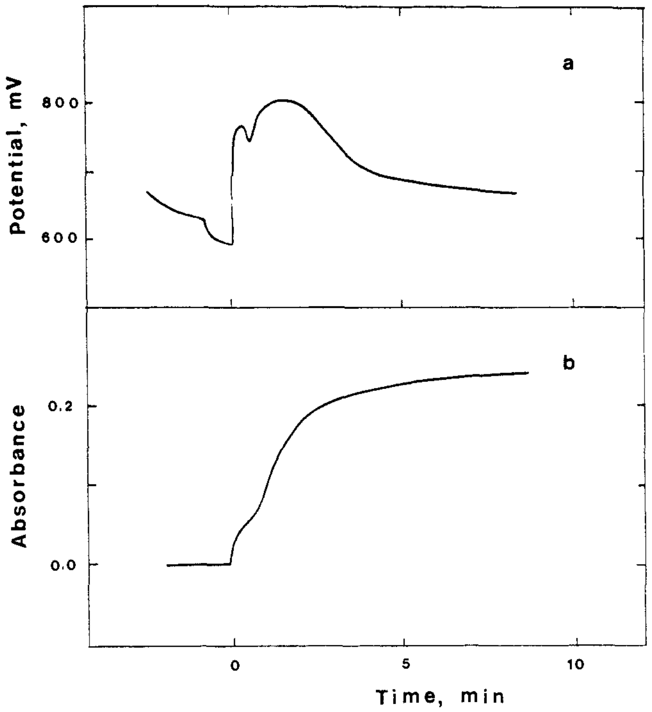

Figure 3. Potential of Pt electrode (a) and light absorbance at 320 nm (b) vs time at the composition of Figure 2. KH_2PO_4 and NaOH were mixed, followed by addition of $MnSO_4$. Reaction was initiated at t = 0 by addition of $KMnO_4$. Path length l = 1.00 cm.

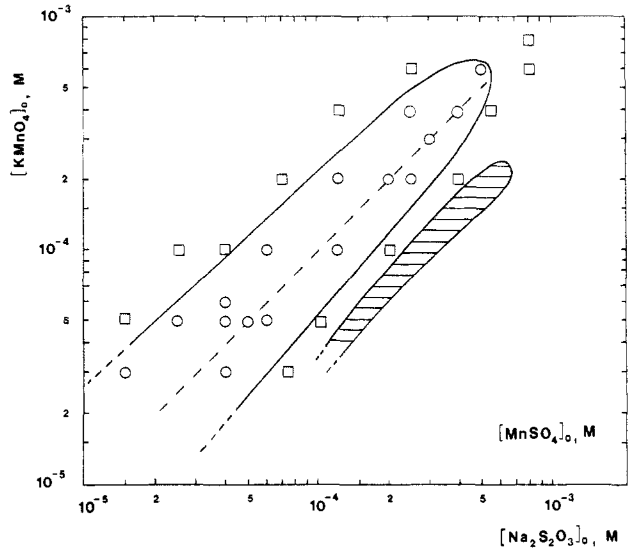

Figure 4. Phase diagram in the $[KMnO_4]_0$–$[Na_2S_2O_3]_0$ plane at fixed inputs $[KH_2PO_4]_0 = 1.5 \times 10^{-3}$ M, $[H_2SO_4]_0 = 2.5 \times 10^{-4}$ M. T = 25 °C. Hatched area is the oscillatory region for the minimal permanganate system in the $[KMnO_4]_0$–$[MnSO_4]_0$ plane. For values of flow rate k_0, see text. Symbols: ○, oscillation, □, nonoscillatory steady state.

oxidation leads to production of OH^-. Therefore, to maintain the proper working pH, we introduced in these systems an H_2SO_4 input solution in place of the NaOH used in the minimal oscillator. The results obtained with these three systems are summarized in the following sections.

$KMnO_4$–$Na_2S_2O_3$–KH_2PO_4–H_2SO_4. As Figure 4 shows, it is considerably easier to find oscillatory conditions in the $KMnO_4$–$Na_2S_2O_3$ reaction than in the minimal system. For comparison, the figure displays the oscillatory domains of both the thiosulfate and the minimal systems. Note the significant extension of the oscillatory region of the minimal system, a feature found in many cases in which a derivative oscillator is generated from a minimal one.[9,10] Unlike the usual concentration–concentration phase diagram where the flow rate is fixed, Figure 4

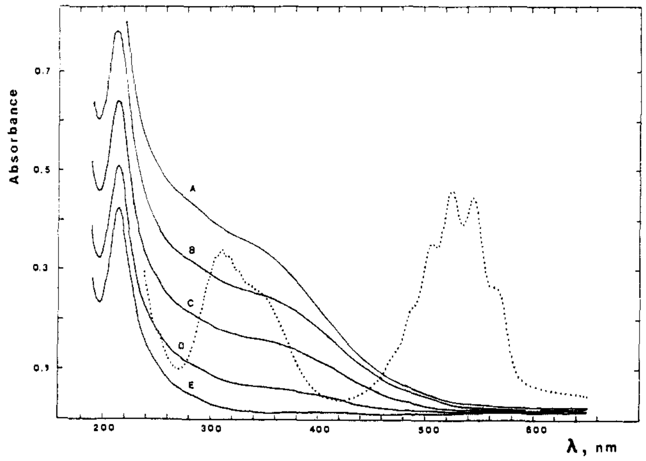

Figure 5. UV/vis absorption spectra in batch reaction with initial concentrations [$KMnO_4$] = 2 × 10^{-4} M, [$Na_2S_2O_3$] = 2.5 × 10^{-4} M, [KH_2PO_4] = 1.5 × 10^{-3} M, [H_2SO_4] = 2.5 × 10^{-4} M. T = 25 °C, l = 1.00 cm. Dotted line: pure 10^{-4} M $KMnO_4$. Curves: (A) 1 min, (B) 4 min, (C) 10 min, (D) 50 min, (E) 100 min.

contains information about a range of flow rates. Along the broken diagonal line oscillations always appear for $0.0080 \leq k_0 \leq 0.0170$ s^{-1}, and in many cases the oscillatory range of k_0 can be expanded above and below this range, to values as low as 0.0040 or as high as 0.020 s^{-1}. Above, the diagonal line the system tends to oscillate at higher values of k_0, while below it the oscillatory range shrinks and shifts to lower values. Very high or low flow rates may result in damped oscillations. The pH is nearly constant during the oscillations at a value between 3.2 and 3.7. The higher the reagent concentrations, the higher is the resulting constant pH. The system is most prone to oscillate when $[KMnO_4]_0:[Na_2S_2O_3]_0$ = 1:1, but oscillations have been observed for ratios ranging from 2:1 to 2:3.

At intermediate flow rates, the potential of the Pt electrode oscillates around a mean of about 600 mV vs SHE. At high and low flow rates this value shifts to 700–800 and 500 mV, respectively. The amplitude of oscillation reaches a maximum at $k_0 \sim 0.012$ s^{-1}. The frequency, however, increases monotonically with the flow rate. The color of the reaction mixture changes significantly with the composition. To the left of the oscillatory region in Figure 4 the solution is red, within the oscillatory domain it is always yellow or brownish yellow, and in the steady state region at the right the solution becomes colorless.

At high concentrations of both reagents (upper right of the oscillatory domain) brown MnO_2 precipitate is formed, but in contrast to the minimal oscillator, in the thiosulfate system oscillations are not always accompanied by precipitation. Below 10^{-4} M input reactant concentrations the solution is free from precipitation whether or not oscillations occur, although in very long experiments a thin brown layer of MnO_2 may form on the walls of the reactor and on the surfaces of the electrodes and the stirrer. The clear solutions made it possible to perform spectrophotometric measurements in both batch and flow configurations.

In Figure 5 we show the spectra of an oscillatory composition taken at different times after mixing. The dotted line shows the situation at $t = 0$, before the reaction starts. Shortly after mixing the $KMnO_4$ disappears, and a broad absorption resembling Figure 2 is measured. This wide band is characteristic of the yellow product, which is formed immediately after mixing and appears to react slowly with $S_2O_3^{2-}$. The sharp peak at λ = 218 nm is the absorption of $S_2O_3^{2-}$. Unfortunately, the product $S_4O_6^{2-}$ has its maximum absorbance at the same value of λ, and its absorption coefficient is approximately double that of $S_2O_3^{2-}$, so we cannot draw conclusions about the stoichiometry from the decrease in this peak.

The spectra presented in Figure 5 were also taken in the absence of KH_2PO_4, and significant differences were found: without KH_2PO_4 the intensity of the broad yellow absorption was about one-fourth of that observed in the presence of KH_2PO_4, and this band disappeared more rapidly. These observations support the view[12] that $H_2PO_4^-$ ions strongly enhance the formation and stability of a soluble manganese(IV) species.

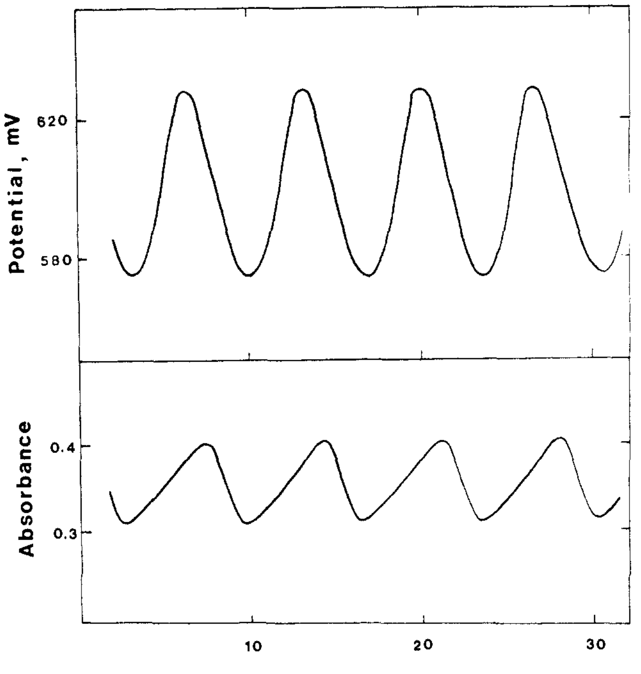

Figure 6. Oscillatory responses in absorbance at 450 nm, $l \approx 4.0$ cm, and in potential of Pt electrode. $[KMnO_4]_0$ = 5 × 10^{-5} M, $[Na_2S_2O_3]_0$ = 5 × 10^{-5} M, $[KH_2PO_4]_0$ = 1.5 × 10^{-3} M, $[H_2SO_4]_0$ = 2.5 × 10^{-4} M, k_0 = 0.0128 s^{-1}, T = 25 °C.

We have also followed the absorbance at different wavelengths of the $KMnO_4$–$Na_2S_2O_3$–KH_2PO_4–H_2SO_4 system in the CSTR. The values of λ were the following: 530 (λ_{max} of $KMnO_4$), 450, 350, and 280 nm. Because of the much longer light path in the flow reactor, we used a more dilute mixture than in Figure 5. We observed oscillatory responses at all four wavelengths. The oscillations were consistent with the data of Figure 2. The lower the wavelength, the higher is the mean value of the absorbance and the bigger the amplitude of oscillation. An example of a simultaneous recording of oscillatory Pt potential and absorbance is shown in Figure 6. Because the absorbance is quite high and changes only by a small fraction at all wavelengths in the visible region, the oscillations are not visible by eye.

As in the case of the minimal permanganate oscillator, the input concentrations of the "extra" species, in this case KH_2PO_4 and H_2SO_4, have a profound effect on the oscillatory behavior of the thiosulfate system. For example, at $[KMnO_4]_0$ = 2 × 10^{-4}, $[Na_2S_2O_3]_0$ = 2.5 × 10^{-4}, $[H_2SO_4]_0$ = 2.5 × 10^{-4} M, oscillations occur only for $1.5 \times 10^{-3} \leq [KH_2PO_4]_0 \leq 3 \times 10^{-3}$ M. With the same input concentrations of permanganate and thiosulfate, if $[KH_2PO_4]_0$ is fixed at 1.5 × 10^{-3} M, $[H_2SO_4]_0$ can be varied by an order of magnitude (10^{-4}–10^{-3} M) without destroying the oscillatory behavior. Changing the input concentration of either reagent causes a pronounced change in the waveform, amplitude, and frequency of the oscillatory traces as well as in the range of flow rates in which the oscillations occur.

$KMnO_4$–Na_2SO_3–KH_2PO_4–H_2SO_4 and $KMnO_4$–Na_2S–KH_2PO_4–H_2SO_4 Systems. Either Na_2SO_3 or Na_2S can be used in place of $MnSO_4$ or $Na_2S_2O_3$ to generate new permanganate oscillators. The experimental conditions for oscillations are similar to those in the thiosulfate system, but the sensitivity of SO_3^{2-} and S^{2-} to air oxygen makes these systems more difficult to control. It is necessary to add more acid, because of the alkaline hydrolysis of SO_3^{2-} and S^{2-}. As a result, the oscillations in pH are more pronounced, and can be as high as 0.2 unit.

We did not attempt, as we did for the thiosulfate system, to delineate in detail the extent of the oscillatory region in phase space

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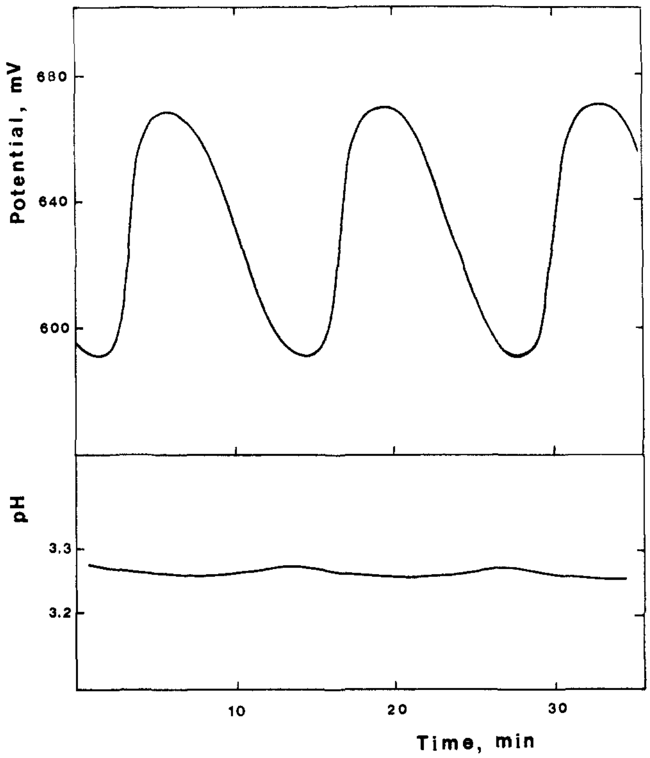

Figure 7. Oscillatory Pt potential and pH in the $KMnO_4$–Na_2SO_3 reaction. $[KMnO_4]_0 = 2 \times 10^{-4}$ M, $[Na_2SO_3]_0 = 1 \times 10^{-4}$ M, $[KH_2PO_4]_0 = 1.5 \times 10^{-3}$ M, $[H_2SO_4]_0 = 5 \times 10^{-4}$ M, $k_0 = 0.0070$ s^{-1}, $T = 25$ °C.

for these systems. Examples of the oscillatory behavior are presented in Figures 7 and 8, and one may use these as starting points to search for more extended regions of oscillation.

Discussion

Of the six possible oxidation states of manganese, only the +2, +4, and +7 states are stable, as Mn^{2+}, MnO_2, and MnO_4^-, respectively, at the pH's where oscillatory MnO_4^- oxidations are observed. The species MnO_4^- and MnO_2 are oxidants having a large potential[13] for reduction to Mn^{2+}.

$$MnO_4^- + 5e^- + 8H^+ = Mn^{2+} + 4H_2O \qquad E^0 = 1.51 \text{ V} \qquad (1)$$

$$MnO_2 + 2e^- + 4H^+ = Mn^{2+} + 2H_2O \qquad E^0 = 1.23 \text{ V} \qquad (2)$$

For the Mn(VII)/Mn(IV) couple, E^0 depends on the pH, being higher in acid (eq 3) and lower in basic solutions[13] (eq 4).

$$MnO_4^- + 3e^- + 4H^+ = MnO_2 + 2H_2O \qquad E^0 = 1.70 \text{ V} \qquad (3)$$

$$MnO_4^- + 3e^- + H_2O = MnO_2 + 4OH^- \qquad E^0 = 0.59 \text{ V} \qquad (4)$$

The reduction of MnO_4^- to Mn^{2+} occurs only in strongly acidic solutions and is catalyzed by the product Mn^{2+}. Reduction to MnO_2 takes place in neutral, weakly acidic, or weakly basic solutions. This reaction is also catalyzed by its product, MnO_2. As a consequence, all MnO_4^-–substrate reactions are autocatalytic if they are carried out in acidic, neutral, or weakly basic solution. Permanganate oxidation reactions are therefore good candidates to generate oscillatory behavior. To enhance the likelihood of oscillations, we need to (a) maintain far from equilibrium conditions, e.g., by conducting the reactions in a CSTR; (b) establish a moderate rate for the overall reaction by appropriate choice of the input concentrations and pH; and (c) find conditions under which intermediate oxidation states may be temporarily stabilized, thereby inducing a delay between component processes of the reaction.[14] These criteria are fulfilled with the conditions described above, but other combinations of parameters may also result in oscillation.

$KMnO_4$–$MnSO_4$–KH_2PO_4–NaOH System. In weakly acid and neutral solution, manganous ions react with permanganate to form manganese dioxide.

$$2MnO_4^- + 3Mn^{2+} + 4OH^- = 5MnO_2 + 2H_2O \qquad (5)$$

Reaction 5 is known as the Guyard[6] reaction and has important applications in analytical chemistry for the volumetric determination of Mn(II) by permanganate in nearly neutral solution. The Guyard reaction is very slow in strong acid, but in weakly acidic and neutral solutions the rate increases significantly. The reaction is catalyzed by the MnO_2 formed, which can precipitate as solid brown product. Often, however, the precipitation is substantially delayed due to formation of a yellow Mn(IV) intermediate. The stability of the yellow Mn(IV) to flocculation into solid is greatly enhanced if phosphate ions are present, and the $H_2PO_4^-$ species appears to serve as the principal stabilizing agent. The soluble form of manganese(IV) can be regarded as a colloidal MnO_2 stabilized by phosphate ions,[12] which does not show light scattering, but which does not rigorously satisfy Beer's law. The visible spectrum of soluble manganese(IV) shows an increasing absorbance with decreasing wavelength[15] from about 600 nm, similar to that shown in Figure 2 for the MnO_4^-–Mn^{2+} batch reaction at an oscillatory composition. The yellow color develops gradually (see Figure 3), reaching a maximum after about 20 min, when precipitation begins. The yellow color disappears much faster if a substrate with a low redox potential, like $S_2O_3^{2-}$, is present, as seen in Figure 5. The rate of conversion of soluble Mn(IV) species into MnO_2 precipitate increases with the initial permanganate concentration, but the precipitation process is inhibited at higher phosphate concentrations.[12] Precipitation is more pronounced in the MnO_4^-–Mn^{2+} system than in the MnO_4^-–Red reactions, indicating a further reaction of MnO_2 with the substrate according to eq 2. At very low concentrations of the MnO_4^-–Red systems the oscillations appear to be free of precipitate.

The presence of phosphate ions appears to be an essential requirement for permanganate oscillators. Phosphate can be introduced as H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, or PO_4^{3-}. At the pH's where the oscillations occur (3.5 and 7), the major species are $H_2PO_4^-$ and HPO_4^{2-}. The phosphate species play a dual role in the oscillatory process. First they stabilize the soluble Mn(IV) against flocculation. Whether this soluble Mn(IV) species is present as colloidal manganese dioxide stabilized in solution by adsorption of phosphate ions on its surface[12] or as a μ-hydroxo-bridged dinuclear phosphate complex[15] is not yet known, but the effect of phosphate in retarding precipitation is well documented. The narrow range of $[H_2PO_4^-]_0$ in which the system will oscillate implies that the stability of the oscillatory behavior is extremely sensitive to the concentration of the soluble Mn(IV) species.

The second role of the phosphate species is to buffer the pH of the reaction mixture. In all MnO_4^- oxidations either acid or base is produced (see eqs 1–5). Since the oxidation rate is strongly pH dependent, the H^+ or OH^- formed must be removed in order to maintain the pH at its optimal value for oscillation. This value is close to 7 in the minimal oscillator, but it can be as low as 3.5 in the MnO_4^-–Red reactions. At high $[KMnO_4]_0$ ($>2.5 \times 10^{-4}$ M) and $[MnSO_4]_0$ ($>7 \times 10^{-4}$ M), the $[H^+]$ or $[OH^-]$ produced can be so high as to exceed the buffer capacity of the $H_2PO_4^-/HPO_4^{2-}$, resulting in termination of the oscillatory domain of Figure 4 at a high pH (≈ 4) steady state.

In light of our experimental observations and considering a mechanism proposed by Tompkins[16] for the Guyard reaction, we suggest the following skeleton mechanism to account for the oscillatory behavior.

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$$MnO_4^- + Mn^{2+} + H_2O \overset{\text{rapid}}{\rightleftarrows} Mn^{3+} + HMnO_4^- + OH^- \qquad (M1)$$

$$HMnO_4^- + Mn^{2+} + OH^- \xrightarrow{\text{slow}} 2\,MnO_2 + H_2O \qquad (M2)$$

$$Mn^{3+} + H_2O \overset{\text{rapid}}{\rightleftarrows} Mn(OH)^{2+} + H^+ \qquad (M3)$$

$$2Mn(OH)^{2+} \rightleftarrows [MnO^{2+}]_{sol} + Mn^{2+} + H_2O \qquad (M4)$$

$$[MnO^{2+}]_{sol} + OH^-/H_2O \xrightarrow{\text{slow}} MnO_2 \qquad (M5)$$

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-} \qquad (M6)$$

Manganese dioxide arises primarily from processes M4 and M5, and the catalytic effect of MnO_2 on its own production is also confined to these steps. Step M2 is even slower than step M5, so that the latter step is the main source of precipitate. Step M3 represents the partial hydrolysis of Mn^{2+}, which yields a soluble hydrated oxide that can be present either as a dimer or in a polymeric form. The hydrated Mn(III) oxide undergoes disproportionation in step M4 to a soluble Mn(IV) species and Mn^{2+}. The $[Mn(IV)]_{sol}$ first forms a supersaturated solution and then generates MnO_2 precipitate autocatalytically as a result of nucleation and surface effects.[12,17] Processes M4 and M5 are strongly affected by HPO_4^{2-} ions, which enhance the supersaturation of $Mn(IV)_{soluble}$ and retard its coagulation and precipitation as MnO_2.

From the experimental fact that the oscillatory composition of the minimal permanganate oscillator has a 1:4 ratio of MnO_4^- to Mn^{2+}, we conclude that the initial composite reaction in the oscillatory process is the production of Mn^{3+} according to eq 6.

$$MnO_4^- + 4Mn^{2+} + 4H_2O = 5Mn^{3+} + 8OH^- \qquad (6)$$

Reaction 6 is equivalent to (M1) + (M2) − 2(M4), if we equate the various forms of Mn(III) and of Mn(IV). In many permanganate oxidation reactions the active oxidant is in fact Mn^{3+} and not MnO_4^-. Trivalent manganese undergoes a rapid disproportionation as in step M4 of the above mechanism, but it can also react with the substrates in the $KMnO_4$–Red reactions.

$KMnO_4$–Red–KH_2PO_4–H_2SO_4 Systems. Permanganate can function as either a one- or two-electron oxidant, depending on the nature of the substrate and the pH of the reaction mixture. In the $KMnO_4$–Red reactions where Red = $S_2O_3^{2-}$, SO_3^{2-}, or S^{2-}, the oxidation of the sulfur species to SO_4^{2-} is fast and complete only in alkaline solution. These proceed with the stoichiometries shown in eqs 7–9.

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^- \qquad (7)$$

$$2MnO_4^- + 3SO_3^{2-} + H_2O \rightarrow 2MnO_2 + 3SO_4^{2-} + 2OH^- \qquad (8)$$

$$8MnO_4^- + 3S^{2-} + 4H_2O \rightarrow 8MnO_2 + 3SO_4^{2-} + 8OH^- \qquad (9)$$

In neutral or weakly acidic media the reactions slow down with decreasing pH and they deviate to some extent from the stoichiometry of eqs 7–9. In neutral solution, Dobbin[18] has shown that eq 7 becomes incomplete and only $^6/_7$ of the total sulfur is converted to SO_4^{2-}; $^1/_7$ goes to $S_4O_6^{2-}$, according to

$$2MnO_4^- + 6S_2O_3^{2-} \rightarrow 2MnO_2 + 3S_4O_6^{2-} + 8OH^- \qquad (10)$$

When the reductant is SO_3^{2-}, the byproduct is $S_2O_6^{2-}$, indicating that both one- and two-electron reaction pathways can exist for this reaction.[19] The one-electron route can be written as

$$2MnO_4^- + 6SO_3^{2-} + 4H_2O \rightarrow 2MnO_2 + 3S_2O_6^{2-} + 8OH^- \qquad (11)$$

Reaction between MnO_4^- and S^{2-} can lead to sulfur and tetrathionate as well as to the major product SO_4^{2-}.[20] Under the conditions where these reactions show oscillation, all the MnO_4^- is converted to MnO_2 whether a unique or a mixed stoichiometry prevails.

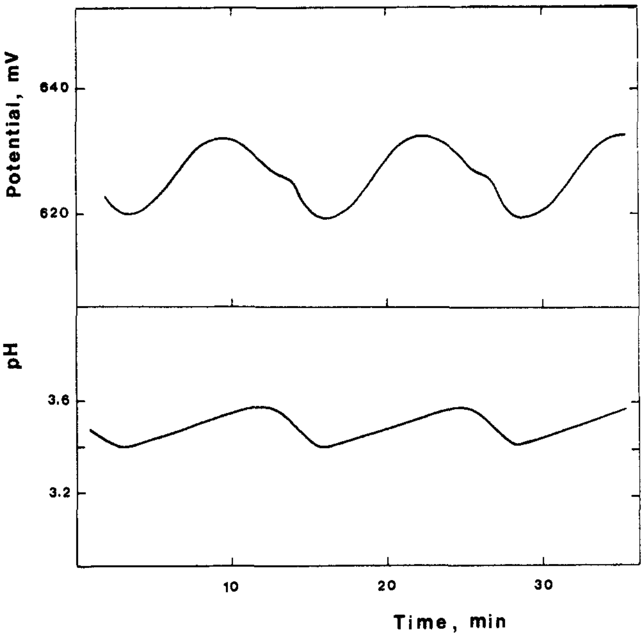

Figure 8. Oscillatory Pt potential and pH in the $KMnO_4$–Na_2S reaction. $[KMnO_4]_0 = 2 \times 10^{-4}$ M, $[Na_2S]_0 = 1.87 \times 10^{-4}$ M, $[KH_2PO_4]_0 = 1.5 \times 10^{-3}$ M, $[H_2SO_4]_0 = 2.5 \times 10^{-4}$ M, $k_0 = 0.011\ s^{-1}$, $T = 25$ °C.

The manganese dioxide can be formed in an oscillatory fashion if its production rate in eqs 7–11 is appropriate. A medium with a pH of about 3.2–3.7 seems to be optimal for the oscillatory oxidation of sulfur species. The chemistry of the individual reactions is very different when Mn^{2+} ions or sulfur ions react with MnO_4^-. Nevertheless, the overall oscillatory mechanisms must be very similar. In each case MnO_2 builds up in a heterogeneous autocatalysis in which the colloid offers its surface for encounter of the reagents; then the autocatalytic species is removed in a linear process by the flow and/or by reaction with the substrate. We suggest that the Guyard reaction represents the core oscillatory system, and the $KMnO_4$–Red oscillators are modifications of this core rather than fundamentally different systems.

The oscillatory mechanism described above is easily extended to the two permanganate oscillators discovered earlier by Nagy and Treindl[2,3] and perhaps also to the $KMnO_4$–KNO_2 system of Morita et al.[4] These oscillators, however, may have some special characteristics not found in our systems. They show bistability between two steady states and one oscillatory state, tristability,[21] birhythmicity, and color oscillations between violet and pink. No MnO_2 precipitate is reported in the $KMnO_4$–H_2O_2 and $KMnO_4$–KNO_2 systems. It is also surprising that the amplitude of the $KMnO_4$–KNO_2 oscillator[4] is more than 400 mV in the Pt potential, even though the initial $KMnO_4$ and Red concentrations are approximately the same as employed in our studies where the oscillatory amplitudes are typically less than 100 mV. Our efforts to reproduce the reported oscillations in the $KMnO_4$–KNO_2–$HCOOH$–CH_3OH system have been unsuccessful to date.

Despite these differences between the oscillators reported in this work and in earlier experiments, it is highly probable that their oscillatory behavior has a common root. The H_2O_2 and KNO_2 systems oscillate at the same pH as the sulfur systems, and this pH permits the reduction of MnO_4^- to take place only via eqs 3 and 4. We may expect the discovery of many more permanganate oscillators as the minimal permanganate system and its relationship to other $KMnO_4$–Red systems comes to be better understood.

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