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Identification of Colloidal Mn(IV) in Permanganate Oscillating Reactions

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Abstract: The responses of permanganate oscillating chemical reactions to factors that govern colloidal stability are examined. Various electrolytes are able to suppress oscillation in the MnO_4^-–Mn^{2+}–$H_2PO_4^-$ and MnO_4^-–H_2O_2–$H_2PO_4^-$ systems, with the strength of the effect depending predominantly on the concentration, charge, and radius of the cation. The hydrophilic colloid gum arabic protects the oscillator against the influence of electrolytes, and the first permanganate oscillator without dihydrogen phosphate, arsenate, or vanadate ions has been designed (MnO_4^- + H_2O_2 + gum arabic). These results identify the central role of colloidal Mn(IV) in these oscillators.

The expansive family of systematically designed chemical oscillators based on the transition metal manganese[1-4] is comprised of reactions consisting either of oxidations by permanganate ion in the presence of a stabilizer[1-3] or of the reduction of periodate ion by manganous ion[4] (Table I) carried out in a continuous-flow stirred tank reactor (CSTR). The primary focus of oscillatory behavior in the permanganate systems is the activity of a Mn(IV) intermediate,[1-3] which must be stabilized and removed from solution at appropriate rates for oscillation to occur. The exact chemical nature of this intermediate remains an unresolved issue. Mn(IV) species have appeared in many chemical systems and have been assigned identities ranging from a colloidal form of hydrous manganese dioxide[5] that can be stabilized by the protective hydrophilic colloid gum arabic (GA)[6,7] or by the adsorption of phosphate ions onto its surface,[8,9] to a Mn(IV)–phosphate complex,[10] H_2MnO_3,[11] ($H_2MnO_4^{2-}$),[12] or dimeric Mn(IV) as either a μ_2-oxo- or a μ_2-hydroxo-bridged dinuclear phosphato complex.[13] The periodic precipitation of MnO_2 during the oscillations and the absolute requirement of oscillation on dihydrogen phosphate, arsenate, or vanadate ions, which are known to stabilize Mn(IV) against flocculation and to adsorb onto MnO_2, suggest that the Mn(IV) intermediate participating in the permanganate oscillators is in the form of a soluble colloid.

Table I. The Family of 29 Manganese Oscillating Reactions[a]

oxidant	reductant	stabilizers
permanganate (MnO_4^-)	Mn^{2+}	P, As, V, GA
	H_2O_2	P, As, GA
	AsO_3^{3-}	P, As, none
	$S_2O_3^{2-}$	P, As
	S^{2-}	P
	SO_3^{2-}	P, As
	SCN^-	P, As
	$(H_2N)_2CS$	P, As
	ascorbic acid	P, As
	NH_3OH^+	P, As
	$S_2O_4^{2-}$	P, As
	NO_2^-	As
periodate (IO_4^-)	Mn^{2+}	IO_4^-(xs), P, As

[a] P, As, and V denote $H_2PO_4^-$, $H_2AsO_4^-$, and $H_2VO_4^-$, respectively.

Species-selective electrodes, spectrophotometry, or chemical methods can detect intermediates contributing to the kinetics of some oscillators, thereby yielding insight into the chemical mechanism of the observed behavior. For example, oscillation in the minimal manganese oscillator[1] (the MMO is composed of MnO_4^-–Mn^{2+}–$H_2PO_4^-$) is completely inhibited by pyrophosphate ions ($P_2O_7^{4-}$) as a result of the rapid formation of the cherry-red $P_2O_7^{4-}$–Mn^{3+} complex,[14] signifying that Mn^{3+} plays a role in producing the oscillations. The colloidal nature of Mn(IV) in the permanganate oscillators can be experimentally detected[15] by observing the effects of coagulants or of deflocculants on these systems. A "minimal" oscillator, that system comprised of the fewest number of chemical species essential for oscillation to occur,[16] is the key to understanding the dynamical behavior for an entire family of oscillators, and so the effects of GA and electrolytes are tested on the MMO. The MnO_4^-–H_2O_2 oscillator functions at lower pH (<3.0) and lower stabilizer concentrations than the remaining permanganate systems,[3] and constant pH can be maintained in this system without introducing additional species to replace the vital role of phosphate ions as a pH buffer.[1] Oscillatory behavior in the MnO_4^-–H_2O_2 reaction and in the MMO is enhanced by the protective action of GA or suppressed by any from an array of electrolytes of various sizes and charges. GA is an effective stabilizer that induces oscillation in the MnO_4^-–H_2O_2 system devoid of a stabilizing oxyanion ($H_2PO_4^-$,

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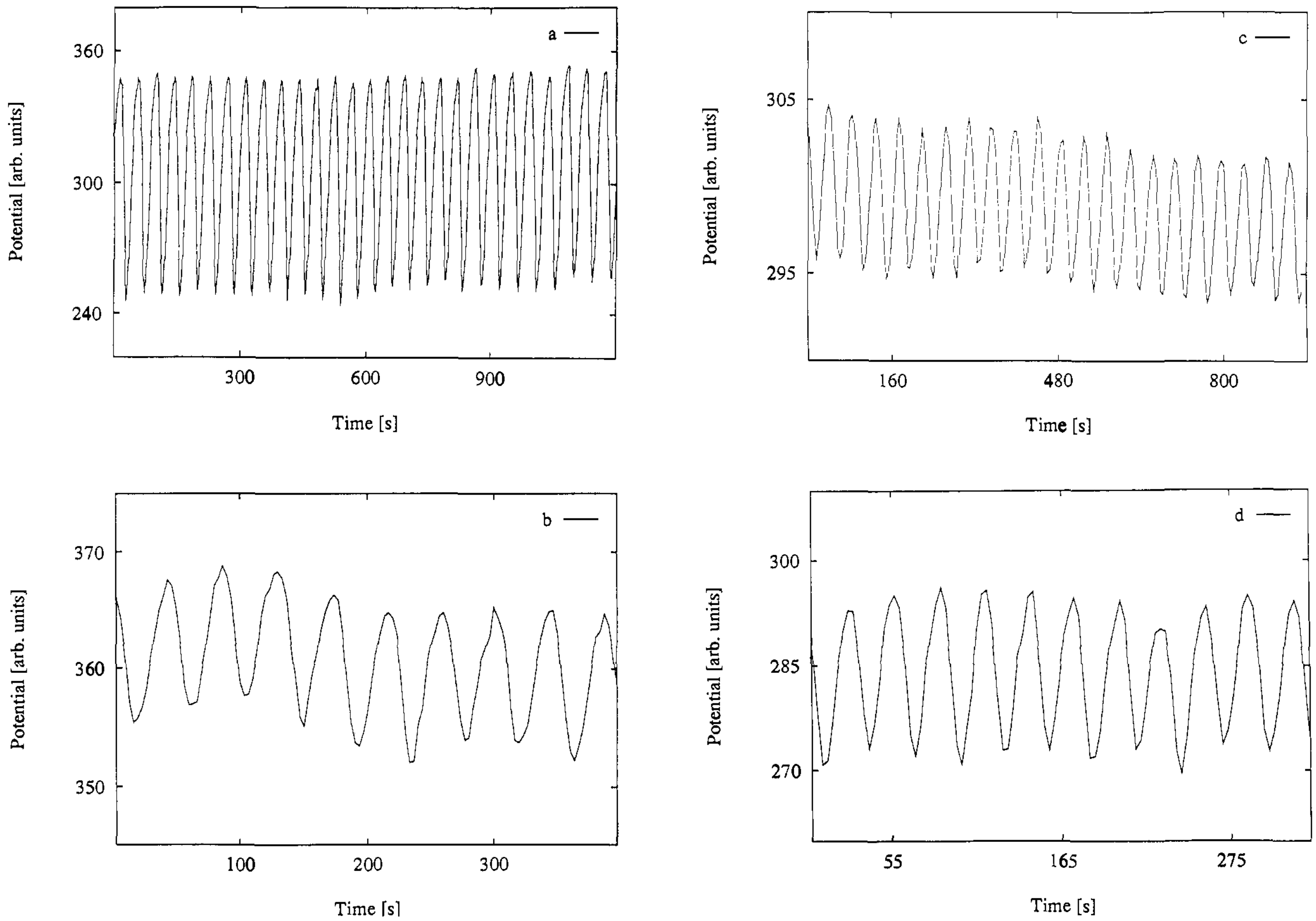

Figure 1. Oscillations in the $KMnO_4$–H_2O_2–GA system with (a) no ions added, (b) 2.4×10^{-3} M $MgCl_2$, (c) 8.7×10^{-3} M KCl, and (d) 1.0×10^{-3} M $MnSO_4$ (see footnote in Table III for experimental conditions).

$H_2AsO_4^-$, or $H_2VO_4^-$). These results confirm the role of colloidal Mn(IV) in the permanganate oscillators.

Experimental Section

Stock solutions of GA (Sigma) and H_2O_2 (Merck) were prepared from analytical grade chemicals every 1–3 days as necessary. Flow experiments were carried out with use of a piston driven syringe pump[17] to regulate the flow of solution into the CSTR (3.8 cm^3 volume) equipped with a stirring bar. A redox electrode consisting of a Pt wire with a Ag/AgCl/KCl internal reference (Ingold) was used to monitor the oscillations. The syringes, tubing, and CSTR were thermostated at $T = 22.2$ °C, and the pH was measured from mixing the reagents in a batch reaction. The experimental conditions were selected from the oscillatory domains characterizing the phosphate-stabilized MnO_4^-–H_2O_2 system[3,18] and the MMO.[1] Simple periodicity is the only oscillatory behavior observed thus far in the manganese systems,[1-4] and outside of the oscillatory regime only stationary state behavior is observed.[1-4]

Results

The addition of a protective colloid or of electrolytes significantly influences the oscillatory behavior in the permanganate systems. These results, segregated according to which reductant was used, are described below and reveal the activity of a colloid in these oscillators.

Table II. Oscillatory Concentrations Range of GA in the MnO_4^-–H_2O_2 System

$[H_2O_2]_0$, $\times 10^4$ M	$[GA]_0$, $\times 10^7$ M	pH	behavior
9.1	1.0	2.8	oscillatory (= OS)
9.3	1.0	2.6	nonoscillatory (= SS)
9.1 or 9.3	2.5	2.7	OS
9.1 or 9.3	5.0	2.6	OS
9.1 or 9.3	7.0	2.7	SS

Permanganate–Hydrogen Peroxide–Gum Arabic Oscillator. The dynamical behavior in the MnO_4^-–H_2O_2–GA system is similar to that seen in the phosphate-stabilized system at identical experimental conditions[3,18] (Figure 1a). Simple oscillations in redox potential are observed with accompanying pink to brown color oscillations. Oscillation in the MnO_4^-–H_2O_2–GA system was examined at the input concentration ratio of $\{[H_2O_2]_0/[MnO_4^-]_0\} \approx 2.3$ corresponding to the permanganate ion concentration range of 2.0–4.0×10^{-4} M, the flow rate range of 0.11–1.30×10^{-3} s^{-1}, and solution pH between 2.6 and 2.9.

The oscillatory range of GA concentration is given in Table II for two different concentrations of H_2O_2. Oscillations in the MnO_4^-–H_2O_2–GA system occur at a much lower stabilizer concentration and are more resistant to the effects of electrolytes than oscillations in the MnO_4^-–H_2O_2–$H_2PO_4^-$ system, which are inhibited by 1.0×10^{-3} M KCl or NaCl. The lifetime of the yellow-brown Mn(IV) intermediate produced in the batch (closed) reaction of permanganate and hydrogen peroxide at oscillatory conditions is suspended significantly longer in the presence of GA (12 min) than in phosphate (5 min) or in the absence of stabilizer (2 min). Adding electrolytes to reaction mixtures containing either stabilizer shortens the duration of the yellow-brown state and hastens the formation of clear Mn(II), the color of the batch reaction. These effects must likewise occur in the reaction in flow conditions and be the manner in which they

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Table III. Effects of Electrolytes on the MnO_4^-–H_2O_2–GA Oscillator[a]

electrolyte	oscillatory concn, ×10^2 M	pH	inhibitory concn, ×10^2 M	pH
chlorides				
NaCl	5.7	2.8	8.6	2.9
KCl	0.87	2.9	1.7	2.9
$MgCl_2$	0.24	2.7	0.48	2.7
$CaCl_2$	0.07	2.7	0.16	2.7
nitrates				
$NaNO_3$	5.7	2.7	8.6	2.7
KNO_3	0.87	2.7	1.7	2.7
$Ca(NO_3)_2$	0.07	2.7	0.16	2.7
$Pb(NO_3)_2$			1.2×10^{-4}	2.7
sulfates				
Na_2SO_4	0.60	2.9	1.5	3.0
K_2SO_4	0.31	2.8	0.64	2.8
$MgSO_4$	0.16	2.8	0.31	2.9
$Al_2(SO_4)_3$	0.003	2.7	0.032	2.7
$MnSO_4$	0.10	2.8	0.14	2.8
others				
KH_2PO_4	0.019	2.7	0.073	2.7
K_2CrO_4			0.44	2.7
$C_8H_5KO_4$			0.10	2.7

[a] $[KMnO_4]_0 = 4 \times 10^{-4}$ M, $[H_2O_2]_0 = 9.3 \times 10^{-4}$ M, $[GA]_0 = 5 \times 10^{-7}$ M, $k_0 = 5.1 \times 10^{-3}$ s^{-1}.

impact the oscillatory behavior. The slow reaction between permanganate and GA does not participate to any appreciable extent in the observed dynamics.

Compiled in Table III are the results of adding a series of chlorides, nitrates, and sulfates to the MnO_4^-–H_2O_2–GA oscillator. The amplitude of oscillation decreases (Figure 1b,c) in the presence of electrolytes. Oscillation occurs at or below the electrolyte concentration corresponding to the designated oscillatory concentration and is inhibited by concentrations equal to or greater than the inhibitory concentration. The lower inhibitory concentration of KCl compared to the oscillatory concentration of NaCl indicates that the colloid is more sensitive to destabilization by cations than anions. For each class of anion, oscillations are more potently suppressed by cations with greater charge and cations of larger radii according to the following sequence of descending inhibitory strength, which parallels the Hofmeister series of flocculation efficiency:[15d] $Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+$. Oscillation is not suppressed more effectively by Mn^{2+} than by the smaller Mg^{2+} due to the catalytic activity of manganese(II),[19] which increases the oscillatory frequency (Figure 1d). The adsorption of sulfate onto Mn(IV)[20] may produce a less stable colloid and account for the stronger inhibitory effect of sulfates than salts containing monovalent anions. Oscillation is suppressed by Pb^{2+}, as well as by the pH buffer potassium phthalate ($C_8H_5KO_4$). Despite functioning as a stabilizer in the MMO, chromate eliminates oscillations due to the formation of a blue chromate–hydrogen peroxide complex.[21] Sodium caprylate or sodium dodecyl sulfate concentrations below 10^{-4} M do not affect the dynamic behavior and are unable to replace phosphate as stabilizers. Oscillations occur with the ionic strength as large as $I = 0.057$, and the inhibition of oscillations at lower I results not from the influence of primary or secondary salt effects on the rate constants but rather by the loss of colloidal stability induced by the electrolytes.

Vigorous stirring is a mechanical means of inducing coagulation of colloidal particles that markedly destabilizes the colloidal state in batch conditions. No significant effects on the dynamical behavior are observed in the MnO_4^-–H_2O_2–GA system with changes in the stirring rate from 743 to 1033 rpm (Table IV) despite 8.0×10^{-3} M KCl being introduced into the system to further destabilize the colloid. These changes in stirring rate do not induce coagulation of colloidal Mn(IV) to the extent of perturbing the system from its oscillatory regime. Mixing imperfections[22] become pronounced at a stirring rate 420 rpm, and oscillations are no longer observable due to the nonuniformities[23] arising in the CSTR from the weak stirring of the reaction mixture.

Table IV. Stirring Rate Effects on the MnO_4^-–H_2O_2–GA Oscillator

$[H_2O_2]_0$, ×10^4 M	$[GA]_0$, ×10^7 M	pH	stirring rates (rpm) 1033	840	743	420
9.1	2.5	2.3	OS	OS	OS	SS
9.3	2.5	2.6	OS	OS	OS	SS
9.1	5.0	2.6	OS	OS	OS	SS
9.3	5.0	2.8	OS	OS	OS	SS

Table V. Effects of Electrolytes on the MMO[a]

electrolyte	concn, ×10^3 M	flow rate, ×10^2 s^{-1} 0.38	1.16
none	0	OS	OS
NaCl	5.0	OS	OS
NaCl	15	OS	SS
$MgCl_2$	0.05	OS	SS
$MgCl_2$	0.10	SS	SS
$Al_2(SO_4)_3$	0.01	SS	SS

[a] $[KMnO_4]_0 = 9 \times 10^{-5}$ M, $[MnSO_4]_0 = 2.1 \times 10^{-4}$ M, $[NaH_2PO_4]_0 = 5 \times 10^{-4}$ M.

Minimal Manganese Oscillator. Responses of the MMO to the addition of electrolytes or of GA parallel those observed with the MnO_4^-–H_2O_2 system (Table V); divalent Mg^{2+} suppresses oscillation more potently than singly charged Na^+, however, the rapid precipitation of white, highly insoluble $Al_2(PO_4)_3$ prevents the flocculation efficiency of Al^{3+} from being determined. Replacing phosphate in the MMO necessitates finding replacements for both the stabilizer and the buffer functions of phosphate.[1] Although the MMO does not oscillate at phosphate concentrations below 5×10^{-4} M, a composition containing 2×10^{-4} M phosphate shows oscillations when both GA (7.1×10^{-6} M) and Mg^{2+} (2.5×10^{-4} M) are present in concentrations that individually suppress oscillation. Adding phthalate ions to replace phosphate ions and buffer the pH at 6.8 is unsuccessful in yielding an oscillatory composition due to the inhibitory effect of phthalate ions on oscillation (Table III). The yellow-brown Mn(IV) produced in the batch reaction of MnO_4^-–Mn^{2+} is also more stable against precipitation as MnO_2 in the presence of GA (120 min) than phosphate (15 min).

Discussion

Chemical oscillation in the MnO_4^-–H_2O_2–GA system serves as an indicator of the colloidal nature of the Mn(IV) intermediate. These results are consistent with batch studies of oxidations by permanganate that have identified a colloidal form of Mn(IV).[6,7,9] The closed reaction of $MnO_4^- + S_2O_3^{2-}$ without phosphate[7] produced a clear solution that precipitated MnO_2 when stirred in the presence of electrolytes in a process that was retarded by GA. An investigation of the kinetics of the Guyard reaction without phosphate[6] showed the autocatalytic activity of the Mn(IV) sol was diminished by vigorously stirring the solution or by adding GA to form a protective layer enveloping the surface of the colloidal particles. Presently, a dependence of chemical oscillation on colloidal stability has been found by extending these same tests of colloidal principles to the permanganate oscillators in flow conditions in a CSTR. Whereas the addition of appropriate concentrations of the deflocculants GA and phosphate ion

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stabilizes the colloidal Mn(IV) autocatalyst for an optimal duration and promotes the evolution of oscillation, electrolytes accelerate the flocculation of the autocatalyst and suppress oscillation.

Expanding the pool of components from which manganese oscillators can be constructed benefits our aim of designing more elaborate manganese systems. First, designing an oscillator by combining both the permanganate-reductant-stabilizer[1-3] and the manganese(II)–periodate[4] classes of oscillators might yield a system exhibiting more complex dynamical behavior beyond simple oscillations. Second, finding oscillation in flow conditions with the synthetic self-replicating system permanganate–octanol–octanoate,[24] in which permanganate oxidizes octanol at the octanoate micelle interface to generate further micelles, would constitute a chemical system exhibiting the principles of self-replication in nonequilibrium conditions in a manner analogous to that occurring in living systems.[25]

Conclusions

Oscillation in the MnO_4^-–H_2O_2–GA system and the inhibitory effects of inert electrolytes on this oscillator confirm the colloidal nature of the Mn(IV) species in these systems, possibly as a colloidal form of MnO_2. There is a critical dependence of oscillation on the stability of the colloidal Mn(IV) autocatalyst, irrespective of whether $H_2PO_4^-$, $H_2AsO_4^-$, $H_2VO_4^-$, or GA acts as the stabilizer. The identical trends of the MMO and the MnO_4^-–H_2O_2 oscillator in response to GA and inert electrolytes therefore suggest that colloidal Mn(IV) has a common function in the remaining manganese oscillators,[1-4] These results yield insight into the chemical mechanism of oscillation in the permanganate systems.

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