well depth ϵ clearly signifies a steady decrease from $TMA\cdot SO_2$ to $HCN\cdot SO_2$. Nevertheless, the absolute values for ϵ are certainly unreliable, at least for the stronger complexes. This procedure underestimates ΔE_{diss} for $TMA\cdot SO_2$ by 5.2 kcal/mol.[1]

As a final measure of the relative stabilities of the two different conformations of pyridine relative to the SO_2 plane (Figure 1) as well as the relative strengths of the adducts from $TMA\cdot SO_2$ to $HCN\cdot SO_2$, ab initio calculations (HF/SCF) were examined. A growing body of work indicates that the relative stabilities of various conformations can be estimated at the HF level although structural details and binding energies will be unreliable in an absolute sense. The structural parameters for the two different conformers (Figure 1) were optimized by using GAUSSIAN86[34] with three different basis sets. The results are given in Table VII. Indeed, the ab initio results favor the experimental conformation by 2–2.5 kcal/mol. Simple electrostatic energy calculations were also carried out for the two conformations using the distributed multipole model of Buckingham and Fowler.[35] The multipole moments for the atoms in pyridine and SO_2 were obtained from the literature.[35,36] The electrostatic interaction energy was calculated at the experimental N···S separation for the two conformations; this also favored the experimental conformation by about 2 kcal/mol. This conformation is consistent with the quadrupole moments for SO_2[37] and pyridine,[38] providing a simple rationale for the observed result.

The optimized calculations at the HF/3-21G* level for $TMA\cdot SO_2$, $DMA\cdot SO_2$, $Py\cdot SO_2$, and $HCN\cdot SO_2$ can also be compared. The calculated ΔE_{diss} for this series varies in a regular fashion (kcal/mol): 17.2, 16.6, 12.6, and 3.34 (Table VI).

We conclude from this evidence that this series represents a transition from a complex with a modest charge-transfer interaction ($TMA\cdot SO_2$) to one with virtually none in $HCN\cdot SO_2$. The dissociation energies decrease from 9.1 kcal/mol (experimental)[8] in $TMA\cdot SO_2$ to roughly 1–3 kcal/mol in $HCN\cdot SO_2$[29] while *d*(N···S) increases by 0.7–0.8 Å. Thus, relatively small changes in the stabilities and the amounts of charge transfer have rather pronounced geometric effects for these complexes.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The research was also supported by the National Science Foundation, Washington, DC.

Registry No. $C_5H_5N\cdot SO_2$, 21326-53-4; $C_5H_5{}^{15}N\cdot SO_2$, 135639-37-1; $C_5D_5N\cdot SO_2$, 135639-38-2; $C_5H_5N\cdot S^{18}O_2$, 135639-39-3; $C_5H_5N\cdot {}^{34}SO_2$, 135639-40-6.

Supplementary Material Available: Tables S1–S6 listing observed and calculated transition frequencies and Stark effect data (6 pages). Ordering information is given on any current masthead page.

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[34] Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, S. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. *GAUSSIAN86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1986.

[35] (a) Buckingham, A. D.; Fowler, P. W. *J. Chem. Phys.* **1983**, *79*, 6426. (b) Buckingham, A. D.; Fowler, P. W. *Can. J. Chem.* **1985**, *63*, 1918.

[36] Price, S. L.; Stone, A. J. *Chem. Phys. Lett.* **1983**, *98* (5), 419.

[37] Pochan, J. M.; Stone, R. G.; Flygare, W. H. *J. Chem. Phys.* **1969**, *51*, 4278.

[38] Harver, E.; Sutter, D. H. *Z. Naturforsch.* **1976**, *31a*, 266.

[39] Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Halsted Press: New York, 1981.

[40] (a) Staley, R. H.; Taagepera, M.; Henderson, W. G.; Koppel, I.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 326. (b) Staley, R. H.; Kleckner, J. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 2081. (c) Kollman, P.; Rothenberg, S. *J. Am. Chem. Soc.* **1977**, *99*, 1333.

Newly Designed Permanganate-Reductant Chemical Oscillators[1]

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Abstract: The subfamily of manganese oscillating chemical reactions containing permanganate as oxidant, plus a reductant, and phosphate to stabilize intermediate Mn oxidation states has been expanded in two ways. The "minimal" manganese oscillator, $MnO_4^- + Mn^{2+} + H_2PO_4^-$, and several of its oscillatory derivatives give oscillation when either arsenate or vanadate replaces phosphate. Oscillatory behavior in a flow reactor has also been found for seven new reductants: arsenite, thiocyanate, thiourea, ascorbic acid, hydroxylamine, dithionite, and nitrite. A two-component permanganate oscillator is constructed using arsenite as the reductant, in which the stabilizing arsenate is generated as a reaction product. Our results yield insight into the roles of the reductant and the stabilizer in promoting oscillation.

The systematic design of chemical oscillators, after having initially focused on halogen chemistry, has progressed through other regions of the periodic table and now includes a family of oscillating reactions based on the chemistry of the transition metal manganese.[2-6] The oscillatory core is the Guyard reaction ($MnO_4^- + Mn^{2+}$)[7] with the addition of dihydrogen phosphate (hereafter referred to as phosphate) performed under flow conditions in a continuously stirred tank reactor (CSTR). This family of oscillators is divided into two subfamilies; the first consists of permanganate and a reductant, and the second consists of manganese(II) and an oxidant.

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[1] Part 74 in the series: Systematic Design of Chemical Oscillators. Part 73: Wang, R. T.; Rábai, G.; Kustin, K. *Int. J. Chem. Kinet.*, in press.

[2] Nagy, A.; Treindl, L. *Nature* **1986**, *320*, 344.

[3] Fazekas, T.; Mrakavova, M.; Nagy, A.; Olexova, A.; Treindl, L. *React. Kinet. Catal. Lett.* **1990**, *42*, 181.

[4] Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1989**, *111*, 8543.

[5] Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 1812.

[6] Orbán, M.; Lengyel, I.; Epstein, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 1978.

[7] Guyard, G. *Bull. Soc. Chim. Fr.* **1864**, *1*, 89.

0002-7863/91/1513-7484$02.50/0

Table I. Effects of Anions on the Behavior of the MnO_4^- – Mn^{2+} Reactions[a]

anion	concn, $\times 10^3$ M	behavior (SS = steady state)	pH	flow rate, $\times 10^3$ s^{-1}
$H_2PO_4^-$ or HPO_4^{2-}	0.7–3	oscillates	6.0–8.0	8–48
$H_2AsO_4^-$ or $HAsO_4^{2-}$	0.5–2.5	oscillates	7.4–8.5	4–15
HVO_4^{2-}	1.0	oscillates	8.8	4
CrO_4^{2-}	0.5–1.5	brown SS	6.9–7.9	3–17
+ $HAsO_4^{2-}$	0.25	oscillates		
HCO_3^-	1.0	brown SS	6.4–7.1	1–15
+ $HAsO_4^{2-}$	0.5	oscillates		
WO_4^{2-}	1.0	orange/pink SS	6.6–10.8	1–15
+ $H_2PO_4^-$	1.0	no oscillation		
$Mo_7O_{24}^{6-}$	1.0	yellow SS	5.4–9.4	1–15
+ $H_2PO_4^-$	1.0	no oscillation		
$H_2P_2O_7^{2-}$	0.5	pink SS	6.8	6
+ HPO_4^{2-}	1.0	no oscillation		
H_3BO_3	1.0	brown SS	4.5–7.9	3–18
IO_4^-	1.0	red-brown SS	4.5–7.4	3–18
SO_4^{2-}	1.0	brown SS	6.0–8.0	1–15
ClO_4^-	1.0	brown SS	6.7	1–15

[a] $[KMnO_4]_0 = 9 \times 10^{-5}$ M, $[MnSO_4 \cdot 2H_2O]_0 = 2.1 \times 10^{-4}$ M.

The design of a chemical oscillator containing manganese in more than a simple catalytic role began with studies of the MnO_4^-–$H_2C_2O_4$ autocatalytic reaction[8,9] and the Ag^+-catalyzed MnO_4^-–H_2O_2–$S_2O_8^{2-}$ system.[10] In these systems, only bistability without oscillation was found. With the introduction of phosphoric acid to stabilize intermediates formed during the reaction, sustained oscillation was discovered in the MnO_4^-–H_2O_2 system,[2] which stimulated further investigations of manganese chemistry as a source of new chemical oscillators.

Additional permanganate–reductant–phosphoric acid oscillators were subsequently reported and probed without detailed consideration of the underlying chemical mechanism involved in the process.[3] The design and discovery of the oscillatory Guyard–phosphate system[4] not only marked the first systematically designed manganese oscillator, but also constituted the minimal manganese oscillator (MMO). A minimal member of a family of oscillators is defined[11] as that system in which the reactants comprise the smallest number of chemical species essential for producing oscillations. These species are common to all members of that family of oscillators as either reactants, intermediates, or products. Derivatives of the MMO have utilized permanganate reductions by sulfur-containing compounds[5] or the manganous ion oxidation by periodate.[6] The presence of phosphate was determined to be vital for the occurrence of oscillation in all of the systems containing permanganate and a reductant.

The subfamily of permanganate oscillators is expanded here by finding alternatives to phosphate for the stabilizing agent and by discovering new systems that employ different reductants. Oxyanions of various sizes and charges have been tested for their ability to replace phosphate in the MMO and some derivative systems. Similarly, new inorganic and organic reductants have been sought to replace Mn^{2+}, with phosphate or a comparable substitute present. In total, we have expanded the subfamily of permanganate chemical oscillators by 19 new members based on variations of the MMO.

Experimental Section

Materials. All chemicals used in these experiments were of analytical grade and required no further purification before use. All compounds, except for arsenite, were dissolved in distilled water to prepare stock solutions. As_2O_3 was heated in base until dissolved, then acidified with dilute sulfuric acid. Stock solutions were typically 10^{-1} to 10^{-2} M, diluted to roughly 10^{-3} to 10^{-5} M immediately before each experiment. Stock solutions were freshly prepared every 48 h, or as necessary.

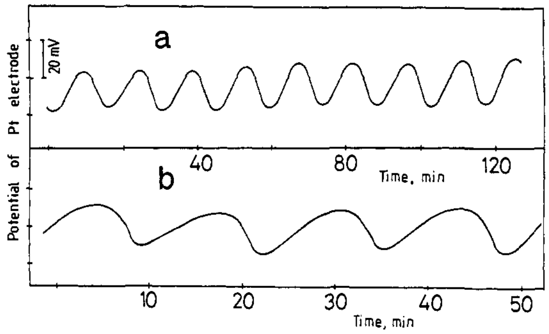

Figure 1. Oscillations with different stabilizers in the Guyard reaction: (a) $[HAsO_4^{2-}]_0 = 1.2 \times 10^{-3}$ M and $k_0 = 0.0080$ s^{-1}. (b) $[HVO_4^{2-}]_0 = 1 \times 10^{-3}$ M and $k_0 = 0.0038$ s^{-1}. In both cases, $[MnO_4^-]_0 = 9 \times 10^{-5}$ M and $[Mn^{2+}]_0 = 2.1 \times 10^{-4}$ M.

Methods. All experiments were carried out under flow conditions in a thermostated glass CSTR of volume 20.5 cm^3 equipped with a magnetic stirring bar and electrodes inserted through holes in the plastic cap. The potential of a Pt electrode (versus $Hg|Hg_2SO_4$, K_2SO_4 reference electrode) and the pH (Radelkis (Hungary) or Aldrich combination calomel-pH electrode connected to an Orion 501 pH meter) were recorded. No effects on the oscillatory behavior were observed with changes in the stirring rate. Peristaltic pumps (Sage Model 375A) were used with either three or four inlet flows, and the flow rate (as reciprocal residence time) was varied from about 0.0002 to 0.0180 s^{-1}.

Results

The experiments can be classified into groups based on the component for which replacements were sought. The first group contains substitutes for the stabilizing agent in the MMO and some derivative systems; the second group consists of the new reductants with appropriate stabilizers. The latter group may be divided into subgroups according to the success of the reductant in producing oscillatory behavior.

New Permanganate Oscillators: Alternative Stabilizers. The effects of the many anions tested to replace phosphate in the MnO_4^-–Mn^{2+}–$H_2PO_4^-$ oscillator are summarized in Table I. Only two oxyanions, hydrogen arsenate and hydrogen orthovanadate (hereafter referred to as arsenate and vanadate, respectively), are capable of fully replacing phosphate and producing oscillations in the MMO (Figure 1). Arsenate produces a slightly higher pH and a darker brown color of the solution and the precipitate than does phosphate. Although it is effective at slightly lower concentrations and flow rates (Figure 2), arsenate is completely interchangeable with phosphate in all members of the manganese family of oscillators. Vanadate produces a sandy brown colored solution that oscillates at a significantly higher pH. Solution speciation, however, prevents systematic replacement of

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(8) Epstein, I. R.; Dateo, C. E.; De Kepper, P.; Kustin, K.; Orbán, M. *Springer Ser. Synerget.* **1981**, *12*, 188.

(9) Reckley, J. S.; Showalter, K. *J. Am. Chem. Soc.* **1981**, *103*, 7012.

(10) De Kepper, P.; Ouyang, Q.; Dulos, E. In *Non-Equilibrium Dynamics in Chemical Systems*; Vidal, C., Pacault, A., Eds.; Springer-Verlag: Berlin, 1984; p 44.

(11) Epstein, I. R.; Orbán, M. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; Wiley: New York, 1985; p 257.

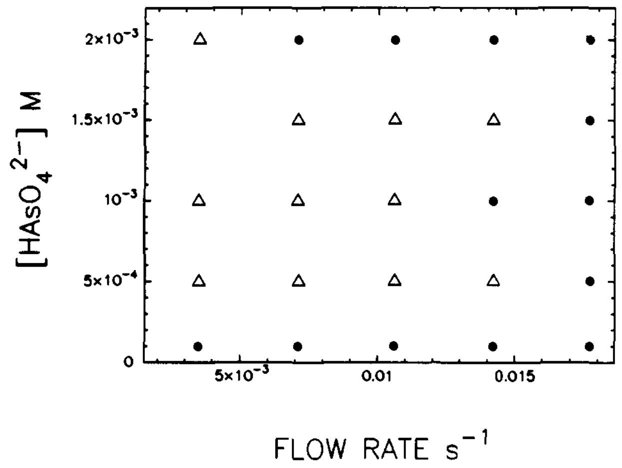

Figure 2. State of MMO at various arsenate concentrations as a function of flow rate. $[MnO_4^-]_0 = 9 \times 10^{-5}$ M and $[Mn^{2+}]_0 = 2.1 \times 10^{-4}$ M. △ = oscillatory state, ● = steady state.

phosphate and arsenate by vanadate in the remaining permanganate oscillators. In the pH range 3–6, vanadate concentrations greater than 10^{-3} M promote the formation of decavanadate isopolyanions, which are not suitable substitutes for phosphate, thereby restricting the range in which vanadate is an effective stabilizer (pH > 8). Substitution with arsenate or vanadate does not require alteration of the concentrations of permanganate or manganous ions in the oscillator. Variations in $[H^+]$ that otherwise would have been detected in the permanganate oscillators are eliminated by the buffering capacity of the stabilizer.

Although none of the remaining metal oxyanions can individually replace phosphate, some of them, in companion roles, can change the oscillatory character of the MMO. Despite showing virtually no effect on the oscillatory behavior of the MMO, chromate ion is able to maintain oscillations when the arsenate concentration is reduced to 1.5×10^{-4} M, below the 2.5×10^{-4} M minimum $[HAsO_4^{2-}]_0$ (the symbol $[\,]_0$ denotes the species inflow concentration divided by the total number of inlet flows) required for oscillation. Conversely, tungstate, pyrophosphate, and molybdate can each suppress oscillations, even when sufficient phosphate or arsenate is present (see Table I). Rapid formation of the cherry-red $P_2O_7^{4-}$–Mn^{3+} complex is well known[12,13] and may be responsible for inhibiting oscillation. The effects of tungstate may also result from its interactions with Mn^{3+} in a manner similar to its role in known tungstate–manganic compounds.[14] Nitrate, perchlorate, carbonate, sulfate, and borate have no apparent effects on the oscillator. Despite acting as a stabilizer of intermediate Mn oxidation states in the oscillatory periodate oxidation of Mn(II),[6] periodate does not induce oscillations in the Guyard reaction.

The previously known MnO_4^-–H_2O_2, $S_2O_3^{2-}$, SO_3^{2-}–$H_nPO_4^{(3-n)-}$ systems all oscillate when arsenate substitutes for phosphate. The most notable among these substituted systems is MnO_4^-–H_2O_2–$HAsO_4^{2-}$, which shows color changes other than those reported for the MnO_4^-–H_2O_2–H_3PO_4 system and which functions at a much lower stabilizer concentration. The phosphoric acid stabilized system was described earlier[2] as showing pink to magenta color changes. In addition to these color oscillations, we found oscillations at higher peroxide concentrations in both the phosphate- and arsenate-stabilized systems from the violet of MnO_4^- to the yellow-brown of manganese(IV) to a colorless solution characteristic of Mn(II). The latter color is the same as in the presence of excess reductant in a batch reaction. Oscillations for the system containing $[MnO_4^-]_0 = 2 \times 10^{-4}$ M and $[H_2O_2]_0 = 4.68 \times 10^{-4}$ M were obtained with $[H_3PO_4]_0 = 1.5 \times 10^{-3}$ M or with $[HAsO_4^{2-}]_0 = 2 \times 10^{-4}$ M. This arsenate concentration, despite being below the minimum needed for oscillation in the MMO (Figure 2), was the greatest with which sustained oscillation could be found in the MnO_4^-–H_2O_2 system. Higher arsenate concentrations inhibit oscillation. Batch experiments suggest that phosphate and arsenate delay the reaction between MnO_4^- and H_2O_2, with arsenate having a more powerful effect. Oscillations in both of these systems occurred only when the pH was maintained between 2.8 and 3.1.

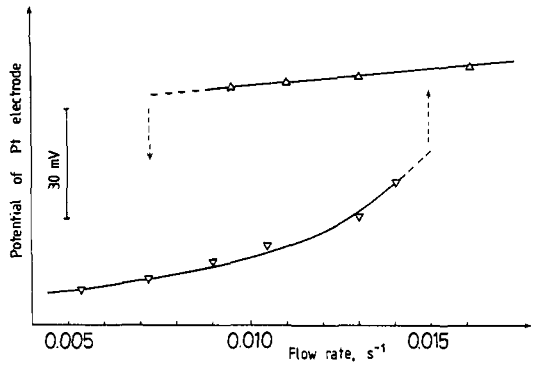

Figure 3. Hysteresis loop showing bistability between two steady states for the composition $[MnO_4^-]_0 = 9 \times 10^{-5}$ M, $[AsO_3^{3-}]_0 = 1.44 \times 10^{-4}$ M, $[HAsO_4^{2-}]_0 = 5 \times 10^{-4}$ M, and $[H_2SO_4]_0 = 2 \times 10^{-4}$ M.

The solution color of the MnO_4^-–$S_2O_3^{2-}$ or SO_3^{2-}–$H_2AsO_4^-$ oscillators is yellow-brown, similar to that produced with phosphate, and precipitate gradually accumulates on the walls of the reactor. Reductant concentrations range from 0.5 (for $S_2O_3^{2-}$) to 0.5–1.6 (for SO_3^{2-}) times that of permanganate. Maintaining the pH between 3.0 and 3.8 is necessary for oscillation to occur. The inflow concentration of the pH regulator, $[H_2SO_4]_0$, is determined by trial and error from the pH resulting at various acid concentrations. Again, arsenate was effective at lower concentrations than phosphate and yielded oscillation in the same span of concentrations as used with the MMO.

New Permanganate Oscillators: Alternative Reductants. A diverse array of reductants, both inorganic and organic, were tested for their ability to produce oscillations with MnO_4^- and a stabilizer. These reductants are classified according to their success in generating oscillating systems.

1. Oscillatory Reductants. The newly found reductants capable of generating sustained oscillation with permanganate and either phosphate or arsenate as the stabilizer are arsenite, thiocyanate, thiourea, ascorbic acid, hydroxylamine, dithionite, and nitrite. Only a single set of conditions for oscillation is determined for each system, because other derivative systems have been thoroughly investigated in previous reports,[5] and similar results are expected for the present derivatives. The oscillatory conditions for the successful substrates are compiled in Table II.

a. Arsenite. Oscillations with arsenite as the reductant differ greatly from those in the thiosulfate systems. Oscillatory behavior occurs at lower flow rates and higher reactant concentrations, with $[AsO_3^{3-}]_0/[MnO_4^-]_0 > 1$. This reductant yields systems exhibiting some of the largest amplitudes (>250 mV) and longest periods (140 min) among the permanganate oscillators. However, like the other derivatives, the systems with arsenite as reductant show the characteristic yellow-brown color with precipitate accumulation in the reactor, require a pH < 3.8, and need a higher ratio of reductant to oxidant concentration when arsenate is the stabilizer. Bistability, which was not found in the MMO or the other derivatives, is observed in the MnO_4^-–AsO_3^{3-}–AsO_4^{3-} system as illustrated by the hysteresis loop in Figure 3. Transitions between the two steady states can be effected by injecting one of the reagents into the reactor.

An oscillator consisting of only two components has also been designed with arsenite as the reductant based on the formation of arsenate as a reaction product. Under certain conditions, sufficient stabilizing arsenate is produced by the oxidation of arsenite, and oscillations are generated without an external input

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[12] Powell, R. T.; Oskin, T.; Ganapathisubramanian, N. *J. Phys. Chem.* **1989**, *93*, 2718.

[13] Adler, S. J.; Noyes, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2036.

[14] Sillén, L. G. *Stability Constants of Metal-Ion Complexes*; The Chemical Society: London, 1971; p 47.

Table II. Oscillatory Conditions for New Reductants

reductant (=Red)	$[Red]_0$, $\times 10^5$ M	$[MnO_4^-]_0$, $\times 10^5$ M	$[H_2PO_4^-]_0$ or $[HAsO_4^{2-}]_0$, $\times 10^4$ M[a]	amplitude, mV	period, min	pH
AsO_3^{3-}	6.5	5	15	50	28	3.4
	24	18	5	230	45	3.8
	63	36	none	110	65	3.1
H_2O_2	47	20	15	16	5	3.1
	47	20	2	18	7.5	2.9
$S_2O_3^{2-}$	12	9	15	70	12	3.4
	4.5	9	5	180	100	3.6
SO_3^{2-}	10	20	15	50	18	3.4
	61	9	8	300	20	2.9
SCN^-	10	10	15	25	20	3.7
	12	9	8	70	35	3.1
$(H_2N)_2CS$	9	9	15	16	10	3.4
	9	9	5	25	6	3.6
ascorbic acid	8	9	15	24	20	3.4
	11	9	8	70	36	3.8
NH_3OH^+	16	20	10	15	20	3.3
	16	20	6	30	30	3.3
$S_2O_4^{2-}$	20	10	10	45	5	3.0
	20	10	5	50	7.5	3.2
NO_2^-	10	10	–	–	–	–
			7	10	3	7.0

[a] First entry is for phosphate stabilizer, second for arsenate.

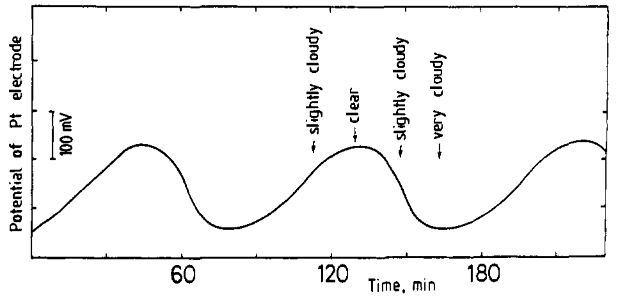

Figure 4. Oscillations in the two-component arsenite–permanganate system. $[MnO_4^-]_0 = 3.6 \times 10^{-4}$ M, $[AsO_3^{3-}]_0 = 6.3 \times 10^{-4}$ M, and $[H_2SO_4]_0 = 1.5 \times 10^{-3}$ M at flow rate $k_0 = 9 \times 10^{-4}$ s^{-1}.

of a stabilizing agent. The permanganate–arsenite system, despite requiring fewer input components than the MMO to oscillate, is not minimal for the entire family of manganese oscillators. Rather, it is a "minimized" version of the MMO with the production of arsenate serving in place of an inflow of stabilizer.

As seen in Figure 4, oscillations in the two-component permanganate–arsenite system have large amplitudes and periods, require high input concentrations of reactants, and occur at low flow rates. Higher reactant concentrations increase the chemical reaction rates and usually require higher flow rates to observe oscillations. The "minimized" system nevertheless oscillates only over a very narrow range of low flow rates with reactant concentrations large enough to produce an adequate amount of stabilizing arsenate. Oscillations require pH < 3.8, and, in contrast to the arsenate-stabilized system, no bistability is observed. An interesting feature observed only in the permanganate–arsenite and permanganate–arsenite–arsenate systems is the periodic formation and disappearance of turbidity that cycles with the decreases and increases in potential, possibly reflecting higher concentrations of stable Mn(IV) colloid formed in the reactor as a result of elevated levels of stabilizing arsenate in these systems.

Oscillatory domains for several systems in permanganate–reductant phase space are shown in Figure 5. The apparent breadth of the oscillatory region for the two-component derivative compared to that of the thiosulfate derivative underscores the sensitivity of the "minimized" system to flow rate. Oscillations occur only over a very narrow range of flow rates, and even small increases in flow rate greatly diminish the area in which oscillation can be found (Figure 5).

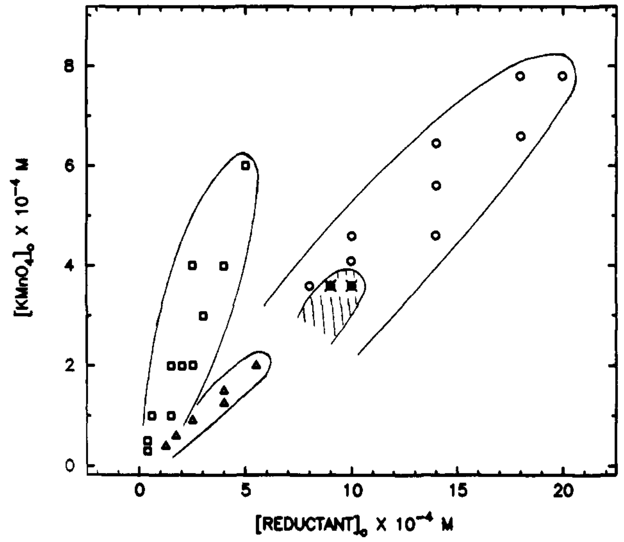

Figure 5. Oscillatory regions in the ($[MnO_4^-]_0$–$[reductant]_0$) plane for the phosphate-stabilized Mn^{2+} (△) and $S_2O_3^{2-}$ (□) systems, as well as for the two-component AsO_3^{3-} (○) system. Oscillations occur for flow rates $0.005 \le k_0 \le 0.020$ s^{-1} in the MMO and $0.004 \le k_0 \le 0.020$ s^{-1} in the thiosulfate system. The oscillatory domain for the "minimized" system at $k_0 = 9.3 \times 10^{-4}$ s^{-1} shrinks to the cross-hatched region at $k_0 = 2.7 \times 10^{-3}$ s^{-1} and is completely eliminated at $k_0 = 6.6 \times 10^{-3}$ s^{-1}.

b. Thiocyanate, Thiourea, L-Ascorbic Acid, and Dithionite. All of the systems involving these reductants oscillate equally well with either phosphate or arsenate as the stabilizing agent. Their pH must be maintained between 3.1 and 3.7, usually with dilute sulfuric acid, to generate sustained oscillations. A yellow-brown precipitate is produced, and, except for slight increases in $[SCN^-]_0$ and $[S_2O_4^{2-}]_0$ in the arsenate-stabilized systems, the oxidant and reductant concentrations are always about 10^{-4} M.

c. Hydroxylamine. In the same concentration range as the above derivatives, the permanganate–hydroxylamine–phosphate oscillator shows periodic visible color changes from the pink of permanganate to the yellow-brown of manganese(IV). Simultaneously increasing both reactant concentrations yields a yellow-brown solution that oscillates at pH ≈ 3.3 in a fashion similar to the other derivative systems. Oscillations show some sensitivity to the manner in which the flow rate is varied. Gradual increments from the highest pump setting to the appropriate flow rate lead to oscillatory behavior, whereas other protocols result in a steady state. The presence of a subcritical Hopf bifurcation with bistability between steady and oscillatory states has been suggested for other systems that show similar sensitivity to the step size in flow rate changes. However, we have no evidence at this time confirming the existence of this phenomenon in the hydroxylamine derivative.

d. Nitrite. The MnO_4^-–NO_2^-–$HAsO_4^{2-}$ system is the only permanganate system other than the MMO that oscillates at neutral pH. Whereas oscillations in the permanganate–manganous–phosphate, arsenate, or vanadate systems occur at pH ≥ 7, the remaining systems containing alternative reductants oscillate only at pH < 3.8. The nitrite system at pH = 7 shows the yellow-brown color typical of permanganate oscillators. At pH ≈ 3.5, however, NO_2^- reduces MnO_4^- to Mn(II) rather than to Mn(IV), the solution becomes colorless, and the system is nonoscillatory.

2. Nonoscillatory Reductants. We were unable to obtain oscillatory behavior with a number of reductants. We describe here our observations.

At pH ≤ 3.8, the reaction between MnO_4^- and some reductants is very fast and proceeds to form Mn(II) rather than Mn(IV) (hydrazine, malic acid, metabisulfite, and ninhydrin). The solution becomes colorless instead of the yellow-brown color characteristic of the oscillatory systems. Chlorite, malonic acid, pyruvate, oxalate, citric acid, L-valine, and methylamine showed almost no reaction with permanganate in the same pH range even when their concentrations were increased several fold. Dimethyl sulfoxide produces a pale brown color when reacted with MnO_4^-, but the color is much fainter than is seen with any of the oscillatory reductants. All of these systems showed little response in potential with large changes in flow rate, and only a single steady state is observed in each case. Increasing the pH above 3.8 induces some of these substrates (hydrazine, malic acid, and ninhydrin) to reduce permanganate to Mn(IV) and form a brown precipitate. Nevertheless, we have not found oscillatory conditions for these reductants. Ferrocyanide, hypophosphite, formic acid, pyrogallol, iodide, vanadyl, diethyldithiocarbamate, and Mohr's salt each reacted with permanganate to produce changes of solution color in the yellow-brown region and show large changes in potential with changes in flow rate without, however, generating oscillations.

Discussion

Arsenate and vanadate are well known to be isomorphous with, to be of similar size as, and to have similar ionization constants as phosphate;[15] their mimicry or ability to be interchanged with phosphate is well known.[15,16] The precise role of these species, all of which presumably act to stabilize some form of Mn(IV), is not well understood. Polissar[17] and Tompkins[18] found that the addition of solid MnO_2 to a Guyard mixture, whose reaction products were some form of Mn(IV), increased the reaction rate and reduced the induction time of the reaction. Furthermore, they found that gum arabic increased the lag time by forming a protective colloid over the surface of the MnO_2. These results imply that surface phenomena are involved in generating autocatalysis.

Recently, several workers have noticed a soluble form of Mn(IV) in solutions containing phosphate. Rayleigh plots have shown that a colloid is present, presumably MnO_2 stabilized by adsorption of phosphate onto its surface.[19] Freeman et al.[20] have shown that phosphate retards flocculation of the soluble Mn(IV) species. Complex formation arising from an undefined Mn(IV)–stabilizer interaction[21] may also give rise to this species. Although it is not certain that the key Mn(IV) species is MnO_2, it is a likely candidate, and so we have looked into the adsorption of phosphate onto MnO_2 for possible insights into the role phosphate plays in the oscillating reactions.

The adsorption of phosphate onto MnO_2 was measured indirectly by Lal, Singh, and Mishra.[22] The disappearance of radioactivity from a phosphate solution containing ^{32}P and MnO_2 obeys the Freundlich isotherm, showing that phosphate does adsorb onto MnO_2. Parida[23] employed titration methods to demonstrate the adsorption of phosphate, arsenate, chromate, and sulfate onto MnO_2. Stronger adsorption is reflected by a larger point of zero charge (pzc) pH, which, for these anions, is 8.85, 8.55, 8.4, and 5.0, respectively. Trivalent anions adsorbed most strongly, followed by divalent anions. Monovalent anions were unable to penetrate the water coordinated to the MnO_2 surface and were not adsorbed. The tri- and divalent anions were proposed to coordinate to the oxide surface either by ligand exchange or by hydrogen bonding to hydroxyl groups present on the oxide surface.

Our results are in agreement with the above analysis. Monovalent anions were completely ineffective in replacing phosphate, and divalent anions were also ineffective for the most part. The maintenance of oscillations by chromate ion in a system deficient in arsenate may reflect the strong adsorption of chromate onto the oxide, as seen by the pzc pH. Apparently, however, this interaction is not quite strong enough for chromate to replace phosphate or arsenate. Vanadate was not tested for adsorption onto MnO_2, but its rapid polymerization at lower pH would present difficulties in the titration method employed.

Conclusion

The interchangeability of a number of reductants and oxyanions with their oscillatory counterparts in the permanganate–reductant–stabilizer systems has been investigated in an attempt to understand better the functions of the individual components in this subfamily of oscillators. We conclude that the activity of Mn(IV), formed by the reduction of permanganate, is the primary focus of the oscillatory behavior. At appropriate rates, Mn(IV) must be formed and removed from solution in order for oscillation to occur. The reductant participates in forming Mn(IV) by reacting with permanganate. Mn(IV) is then stabilized for some optimal duration by certain oxyanions, which thereby regulate the removal rate of the autocatalyst.

Composing many new oscillators from diverse classes of substrates affords insight into the principal role of the reductant. That role can be defined simply as providing a source of Mn(IV) by reacting with MnO_4^-. Conditions may exist to accommodate many more reductants by adjusting some of the parameters (e.g., reagent concentrations and proportions, pH, flow rate, temperature). Although our unsuccessful reductants will not give oscillations in the conditions employed here, we cannot preclude the possibility that conditions may be attainable for which these substrates will yield oscillation. In order to be effective, however, a change in parameters must not perturb the generation or removal rates or the activity of Mn(IV) away from their respective oscillatory regimes.

Whereas reductants virtually need only react with MnO_4^- to participate in an oscillator, far more restrictive requirements apply for a compound to be effective as a stabilizer. The only three stabilizers capable of bringing about oscillations are also the only oxyanions that share the same geometry, degree of protonation in the applicable pH range, and net ionic charge. Through interactions based on these common features, we surmise, the requirements for efficacy are satisfied, and phosphate, arsenate, and vanadate can interact similarly with Mn(IV) to stabilize it and delay its flocculation. Tetrahedral geometry may be essential for establishing the undefined Mn(IV)–stabilizer interaction that results in formation of either a soluble MnO_2 colloid or a complex. Protons may impart stability through hydrogen bonding, and charge may contribute by preventing aggregation of the colloidal particles, thereby slowing the precipitation process.

As already indicated, the autocatalyst in all oxidations by permanganate at pH > 3 is Mn(IV), possibly in the form of colloidal MnO_2. Model calculations yielding oscillations in flow conditions require a very specific rate for the removal of this species from solution. This removal rate is regulated by the oxyanions that control the lifetime of the Mn(IV) species by stabilizing it

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(15) Kustin, K.; Macara, I. G. *Commun. Inorg. Chem.* **1982**, *2*, 1.

(16) Drueckhammer, D. G.; Durrwachter, J. R.; Pederson, R. L., Crans, D. C.; Daniels, L.; Wong, C.-H. *J. Org. Chem.* **1989**, *54*, 70.

(17) Polissar, M. J. *J. Phys. Chem.* **1935**, *39*, 1057.

(18) Tompkins, F. C. *Trans. Faraday Soc.* **1942**, *38*, 131.

(19) Mata-Pérez. F.; Pérez-Benito, J. F. *Can. J. Chem.* **1985**, *63*, 988.

(20) Freeman, F.; Kappos, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6628.

(21) Jáky, M.; Simándi, L. I.; Shafirovich, Vi. Y. *Inorg. Chim. Acta* **1984**, *90*, L39.

(22) Lal, N. S.; Mishra, S. P.; Singh, T. B. In *Proceedings of the International Symposium on Applications and Technology of Ionizing Radiation*; King Saud University Libraries: Riyadh, Saudi Arabia, 1982; p 921.

(23) Parida, K. M.; *J. Electrochem. Soc. India* **1988**, *37*, 3.

against flocculation. The results described here give some possible explanations for the roles of the reductant and the stabilizer and greatly expand the subfamily of MnO_4^-–reductant oscillating chemical reactions.

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"Gas-Phase-like" Behavior in Solution Chemistry[†]

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Abstract: Using data from this work and from the literature, the standard free-energy changes for reactions i and ii, $\Delta G_{H^+}(g)$ and $\Delta G°_{I_2}(soln)$, are compared: $B(g) + H^+(g) \rightleftharpoons BH^+(g)$ (i); $B(soln) + I_2(soln) \rightleftharpoons B\cdots I_2(soln)$ (ii). B's are $S(sp^3)$ and $N(sp^2$ and $sp^3)$ n-donor bases (all compounds for which data sets are extensive and reliable), spanning a range of $\Delta G_{H^+}(g)$ of ca. 65 kcal·mol^{-1}. Within families, $\Delta G_{H^+}(g)$ and $\Delta G°_{I_2}(soln)$ are linearly related. Thus, a pattern of reactivity similar to that prevailing in the gas phase can be found in acid–base reactions in solution, provided charge dispersal through hydrogen bonding to the solvent is minimized.

I. Introduction

The development of experimental techniques for the study of proton-transfer reactions in the gas phase[1] has allowed the determination of gas-phase basicities (GB) and proton affinities (PA) for a substantial number of compounds. For a given base B, these magnitudes are defined as $GB(B) = \Delta G_{H^+}(g)$ and $PA(B) = -\Delta H_{H^+}(g)$, $\Delta G_{H^+}(g)$ and $\Delta H_{H^+}(g)$ being the standard free-energy and enthalpy changes for the reactions

$$B(g) + H^+(g) \rightarrow BH^+(g) \quad \Delta G_{H^+}(g), \Delta H_{H^+}(g) \qquad (1)$$

The pattern of structural effects on the aqueous basicities of organic compounds is dominated by the solvation of the onium ions, largely by charge dispersal through hydrogen bonding to water.[2] When solvation is not sterically hindered and the basic center as well as the number of acidic hydrogens are kept constant, as it is the case for pyridinium ions,[3] gas-phase and aqueous basicities are linearly related, provided allowance is made for an almost complete loss of polarizability[3] stabilization in aqueous solution. It is also known that extensive charge delocalization within the protonated base provides an efficient "internal solvation" leading to a very precise matching of structural effects on gas-phase and aqueous solution basicities.[4]

It is then fair to ask whether a *general* "gas-phase pattern of reactivity" can be observed in solution. From the above *it is clear that if a general "gas-phase ranking" of basicities is ever to be found in solution chemistry, charge dispersal through hydrogen bonding to the solvent has to be avoided.* This is a very difficult requirement for protonation reactions to fulfill,[5] but charge-transfer (CT)[7] association between neutral bases B and molecular iodine in solution (reaction 2) is a Lewis acid–base reaction that seems promising for this purpose.

$$B + I_2 \underset{soln}{\overset{K_c}{\rightleftharpoons}} B\cdots I_2 \qquad \Delta G°_{I_2}(soln) \qquad (2)$$

This work is thus aimed at comparing gas-phase proton basicity and solution molecular iodine basicity [defined as $IB = \Delta G°_{I_2}(soln)$] as determined in "inert" media (saturated hydrocarbons or dichloromethane).

Because data on $N(sp^2)$, $N(sp^3)$, and $S(sp^3)$ n-donor bases are more numerous and span a range of GBs of some 65 kcal·mol^{-1}, we have chosen to carry out a thorough study of these compounds.

II. Experimental Results and Discussion

For the purpose of extending the range of structural variations, a number of new IB values were determined in this study. They are presented in Table I together with data from other workers.

Most GB values given in Table I are taken with respect to the

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[†] Dedicated to Prof. E. M. Arnett on the occasion of his 69th birthday.

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(1) (a) *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York; Vol. 1 and 2, 1979; Vol. 3, 1984. (b) Lehman, A. T.; Bursey, M. M. *Ion Cyclotron Resonance Spectrometry*; John Wiley: New York, 1976. (c) *Fourier Transform Mass Spectrometry, Evolution, Innovation and Application*; Buchanan, M. V., Ed.; ACS Symposium Series 359; American Chemical Society: Washington, DC, 1987.

(2) See, e.g.: (a) Arnett, E. M.; Scorrano, G. *Adv. Phys. Org. Chem.* **1976**, *13*, 83. (b) Taft. R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247. (c) Taft. R. W. In *Proton Transfer Reactions*; Caldin, E. F., Gold, V., Eds.; Chapman and Hall: London, 1972; Chapter 2. (d) Arnett, E. M., *Ibid.*, Chapter 3.

(3) (a) Abboud, J.-L. M.; Catalán, J.; Elguero, J.; Taft, R. W. *J. Org. Chem.* **1988**, *53*, 1137. (b) Maria, P.-C.; Gal, J.-F.; Taft, R. W. *New. J. Chem.* **1987**, *11*, 617. (c) Aue, D. H.; Webb, H. M.; Davidson, W. R.; Toure, P.; Hopkins, H. P., Jr.; Moulik, S. P.; Jahagirdar, D. V. *J. Am. Chem. Soc.* **1991**, *113*, 1770.

(4) Wolf, J. F.; Abboud, J.-L. M.; Taft, R. W. *J. Org. Chem.* **1977**, *42*, 3316.

(5) This is so because dipolar solvents, however weakly basic (through hydrogen bonding),[6] lead to fairly strong hydrogen bonds with onium ions. This happens, for instance, in MeCN,[6] as shown by the pK_as of ammonia and the methylamines in this solvent (*Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions*; Palm, V. A., Ed.; Biniti: Moscow, 1976; Vol. 2, p 171).

(6) MeCN is a rather weak hydrogen-bonding base. See, e.g.: Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(7) (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600. (b) Mulliken, R. S.; Person, W. B. *Molecular Complexes—A Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969. (c) Briegleb, G. *Elektronen-Donator-Acceptor Komplexe*; Springer: Berlin, 1961. (d) Foster, R. *Organic Charge Transfer Complexes*; Academic Press: London, 1969. (e) *Molecular Complexes*; Foster, R., Ed.; Elek Science: London 1973; Vol. 1.

0002-7863/91/1513-7489$02.50/0