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An Inorganic Bromate Oscillator Incorporating Permanganate as a Reagent

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In the study reported here an attempt was made to determine whether oscillatory behaviour could be identified for a multicomponent, purely inorganic system. Organic substrates are invariably involved in bromate oscillators which have been widely studied from both experimental and mechanistic points of view [1, 2]. However, completely inorganic oscillators based on chlorite [3] are now known, and bistability has been established for a system containing only bromate, bromide and cerium [4]. Recently the predicted existence of a region of small amplitude oscillations for this latter system [5] was experimentally confirmed [6]. Under a very narrow range of conditions, sustained oscillations of electric potentials at Pt and bromide selective electrodes and of optical absorbance at 350 nm were observed in a stirred tank reactor (CSTR). We have identified and characterised very similar oscillatory behaviour for a system consisting of bromate (BrO_3^-), oxalate ($C_2O_4^{2-}$), permanganate (MnO_4^-), acid (H_2SO_4) and either Mn^{2+}, Fe^{2+}, or Ce^{3+} ions.

Experimental

A variable flow procedure was used whereby solutions were added from individual storage bottles by gravity feed into a CSTR of 138 cm^3 volume. Oscillatory behaviour was monitored by changes in the electrical potential of the solutions. Details of input concentrations and flow rates for the individual reagents, potassium bromate, sulphuric acid, catalyst (Fe^{2+}, Mn^{2+} or Ce^{3+} (anion, SO_4^{2-})) potassium permanganate and sodium oxalate are given in Table I.

Changes in the concentrations of Br_2 and Fe^{3+} were spectrophotometrically monitored for the iron catalysed oscillator. Samples were extracted from the CSTR with CCl_4 at appropriate stages of the oscillation. The Br_2 visible absorption at 415 nm was used to analyse for Br_2. For Fe^{3+}, complexation with thiocyanate (0.035 *M* SCN^- in 60% acetone [7]) was used. The complex formed, $[Fe(H_2O)_5(SCN)]^{2+}$, absorbs at ~480 nm.

Results and Discussion

Characteristics of the oscillatory behaviour of the three different systems studied are given in Table I. Details of the electrical potential profiles are shown in Fig. 1. As also reported for the 'minimal bromate oscillator' [6] oscillation occurred over a narrow range of conditions and for the particular apparatus used here, where some drift of flow rates inevitably occurs, small adjustments to individual flow rates were necessary in order to maintain oscillatory behaviour. However, for the Ce^{3+} system in particular oscillation was quite readily obtained and sustained, indicating the existence of a reasonably versatile reaction network.

A wide range of tests was carried out in order to ensure that all of the reagents listed (in particular permanganate) are required for oscillation to occur and that the same kind of behaviour cannot be obtained for fewer reagents (having different concentration/flow rate features). The general similarity of the features of the oscillations with those for the bromate/bromide/cerium system [6] (Table I) shows that similar inter-related reactions are involved. Thus these more complex systems could be incorporated into the new class of bromate/bromide/catalyst/oxidising substrate oscillator referred to by Orbán *et al.* [6, 8].

Bistability has been reported for the oxalate/permanganate/acid system carried out in a CSTR [9] but very much higher flow rates were employed than used here. Also the solution colour indicated that a comparable, relatively high permanganate composition domain was not involved in our systems. Indeed

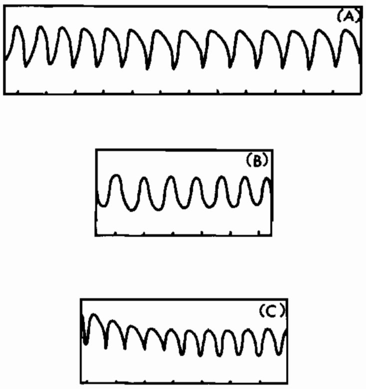

Fig. 1. Representative traces of Pt electrode potential changes for three metal ion catalysed, $BrO_3^-/MnO_4^-/C_2O_4^{2-}/H^+$, systems (A) Fe^{2+} (B) Ce^{3+} (C) Mn^{2+}. (The marked divisions are two minute time intervals in each case. The magnitude of the electrode potential changes (uncalibrated) was estimated to be within the 10–40 mV range.)

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TABLE I. Data for CSTR Bromate Oscillators.

System[a]	A[d]	B[d]	C[d]	D	E
Period of Oscillation (sec)	240–270	95–120	72–84	240	240[c]
Amplitude of oscillation (mV)	(within ~10–40 range)			28	28[c]
Temperature (aq) (°C)	22.5	22.0	22.0	25.0	25.0
CSTR Volume (cm^3)	138	138	138	21(28.7)[b]	21(28.7)[b]
BrO_3^- input molarity	0.030	0.030	0.030	0.048	0.072
H_3O^+ input molarity	1.87	1.87	1.87	1.5	1.5
Cation (M^{n+}) input molarity	8.1×10^{-3}	8.4×10^{-3}	3.3×10^{-3}	1.02×10^{-4}	1.02×10^{-4}[c]
MnO_4^- input molarity	0.006	0.006	0.006		
$C_2O_4^{2-}$ input molarity	0.060	0.060	0.060		
Br^- input molarity				9.8×10^{-5}	1.22×10^{-4}
BrO_3^- inflow rate (mls/min)	2.71	5.72	5.58	4.03	4.03[c]
H_3O^+ inflow rate (mls/min)	1.66	2.43	3.77	4.03	4.03[c]
Cation (M^{n+}) inflow rate (mls/min)	0.82	1.38	0.24	4.03	4.03[c]
MnO_4^- inflow rate (mls/min)	1.21	0.72	0.85		
$C_2O_4^{2-}$ inflow rate (mls/min)	1.01	1.45	1.36		
Br^- inflow rate (mls/min)				4.03	4.03[c]
Total inflow/outflow rate (mls/min)	7.41	11.70	11.80	16.13	16.13[c]
k_o (reciprocal residence time) (s^{-1})	0.0009	0.0014	0.0014	0.0128	0.0128[c]
$[BrO_3^-]$ for no reaction[e]	0.011	0.015	0.014	0.012	0.018
$[H_3O^+]$ for no reaction[e]	0.419	0.388	0.597	0.375	0.375
[Cation (M^{n+})] for no reaction[e]	8.96×10^{-4}	9.91×10^{-4}	6.71×10^{-5}	2.55×10^{-5}	2.55×10^{-5}[c]
$[MnO_4^-]$ for no reaction[e]	9.8×10^{-4}	3.7×10^{-4}	4.3×10^{-4}		
$[C_2O_4^{2-}]$ for no reaction[e]	8.2×10^{-3}	7.4×10^{-3}	6.9×10^{-3}		
$[Br^-]$ for no reaction[e]				2.45×10^{-5}	3.05×10^{-5}

[a] System: A = $Fe^{2+}/BrO_3^-/H_3O^+/MnO_4^-/C_2O_4^{2-}$; B = $Ce^{3+}/BrO_3^-/H_3O^+/MnO_4^-/C_2O_4^{2-}$; C = $Mn^{2+}/BrO_3^-/H_3O^+/MnO_4^-/C_2O_4^{2-}$; D = $Mn^{2+}/BrO_3^-/H_3O^+/Br^-$ (ref. 6). E = $Ce^{3+}/BrO_3^-/H_3O^+/Br^-$ (ref. 6). [b] Two reactor volumes were specified; calculations were carried out using the 21 cm^3 volume only. [c] Although not stated in ref. 6 these are assumed to be the same as for system D. [d] Error estimates for A, B, C-CSTR Volume ±2%; Input molarities ±1%; Flow rates ±4%; Total = 7% error in calculated, no-reaction concentrations. [e] Concentrations of reagents in reactor (moles/litre) for hypothetical no-reaction situation.

the concentrations and flow rates of the reactants used here show oxalate to be in excess of that required for stoichiometric reaction with permanganate. This feature highlights the similarity of the system with the oxalate/bromate/catalyst heterogeneous oscillator reported by Noszticzius and Bódiss [10].

Oscillatory behaviour was achieved in the latter case, for a closed system, by using an inert carrier gas to remove gaseous reaction products. Attention was focussed [10] on the direct role that molecular bromine, Br_2, may play (in place of or in addition to Br^-) in this oscillating reaction and in Belousov-Zhabotinskii (BZ) reactions in general. Citing evidence for the oscillation in the concentration of Br_2 for the original BZ reaction [11], Noszticzius and Bódiss suggest [10] that removal of Br_2 by the gas stream in their system was equivalent, kinetically, to the role of malonic acid (or its organic analogue) in reacting with Br_2 in homogeneous BZ reactions.

Although bromine does react with oxalate, this reaction is considered to be too slow (for the acidic conditions used) to be significant in the Noszticzius-Bódiss reaction [10]. This is probably also the case for the systems reported here. However preliminary studies indicate that bromine may be removed in these systems by reaction with intermediate manganese oxalato species [12]. When aqueous bromine is added to an almost completely reacted $MnO_4^-/C_2O_4^{2-}$/acid mixture it is quite rapidly reduced to bromide. Consequently it can be proposed that MnO_4^- (*via* its reaction with $C_2O_4^{2-}$) facilitates the removal of Br_2. Thus the system may be related to the standard BZ reaction in an analogous manner to that proposed for the Noszticzius-Bódiss reaction [10].

This system also shows a variation in the concentration of Br_2, and that of Fe^{3+} (when Fe^{2+} was used as the catalyst), along the electrode potential oscillatory profile. Quantitative extraction of CSTR samples with CCl_4 at maximum and minimum potential positions showed clear differences in absorbances at 415 nm corresponding to the visible Br_2 absorption. Similarly, a small but measurable difference in the concentration of Fe^{3+} was also demonstrated by measuring the absorbance of the derived $[Fe(H_2O)_5\cdot SCN]^{2+}$ species at 480 nm.

The presence of permanganate appears to extend the domain of oscillation of the 'minimal bromate oscillator' [6] to some extent, although the overall characteristics of the two systems (which are compared in Table I) are similar. In terms of this comparison it may be envisaged that admixture of oxalate and permanganate with bromate under acid conditions produces the right amount of bromide required for 'minimal' bromate/bromide/catalyst oscillatory behaviour.

However, as described above, the system reported here is probably more readily understood, mechanistically, in relation to the Noszticzius and Bódiss heterogeneous system [10]. Thus permanganate may be regarded as an effective chemical replacement for the inert carrier gas as a means by which Br_2 is removed from the system. It is probably the existence of intermediate manganese oxalato complexes (formed in the MnO_4^-–$C_2O_4^{2-}$ reaction) which enables oscillatory behaviour to be realised for this multicomponent inorganic system.

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