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Mechanistic studies on the bromate–1,4-cyclohexanedione–ferroin oscillatory system

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A chemical mechanism including 22 reactions and 15 species is suggested for describing the dynamical behavior of the ferroin controlled BrO_3^-–1,4-cyclohexanedione (CHD) batch oscillator. The model represents an extended version of the mechanism developed to explain the oscillations in the ferroin-free BrO_3^-–CHD system. The kinetics and rate constants for some additional reactions such as ones between ferriin and CHD, BrCHD (2-bromo-1,4-cyclohexanedione) and H_2Q (1,4-hydroquinone) and between ferroin and bromate were determined and incorporated in the mechanism of the BrO_3^-–CHD reaction. The model proposed here simulates satisfactorily the behavior of the BrO_3^-–CHD–ferroin oscillator at increasing concentration of ferroin and at the condition of [ferroin] $= 0$ mol dm^{-3}.

1 Introduction

The bromate–1,4-cyclohexanedione(CHD)–indicator oscillatory batch systems, where the indicator can be ferroin, Ru(II)–bipyridine complex, erioglaucine, diphenylamine and its derivatives, or some azo-dyestuffs, like *p*-ethoxychrysoidine and chrysoidine, were shown to be well suited for generating two-dimensional patterns.[1,2] Due to their bubble-free, long-lived and light sensitive character these systems are, in some sense, superior to the classical bromate–malonic acid–catalyst reaction (known as the BZ reaction) in studying reaction–diffusion structures. Especially the bromate–CHD–ferroin system has become the subject of many recent studies. Winfree *et al.* preferred to use this reaction instead of BZ to visualize organizing centers in an excitable chemical medium.[3] Komlósi *et al.* studied the interaction of chemical waves and convection in the bubble-free BrO_3^-–CHD–ferroin reaction.[4] Various bifurcation points and bistability were shown to exist during the long lifetime of the bromate–CHD–ferroin batch reaction and different propagation speeds for the reduction and oxidation waves were measured in 1D capillary tube by Chen.[5] One of the most striking results obtained in the 1D and 2D bromate–CHD–ferroin excitable systems were reported by Steinbock *et al.*[6,7] who observed an anomalous dispersion relation resulting in new dynamical phenomena, like stacking and merging of waves, which are not known for the BZ reaction with malonic acid.

The major drawback in the application of the bromate–CHD–ferroin system as model reaction for studying nonlinear chemical behaviour is its poorly known chemistry. Here we propose a chemical mechanism which hopefully helps to describe and to model the temporal and spatial phenomena observed in the title reaction.

2 Experimental

H_2SO_4 (Chemolab 96%), 1,4-cyclohexanedione (Aldrich 98%), KBr (Reanal p.a.), $NaBrO_3$ (Fluka p.a.), 0.025 mol dm^{-3} ferroin (prepared from a calculated amount of $FeSO_4 \cdot 7H_2O$ (Reanal p.a.) and 1,10-phenanthroline (Aldrich 99%)) and bidistilled water were used to prepare the working solutions.

Stock solution of ferriin was prepared from the stock solution of ferroin by oxidation with solid PbO_2 followed by filtration. Because of its instability, the ferriin solution was stored in the dark and used within 1 h.

The bromo derivative of CHD, abbreviated as BrCHD, was prepared by mixing CHD with stoichiometric amount of bromine. The reaction is regarded to be complete when the color of bromine disappears. It takes a relatively long time, and therefore the decomposition of BrCHD according to eqns. (R9) and (R10) should be considered when the initial concentration of BrCHD used in the ferriin–BrCHD reaction is calculated. For example, when 5×10^{-3} mol dm^{-3} CHD and 5×10^{-3} mol dm^{-3} bromine were mixed, 90 min was needed for the consumption of bromine, and in a good approximation 3×10^{-3} mol dm^{-3} BrCHD was calculated and used as initial concentration in the experiments shown in Fig. 2.

The spectra for the kinetic measurements were taken on a Milton Roy 3000 diode array spectrophotometer equipped with quartz cells (path length 1 cm, volume 2 ml). The uncatalyzed oscillatory reaction occurring between bromate and 1,4-cyclohexanedione was monitored by using a smooth Pt electrode (Radelkis) and a $Hg/Hg_2SO_4/K_2SO_4$(sat.) reference electrode (Radiometer). The analog signals were digitized by a 12-bit AD converter (Labtech PCL-711 S) and processed by a PC. The temperature was kept at 20.0(±0.1) °C, and the solutions in the cell were mixed by a magnetic stirrer.

The simulations were done with the program LSODE.[8] The parameter estimations were carried out by the MULTIMRQ program, which uses the Marquardt method. Fitted parameters are given at 95% significance level.

3 Results

3.1 The bromate–CHD oscillator

The reaction between acidic bromate and CHD was reported to exhibit long-lasting (200–300 cycles) batch oscillations which could be recorded in a galvanic cell arrangement using Pt *vs.* reference electrodes. Adding ferroin redox indicator to the reaction mixture, the oscillations can be visualized, *i.e.* the color changes periodically between blue and red.[1,9]

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A chemical mechanism for explaining the origin of the batch oscillations in the ferroin-free system was proposed by Szalai and Kőrös.[10,11] In the mechanism the CHD is oxidized by bromate ions to 1,4-benzoquinone (Q) through a stable intermediate 1,4-hydroquinone (H_2Q), which is produced continuously from 2-bromo-1,4-cyclohexanedione (BrCHD) *via* 2-cyclohexene-1,4-dione (CHED) but oxidized in an autocatalytic fashion by $BrO_2^{\bullet}$. A protonation equilibrium leading to the enol form of CHD (CHDE) precedes the bromination. Schematically the oxidation of CHD can be described as follows:

$$\mathrm{CHD} \xrightleftharpoons{\mathrm{H^+}} \mathrm{CHDE} \xrightarrow{\mathrm{Br_2}} \mathrm{BrCHD} \xrightarrow{\mathrm{H^+}}$$

$$\mathrm{CHED} \xrightarrow{\mathrm{H^+}} \mathrm{H_2Q} \xrightarrow{\mathrm{BrO_2^{\bullet}}} \mathrm{Q}$$

This sequence of reactions for the oxidation of CHD by bromate may be applied in the presence of ferroin as well.

3.2 Effect of ferroin on the BrO_3^-–CHD oscillator

Adding ferroin to the BrO_3^-–CHD oscillator strongly affects its dynamical behaviour. For example:

(i) In a well stirred mixture, the amplitude increases and the period decreases proportionally with increasing concentration of ferroin. [At high value of ferroin concentration the system approaches the oxidized (blue) state.][1]

(ii) The added ferroin is able to reinitiate new oscillations after the oscillations have terminated in a ferroin-free system.[2]

(iii) There is a pronounced dependence of the wave velocity on the initial concentration of ferroin in the BrO_3^-–CHD system, while the dynamics of the ferroin front is independent of the catalyst concentration in the classical BZ with malonic acid.[7]

In order to construct a chemically realistic model for the BrO_3^-–CHD–ferroin oscillator we have to combine the mechanism developed for the BrO_3^-–CHD system and the reactions of ferriin and ferroin with initial reagents and some intermediates. The oxidation of CHD, BrCHD and H_2Q by ferriin and the reduction of BrO_3^- by ferroin were studied in detail.

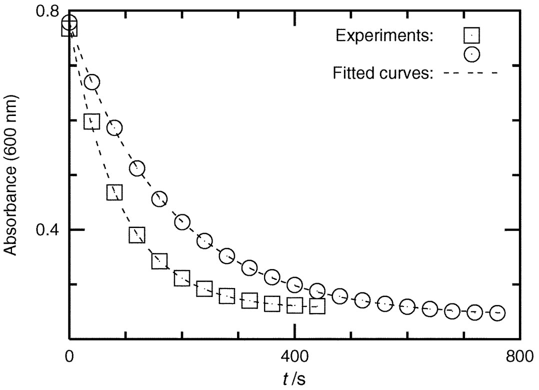

Fig. 1 Oxidation of CHD by ferriin. Experimental conditions: $[H_2SO_4] = 1.0$ mol dm^{-3}; [ferriin] $= 7.0 \times 10^{-4}$ mol dm^{-3}; [CHD] $= 5.0 \times 10^{-2}$ mol dm^{-3} (⊡); [CHD] $= 2.5 \times 10^{-2}$ mol dm^{-3} (⊙); $\varepsilon_{600}{}^{\mathrm{ferriin}} = 1010$ mol^{-1} dm^3 cm^{-1}; $\varepsilon_{600}{}^{\mathrm{ferroin}} = 270$ mol^{-1} dm^3 cm^{-1}; $T = 20\,°\mathrm{C}$.

3.3 Oxidation of CHD and BrCHD by ferriin

The rate of the reaction between CHD or BrCHD and ferriin was measured by following the decrease in the absorbance *vs.* time at $\lambda = 600$ nm (characteristic of the absorption of ferriin).

The rate equation and the rate constant related to the CHD–ferriin reaction were established from experiments carried out at 10 combinations of the initial concentrations of CHD (0.01–0.1 mol dm^{-3}), ferriin (10^{-5}–10^{-4} mol dm^{-3}) and sulfuric acid (1.0–2.5 mol dm^{-3}). Fig. 1 presents the experimentally obtained absorbance *vs.* time curves at two initial concentrations of CHD (symbols ⊡ and ⊙) and it shows the fitted curves (dotted lines) for determination of the rate constants. The results are summarized in reaction (R16) (see section 3.6 and Tables 1 and 2):

$$2\mathrm{Fe(phen)_3}^{3+} + \mathrm{CHD} \rightarrow 2\mathrm{Fe(phen)_3}^{2+} + \mathrm{H_2Q} + 2\mathrm{H^+}$$

$$v_{16} = \frac{k_{16}}{[\mathrm{H^+}]}[\mathrm{Fe(phen)_3}^{3+}][\mathrm{CHD}]$$

$$k_{16} = 0.14(\pm 0.01)\,\mathrm{s^{-1}} \qquad \mathbf{(R16)}$$

Table 1 Model for the bromate–CHD–ferroin oscillatory system. Symbols for the organic species: CHD = 1,4-cyclohexanedione; CHDE = enol form of CHD; BrCHD = 2-bromo-1,4-cyclohexanedione; CHED = 2-cyclohexene-1,4-dione; H_2Q = 1,4-hydroquinone; Q = 1,4-benzoquinone

	Reactions
(R1)	$\mathrm{Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O}$
(R2)	$\mathrm{Br^- + HBrO_2 + H^+ \rightleftharpoons 2HOBr}$
(R3)	$\mathrm{Br^- + BrO_3^- + 2H^+ \rightleftharpoons 2HOBr + HBrO_2}$
(R4a)	$\mathrm{HBrO_2 + H^+ \rightleftharpoons H_2BrO_2^+}$
(R4b)	$\mathrm{HBrO_2 + H_2BrO_2^+ \rightarrow BrO_3^- + HOBr + H^+}$
(R5a)	$\mathrm{HBrO_2 + BrO_3^- + H^+ \rightleftharpoons Br_2O_4 + H_2O}$
(R5b)	$\mathrm{Br_2O_4 \rightleftharpoons 2BrO_2^{\bullet}}$
(R6a)	$\mathrm{H_2Q + 2BrO_2^{\bullet} \rightarrow 2HBrO_2 + Q}$
(R6b)	$\mathrm{Fe(phen)_3^{2+} + BrO_2^{\bullet} + H^+ \rightarrow Fe(phen)_3^{3+} + HBrO_2}$
(R7)	$\mathrm{CHD + H^+ \rightleftharpoons CHDE + H^+}$
(R8)	$\mathrm{CHDE + Br_2 \rightarrow BrCHD + Br^- + H^+}$
(R9)	$\mathrm{BrCHD + H^+ \rightarrow CHED + Br^- + 2H^+}$
(R10)	$\mathrm{CHED + H^+ \rightarrow H_2Q + H^+}$
(R11)	$\mathrm{CHD + BrO_3^- + H^+ \rightarrow H_2Q + HBrO_2 + H_2O}$
(R12)	$\mathrm{CHD + HBrO_2 \rightarrow H_2Q + HOBr + H_2O}$
(R13)	$\mathrm{H_2Q + BrO_3^- + H^+ \rightarrow Q + HBrO_2 + H_2O}$
(R14)	$\mathrm{H_2Q + HOBr \rightarrow Q + Br^- + H^+ + H_2O}$
(R15)	$\mathrm{H_2Q + Br_2 \rightarrow Q + 2Br^- + 2H^+}$
(R16)	$\mathrm{2Fe(phen)_3^{3+} + CHD \rightarrow 2Fe(phen)_3^{2+} + H_2Q + 2H^+}$
(R17)	$\mathrm{2Fe(phen)_3^{3+} + BrCHD \rightarrow Q + Br^- + 3H^+ + 2Fe(phen)_3^{2+}}$
(R18)	$\mathrm{2Fe(phen)_3^{3+} + H_2Q \rightarrow 2Fe(phen)_3^{2+} + Q + 2H^+}$
(R19)	$\mathrm{2Fe(phen)_3^{2+} + BrO_3^- + 3H^+ \rightarrow 2Fe(phen)_3^{3+} + HBrO_2 + H_2O}$

Table 2 Rate constants for the model of the bromate–CHD–ferroin oscillatory system. The values refer to a temperature of 20 °C. $[H_2O] = 55$ mol dm^{-3} is included in the rate constant. We used hydrogen ion concentrations reported by Robertson and Dunford.[19] This is a mass action kinetic model with the exception of $v_{6a} = k_{6a} \times [H_2Q] \times [BrO_2^{\bullet}]$, $v_{16} = (k_{16}/[H^+]) \times [Fe(phen)_3{}^{3+}] \times [CHD]$, $v_{17} = k_{17} \times [Fe(phen)_3{}^{3+}] \times [BrCHD]$, $v_{18} = k_{18} \times [Fe(phen)_3{}^{3+}] \times [H_2Q]$, $v_{19} = k_{19} \times [Fe(phen)_3{}^{2+}] \times [BrO_3{}^-] \times [H^+]^2$.Values marked by an asterisk are slightly modified compared to ref. 10.

	$k_{forward}$	$k_{reverse}$	Ref.
(R1)	8×10^9 mol^{-2} dm^6 s^{-1}	80 s^{-1}	16
(R2)	2.5×10^6 mol^{-2} dm^6 s^{-1}	2×10^{-5} mol^{-1} dm^3 s^{-1}	16
(R3)	1.2 mol^{-3} dm^9 s^{-1}	3.2 mol^{-2} dm^6 s^{-1}	18
(R4a)	2×10^6 mol^{-1} dm^3 s^{-1}	1×10^8 s^{-1}	17
(R4b)	1.7×10^5 mol^{-1} dm^3 s^{-1}		17
(R5a)	48 mol^{-2} dm^6 s^{-1}	3.2×10^3 s^{-1}	18
(R5b)	7.5×10^4 s^{-1}	1.4×10^9 mol^{-1} dm^3 s^{-1}	18
(R6a)	2×10^6 mol^{-1} dm^3 s^{-1}		10*
(R6b)	1×10^7 mol^{-1} dm^3 s^{-1}		15
(R7)	2.1×10^{-4} mol^{-1} dm^3 s^{-1}	5.2×10^2 mol^{-1} dm^3 s^{-1}	10
(R8)	2.8×10^9 mol^{-1} dm^3 s^{-1}		10
(R9)	5×10^{-5} mol^{-1} dm^3 s^{-1}		10
(R10)	1.9×10^{-4} mol^{-1} dm^3 s^{-1}		10
(R11)	2×10^{-5} mol^{-2} dm^6 s^{-1}		10*
(R12)	5 mol^{-2} dm^6 s^{-1}		this work
(R13)	2×10^{-2} mol^{-2} dm^6 s^{-1}		10
(R14)	6×10^5 mol^{-1} dm^3 s^{-1}		10
(R15)	1×10^4 mol^{-1} dm^3 s^{-1}		10*
(R16)	0.14 s^{-1}		this work
(R17)	0.051 mol^{-1} dm^3 s^{-1}		this work
(R18)	6×10^3 mol^{-1} dm^3 s^{-1}		this work
(R19)	2×10^{-2} mol^{-3} dm^9 s^{-1}		this work

Fig. 2 shows the absorbance *vs.* time curve taken for the reaction between BrCHD and ferriin (symbol ⊡) and the result of simulation (dotted line) for determining the rate of process (R17):

$$2Fe(phen)_3{}^{3+} + BrCHD \rightarrow Q + Br^- + 3H^+ + 2Fe(phen)_3{}^{2+}$$
$$v_{17} = k_{17}[Fe(phen)_3{}^{3+}][BrCHD]$$
$$k_{17} = 0.051(\pm 0.001)\,mol^{-1}\,dm^3\,s^{-1} \qquad (R17)$$

3.4 Oxidation of H_2Q by ferriin

The oxidation of H_2Q, one of the key intermediates in the $BrO_3{}^-$–CHD oscillator, by ferriin is too fast to be able to measure its rate with our experimental setup. The reaction is supposed to take place according to the stoichiometry of reaction (R18). This assumption is based on analogous reactions occurring between H_2Q and one-electron oxidants, like Ce^{4+}, Co^{3+}, Mn^{3+} and Fe^{3+} studied by Wells and Kuritsyn[12] and Baxendale *et al.*.[13] Thus:

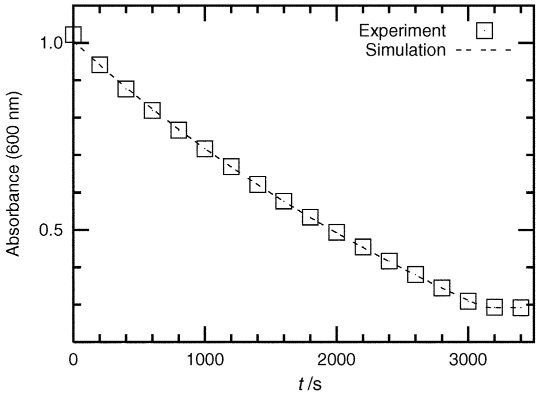

Fig. 2 Oxidation of BrCHD by ferriin. Experimental conditions: $[H_2SO_4] = 1.0$ mol dm^{-3}; $[BrCHD] = 3.0 \times 10^{-3}$ mol dm^{-3}; $[ferriin] = 9.0 \times 10^{-4}$ mol dm^{-3}; $\varepsilon_{600}{}^{ferriin} = 1010$ mol^{-1} dm^3 cm^{-1}; $\varepsilon_{600}{}^{ferroin} = 270$ mol^{-1} dm^3 cm^{-1}; $T = 20$ °C.

$$2Fe(phen)_3{}^{3+} + H_2Q \rightarrow 2Fe(phen)_3{}^{2+} + Q + 2H^+$$
$$v_{18} = k_{18}[Fe(phen)_3{}^{3+}][H_2Q]$$
$$k_{18} = 6 \times 10^3\,mol^{-1}\,dm^3\,s^{-1} \qquad (R18)$$

The rate constant for reaction (R18) was treated as an adjustable parameter in the simulations, but its final value falls within the range found for similar reactions discussed in refs. 11 and 12.

3.5 Reduction of bromate by ferroin

Kéki *et al.*[14] pointed out that the reactions between the ferroin and oxybromine species ($BrO_3{}^-$, $BrO_2{}^{\bullet}$, $HBrO_2$) play an important role in the dynamics of the ferroin-catalyzed BZ reaction. In our model we considered only two reactions, (R6b) and (R19), to be essential for simulation of the autocatalysis in the bromate–ferroin reaction:

$$Fe(phen)_3{}^{2+} + BrO_2{}^{\bullet} + H^+ \rightarrow Fe(phen)_3{}^{3+} + HBrO_2$$
$$v_{6b} = k_{6b}[Fe(phen)_3{}^{2+}][BrO_2{}^{\bullet}][H^+]$$
$$k_{6b} = 1 \times 10^7\,mol^{-2}\,dm^6\,s^{-1} \qquad (R6b)$$

$$2Fe(phen)_3{}^{2+} + BrO_3{}^- + 3H^+ \rightarrow 2Fe(phen)_3{}^{3+} + HBrO_2 + H_2O$$
$$v_{19} = k_{19}[Fe(phen)_3{}^{2+}][BrO_3{}^-][H^+]^2$$
$$k_{19} = 2 \times 10^{-2}\,mol^{-3}\,dm^9\,s^{-1} \qquad (R19)$$

Fig. 3 shows the experimental and simulated autocatalytic curves. For simulations k_{6b} was taken from ref. 14 and k_{19} was derived from the simulated curve of Fig. 3.

3.6 The model for the $BrO_3{}^-$–CHD–ferroin oscillator

The mechanistic model constructed for the $BrO_3{}^-$–CHD–ferroin oscillator is an extended version of the mechanism devel-

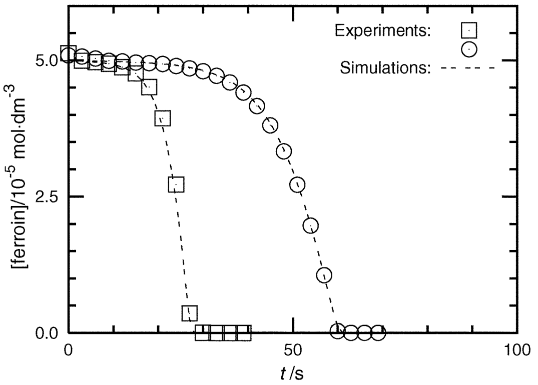

Fig. 3 Autocatalytic reaction between bromate and ferroin. Experimental conditions: $[H_2SO_4] = 1.0$ mol dm^{-3}; [ferroin] $= 5.0 \times 10^{-5}$ mol dm^{-3}; $[BrO_3^-]_0 = 5.0 \times 10^{-2}$ mol dm^{-3} (☐); $[BrO_3^-]_0 = 2.5 \times 10^{-3}$ mol dm^{-3} (⊙); $T = 20\,°C$.

oped for the ferroin-free BrO_3^-–CHD oscillatory system. Some sequences of reactions are common in both models, like reactions (R1)–(R6a), which represent the known chemistry of the oxybromine species, and steps (R7)–(R15) showing the oxidation of CHD to 1,4-benzoquinone. For a better description of the induction period, the rate constants of reactions (R6a), (R11) and (R15) were slightly modified and a new step, the reaction between CHD and $HBrO_2$, was added as reaction (R12). The model was completed with all the important reactions that take place between ferroin and bromo species or between ferriin and CHD derivatives. The complete model and corresponding rate constants are summarized in Tables 1 and 2.

4 Discussion

In the mechanism suggested for the BrO_3^-–CHD–ferroin oscillator and presented in Table 1, the Br^- consumption processes (R1)–(R3) are identical with those involved in the ferroin-free version. The reaction between ferriin and Br^- is too slow to be considered as a Br^- removal step in the mechanism. There are two pathways for the autocatalytic production of $HBrO_2$. $BrO_2^\bullet$ is reduced to $HBrO_2$ concurrently by intermediate H_2Q (R6a) and ferroin (R6b). Regeneration of Br^- can occur in several steps, but the major source of Br^- is BrCHD formed in step (R8) and decomposed in (R9) and its oxidation by ferriin in step (R17).

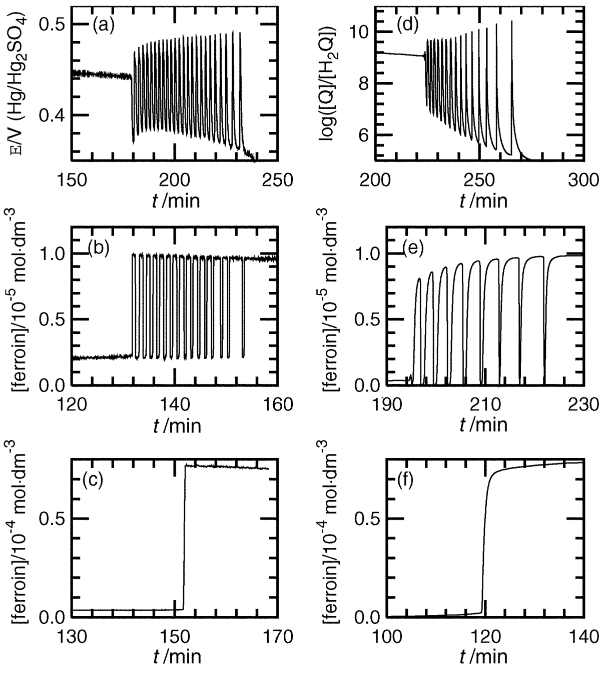

Fig. 4 Comparison of experimental [curves (a)–(c)] and simulated [curves (d)–(f)] results. Experimental conditions: [CHD] $= 0.1$ mol dm^{-3}; $[BrO_3^-] = 0.1$ mol dm^{-3}; (a) and (d) ferroin-free system; (b) and (e) [ferroin] $= 1.0 \times 10^{-5}$ mol dm^{-3}; (c) and (f) [ferroin] $= 8.0 \times 10^{-5}$ mol dm^{-3}; $T = 20\,°C$.

The attractive feature of the mechanism is its applicability to both BrO_3^-–CHD–ferroin and BrO_3^-–CHD oscillators. The model includes all essential steps required to simulate the oscillations observed in the ferroin-free BrO_3^-–CHD system but it also works well in its more complex form when all important reactions of ferroin and ferriin are incorporated. Using the mechanism in Table 1 and rate constants in Table 2, the dynamical behavior at $[BrO_3^-] = [CHD] = 0.1$ mol dm^{-3} and $[H_2SO_4] = 1.0$ mol dm^{-3} was calculated using a concentration of ferroin from 0 to 8×10^{-5} mol dm^{-3}. The agreement between the experimental and simulated behaviors is satisfactory.

We can conclude that the mechanism proposed in Table 1 provides a qualitative description of the BrO_3^-–CHD–ferroin oscillator. Further improvement of the model requires additional rate measurements, *e.g.* the dependence of some rate constants on the acidity and temperature should be determined. In order to simulate the reported bistability, target patterns, some wave phenomena, like stacking or merging, *etc.*, we plan also to construct a reduced model containing no more than three variables. For abstracting a reduced model, sensitivity analysis will be applied to identify the most important reactions in the present mechanism.

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