On the Reduction of Iodate in Briggs–Rauscher Type Chemical Oscillators

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Oxidation of organic compounds in the presence of iodate ion is significant to the behaviour of the Briggs–Rauscher oscillating system; a new induced reaction in which iodine is liberated from iodate during the oxidation of oxalic acid by a one electron oxidant is described.

The Briggs–Rauscher reaction[1] is an oscillating system based on the manganese(II) catalysed iodate–peroxide reaction. Oscillations are obtained in the presence of an organic substrate such as malonic acid[2,3] or acetone.[4] The behaviour of these two substrates is significantly different as a result of greater oxidation of organic material in the malonic acid system. The reactions are now becoming well understood and mathematical modelling of the malonic acid system has yielded a fair approximation to the observed behaviour.[3] Discrepancies, at least in part, result from considerations involving oxidation of the organic substrate and material derived from it. Combination of the two substrates leads to an interesting 'double barrelled' oscillatory system the two oscillatory phases of which are separated by a period involving oxidation of malonic acid–iodomalonic acid.[5]

During the examination of some organic substrate–halate reactions of relevance to these systems it has been demonstrated that iodate may be reduced by free radicals generated in the oxidation of the organic substrate, an observation of particular significance to the oscillatory behaviour. The following serves to illustrate the possibilities.†

When manganese(III) is added to an iodate–oxalic acid–sulphuric acid solution iodine is produced. Experimental data are shown in Figure 1. The rate of iodine production increases with increasing iodate at low iodate concentration but is virtually independent of iodate at high concentration. At high iodate concentration iodine production continues to precipitation. Continuous extraction of the iodine produced enables observation of the behaviour of Mn^{III} in the system and in this case, at high iodate concentration, the rate of loss of Mn^{III} is low to non-existent (Figure 1c). Removal of iodine with

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† Oxalic acid has been chosen to illustrate these effects as quantitative results are easier to obtain than in the case of malonic acid.

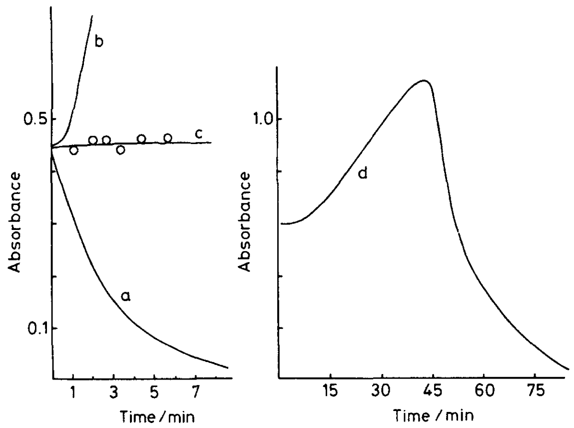

Figure 1. Absorbance *vs.* time behaviour for the Mn^{III}–oxalic acid–iodate system: $\lambda = 460$ nm, $T = 25$ °C, $[Mn^{III}] = 3.84 \times 10^{-3}$ M, $[Mn^{II}] = 9.85 \times 10^{-3}$ M, $[H_2SO_4] = 6.77 \times 10^{-2}$ M, $[Na_2P_2O_7] = 1.35 \times 10^{-1}$ M, $[H_2C_2O_4] = 2.15 \times 10^{-2}$ M. a, No iodate; b, $[KIO_3] = 2.5 \times 10^{-2}$ M (absorbance is the sum of Mn^{III} and iodine); c, $[KIO_3] = 2.5 \times 10^{-2}$ M; ○ Iodine removed by extraction with decane; solid line, iodine removed [*via* (1)] with acetone; d, behaviour at low iodate concentration, $[KIO_3] = 2.5 \times 10^{-3}$ M (iodine initially produced is eventually reduced to iodide ion).

acetone, reaction (1), rather than with decane did not affect the rate of consumption of Mn. It is noted that cerium(IV) can replace Mn^{III}; hence a one electron transfer is clearly implicated. The initiation of the iodine production appears to be *via* reactions (2)—(4).

$$5Me_2CO + 2I_2 + IO_3^- \longrightarrow 5ICH_2COMe + 2H^+ + 3H_2O \quad (1)$$

$$Mn^{III} + C_2O_4^{2-} \rightarrow CO_2^{\cdot -} + Mn^{II} + CO_2 \quad (2)$$

$$CO_2^{\cdot -} + IO_3^- + H^+ \rightarrow CO_2 + IO_2^{\cdot} + H_2O \quad (3)$$

$$IO_2^{\cdot} + Mn^{II} + H^+ \rightarrow Mn^{III} + HIO_2 \quad (4)$$

The failure of acetone to prevent maintenance of a steady state Mn^{III} concentration during iodine production with the system at high iodate concentration (Figure 1c) indicates that iodide ion produced *via* reaction (5) does not inhibit the oxidation through reaction (6) preventing (7) as it does in the Mn^{II}–iodate–hydrogen peroxide reaction. Sustained iodine dioxide production *via* reactions (2)—(4) appears responsible. The ability of iodine dioxide to oxidize Mn^{II} in these reactions again illustrates the limited number of fates open to iodine dioxide once produced in a halate system.[3] With reference to the Briggs–Rauscher reaction it is clear that cycles involving iodine dioxide can in principle be maintained through oxidation, by any species, of the organic substrate even during periods of relatively high iodide ion concentration.

$$MeCOMe + I_2 \rightarrow MeCOCH_2I + I^- + H^+ \quad (5)$$

$$HIO_2 + I^- + H^+ \rightarrow 2HIO \quad (6)$$

$$HIO_2 + H^+ + IO_3^- \rightarrow 2IO_2^{\cdot} + H_2O \quad (7)$$

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