The Singular Autocatalytic Behaviour of the Oxidation of Acetic Acid by Methyltributylammonium Permanganate in Methylene Chloride

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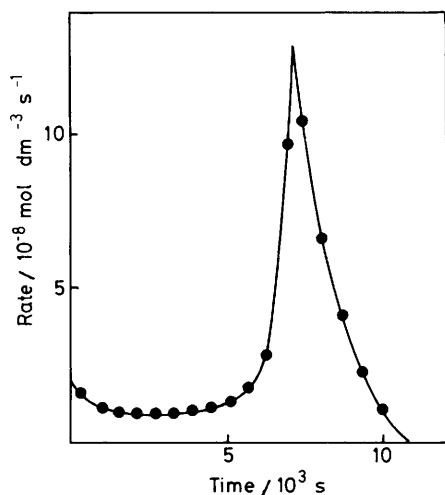
The oxidation of acetic acid by methyltributylammonium permanganate in methylene chloride shows an anomalous kinetic behaviour: the rate first decreases, then remains stationary for a long time and, finally, increases suddenly until permanganate consumption causes the reaction to stop.

Autocatalysis is known to be a widespread phenomenon. In particular, many permanganate reactions carried out in water[1,2] and methylene chloride[3] solutions have been reported to be autocatalytic. However, the mechanistic details of the autocatalytic pathway are in most cases still unresolved. In this paper, an intriguing case of autocatalysis, different from those previously reported, is presented.

The solvent used in the experiments was anhydrous methylene chloride purified by double distillation over 4 Å molecular sieve. The oxidizing agent was methyltributylammonium permanganate obtained by precipitation from an aqueous mixture of potassium permanganate and methyltributylammonium bromide.[4] The reducing agent was acetic acid

purified by distillation. In a typical experiment, the concentrations of quaternary ammonium permanganate and acetic acid in methylene chloride were 3×10^{-4} M and 0.70 M, respectively; thus, there was a large excess of reductant with respect to oxidant. The reactions were monitored by following the disappearance of permanganate at 526 nm by means of an HP 8450A u.v.–visible spectrophotometer. The extinction coefficient of methyltributylammonium permangate in a methylene chloride solution at that wavelength is 2.63×10^3 dm³ mol⁻¹ cm⁻¹. The spectrophotometer was provided with a thermostated cuvette holder.

A typical reaction rate vs. time plot is shown in Figure 1. It is interesting to note that roughly half of the total time spent in

Figure 1. Reaction rate vs. time plot for the oxidation of acetic acid (0.70 M) by methyltributylammonium permanganate (2.91×10^{-4} M) in methylene chloride at 25.0 °C.
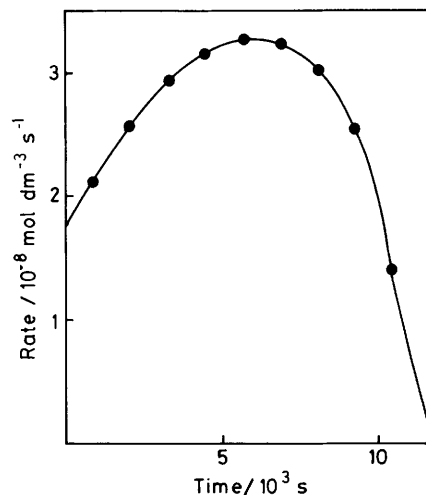
Figure 2. Reaction rate vs. time plot for the oxidation of methyl formate (0.65 M) by methyltributylammonium permanganate (2.99×10^{-4} M) in methylene chloride at 25.0 °C.
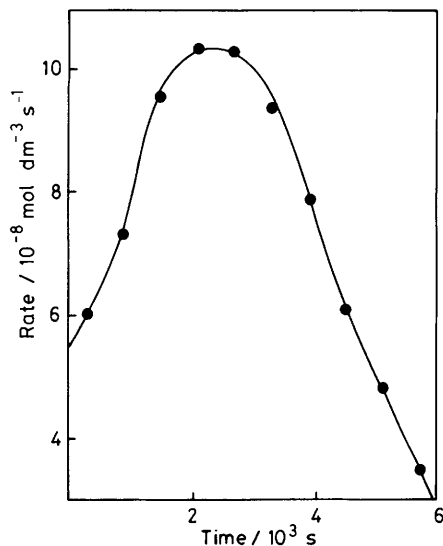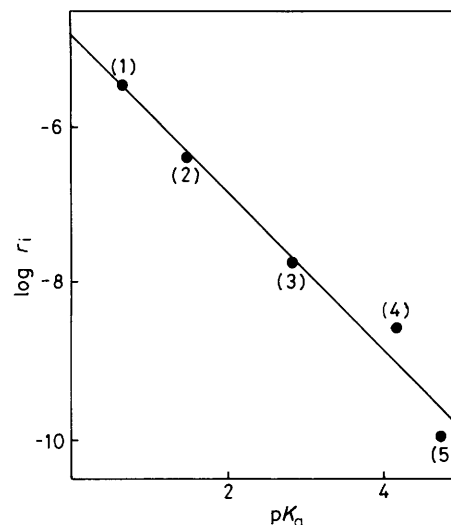
Figure 3. Reaction rate vs. time plot for the oxidation of ethylamine (1.25 M) by potassium permanganate (5.02 × 10^{-4} M) in an aqueous phosphate buffer at pH 8.0 and 25.0 °C.

Figure 4. Logarithm of the initial rate (in mol dm^{-3} s^{-1}) for the oxidation of several carboxylic acids (0.01 M) by methyltributylammonium permanganate (3.00 × 10^{-4} M) in methylene chloride at 25.0 °C vs. the pK_a of each acid in aqueous solution at the same temperature ($r = 0.982$). Acids: (1) trichloroacetic, (2) dichloroacetic, (3) 2-chloropropionic, (4) benzoic, and (5) acetic.

the reaction had elapsed before autocatalysis took place and that when this occurred, the maximum rate value was around seven times higher than the initial rate. The reaction rate vs. time plots corresponding to the reactions between methyltri-butylammonium permanganate and methyl formate in methylene chloride and between potassium permanganate and ethylamine in water are shown in Figures 2 and 3, respectively. We observe that in both cases autocatalysis starts immediately after the beginning of the reaction and the maximum rate values are only about twice as high as the initial rates.

A study was undertaken to check whether other carboxylic acids behave like acetic acid towards quaternary ammonium permangate in methylene chloride solutions. We found that all the acids tested failed to show the reaction rate vs. time pattern displayed in Figure 1. However, it was possible to demonstrate that the logarithm of the initial rate follows a Brønsted correlation[5] when plotted against the pK_a of each acid (see Figure 4). In spite of the fact that the pK_a values in aqueous solutions were used (the corresponding data in methylene chloride solutions are not available in the literature), a quite satisfactory correlation was obtained.

Although most autocatalytic reactions show a bell-shaped profile when the reaction rate is plotted against time, with autocatalysis occurring immediately after the products start forming (see Figures 2 and 3), this is not the case for the oxidation of acetic acid by methyltributylammonium permanganate carried out in a methylene chloride solution (see Figure 1). Given the fact that the kinetic data available for autocatalytic reactions are usually referred to aqueous media, one might suspect that the kind of behaviour shown in Figure 1 is typical of autocatalytic processes performed in methylene chloride solutions. Nevertheless, we can see in Figure 2 that the kind of autocatalysis found in the permanganate oxidation of methyl formate in methylene chloride does not differ significantly from that observed in aqueous media (see Figure 3). Neither is the behaviour shown in Figure 1 common to all the carboxylic acids when they are oxidized by quaternary ammonium permanganate in methylene chloride, for only acetic acid seems to react in this way (the oxidation of the

other acids given in Figure 4 is not autocatalytic).

We could infer from Figure 1 that the autocatalytic mechanism is inhibited by one of the reactants, whose concentration must decrease under a certain limit for autocatalysis to become evident. This reactant cannot be acetic acid since it is present in great excess and its concentration is constant for all practical ends. However, it cannot be permanganate either, since when the reaction is performed in the presence of very dilute permanganate the kind of plot shown in Figure 1 still holds.

It has been reported that many permanganate reactions undergo autocatalysis by a soluble form of colloidal manganese dioxide generated as a reaction product[2,3] and that this soluble colloid is also formed when quaternary ammonium permanganate is reduced by most organic substrates in methylene chloride solutions.[6] Thus, an attractive explanation could be that the autocatalysis is due to some kind of retarded activation of the acetic acid molecule after it has been adsorbed on the colloid surface; later, this activated acetic acid might suffer a very fast oxidation by permanganate. However, the mechanistic details of the activation process are as yet unknown.

Figure 4 shows that the initial oxidation of carboxylic acids by quaternary ammonium permanganate in methylene chloride indicates general acid catalysis, the acid being at the same time both reducing agent and catalyst. This could be explained in principle by proton transfer to generate a very active oxidizing agent (permanganic acid[7]) capable of reacting with the organic substrate, according to equations (1) and (2).

$$RCOOH + QMnO_4 \rightleftharpoons RCOOQ + HMnO_4 \quad (1)$$

$$RCOOH + HMnO_4 \longrightarrow Products \quad (2)$$
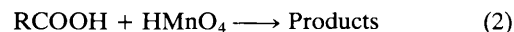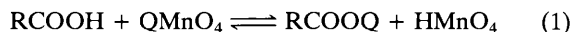
Although the mechanism proposed in these equations is only speculative, if it were confirmed it would be the first evidence of permanganic acid formation in an anhydrous medium such as methylene chloride.

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