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Iodine Concentration Behaviour of the Hydrogen Peroxide–Iodic Acid–Manganese(II)–Malonic Acid Oscillating System

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The iodine concentration behaviour of the title reaction has been investigated. Production and consumption rates under various conditions are reported. Some mechanistic details are suggested.

Introduction

This oscillating reaction intimately related to the Bray [1] and Belousov-Zhabotinskii [2] reactions and discovered by Rauscher and Briggs [3] is at present of particular interest [4, 5, 12]. As part of the continued investigation of this system [6–8] the iodine concentration behaviour has been examined. Some mechanistic conclusions are given. Thermometric measurements have been used as an indication of the oxidation of malonic acid and iodinated malonic acid.

Experimental

The iodine concentration oscillations were monitored using a filter photometer (λ_{max} 430 nm) and signals displayed on a potentiometric recorder. The reaction mixtures were stirred throughout. Thermometric measurements were carried out using a thermistor–Wheatstone bridge circuit with the reaction mixture in a small thermos flask stirred mechanically. The reaction was initiated with hydrogen peroxide. High purity (Hopkin and Williams) materials were used throughout. Manganese(II) was supplied as the sulphate and iodate as the potassium salt.

Results

It is apparent that all concentration variables affect all phases of the reaction. The behaviour is complicated by the fact that the iodine production and consumption rates can vary considerably with oscillation number. Broadly speaking, it may be considered that the iodine production rate increases with increasing oscillation number and that the consumption rate decreases with increasing oscillation number.

The reaction may be characterised by several factors, these are considered as follows.

The Induction Period

Under suitable conditions the oscillations are preceded by an induction period. The effect of manganese(II), malonic acid, hydrogen peroxide, iodate and sulphuric acid are shown in Fig. 1.

The Waveshape

The waveshape of the iodine oscillations does not change appreciably with the concentration of any species. A saw tooth appearance is generally observed but the oscillations may approach sinusoidal at low sulphuric acid or high malonic acid concentration. Some typical traces are shown in Fig. 2. The first iodine production rate is always greater than the consumption rate.

The Time Periods

The effect of manganese(II), malonic acid, hydrogen peroxide, iodate and sulphuric acid on the time period are shown in Fig. 3.

Iodine Maxima

An increase in iodate and sulphuric acid concentration increases the iodine maxima and minima. An increase in malonic acid decreases both the maxima and minima. Manganese(II) and hydrogen peroxide both increase the maxima but the effect is slight except at very high hydrogen peroxide concentration where both maxima and minima are increased.

The Mode of Conclusion of the Reaction

Oscillations may end abruptly with production and precipitation of iodine, may damp away to be followed at some later time by production of iodine or the reaction may cease in the absence of iodine. Where observed the rate of final iodine production is increased by increasing malonic acid (considered in this phase as iodomalonic acid) and decreased by increasing hydrogen peroxide, sulphuric acid and manganese(II).

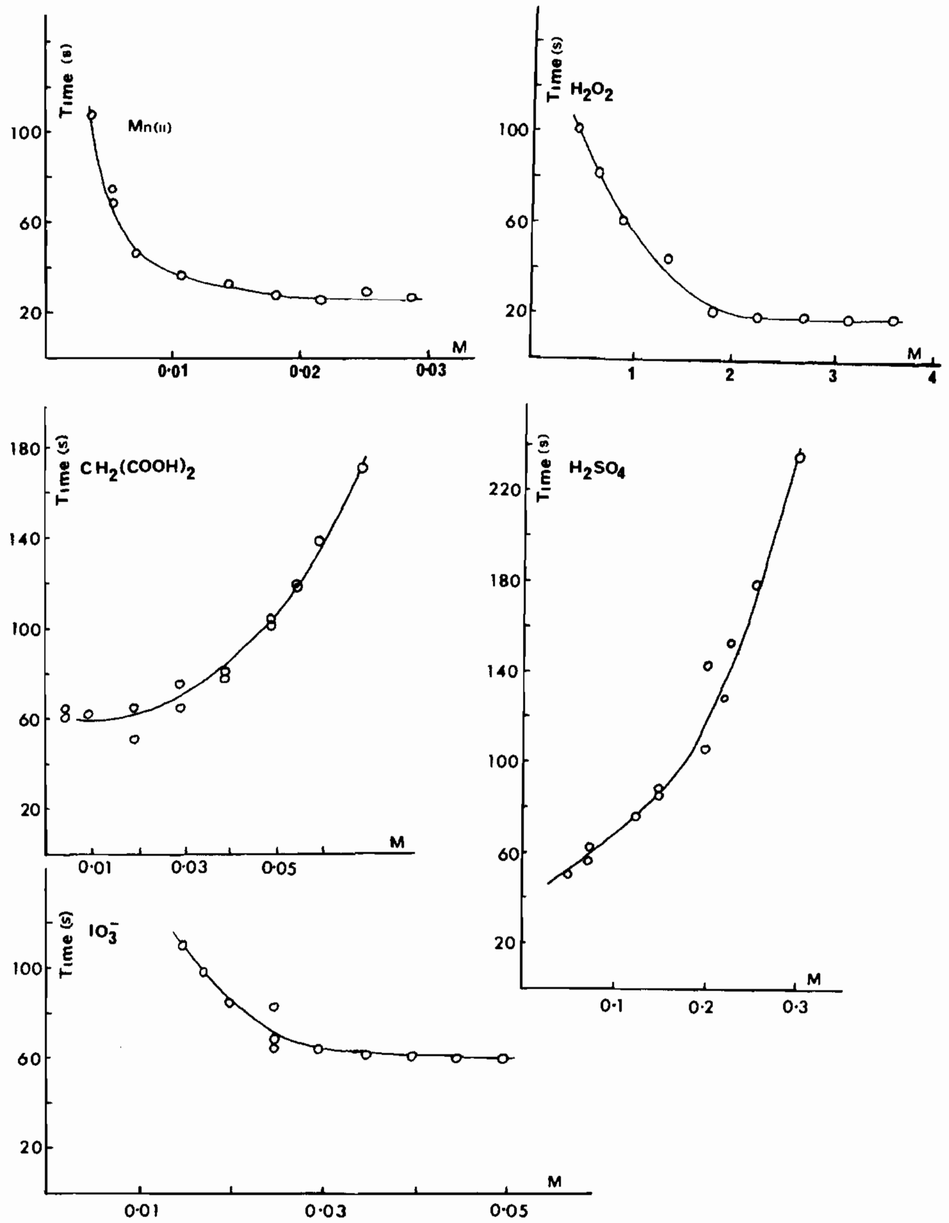


Fig. 1. Concentration effects on the induction period. Standard conditions are $[IO_3^-] = 0.025\ M$, $[H_2SO_4] = 0.10\ M$, $[H_2O_2] = 0.91\ M$, $[Mn(II)] = 0.005\ M$, $[CH_2(COOH)_2] = 0.03\ M$. In each plot the concentration of all species except that being examined is as for the standard conditions T = 23 °C.

The Iodine Production and Comsumption Rates

Production and consumption rates which may be considered are first, second (early) and late. There are significant effects dependent on the existence of any induction period and on the mode of conclusion of the reaction.

Reliable first production rates are under most circumstances difficult to obtain as a result of the very high evolution of oxygen on mixing. The first consumption rate does not generally differ appreciably from the early consumption rates. Some production and consumption rates for a typical system *versus* manganese(II), malonic acid, hydrogen peroxide, iodate and sulphuric acid are shown in Fig. 4. For these oscillators the first production rate is somewhat slower than the second or early rate. Where an appreciable induction period is observed, the exponential rise in iodine concentration on completion of this phase is increased by increasing sulphuric acid, manganese(II), hydrogen peroxide and iodate but is decreased by increasing malonic acid.

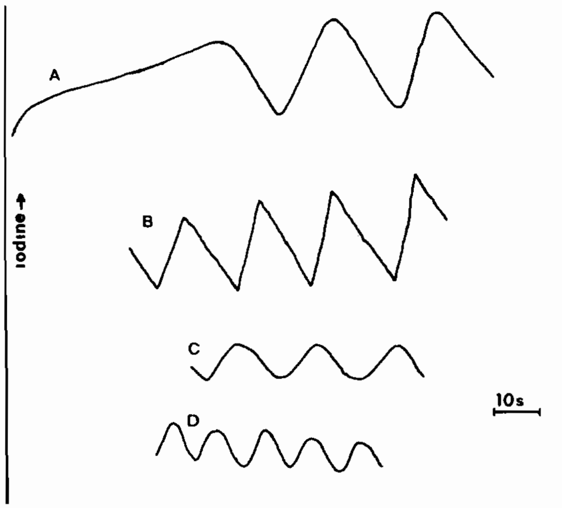


Fig. 2. Iodine concentration *versus* time traces for typical oscillators:

A) $[\mathrm{IO}_3^-]$ = 0.25 *M*, $[H_2SO_4]$ = 0.10 *M*, $[H_2O_2]$ = 0.91 *M*, [Mn(II)] = 0.005 *M*, $[CH_2(COOH)_2]$ = 0.03 *M*

B) $[\mathrm{IO}_3^-]$ = 0.025 *M*, $[H_2SO_4]$ = 0.10 *M*, $[H_2O_2]$ = 0.91 *M*, [Mn(II)] = 0.02 *M*, $[CH_2(COOH)_2]$ = 0.03 *M*

C) $[\mathrm{IO}_3^-]$ = 0.025 *M*, $[H_2SO_4]$ = 0.05 *M*, $[H_2O_2]$ = 0.91 *M*, [Mn(II)] = 0.005 *M*, $[CH_2(COOH)_2]$ = 0.03 *M*

D) $[\mathrm{IO}_3^-]$ = 0.025 *M*, $[H_2SO_4]$ = 0.10 *M*, $[H_2O_2]$ = 0.91 *M*, [Mn(II)] = 0.005 *M*, $[CH_2(COOH)_2]$ = 0.07 *M*.

For the second (early) production rates the production is for low concentrations of manganese(II) reasonably represented

$$\frac{d[I_2]}{dt} = k[H_2O_2]\,[\mathrm{Mn(II)}]\,[\mathrm{IO}_3^-]\,[H_2SO_4]$$

From the above data (Fig. 5) we have $k_{23\,^\circ\mathrm{C}} = 2.0 \pm 0.25\ M^{-3}\ s^{-1}$. Malonic acid in the range 0.015–0.05 *M* had no significant effect.

The consumption rate within the oscillator is slower than that for the added iodine–hydrogen peroxide–iodate–sulphuric acid–malonic acid reaction under the same conditions. This reflects the importance of iodine production via iodinated malonic acid.

Thermochemical Behaviour

High heat output within the reaction is observed at high malonic acid and low hydrogen peroxide concentrations. Increasing the iodate and sulphuric acid concentrations increases the initial rate of heat output. Manganese(II) has little effect. The heat output of the system when in the oscillatory phase is a stepwise function and is at its highest during the iodine production phase. It is considered that the heat output is a measure of the oxidation of organic material and an indication of the free radical concentration of the reaction mixture. Typical behaviour is shown in Fig. 6.

Discussion

The gross reactions we are considering are represented:

iodine production

$$2HIO_3 + 5H_2O_2 \rightarrow 5O_2 + I_2 + 6H_2O \qquad (1)$$

iodine consumption

$$CH_2(COOH)_2 + I_2 \rightleftharpoons CHI(COOH)_2 + H^+ + I^- \qquad (2)$$

The Induction Period

The induction period results from conditions where the rate of consumption of iodine can compete favourably with the production. Hydrogen peroxide and manganese(II) which favour iodine production decrease the induction period, malonic acid which favours consumption increases the period. Sulphuric acid increases the induction period to a much greater extent than anticipated from its effect on the two isolated reactions (1) and (2). At high sulphuric acid concentration oxygen evolution during the induction period at low to non-existent iodine concentration is very high indeed. The rate of iodine removal is decreased during the induction period as a result of lower malonic acid concentration through

(a) *iodination*
(b) *removal through oxidation.*

The rate of iodine production is expected to increase during this period as a result of oxidation of iodinated organic material and to decrease through a decrease in iodate and hydrogen peroxide concentrations. Thermochemical evidence (Fig. 6) indicates extensive oxidation during the induction period. The rate of consumption of iodine *vs.* malonic acid concentration (Fig. 4) indicates that at high malonic acid concentration this species is adjusted during the induction period as must be the hydrogen peroxide concentration.

The Time Periods

It appears that little mechanistic information can be obtained from the time periods in the present system. The decrease in time period with increase in malonic acid concentration is considered to result from the rise in iodide ion concentration being able to inhibit the iodine production at lower iodide ion concentation. The increase in period with acid probably results from suppression of the iodide ion concentration. In agreement with this the iodine maxima are higher at high acidity.

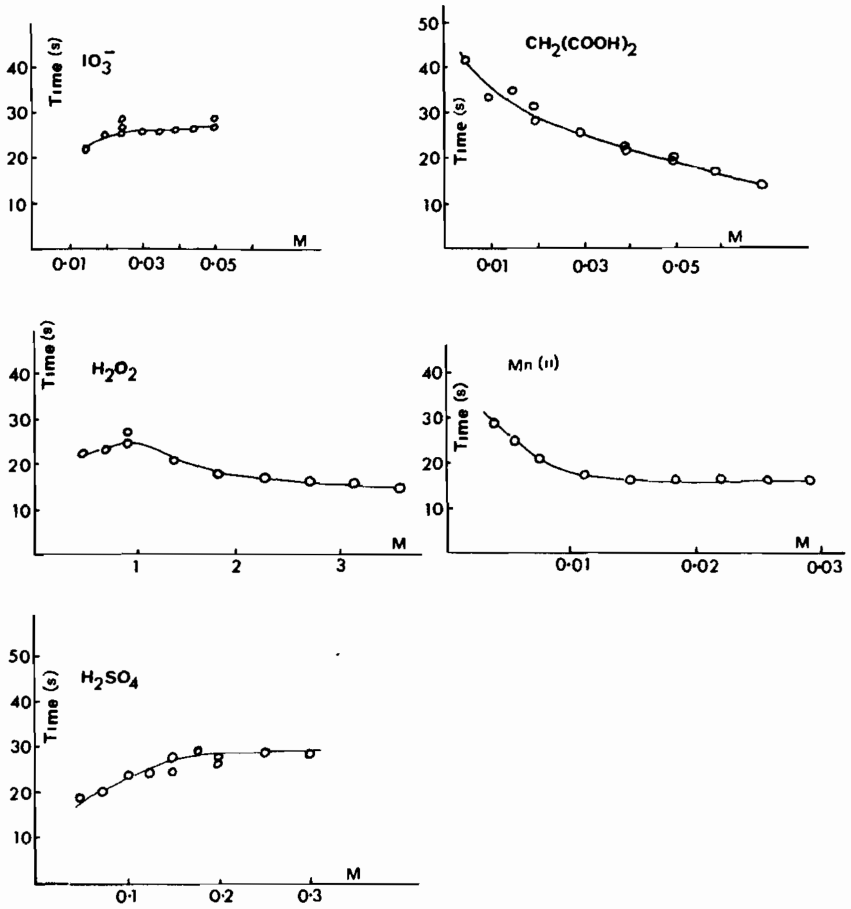


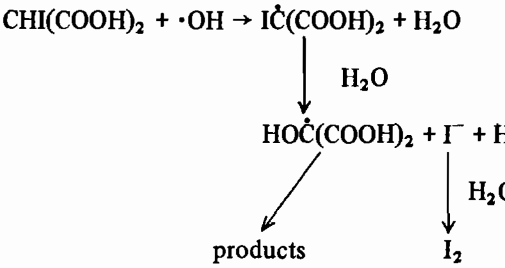
Fig. 3. Concentration effects on the time period. Standard conditions are $[IO_3^-] = 0.025\ M$, $[H_2SO_4] = 0.10\ M$, $[H_2O_2] = 0.91\ M$, $[Mn(II)] = 0.005\ M$, $[CH_2(COOH)_2] = 0.03\ M$. In each plot the concentration of all species except that being examined is as for the standard conditions T = 23 °C.

The Mode of Conclusion of the Reaction

Cessation of the oscillations with iodine production leading to precipitation is favoured by an increase in sulphuric acid, iodate, malonic acid and manganese(II) concentration and by a decrease in hydrogen peroxide concentration. It is clear that the final iodine production in these cases results from conditions when iodine production through oxidation of iodomalonic acid and the manganese(II)–hydrogen peroxide–iodate reaction can be maintained greater than the rate of iodination of malonic acid despite some considerable increase in the iodide ion concentration.

It is evident that the particular mode of conclusion is dependent on the iodate concentration being low. It appears that the iodomalonic acid concentration cannot be high in comparison to the malonic acid concentration.

Thermochemical evidence (Fig. 6) indicates that appreciable oxidation of organic material proceeds only during the iodine production phase. The oxidant is apparently an intermediate in this reaction. Hydroxyl radicals would appear the most likely candidate. This suggestion is in agreement with the fact that the final production rate is decreased by increasing hydrogen peroxide concentration, the competition between organic material and hydrogen peroxide for hydroxyl radical being the significant factor. The oxidation of iodomalonic acid to yield iodide ion can then be represented:



$$\begin{tikzcd}
\mathrm{CHI(COOH)_2} + \cdot\mathrm{OH} \arrow[r] & \mathrm{I\dot{C}(COOH)_2} + \mathrm{H_2O} \arrow[d, "\mathrm{H_2O}"] & \\
& \mathrm{HO\dot{C}(COOH)_2} \arrow[dl] & + \mathrm{I^-} + \mathrm{H^+} \arrow[d, "\mathrm{H_2O_2}"] \\
\text{products} & & \mathrm{I_2}
\end{tikzcd} \qquad (3)$$

It is anticipated that manganese(II) may also compete for hydroxyl radical [9]

$$\mathrm{Mn^{2+}} + \cdot\mathrm{OH} + \mathrm{H^+} \rightarrow \mathrm{Mn(III)} + \mathrm{H_2O} \qquad (4)$$

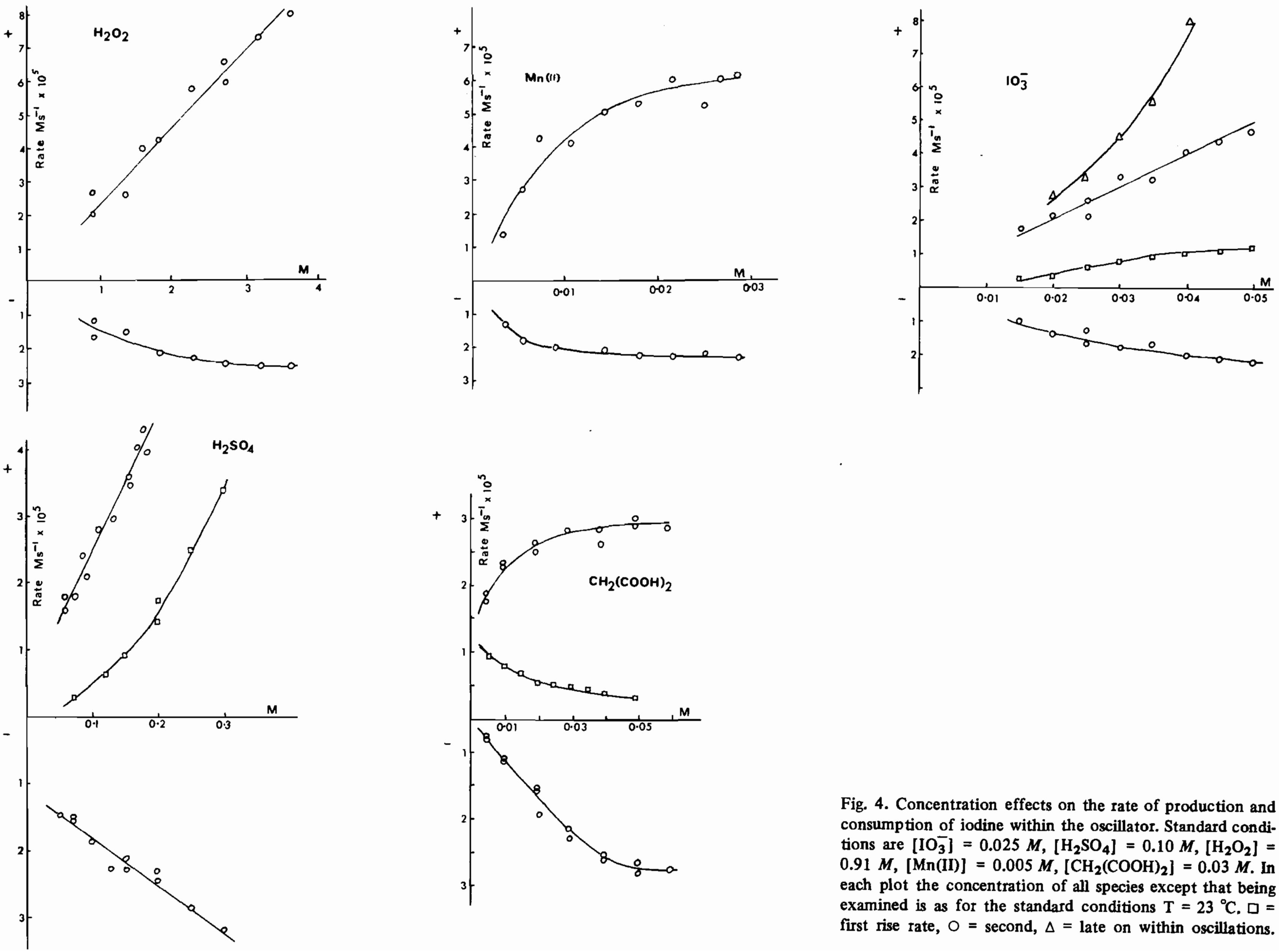


Fig. 4. Concentration effects on the rate of production and consumption of iodine within the oscillator. Standard conditions are $[IO_3^-]$ = 0.025 *M*, $[H_2SO_4]$ = 0.10 *M*, $[H_2O_2]$ = 0.91 *M*, [Mn(II)] = 0.005 *M*, $[CH_2(COOH)_2]$ = 0.03 *M*. In each plot the concentration of all species except that being examined is as for the standard conditions T = 23 °C. □ = first rise rate, ○ = second, △ = late on within oscillations.

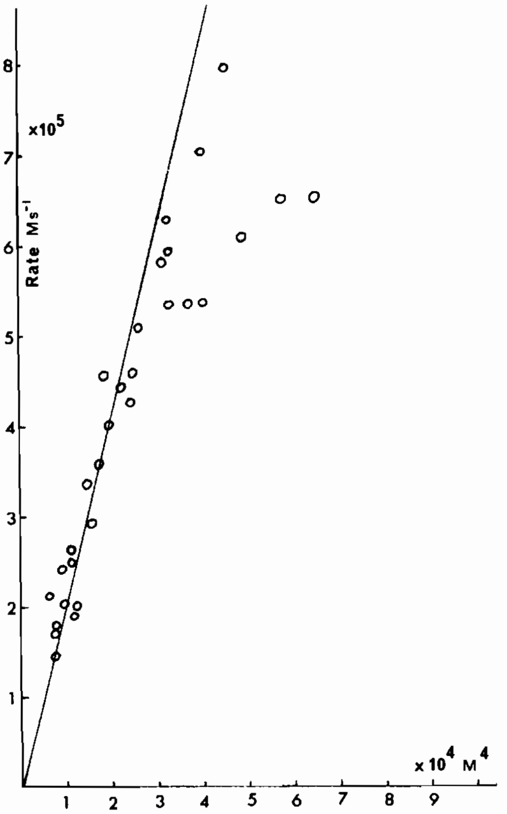


Fig. 5. Plot of production rate *vs.* the product $[H_2O_2][Mn(II)][IO_3^-][H_2SO_4]$ for the second rise rate within the oscillator (data from Fig. 4).

$$Mn(III) + H_2O_2 \rightarrow Mn(II) + H^+ + {\cdot}OOH \tag{5}$$

The onset of the final production of iodine is sooner in the absence of stirring. This appears to implicate oxygen in the oxidation pathway.

Iodine Production

The concentration effects on the iodine production rates appear similar to those in the manganese(II) catalysed hydrogen peroxide–iodate reaction (absence of malonic acid) [10]. However, in the absence of malonic acid reoxidation of iodine is of obvious importance [10] and the reaction may be considered as a combination of

$$5H_2O_2 + 2HIO_3 \rightarrow 5O_2 + I_2 + 6H_2O \tag{1}$$

and

$$I_2 + 5H_2O_2 \rightarrow 2HIO_3 + 4H_2O \tag{6}$$

Our interpretation [10] of this reaction involves the iodine dioxide oxidation of manganese(II) with subsequent rapid reoxidation by hydrogen peroxide and is represented

$$HIO_3 + I^- + H^+ \rightarrow HIO_2 + HIO \tag{7}$$

$$HIO_3 + H_2O_2 \rightarrow HIO_2 + H_2O + O_2 \tag{8}$$

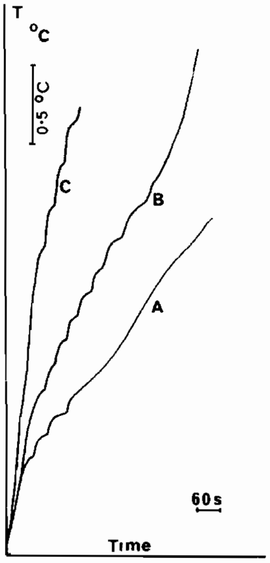


Fig. 6. Temperature *vs.* time curves for the oscillator $[IO_3^-]$ = 0.04 *M*, $[H_2SO_4]$ = 0.10 *M*, $[H_2O_2]$ = 0.91 *M*, [Mn(II)] = 0.0072 *M*, $[CH_2(COOH)_2]$ = A) 0.02 *M*, B) 0.04 *M*, C) = 0.06 *M*. Total volume = 50 cm^3.

$$HIO_3 + HIO_2 \rightleftharpoons 2IO_2^{\cdot} + H_2O \tag{9}$$

$$IO_2^{\cdot} + Mn(II) + H^+ \rightleftharpoons Mn(III) + HIO_2 \tag{10}$$

$$Mn(III) + H_2O_2 \rightleftharpoons Mn(II) + {\cdot}OOH + H^+ \tag{11}$$

$$2\ {\cdot}OOH \rightarrow H_2O_2 + O_2 \tag{12}$$

$$2HIO_2 \rightarrow HIO_3 + HIO \tag{13}$$

$$HIO + H_2O_2 \rightarrow H^+ + I^- + O_2 + H_2O \tag{14}$$

$$HIO + I^- + H^+ \rightleftharpoons H_2O + I_2 \tag{15}$$

This reaction scheme is analogous to the suggested mechanism for the bromate oxidation of manganese(II) in the absence of hydrogen peroxide. The nonexistence of the analogous iodate reaction (absence of hydrogen peroxide) is considered to result from the equilibrium (10) lying well to the left. In the presence of hydrogen-peroxide (10) is driven to the right via rapid removal of manganese(III) via (11).

The reoxidation of iodine to iodate (6) has been examined by Noyes and Sharma [1] and is considered to obey the stoichiometry (16)

$$I_2 + 11H_2O_2 \rightarrow 2IO_3^- + 2H^+ + 3O_2 + 10H_2O \tag{16}$$

and to be initiated via the perhydroxyl radical [1]. The conditions expected to favour this reaction are those prevailing during the iodine production phase. The iodine removal rates and high iodide ion concentration mitigate against the importance of this reaction during the iodine consumption phase of the oscillator. With the iodide ion concentration high (via 2) the iodous acid concentration is anticipated to be low through (17) and

$$HIO_2 + I^- + H^+ \rightarrow 2HIO \qquad (17)$$

the radical production correspondingly low as a result of the non-existence of (9).

Consumption of Iodine

The consumption of iodine through iodination of malonic acid is represented by (2). In the presence of iodate the stoichiometry is represented

$$5CH_2(COOH)_2 + H^+ + 2I_2 + IO_3^- \rightarrow 5CHI(COOH)_2 + 3H_2O \qquad (18)$$

and in the presence of hydrogen peroxide

$$2CH_2(COOH)_2 + I_2 + H_2O_2 \rightarrow 2CHI(COOH)_2 + 2H_2O \qquad (19)$$

Under the oscillatory conditions the oxidation of iodide by iodate is faster than that by hydrogen peroxide. Manganese(II) in the absence of hydrogen peroxide and iodate does not affect the rate of iodination. pH measurements on malonic acid–manganese(II) sulphate solutions do not indicate significant complexation.

The iodination of malonic acid in the presence of triiodide ion has been examined by Leopold and Haim [11] who report the rate equation

$$\frac{-d[I_3^-]}{dt} = [HOOCCH_2COO^-]\{k[I_2] + k'[I_3^-]\} + [(CH_2(COOH)_2)]\{k''[I_2] + k''i[I_3^-]\} + k''''[H^+][I_3^-][CH_2(COOH)_2]$$

The same workers report the rate of enolization to be represented (25 °C)

$$\nu = 2 \times 10^{-3}[CH_2(COOH)_2] + 10^{-2}[CH_2(COOH)_2]^2$$

The iodide ion concentration is low in the oscillatory system and except during the iodine consumption at high iodine concentration iodine rather than the triiodide ion is the dominant species. In the presence of iodine with no iodide ion other than that present through hydrolysis the present work indicates that for $[CH_2(COOH)_2] < 0.05\ M$ and $[H_2SO_4] = 0.1\ M$ (the conditions for oscillatory behaviour (Fig. 5)) the iodination is reasonably well represented by

$$\frac{-d[I_2]}{dt} = k'[CH_2(COOH)_2] + k'''[I_3^-]\} + k''[CH_2(COOH)_2][I_2]$$

Considering the k′ pathway as enolization we have, 25 °C, $k' = 2 \times 10^{-3}\ s^{-1}$ and $k'' = 1.0 \pm 0.2\ mol^{-1}\ l\ s^{-1}$.

Sulphuric acid has a small positive effect on the rate.

Oscillatory Behaviour

Considering the system as switched between two steady states of high and low iodide ion concentration [4] we now have a reaction analogous to that of the Belousov-Zhabotinskii reaction and with iodous acid playing a similar role to bromous acid in that system.

For radical production leading to iodine we have the principal fate of iodous acid as (9):

$$HIO_3 + HIO_2 \rightleftharpoons 2IO_2^{\bullet} + H_2O \qquad (9)$$

and for high iodide ion concentration (the conditions prevailing during iodine consumption) the principal fate of iodous acid is (17):

$$HIO_2 + I^- + H^+ \rightarrow 2HIO \qquad (17)$$

Switching is anticipated to occur whenever the iodide ion concentration passes through the value

$$[I^-] = \frac{k_9}{k_{17}}[IO_3^-]$$

For $[I^-]$ less than this value iodine production will dominate leading to an autocatalytic rise in iodous acid limited by the second order disproportionation of this species. For $[I^-]$ greater than this value iodine consumption dominates and the iodous acid concentration is maintained low.

Acknowledgements

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