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## A new chemical system for studying pattern formation: Bromate–hypophosphite–acetone–dual catalyst

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Miklós Orbán,<sup>\*a</sup> Krisztina Kurin-Csörgei,<sup>a</sup> Anatol M. Zhabotinsky<sup>b</sup> and  
Irving R. Epstein<sup>b</sup>

<sup>a</sup> Department of Inorganic and Analytical Chemistry, L. Eötvös University,  
H-1518 Budapest 112, P.O.Box 32, Hungary

<sup>b</sup> Department of Chemistry, MS 015 Brandeis University, Waltham, Massachusetts  
02454-9110, USA

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A modified version of the short-lived  $\text{BrO}_3^-$ – $\text{H}_2\text{PO}_2^-$ –Mn(II)– $\text{N}_2$  oscillator, the  $\text{BrO}_3^-$ – $\text{H}_2\text{PO}_2^-$ –acetone–dual catalyst system, where the catalyst pair can be Mn(II)–Ru(bpy)<sub>3</sub>SO<sub>4</sub>, or Mn(II)–ferroin, or Mn(II)–diphenylamine, shows long-lasting batch oscillations in the potential of a Pt electrode and in colour, accompanying periodic transitions between the oxidised and reduced forms of the catalysts. Experimental conditions for the oscillations are established. The origin of the batch oscillations and the role of the catalyst pair in the oscillatory behaviour are discussed. The new system is ideally suited to the study of waves and patterns in reaction–diffusion systems, since in addition to the longevity of its spatial behaviour in batch, it produces no gaseous or solid products and exhibits significant photosensitivity.

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### Introduction

Interest in nonlinear chemical dynamics has recently focused on seeking new kinds of reaction–diffusion phenomena. Approaches to this goal include manipulation by external forces (*e.g.* light, electric or magnetic fields) of target patterns, spirals and Turing structures observed in the Belousov–Zhabotinsky (BZ) or chlorite–iodide–malonic acid (CIMA) systems, and development of new reactions capable of forming two-dimensional patterns.

While the BZ and CIMA reactions and their variants provide powerful tools for studying chemical waves and patterns, neither is ideal. The standard BZ reaction ( $\text{BrO}_3^-$ –MA– $\text{H}_2\text{SO}_4$ –ferroin) generates bubbles of carbon dioxide, which hamper observation in experiments of long duration. Some uncatalysed bromate oscillators, variants of BZ, are bubble-free, but short-lived, and tend to form precipitates. The CIMA system requires an unstirred flow reactor, a cumbersome technology, because the patterns last for only a relatively short time without the inflow of fresh reactants. Also, the traveling waves and Turing patterns in this system must be studied at temperatures (typically at 4–6 °C) significantly below ambient.

Until now, little progress has been achieved toward eliminating bubble or precipitate formation, the two major factors that militate against long-lasting pattern evolution. Ouyang *et al.*<sup>1</sup> suggested that it might be possible to generate a bubble-free bromate oscillator by employing two substrates, one being oxidised to a product other than CO<sub>2</sub>, the other binding Br<sub>2</sub>, an intermediate of bromate reduction. One possibility they considered was the Mn(II)-catalysed bromate–

hypophosphite–acetone system. In this reaction,  $\text{H}_2\text{PO}_2^-$  is oxidised to  $\text{H}_3\text{PO}_3$ , and the acetone serves to bind bromine. They had only limited success, however, in finding suitable compositions for oscillations and pattern formation.

Aside from the recently published results of Kurin-Csörgi *et al.*,<sup>2</sup> who observed long lasting traveling waves in the bromate–cyclohexanedione(CHD)–ferroin system without formation of bubbles or precipitate, we are unaware of work directed at developing novel systems with the desired properties.

Our plan is to find new chemical systems for studying two-dimensional patterns in a thin layer of solution. Ideally, a new system would have the following properties:

Oscillate in batch at room temperature for an extended period of time, several hours at a minimum; produce no gaseous or solid products; give rise to easily visible spatial waves and patterns with a convenient wavelength and velocity; be susceptible to perturbation or control, *e.g.*, photochemically; and have a relatively simple mechanism to facilitate modelling.

Here we report a new chemical system, a highly improved version of the bromate–hypophosphite–manganese(II)–N<sub>2</sub> batch oscillator, for the investigation of pattern formation in a thin unstirred solution layer. The bromate–hypophosphite–acetone–dual catalyst reaction meets almost all of the requirements listed above. It is well suited to the generation of high quality traveling waves that are close to ideal for studying sustained pattern evolution.

## Experimental

### Chemicals

$\text{NaBrO}_3$  (Aldrich),  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  (Sigma),  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (Aldrich),  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (Aldrich),  $\text{Ce}(\text{SO}_4)_2$  (Aldrich), 1,10-phenanthroline (Aldrich), diphenylamine sulfate (Aldrich), and acetone (Fisher) were of the highest grade commercially available and were used without purification.

The other reagents were prepared as follows:

$\text{Ru}(\text{bpy})_3\text{SO}_4$  was obtained from  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  by converting the chloride salt to the sulfato form using the recipe suggested by Gao and Försterling.<sup>3</sup> The removal of chloride is necessary because of its known inhibitory effect on bromate oscillators. The concentration of the aqueous stock solution of  $\text{Ru}(\text{bpy})_3\text{SO}_4$  ( $c = 3.75 \times 10^{-2}$  M) was determined spectrophotometrically ( $\lambda = 452$  nm,  $\epsilon = 14\,800$ ).

$\text{Fe}(\text{phen})_3\text{SO}_4$  (ferroin) stock solution ( $c = 2.5 \times 10^{-2}$  M) was prepared by mixing 1,10-phenanthroline and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in stoichiometric ratio. The stock solutions of the Ru(II) and Fe(II) complexes were found to be stable for days when stored in amber glass.

$\text{Ru}(\text{bpy})_3^{3+}$  sulfate and  $\text{Fe}(\text{phen})_3^{3+}$  sulfate were obtained by oxidation of the Ru(II) and Fe(II) complexes with solid  $\text{PbO}_2$  in 1 M  $\text{H}_2\text{SO}_4$ . The oxidation is complete within a few minutes: the orange Ru(II) compound turns to green Ru(III); the red Fe(II) complex is transformed into the dark blue Fe(III) complex. The excess  $\text{PbO}_2$  is removed using a glass filter. The Ru(III) and Fe(III) complexes were stored in darkness and used within 1 h.

Diphenylamine (DPA) stock solution ( $c = 2 \times 10^{-2}$  M) was made by dissolving diphenylamine sulfate in hot 10 M  $\text{H}_2\text{SO}_4$ .

$\text{Mn}_2(\text{SO}_4)_3$  stock solution ( $c = 10^{-2}$  M) was prepared by reacting a known amount of  $\text{KMnO}_4$  with a 50-fold excess of  $\text{MnSO}_4$  in 2 M  $\text{H}_2\text{SO}_4$ .

### Methods

Standard methods for monitoring the oscillations and observing pattern formation were employed. First, conditions for long-lasting batch oscillations and wave formation were established. Then, kinetic runs were carried out to estimate the relative rates of several composite reactions in order to reveal, at least qualitatively, the chemistry underlying the dynamical behaviour of the title system.

**Oscillations.** Chemical oscillations in the system were followed visually by the change in colour due to the periodic transition between the oxidised and reduced forms of the catalyst. The oscillations were recorded by measuring the potential of a Pt *vs.* Hg |  $\text{Hg}_2\text{SO}_4$  |  $\text{K}_2\text{SO}_4$  electrode pair immersed in the reaction mixture. The reaction was carried out in a thermostatted beaker ( $V = 30$

$\text{cm}^3$ ) covered with a Teflon cap. There was an air gap between the cap and the surface of the reaction mixture. The amplitude and frequency of the oscillations were dependent on the stirring rate. Therefore, a constant rate of 300 rpm was maintained in all batch experiments using a 2 cm long, 8 mm id Teflon coated stirring bar.

**Patterns.** When the oscillatory reaction mixture was spread in a covered Petri dish (id 9 cm) to form a 1–2 mm solution layer, target patterns or spirals began to develop. The waves were observable by eye, but for better contrast and for better recording appropriate optical filters were used. Pictures were taken with a CCD video camera connected to a camera controller and a PC. The pictures were processed with image analysis software.

**Kinetic runs.** The relative rates of some reactions were measured by recording the absorption spectra of the reaction mixture at different times. The ZITA program package<sup>4</sup> was used for data evaluation.

## Results

### Oscillations

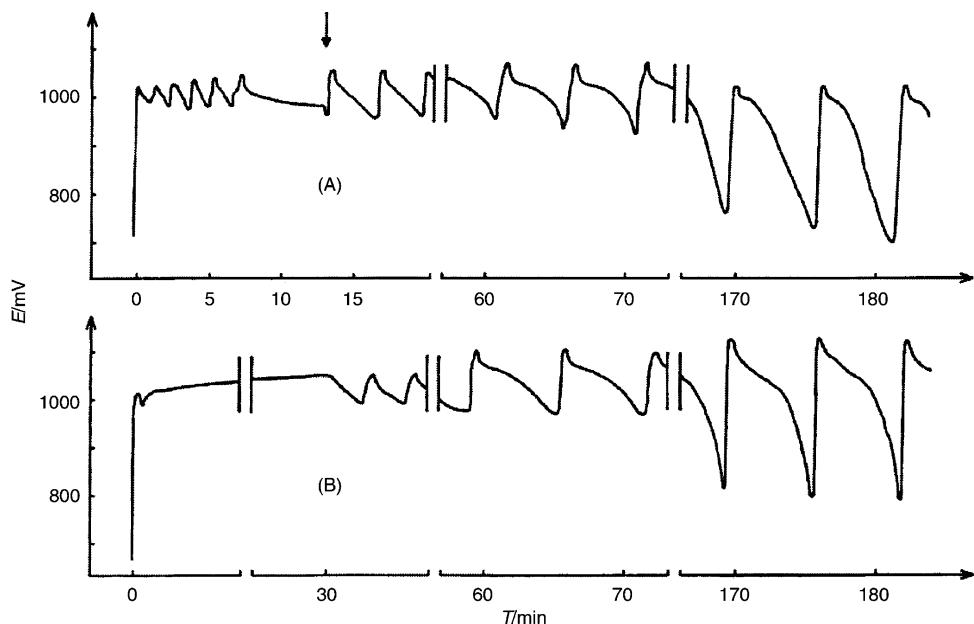
The reaction between bromate and hypophosphite ions in the presence of a metal ion catalyst ( $\text{Mn(II)}$ ,  $\text{Ce(III)}$ , ferroin) in sulfuric acid was reported by Adamčíkova and Sevcík<sup>5</sup> to show a few (4–8) oscillations in batch, if a flow of  $\text{N}_2$  was used to purge the intermediate bromine. As a system for pattern formation, this reaction suffers from two drawbacks: the oscillations persist only for a short time, and the  $\text{N}_2$  flow would be as disruptive to pattern formation as the production of bubbles.

An alternative approach is to remove the bromine by adding acetone, with which the  $\text{Br}_2$  reacts to form an inert product. This oscillator was tested for pattern formation by Ouyang *et al.*<sup>1</sup> In the  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^-$ -acetone reaction they could use only  $\text{Mn(II)}$  as the oscillatory catalyst; all other BZ catalysts,  $\text{Ce(IV)}$ , ferroin and  $\text{Ru(bpy)}_3\text{SO}_4$ , were ineffective. This finding is in contrast to the report of Adamčíkova and Sevcík, but it is in agreement with our results. Using  $\text{Mn(II)}$ , however, did not allow visual observation of patterns—if they formed at all—owing to the pale colour changes accompanying the  $\text{Mn(II)} \leftrightarrow \text{Mn(III)}$  transitions. When Ouyang *et al.* used a mixture of  $\text{Mn(II)}$  and ferroin, where  $\text{Mn(II)}$  served as the catalyst and ferroin as an indicator for visualisation of the periodic behaviour, they noted the appearance of two-dimensional patterns, but gave no further details.

Following up on the idea of employing two BZ catalysts, we were able to identify compositions at which  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^-$ -acetone- $\text{Mn(II)}$ -second catalyst systems produce long-lasting batch oscillations and patterns. We have found that with a dual catalyst sustained oscillations in the  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^-$ -acetone batch system can be obtained in the potential of a Pt electrode and in the colour. The presence of  $\text{Mn(II)}$  as a member of the catalyst pair is essential. As the second catalyst,  $\text{Ru(bpy)}_3\text{SO}_4$  is by far the most effective, but ferroin or diphenylamine can also be used,  $\text{Ce(IV)}$ , however, is ineffective in any combination.

Only a small amount of the second catalyst ( $10^{-5}$ – $10^{-4}$  M  $\text{Ru(bpy)}_3\text{SO}_4$ , ferroin or diphenylamine compared to  $[\text{Mn(II)}] > 10^{-3}$  M) is required to generate long-lasting oscillations. This amount can be added either together with the  $\text{Mn(II)}$  or when the short-lived  $\text{Mn(II)}$ -catalyzed oscillations cease.

Typical sequences of oscillations are presented in Fig. 1. Fig. 1A shows the potential of the Pt electrode *vs.* time recorded when the two catalysts,  $\text{MnSO}_4$  and  $\text{Ru(bpy)}_3\text{SO}_4$ , are added separately to the  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^-$ -acetone- $\text{H}_2\text{SO}_4$  system. Oscillations start immediately after adding  $\text{BrO}_3^-$  to the rest of the mixture, resulting in 5 cycles at this composition. The amplitude and period increase in time from 50 to 60 mV and from 60 to 120 s, respectively. This is identical to the time evolution of the system when only  $\text{Mn(II)}$  is added. When these oscillations terminate (after about 10 min), introducing 2 drops of  $1.56 \times 10^{-2}$  M  $\text{Ru(bpy)}_3\text{SO}_4$  solution (the final concentration is  $4 \times 10^{-5}$  M) generates new oscillations which last for more than 4 h. During that time, the period gradually becomes longer (7–8 min) and the amplitude increases and reaches a value of 370 mV after 4 h. The colour changes between green and yellow during the cycles result



**Fig. 1** Oscillations in the  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^- - \text{acetone} - \text{H}_2\text{SO}_4$ -dual catalyst system. A: The catalysts are added separately.  $\text{MnSO}_4$  is introduced at  $t = 0$ ,  $\text{Ru}(\text{bpy})_3\text{SO}_4$  at the time (in min) shown by the arrow. B: The catalysts are applied together at  $t = 0$ . Compositions:  $[\text{BrO}_3^-] = 2.1 \times 10^{-2}$  M;  $[\text{H}_2\text{PO}_2^-] = 1.13 \times 10^{-1}$  M;  $[\text{Mn(II)}] = 3.1 \times 10^{-3}$  M;  $[\text{acetone}] = 1.2 \times 10^{-1}$  M;  $[\text{H}_2\text{SO}_4] = 1.33$  M;  $[\text{Ru}(\text{bpy})_3\text{SO}_4] = 4 \times 10^{-5}$  M.  $T = 25^\circ\text{C}$ . Stirring rate: 300 rpm.

from the periodic oxidation and reduction of the second catalyst, the Ru-complex. Fig. 1B shows the time course of the system when the two catalysts are added together to the reaction mixture. In that case, an induction period of 30 min is followed by sustained oscillations, which strongly resemble in amplitude and frequency those seen after the arrow in Fig. 1A.

In most cases, the long-lasting oscillations begin after an induction period whose length depends upon the identity and the quantity of second catalyst and on the order in which the members of the dual catalyst pair are introduced into the reaction mixture. For example, when  $[\text{Rubpy}_3\text{SO}_4] = 4 \times 10^{-5}$  M was applied separately from Mn(II) (Fig. 1A), the second sequence of oscillations started immediately, but an induction period of 30 min appeared if the  $\text{Ru}(\text{bpy})_3\text{SO}_4$  and Mn(II) were added together (Fig. 1B). The induction time further increased to 50 and 100 min when larger quantities of  $[\text{Ru}(\text{bpy})_3\text{SO}_4]$ ,  $5 \times 10^{-5}$  and  $1 \times 10^{-4}$  M, respectively, were premixed with Mn(II). In general, an induction time always occurs if the two catalysts are introduced simultaneously. Separate addition of the second catalyst may eliminate the induction time if  $\text{Ru}(\text{bpy})_3\text{SO}_4$  or DPA, but not ferroin, is employed at low concentration ( $< 10^{-4}$  M). When  $[\text{ferroin}] = 10^{-4}$  and  $2 \times 10^{-4}$  M were applied instead of  $\text{Ru}(\text{bpy})_2\text{SO}_4$  under the conditions of Fig. 1A, induction times of 70 and 110 min, respectively, were measured. A higher concentration of the second catalyst results in a higher amplitude, longer period and longer sequence of oscillations. For example, with  $[\text{ferroin}] = 10^{-4}$  and  $2 \times 10^{-4}$  M (other concentrations as in Fig. 1), the following data were recorded: period = 15 and 36 min; initial amplitude of oscillations = 170 and 190 mV, respectively; duration of oscillations  $> 6$  h in both experiments. The data above are informative about the time expected for the appearance and the persistence of two-dimensional patterns when a mixture of oscillatory composition is spread in a Petri dish.

#### Effect of composition on the oscillatory behaviour

Long-lasting batch oscillations in the  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^- - \text{acetone} - \text{H}_2\text{SO}_4$  system with dual catalyst pairs Mn(II)- $\text{Ru}(\text{bpy})_3\text{SO}_4$ , Mn(II)-ferroin or Mn(II)-DPA were observed in the following ranges

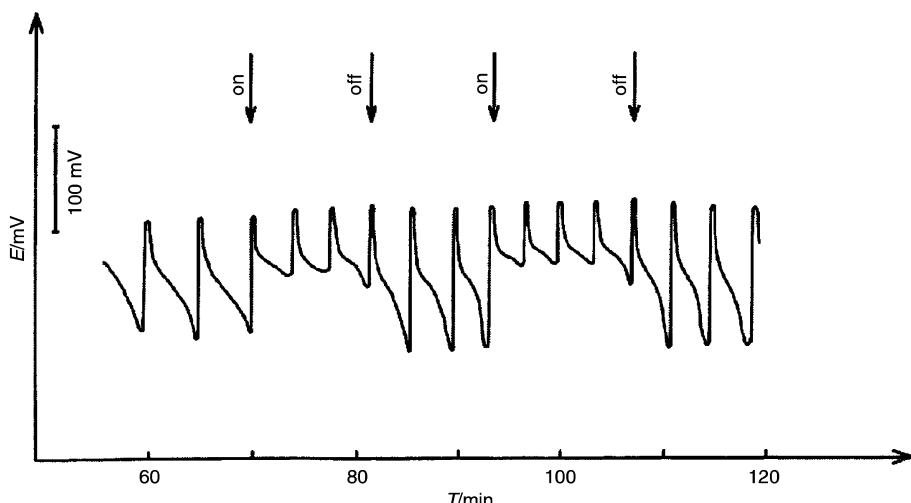
of concentration:  $[\text{BrO}_3^-] = 8 \times 10^{-3}$ - $3.2 \times 10^{-2}$  M,  $[\text{H}_2\text{PO}_2^-] = 9 \times 10^{-2}$ - $1.7 \times 10^{-1}$  M,  $[\text{acetone}] = 9 \times 10^{-2}$ - $2.5 \times 10^{-1}$  M,  $[\text{MnSO}_4] = 2 \times 10^{-3}$ - $3.5 \times 10^{-3}$  M,  $[\text{H}_2\text{SO}_4] = 1.0$ - $2.5$  M,  $[\text{Ru(bpy)}_3\text{SO}_4] = 10^{-5}$ - $3 \times 10^{-4}$  M,  $[\text{ferroin}] = 5 \times 10^{-5}$ - $3.3 \times 10^{-4}$  M,  $[\text{DPA}] = 5 \times 10^{-5}$ - $10^{-4}$  M. The best compositions for producing long-lasting oscillations are similar to those shown in Fig. 1. Significant changes in the characteristics of the oscillations (induction time, amplitude, period, duration of oscillations) are observed near the ends of the concentration ranges.

When DPA served as the second catalyst, the duration of the second sequence of oscillations was much shorter than with  $\text{Ru(bpy)}_3\text{SO}_4$  or ferroin. For example, with  $[\text{BrO}_3^-] = 8.5 \times 10^{-3}$  M,  $[\text{H}_2\text{PO}_2^-] = 9.2 \times 10^{-2}$  M,  $[\text{H}_2\text{SO}_4] = 2.0$  M,  $[\text{acetone}] = 8.9 \times 10^{-2}$  M,  $[\text{Mn(II)}] = 2 \times 10^{-3}$  M,  $[\text{DPA}] = 5 \times 10^{-5}$  M and Mn(II) and DPA added simultaneously as in Fig. 1A, the DPA-induced oscillations started as soon as DPA was introduced but died away after about 2 h. During this time the amplitude of Pt oscillations first increased from 50 to 190 mV (period is 4–6 min), then gradually decreased to zero. The solution oscillated between dark blue and colourless. The termination of oscillations is a consequence of the slow decomposition of DPA by  $\text{BrO}_3^-$  oxidation; a new addition of DPA engenders a new (much shorter-lived) oscillatory state.

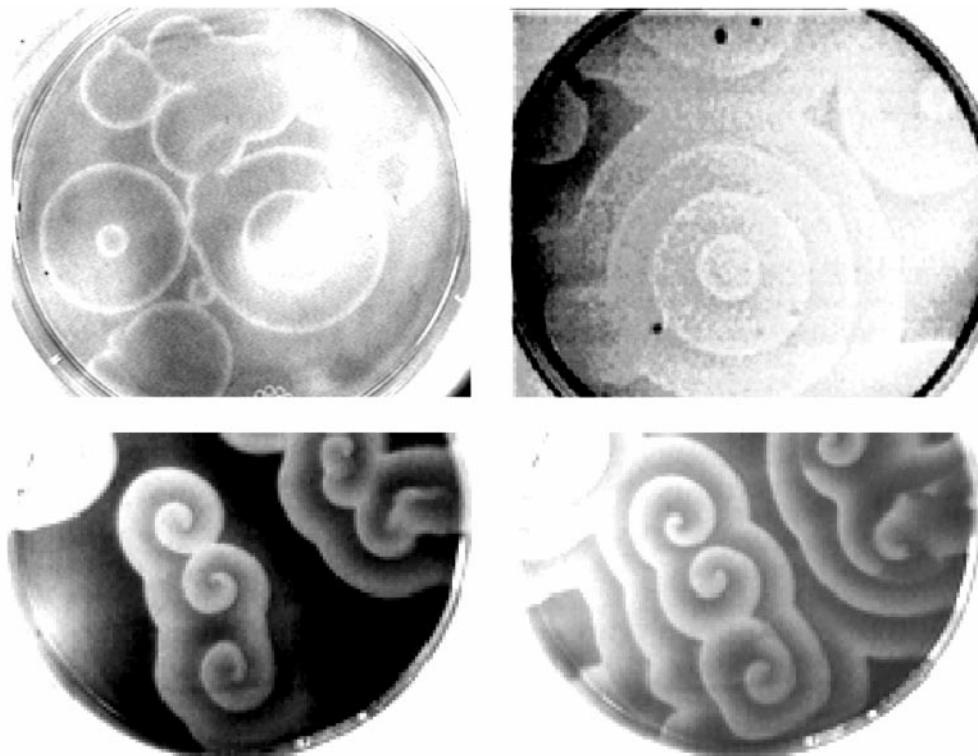
#### Effect of light and stirring rate on the oscillatory behavior

Chemical oscillators that contain photosensitive species usually show sensitivity to illumination. Because Ru(II) complexes are easily excited by visible light, the  $\text{BrO}_3^-$ - $\text{H}_2\text{PO}_2^-$ -acetone-Mn(II)- $\text{Ru(bpy)}_3\text{SO}_4$  system is expected to be sensitive to light. When the oscillator shown in Fig. 1 was illuminated with the 300 W halogen lamp of a Fiber Optic Illuminator (Dolan-Jenner Ind. Inc., Model 190), the period and amplitude immediately decreased by 25% and 50%, respectively. When the light source was turned off, the system soon recovered to its original amplitude and frequency. The effect of light on the oscillatory state is illustrated in Fig. 2.

We found a strong dependence on the stirring rate of the induction period, amplitude and frequency of the oscillations, a dependence that is not characteristic of other bromate oscillators. Sensitivity to the stirring rate is probably associated with the escape of volatile reagents (acetone) and/or products (bromoacetone, bromine) from the reaction mixture. In order to assure reproducibility, a constant stirring rate (300 rpm) was used and the air gap between the surface of the reaction mixture and the cap was always kept the same.



**Fig. 2** Effect of light on oscillations in the potential of a Pt electrode in the  $\text{BrO}_3^-$ - $\text{H}_2\text{PO}_2^-$ -acetone- $\text{H}_2\text{SO}_4$ -Mn(II)- $\text{Ru(bpy)}_3\text{SO}_4$  system. Light source is switched on and off at the times shown by the arrows. Composition as in Fig. 1.



**Fig. 3** Traveling chemical waves and spirals in a thin ( $\sim 1$  mm) solution layer. Composition:  $[\text{BrO}_3^-] = 3.2 \times 10^{-2}$  M;  $[\text{H}_2\text{PO}_2^-] = 1.13 \times 10^{-1}$  M;  $[\text{Mn(II)}] = 3.1 \times 10^{-3}$  M;  $[\text{Ru(bpy)}_3\text{SO}_4] = 5 \times 10^{-5}$  M; [acetone] =  $1.2 \times 10^{-1}$  M;  $[\text{H}_2\text{SO}_4] = 1.33$  M.

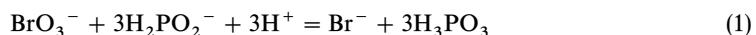
### Wave and spiral formation

In the oscillatory  $\text{BrO}_3^-$ - $\text{H}_2\text{PO}_2^-$ -acetone- $\text{H}_2\text{SO}_4$ -Mn(II)-second catalyst system, the changes in colour due to the  $\text{Ru(II)} \leftrightarrow \text{Ru(III)}$ , ferroin  $\leftrightarrow$  ferritin or diphenylamine  $\leftrightarrow$  diphenylbenzidine transitions are visible only if the amplitude of oscillations exceeds 100 mV. This requirement can easily be fulfilled by using a  $10^{-4}$  M or higher concentration of the second catalyst.

When a solution which is in an oscillatory state is spread in a Petri dish, target patterns develop and move with a speed of about  $1 \text{ mm min}^{-1}$  and a wavelength of 1–3 cm. Mechanical disturbance of a target pattern at an early stage results in the formation of a spiral wave. For generation of patterns the Mn(II)-Ru(bpy)<sub>3</sub>SO<sub>4</sub> and the Mn(II)-ferroin catalyst pairs are equally good but poor results were obtained with Mn(II)-DPA. The evolution of the waves continues for as long as the batch oscillations persist, often many hours. We observed formation of new traveling waves 7 h after the first wave appeared in the Petri dish. The wave fronts are quite sharp, as illustrated in Fig. 3. The patterns are free of bubbles and precipitate during their entire lifetime, and they readily reform after being destroyed by swirling the solution layer.

### Discussion

The overall reaction between the two main components of the  $\text{BrO}_3^-$ - $\text{H}_2\text{PO}_2^-$  oscillators is described by eqn. (1):



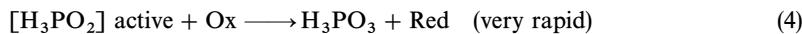
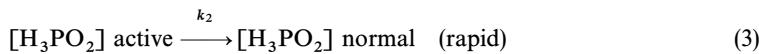
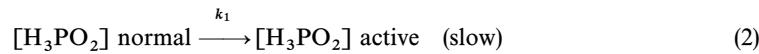
Reaction (1) is reported to be quite slow<sup>6,7</sup> and is autocatalytic in bromide ions, with an induction period inversely proportional to the concentrations of the reactants.<sup>7</sup> Reaction (1) was found to be catalysed and oscillatory only with Mn(II). No catalysis or oscillations were observed using other BZ-catalysts: Ce(III), ferroin or Ru(II)-complex.

In order to understand better the short-lived batch oscillations in the  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^- - \text{Mn}(\text{II}) - \text{N}_2$  or  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^- - \text{acetone} - \text{Mn}(\text{II})$  systems and the sustained batch oscillations in the  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^- - \text{acetone} - \text{Mn}(\text{II}) - \text{second catalyst}$  systems, we consider the following questions:

- (i) What is the origin of the batch oscillations?
- (ii) Why is Mn(II) the only effective catalyst in the  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^-$  reaction?
- (iii) How is a small amount of  $\text{Ru}(\text{bpy})_3\text{SO}_4$  or ferroin added to an exhausted  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^- - \text{Mn}(\text{II}) - \text{acetone}$  system able to reinitiate and to maintain the oscillations for many hours, while these catalysts are completely ineffective in the absence of Mn(II)?

Questions (i)–(iii) may be, at least qualitatively, answered as follows:

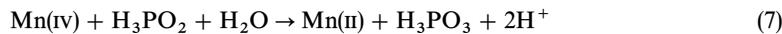
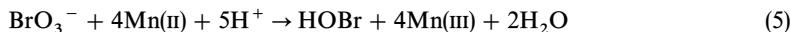
(i) Studies have shown that when  $\text{H}_2\text{PO}_2^-$  is oxidised to  $\text{H}_3\text{PO}_3$  by a variety of oxidising agents ( $\text{Br}_2$ ,  $\text{IO}_3^-$ ,  $\text{Cl}_2$ ,  $\text{HgCl}_2$ ) the rate law and rate constant for the reaction are about the same and the velocity is independent of the concentration of the oxidant.<sup>8</sup> This observation was explained by assuming  $\text{H}_3\text{PO}_2$  to exist in two forms, which differ strongly in reactivity: the “normal” form, four-coordinated  $\text{H}_2\text{PO}(\text{OH})$ , is unreactive, and the “active” form, three-coordinated  $\text{HP}(\text{OH})_2$ , reacts rapidly with oxidants, according to the following mechanism:



The “active”  $\text{H}_3\text{PO}_2$  is formed in the slow acid-catalysed tautomerisation reaction in process (2) from “normal”  $\text{H}_3\text{PO}_2$  and serves as a constant source of reactive reductant required for all variants of batch oscillators based on the reaction between  $\text{BrO}_3^-$  and  $\text{H}_2\text{PO}_2^-$ .

The appearance of the sustained batch oscillations shown in Fig. 1 suggests a very low conversion of  $\text{H}_3\text{PO}_2$  to  $\text{H}_3\text{PO}_3$  during each oscillatory period. Therefore, even if the “active”  $\text{H}_3\text{PO}_2$  is completely consumed in one cycle, the initial concentration of reagent  $\text{H}_2\text{PO}_2^-$  can support many oscillations *via* step (2) without the need for a continuous supply by input mass transport in a CSTR.

(ii) The effectiveness of the Mn(II) catalyst in the reaction between  $\text{BrO}_3^-$  and  $\text{H}_2\text{PO}_2^-$  results from the ability of its oxidised forms to exchange two electrons during bromate oxidation of  $\text{H}_3\text{PO}_2$  to  $\text{H}_3\text{PO}_3$ , according to the following steps:



Ferroin, Ce(III) and  $\text{Ru}(\text{bpy})_3\text{SO}_4$  are also readily oxidised by  $\text{BrO}_3^-$ , but their oxidised forms can exchange only a single electron with the substrate, which does not favour oxidation of  $\text{H}_3\text{PO}_2$ . We have measured the rate of oxidation of  $\text{H}_3\text{PO}_2$  by Mn(III), Ce(IV), ferriin and Ru(III) complex and found the following sequence:  $\text{Mn}(\text{III}) > \text{Ce}(\text{IV}) > \text{Ru}(\text{III}) > \text{ferriin}$ ; with pseudo-first order rate constants  $k' = 0.013 > 0.0012 > 9.9 \times 10^{-5} > 8.3 \times 10^{-6} \text{ s}^{-1}$ , respectively.

We also found that soluble Mn(IV) (stabilised with polyphosphate) oxidises  $\text{H}_2\text{PO}_2^-$  several orders of magnitude faster than Mn(III). The reaction is autocatalytic, shows a dependence on  $[\text{H}^+]$ , and needs further study to establish  $k'$ . These rates show the superiority of manganese species over the other ions as catalysts for the oxidation of  $\text{H}_2\text{PO}_2^-$ .

(iii) The role of the second catalyst in inducing a new sequence of oscillations in the exhausted  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^- - \text{acetone} - \text{Mn}(\text{II}) - \text{Ru}(\text{bpy})_3\text{SO}_4$  system still awaits explanation. Even the mechanism of the short-lived oscillator, the  $\text{BrO}_3^- - \text{H}_2\text{PO}_2^- - \text{Mn}(\text{II}) - \text{acetone}$  reaction, is not yet clear.

In Table 1 we suggest a skeleton mechanism that accounts for the “exotic” behaviour observed

**Table 1** Skeleton mechanism for the  $\text{BrO}_3^-$ – $\text{H}_2\text{PO}_2^-$ –acetone–Mn(II)–Ru(bpy)<sub>3</sub>SO<sub>4</sub> oscillatory system (the reactions are unbalanced)

$\text{BrO}_3^- + \text{Mn}(\text{II}) \rightarrow \text{Br}(\text{I}) + \text{Mn}(\text{III})$	(M1)
$2\text{Mn}(\text{III}) \rightarrow \text{Mn}(\text{II}) + \text{Mn}(\text{IV})$	(M2)
$\text{Mn}(\text{IV}) + \text{H}_2\text{PO}_2^- \rightarrow \text{Mn}(\text{II}) + \text{H}_3\text{PO}_3$	(M3)
$\text{Br}(\text{I}) + \text{Br}^- \rightarrow \text{Br}_2$	(M4)
$\text{Br}_2 + \text{Acetone} \rightarrow \text{Br-Ac} + \text{Br}^-$	(M5)
$\text{Mn}(\text{III}) + \text{Ru}(\text{II}) \rightarrow \text{Mn}(\text{II}) + \text{Ru}(\text{III})$	(M6)
$\text{Ru}(\text{III}) + \text{Br}^- \rightarrow \text{Ru}(\text{II}) + \text{Br}_2$	(M7)

in the  $\text{BrO}_3^-$ – $\text{H}_2\text{PO}_2^-$ –acetone–Mn(II)–Ru(bpy)<sub>3</sub>SO<sub>4</sub> system and that may explain the function of the second catalyst Ru(bpy)<sub>3</sub>SO<sub>4</sub> in maintaining the oscillatory state.

In the skeleton mechanism, reactions (M1)–(M5) explain the short-lived Mn(II)-catalyzed batch oscillations, which turn into long-lasting ones when steps (M6) and (M7) are included. The reagents in step (M1), together with Br<sup>-</sup> inflow, constitute the simplest bromate oscillator (or minimal bromate oscillator) when the reaction is run in a continuous-flow stirred tank reactor (CSTR).<sup>9</sup> This system can oscillate between two kinetic states associated with low and high concentrations of Br<sup>-</sup>. Bromide ions act as the control intermediate in the oscillatory mechanism.

Step (M3) makes the oscillations possible in batch. The “active”  $\text{H}_2\text{PO}_2^-$  supplied continuously by process (2) reacts with Mn(IV) in a slow reaction that restores Mn(II). The Br<sub>2</sub> produced in (M4) is chemically bound in (M5). The oscillations continue as long as the concentration of the control intermediate Br<sup>-</sup> lies within a critical range, but cease when (M5) causes [Br<sup>-</sup>] to increase above this range. The existence of short-lived oscillations in the  $\text{BrO}_3^-$ – $\text{H}_2\text{PO}_2^-$ –Mn(II)–acetone system suggests that the proper balance can be maintained only briefly and the oscillations stop as (M5) becomes dominant.

Steps (M6) and (M7) account for the role of the second catalyst Ru(bpy)<sub>3</sub>SO<sub>4</sub> in the oscillatory cycle. Ru(II) is readily oxidised in (M6) [ $k_{M6} = 267 \text{ M}^{-1} \text{ s}^{-1}$ ], and Ru(III) consumes Br<sup>-</sup> in (M7), bringing its level back into the critical range where oscillations can occur.

We performed kinetic runs to establish the relative rates of oxidation of Br<sup>-</sup> by the oxidised form of the BZ-catalysts, and found the following order: Mn(III) > Ru(III) ~ ferritin > Ce(IV). This order, plus the sequence of  $k'$  values for oxidation of  $\text{H}_2\text{PO}_2^-$ , suggest that Ru(III) and ferritin are not consumed in the reaction with  $\text{H}_2\text{PO}_2^-$ , but contribute significantly to the removal of Br<sup>-</sup>, adjusting [Br<sup>-</sup>] to an optimum range where long-lasting oscillations occur.

Simulations are in progress to check the validity of the skeleton mechanism and to work out the detailed description of the reactions in order to explain the “exotic” phenomena observed in the  $\text{BrO}_3^-$ – $\text{H}_2\text{PO}_2^-$ –acetone–dual catalyst system.

## Conclusion

The bromate–hypophosphite–acetone–dual catalyst oscillatory batch system may well turn out to be superior to either of the current systems for producing and studying two-dimensional pattern formation. The only disadvantage of the patterns produced by the present system is the relatively long (1–3 cm) wavelength, which prevents the development of large numbers of waves and spirals in the Petri dish. This drawback, however, is more than compensated by the advantages of long-lasting, gas- and precipitate-free pattern evolution—much longer than in the other systems—and the fact that the wave fronts appearing in the clear layer of reaction mixture can easily be observed, recorded and/or manipulated by external forces.

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