# Inhibition of a Homogeneous Periodic Reaction by Radical Scavengers

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*Summary* The periodic reaction between malonic acid, sulphuric acid, potassium bromate, and a catalyst is inhibited by molecular oxygen, hydrogen peroxide, and acrylonitrile, and hence has a free-radical mechanism.

A POTENTIOMETRIC study of the periodic reaction between malonic acid, sulphuric acid, potassium bromate, and a catalyst is reported.[1-5] In an oscillating reaction, a number of maxima and minima occur on the concentration *versus* time curve. We followed the reaction by measuring the change of the redox potential with time. Manganese(II), cerium(III), and tris-(1,10-phenanthroline)iron(II) were used as catalysts. The potential of a bright platinum electrode at 25° was measured, using a saturated calomel reference electrode. A potassium nitrate salt bridge was used to avoid contamination of the reaction mixture by chloride ions.

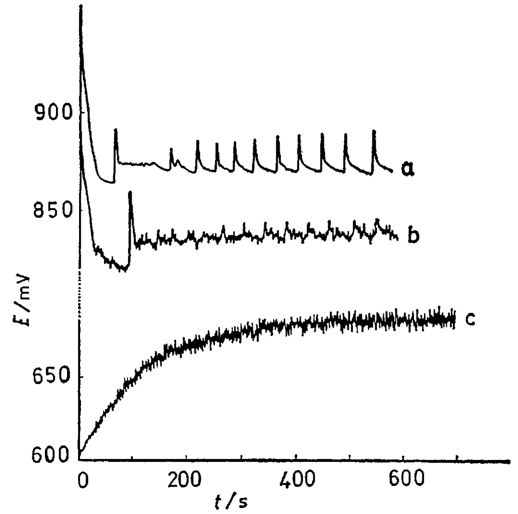

FIGURE 1. *Effect of hydrogen peroxide on the frequency and amplitude of the bromate–malonate reaction with tris-*(1,10-*phenanthroline*)*iron*(II) *catalyst. Compositions of the reaction mixtures* (*in* mol dm$^{-3}$) *potassium bromate* 6·98 × 10$^{-2}$, *malonic acid* 2·96 × 10$^{-1}$, *sulphuric acid* 4·50 × 10$^{-1}$, *tris-*(1,10-*phenanthroline*)-*iron*(II) 4·40 × 10$^{-4}$, *hydrogen peroxide* (*curve a*) 4·70 × 10$^{-4}$, (*curve b*) 1·37 × 10$^{-3}$, (*curve c*) 9·10 × 10$^{-2}$; *volume:* 20 ml.

Molecular oxygen was found to inhibit the periodic reaction. When tris-(1,10-phenanthroline)iron(II) was used as catalyst, and nitrogen containing 1% oxygen was bubbled through the system, complete inhibition resulted. Manganese(II) and cerium(III) were less sensitive catalysts, under similar conditions oscillations were merely modified. Pure oxygen at a flow rate of 20 ml s$^{-1}$, gave complete inhibition with these two catalysts. The extent of inhibition depends on the acidity of the system. At high acid concentrations the oxygen sensitivity decreases and the periodic reactions in oxygen and in nitrogen atmospheres are similar particularly with manganese(II) and cerium(III) catalysts. Previous investigations using cerium(III) catalysts were carried out almost exclusively at high acidities, the inhibition by oxygen was therefore not observed. Molecular oxygen is consumed during the reaction. When passage of gas through the system was stopped the reaction was no longer inhibited. Inhibition by oxygen does not mean the complete cessation of reaction. The decrease of the oxidizing power of the reaction mixture was followed iodometrically. The initial rates of the decrease in oxidizing power in oxygen and in nitrogen atmospheres were found to be the same; the oxygen experiment later shows a sharper decrease than the nitrogen experiment. This shows that the oxygen takes part in an induced oxidation, the oxidation of malonic acid also occurs by another reaction path,[6] and so the reduction of the bromate (which determines the decrease of the oxidizing power) occurs to only a small extent.

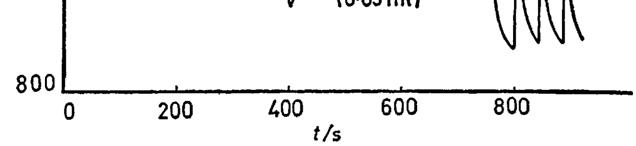

FIGURE 2. *Inhibition of the reaction by acrylonitrile. The composition and volume as in Figure* 1.

Hydrogen peroxide also inhibits the reaction and can transform the ordered oscillation into an aperiodic one of high frequency (Figure 1). If the amount of hydrogen peroxide is further increased the high-frequency phenomenon is lost. This phenomenon is a combination of free-radical decomposition of hydrogen peroxide and inhibition of the periodic reaction.

Acrylonitrile also acts as an inhibitor (Figure 2). The monomeric acrylonitrile is polymerized by radicals formed in the periodic reaction and the flocculent polymeric product is precipitated from the reaction mixture. When a high concentration of monomer is added the period during which the redox potential falls steadily is longer. The period of inhibition is directly proportional to the concentration of the monomer.

The effect on the periodic reaction of oxygen, hydrogen peroxide, and acrylonitrile (all compounds which inhibit free-radical stages) confirms the assumption that the oscillating reaction in the malonic acid–potassium bromate–catalyst–sulphuric acid system takes place by a free-radical mechanism.[3]

Chloride ions act by a different mechanism from that of the radical-scavenging inhibitors. When chloride ions are added, the induction period of the oscillating reaction is lengthened, and when they are present in concentrations above $1{\cdot}3 \times 10^{-3}$ mol dm$^{-3}$ the reaction is no longer periodic. The effect of chloride ions is due to the inhibition of the catalytic bromination of malonic acid. The bromide ion is known to be a strong inhibitor,[5] here the chloride ion acts similarly and inhibits the formation of bromomalonic acid. The oscillating reaction begins only when the concentration of bromomalonic acid reaches a critical value.

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