The Hydrogen Peroxide–Iodic acid–Manganese(II)–Acetone Oscillating System

By David O. Cooke

(*Hastings College of Further Education, St. Leonards on Sea, Sussex* TN38 OHX)

Summary A new oscillatory system involving acetone is described; sustained oscillations which may be regenerated by replenishment of the reagents have been obtained and some mechanistic details are given.

During the investigation of the H_2O_2–HIO_3–Mn^{II}–$CH_2(CO_2H)_2$ oscillating system[1] it became of interest to examine the behaviour of organic species other than malonic acid. As a result of this investigation a significant new oscillatory system involving acetone in place of malonic acid was discovered.† The present system is related to both Belousov's reaction[2] [$CH_2(CO_2H)_2$–$HBrO_3$–Mn^{II} or Ce^{III}] and Bray's reaction[3] (H_2O_2–HIO_3), two of the three known liquid phase 'inorganic' oscillatory systems.[4] Although malonic acid may be replaced in Belousov's reaction by a large number of species,[5–7] simple ketones have not yielded good oscillations.[7] In the present case, however, sustained oscillations have been obtained over a wide concentration range. The exact inter-relationship and ranges have not been determined. Oscillations in iodide ion, tri-iodide ion and iodine concentrations, and redox potential were observed. The redox potential was monitored using a platinum electrode *vs.* S.C.E.[1] Oscillations in iodide and tri-iodide ion, and iodine concentrations were observed spectrophotometrically.[8] No absorption in the visible region attributable to manganese could be detected.

The oscillations are affected little by the undisclosed inhibitor present in the H_2O_2 obtained from Hopkin and Williams. The results quoted refer to the system with unstabilised H_2O_2 obtained from Laporte Industries Ltd. It has been concluded that commercial inhibitors are not significant to the oscillatory behaviour.

The acetone system differs considerably from the malonic acid reaction[1] in several respects. Oscillations may be sustained for *ca.* 1 h; several hours with appropriate replenishment. Several distinct phases may be recognised from the redox potential plots in the acetone system (Figure). The oscillations may be reinitiated by addition of iodate ions. The frequency and wave shape are then controlled by the added reagent concentration. The acetone system has not been observed to terminate with production of iodine whereas the malonic acid reaction generally finishes in this

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† Hazards associated with Me_2CO–H_2O_2 mixtures have been discussed (*Chem. in Britain*, **1975**, **11**, **335**, and references therein).

manner.[1] Stirring increases the amplitude of the redox potential oscillation. Irradiation (500 W photoflood, 30 cm) of the system decreased the amplitude of the redox potential oscillation by *ca.* 30%. Under similar irradiation oscillations in the malonic acid system were completely inhibited with the production of iodine. In the absence of stirring the temperature increases monotonically in a stepwise manner. The overall change (<1 °C for a typical train of oscillations) is very much less than that for the malonic acid system.[1]

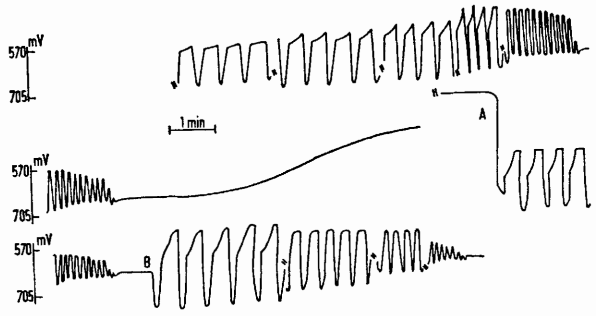
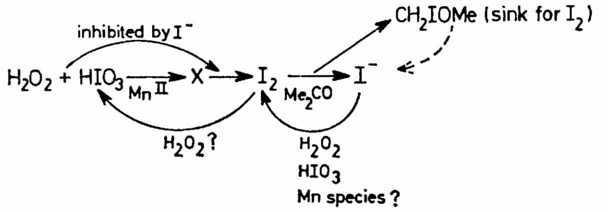


FIGURE. Typical changes in wave shape and frequency with time for the redox potential oscillations KIO_3 0·0360 M, H_2SO_4 0·0769 M, H_2O_2 0·709 M, Me_2CO 3·14 M, and $MnSO_4 . 4H_2O$ 0·0055M; initial volume 65·0 cm^3; duration of initial oscillations *ca.* 43 min; $T_{\text{initial}} = 21$ °C. 4th reinitiation (A) and 5th reinitiation (B), each with 5·0 cm^3 0·093 M KIO_3.

Mechanistic details of the H_2O_2–HIO_3–Mn^{II}–organic species systems have not been reported previously. It is observed that the production of the highly oxidising state of these systems is inhibited by I^-. The reaction apparently consists of two phases switched on and off by the iodide ion concentration. In this respect iodide is analogous to bromide in Belousov's reaction.[2] The first phase consists of the manganese(II)- catalysed production of iodine from the H_2O_2–HIO_3 reaction. This apparently does not proceed when the concentration of the iodide ion is high. At low manganese(II) concentration this isolated reaction exhibits an induction period and is autocatalytic; the total iodine produced is, however, limited as a result of the reoxidation of iodine to iodate by H_2O_2. This reoxidation, inhibited by H_2O_2 eventually (~ hours) results in removal of all the iodine produced in the initial reaction. This reaction is under investigation.



SCHEME

The second phase is the consumption of iodine–iodide principally *via* iodination of acetone. A possible mechanism is shown in the Scheme. The reoxidation of iodine to iodate[9] has not yet been confirmed within the oscillatory system although from the known mechanism[3,9] it would be expected to be catalysed by I^-. Interestingly, Degn[13] has reported that this reaction is catalysed by Cl^- which would in part be in agreement with the inhibitory effect of high concentrations of Cl^- on the oscillating system. The changes in the redox potential oscillations on successive reinitiation of the oscillations with iodate (Figure) suggest that iodoacetone may have some part in the reaction. An increase in the acidity of the system is observed to increase the stability of the highly oxidising state as expected from its effect on the H_2O_2–I^-,[10] HIO_3–I^-[11] and Me_2CO–I_2[12] reactions and its likely effect on any reactions involving HIO_2, the product in the rate determining step in the uncatalysed HIO_3–H_2O_2 reaction.[14]

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