substrate-directed oxidation, activated in the presence of Ni(II) and peracid (25 °C, pH 7.5).

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Batch Oscillation in the Reaction of Chlorine Dioxide with Iodine and Malonic Acid[1]

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The reaction of chlorite, iodide, and malonic acid (MA) is one of a handful of chemical reactions to oscillate in a closed (batch) system.[3] This reaction has recently been used in the first experimental demonstration[4] of the symmetry-breaking, reaction-diffusion structures predicted by Turing[5] nearly 40 years ago. We have discovered that the source of oscillation in the ClO_2^-–I^-–MA reaction is the chlorine dioxide–iodine–malonic acid reaction. From this knowledge, we can construct a simple model that explains the temporal behavior of the system and should serve as a basis for theoretical studies of the Turing structures.

Batch oscillations in the ClO_2^-–I^-–MA reaction were studied at 25 °C and 400 rpm in an HP8452A diode array spectrophotometer. The diode array instrument enabled us to monitor many wavelengths simultaneously, making it possible to follow several intermediates and products during the reaction.

In Figure 1, we show a representative experiment at two different wavelengths: 468 nm, the isosbestic point of I_2 and I_3^- ($\epsilon = 740$ cm^{-1} M^{-1}), and 280 nm, where iodomalonic acid (IMA) and triiodide ion ($\epsilon = 32000$ cm^{-1} M^{-1}) both have significant absorptivity. The envelope of minima in the 280-nm curve corresponds to a first-order increase in [IMA] at a rate equal to that of the disappearance of I_2 in the 468-nm curve. In view of the much larger molar absorptivity of I_3^- at 280 nm, we conclude that $[I_2] \gg [I_3^-]$ and that the oscillations result from changes in $[I_3^-]$.

In the preoscillatory period, the autocatalytic increase in $[I_2]$ followed by a sharp decrease and a slow recovery resembles the behavior of the chlorite–iodide reaction in the absence of MA.[6] This similarity suggests that in the presence of MA the ClO_2^-–I^- reaction is complete before oscillations start, and one or more products of this reaction plays a crucial role in the subsequent periodic behavior. From $[I_2]$ determined from the absorbance at 468 nm, we can estimate $[IO_3^-]$ using the stoichiometric equations

$$ClO_2^- + 4I^- + 4H^+ = Cl^- + 2I_2 + 2H_2O \qquad (1)$$

$$5ClO_2^- + 2I_2 + 2H_2O = 5Cl^- + 4IO_3^- + 4H^+ \qquad (2)$$

Rábai and Beck[7] showed that reaction 2 is accompanied by formation of chlorine dioxide. The $[ClO_2^\bullet]$ formed during the chlorite–iodide reaction (at the same initial concentrations used in the chlorite–iodide–malonic acid oscillator) can be determined from the spectrum of the reaction mixture. If we mix the amounts of I_2, IO_3^-, and $ClO_2^\bullet$ formed in the chlorite–iodide reaction with MA and H_2SO_4 at the concentrations used in the oscillatory reaction, oscillation appears with no induction period. Further study reveals that iodate ion is not required for oscillation. These experiments demonstrate that *malonic acid*, *chlorine dioxide*, *and iodine* are responsible for the oscillation. In Figure 2, we show three oscillatory curves at different $[ClO_2^\bullet]_0$.

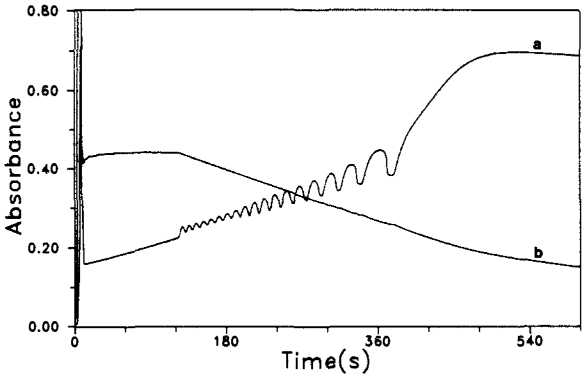

Figure 1. Absorbance at (a) 280 nm and (b) 468 nm in the chlorite–iodide–malonic acid reaction. $[ClO_2^-]_0 = 5.71 \times 10^{-3}$ M, $[I^-]_0 = 4.57 \times 10^{-3}$ M, $[MA]_0 = 1.0 \times 10^{-3}$ M, $[H_2SO_4]_0 = 5.0 \times 10^{-3}$ M.

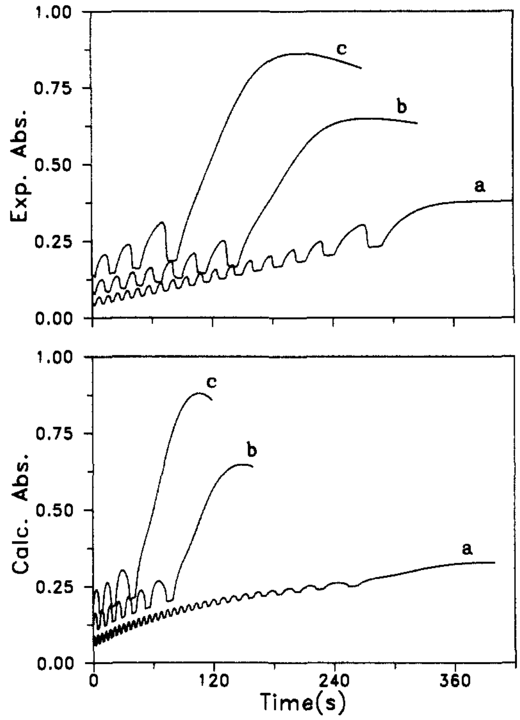

Figure 2. Experimental and calculated oscillations in absorbance (280 nm) in the chlorine dioxide–iodine–malonic acid reaction. Molar absorbances for I_3^-, I_2, $ClO_2^\bullet$, and iodomalonic acid are 32000, 100, 88, and 300 M^{-1} cm^{-1}, respectively. $[I_2]_0 = 5.0 \times 10^{-4}$ M, $[MA]_0 = 1.0 \times 10^{-3}$ M, $[H_2SO_4]_0 = 5.0 \times 10^{-3}$ M, $[ClO_2^\bullet]_0 = 1.7 \times 10^{-4}$ (a), 1.0×10^{-4} (b), and 7.1×10^{-5} M (c). For clarity, curves b and c have been shifted upward by 0.05 and 0.10 absorbance units, respectively, since in the absence of a shift the curves overlap significantly.

Malonic acid can be replaced by ethyl acetoacetate at the same concentration. This suggests that MA serves primarily to generate I^- from I_2 and that in an open system the reaction of chlorine dioxide with iodide should be oscillatory. Our experiments confirm this prediction over a broad range of initial concentrations and residence times.[8]

On the basis of these observations, we propose a model consisting of three component processes. The first is the reaction between (MA) and I_2.

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(8) A typical reaction mixture consists of $[ClO_2]_0 = 1 \times 10^{-4}$ M, $[I^-]_0 = 1 \times 10^{-4}$ M, $[H_2SO_4]_0 = 5 \times 10^{-3}$ M at a reciprocal residence time $k_0 = 5 \times 10^{-3}$ s^{-1}. The oscillations were monitored with an iodide-selective electrode.

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$$\mathrm{MA} + \mathrm{I_2} \rightarrow \mathrm{IMA} + \mathrm{I^-} + \mathrm{H^+} \qquad (3)$$

The rate-determining step is the enolization of malonic acid, which is followed by the fast reaction between the enol form and iodine. The rate law for this process is[9,10]

$$v_3 = -\frac{\mathrm{d}[\mathrm{I_2}]}{\mathrm{d}t} = \frac{(4 \times 10^{-3})[\mathrm{MA}][\mathrm{I_2}]}{(1 \times 10^{-4}) + [\mathrm{I_2}]} \qquad (3')$$

The second component reaction occurs between chlorine dioxide and iodide ion.

$$\mathrm{ClO_2} + \mathrm{I^-} \rightarrow \tfrac{1}{2}\mathrm{I_2} + \mathrm{ClO_2^-} \qquad (4)$$

We have redetermined the kinetics of this reaction, which was first studied by Fukutomi and Gordon.[11] Using a more modern stopped-flow instrument and conditions more appropriate for the oscillatory system, we obtained the following rate law, which is independent of both pH between 2.0 and 5.0 and ionic strength (0.1–1.0 M).

$$v_4 = 2\mathrm{d}[\mathrm{I_2}]/\mathrm{d}t = (6 \times 10^3)[\mathrm{ClO_2^\bullet}][\mathrm{I^-}] \qquad (4')$$

The third component reaction, between chlorite and iodide ions, was studied by Kern and Kim[12] and by De Meeus and Sigalla.[13]

$$\mathrm{ClO_2^-} + 4\mathrm{I^-} + 4\mathrm{H^+} \rightarrow \mathrm{Cl^-} + 2\mathrm{I_2} + 2\mathrm{H_2O} \qquad (5)$$

The rate equation of Kern and Kim is

$$r_5 = (4.6 \times 10^2)[\mathrm{ClO_2^-}][\mathrm{I^-}][\mathrm{H^+}] + (2.65 \times 10^{-3})[\mathrm{ClO_2^-}][\mathrm{I_2}]/[\mathrm{I^-}] \qquad (5')$$

The selfinhibition[14] of reaction 5 by iodide is much more important than the autocatalysis by iodine, because $[\mathrm{I_2}]$ is nearly constant during an oscillatory period, while $[\mathrm{I^-}]$ varies by several orders of magnitude. The second term of rate law (5′) cannot be valid when the $[\mathrm{I^-}]$ tends to zero, because this term becomes infinite, while the rate must go to zero if the concentration of one of the reactants vanishes. To alleviate this situation, we replace eq 5′ by

$$r_3 = (4.6 \times 10^2)[\mathrm{ClO_2^-}][\mathrm{I^-}][\mathrm{H^+}] + (2.65 \times 10^{-3})[\mathrm{ClO_2^-}][\mathrm{I_2}][\mathrm{I^-}]/(u + [\mathrm{I^-}]^2) \qquad (5'')$$

with $u = 1 \times 10^{-13}$ M^2. The second term goes smoothly to zero as $[\mathrm{I^-}] \rightarrow 0$, and gives Kern and Kim's expression (5′) when $[\mathrm{I^-}] \gg 10^{-6}$ M.

The simple model consisting of reactions 3–5 and the corresponding rate equations describes both the batch oscillations in the $\mathrm{ClO_2^\bullet}$–$\mathrm{I_2}$–MA system, as shown in Figure 2, and the oscillatory behavior of the $\mathrm{ClO_2^\bullet}$–$\mathrm{I^-}$ reaction in a flow reactor. By treating the concentrations of $\mathrm{I_2}$, MA, and $\mathrm{ClO_2^\bullet}$ as constant, we obtain a two-variable ($[\mathrm{I^-}]$, $[\mathrm{ClO_2^-}]$) model, which gives good agreement with the observed dynamics.[15] Such a model is amenable to a variety of analytical techniques for studying both the temporal and the spatial behavior of this system. A more detailed analysis of the experimental kinetics and of the predictions of the model will be presented elsewhere.

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Chiral Pentaisopropyl–Cyclopentadienyl and Pentaisopentyl–Cyclopentadienyl Complexes: One-Pot Synthesis by Formation of 10 Carbon–Carbon Bonds from Pentamethylcobalticinium

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Following explosive developments in $\mathrm{C_5Me_5}$–transition-metal chemistry, considerable interest has recently appeared for the design of new pentasubstituted Cp ligands[1] such as $\mathrm{C_5Et_5}$[1a,b] (and $\mathrm{C_5Et_4R}$[1c,d]), $\mathrm{C_5Ph_5}$,[1e] $\mathrm{C_5(CH_2Ph)_5}$,[1f] and $\mathrm{C_5Me_4R}$ (R = alkyl),[1g] and attempts to synthesize the $\mathrm{C_5}(i\text{-Pr})_5$ ligand have been published.[1h]

This report shows a one-pot route to the first pentaisoalkylcyclopentadienyl complexes involving the formation of 10 C–C bonds with the hope that, beyond their topological interest, these novel bulky ligands will also find future use in organometallic chemistry and catalysis.

We already know that the hexaalkylation of $[\mathrm{FeCp(C_6Me_6)}]^+$ using a base and a halide proceeds according to eq 1, with replacement of one hydrogen by an alkyl substituent on each methyl group[2] (single branching).

$$[\mathrm{FeCp(C_6Me_6)}]^+ \xrightarrow[\text{RX (R = alkyl, allyl, benzyl)}]{\text{KOR}'\ (\text{R}' = \text{H},\ t\text{-Bu}),} [\mathrm{FeCp[C_6(CH_2R)_6]}]^+ \qquad (1)$$

We now find that 1,2,3,4,5-pentamethylcobalticinium (**1**)[3] reacts with excess (20 equiv) t-BuOK and $\mathrm{CH_3I}$ (THF, 60 °C, 14 h) to give pure 1,2,3,4,5-pentaisopropylcobalticinium ($\mathrm{PF_6^-}$ salt (**2**), Scheme I, double branching), as indicated by ^{1}H NMR of the crude reaction product.

Recrystallization from acetone/ethanol (1/1) gave an 81% yield of yellow crystals of **2**.[4] Its ^{1}H NMR spectrum ($\mathrm{CDCl_3}$) shows two doublets at δ 1.17 and 1.51 ppm for the non-equivalent (endo and exo) methyl groups and only one $\mathrm{C_5H_5}$ peak (δ 5.54 ppm) whereas the [^{1}H]^{13}C spectrum ($\mathrm{CDCl_3}$) also shows two methyl peaks at δ 21.4 and 24.3 ppm and only one methine peak at δ 25 ppm (Table I, supplementary material).[4] Thus, of the four possible pairs of enantiomers of variable energy, only the low-energy one, in which all the methine C–H bonds are pointing in the same direction, is observed. This is due to the "requirement that each isopropyl group interlocks exactly with its neighbours on either side" as stated in the case of hexaisopropylbenzene[5] (of which no

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