p-Xylene Autoxidation Studies. Oxidation of Cobalt(II) and Manganese(II) Acetates by Peracids

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Summary The stoicheiometric oxidations of both cobalt(II) and manganese(II) acetates in aqueous acetic acid by *m*-chloroperbenzoic acid are non-free radical processes, the former proceeding *via* a peracid·Co^{II}_2 complex to give an active form of cobalt(III) which rearranges to a more stable form, and the latter proceeding in an autocatalytic fashion *via* a peracid·Mn^{III}_2 complex to give, in the presence of excess peracid, manganese(IV).

THE final step during autoxidation of a methyl aromatic compound to a carboxylic acid in aqueous acetic acid, catalysed by metals such as cobalt and manganese, involves reduction of the intermediate peracid, a reaction described in the review literature[1] as proceeding *via* free radicals [reactions (1) and (2)].

$$\mathrm{ArCOOOH} + \mathrm{M}^{n+} \rightarrow \mathrm{ArCOO}^- + \mathrm{OH}\cdot + \mathrm{M}^{(n+1)+} \quad (1)$$

$$\mathrm{ArCOOOH} + \mathrm{M}^{n+} \rightarrow \mathrm{ArCOO}\cdot + \mathrm{OH}^- + \mathrm{M}^{(n+1)+} \quad (2)$$

The finding of a precise stoicheiometry of 2:1 for the oxidation of cobalt(II) acetate in 95% HOAc by peracids such as peracetic and *m*-chloroperbenzoic[2] (recently confirmed for peracetic and perbenzoic[3]), together with a failure to find evidence for the intermediacy of either OH· or ArCOO·,[2] prompted a kinetic and spectroscopic investigation of this reaction.

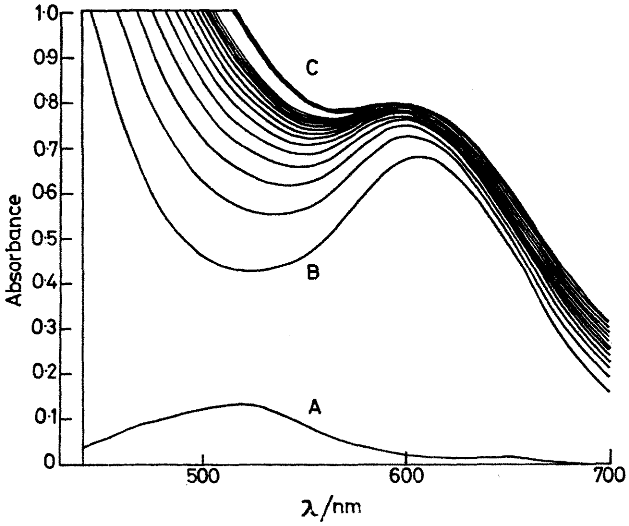

FIGURE 1. *m*-Chloroperbenzoic acid oxidation of cobalt(II) acetate in 95% acetic acid. Conditions: 95% HOAc–5% H_2O; 2 °C; 1×10^{-2} M $Co(OAc)_2$; $2{\cdot}5 \times 10^{-3}$ M ClC_6H_4COOOH (excess Co^{II}). Unicam SP8000 spectrophotometer; path length 10 mm. A = 1×10^{-2} M $Co(OAc)_2$; B = products immediately after mixing; B → C: scan time = 75 s; scan repeat = 5 min; C = 3 h after mixing.

Whilst the rapid pink [cobalt(II)] → green [cobalt(III)] colour change which accompanies the addition of a peracid to cobalt(II) acetate in aqueous acetic acid has been frequently noted, that the reaction proceeds *via* two distinct colour changes appears to have been previously overlooked. Figure 1 shows the spectral changes which accompany the reaction in 95% HOAc at 2 °C. A rapid initial change from pink to apple green, A → B, complete in a few seconds, is followed by a much slower converson, B → C, to give a stable olive green solution. The rates of both processes are strongly dependent upon water concentration, though the former is always much the faster. Monitored by stopped-flow, A → B involves a process which is first order in peracid and second order in cobalt(II). Monitored by conventional spectrophotometry, the process B → C is first order in the apple green species when peracid is in excess [to eliminate residual cobalt(II)], but includes a second order term when cobalt(II) is in excess.

A mechanism which appears consistent with these observations† assumes that the apple green colour is due to the formation of an active form of cobalt(III), denoted Co^{IIIa}, resulting from the redox step (4), and that a rapid monomer–dimer equilibrium[4] (3), favouring monomer, precedes this step. The olive green species appears to be a stable form, denoted Co^{IIIs}, to which the active form subsequently rearranges, the precise nature of the species undergoing rearrangement, Co^{IIIa}_2 or $Co^{IIIa}{\cdot}Co^{II}$, being dependent upon the absence [equation (6)] or presence [equation (7)] of excess cobalt(II).

$$2\,\mathrm{Co}^{II} \rightleftharpoons \mathrm{Co}^{II}_2 \quad (3)$$

$$\mathrm{ClC_6H_4COOOH} + \mathrm{Co}^{II}_2 \rightarrow \mathrm{ClC_6H_4COOH} + \mathrm{Co}^{IIIa}_2 \quad (4)$$

$$\frac{d[\mathrm{Co}^{IIIa}]}{dt} \propto [\mathrm{peracid}][\mathrm{Co}^{II}]^2 \quad (5)$$

$$\mathrm{Co}^{IIIa}_2 \rightarrow \mathrm{Co}^{IIIs}_2 \quad (6)$$

$$2\,\mathrm{Co}^{IIIa}{\cdot}\mathrm{Co}^{II} \rightarrow \mathrm{Co}^{IIIs}_2 + 2\,\mathrm{Co}^{II} \quad (7)$$

The characteristics of the stable olive green species are consistent with it being the 'cobaltic acetate' reported in the past as being isolated by bulk preparation by a variety of methods.[5] Whilst the active cobalt(III) dimer is apparently in equilibrium with monomer, the stable dimer (from comparative experiments in glacial and 70% HOAc) is not. During hydrocarbon autoxidation (at least for those reactions which proceed *via* peracids) both forms of cobalt(III), which can differ vastly in reactivity, would be expected to be present. Since the relative steady-state concentrations of the two species will be a function of experimental conditions, the observations outlined here may help to resolve some apparently conflicting rate laws obtained for cobalt-catalysed oxidations.[6]

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† Reaction of cobalt(II) with ozone in aqueous acetic acid gives rise to the same sequence of colour changes.

Although superficially a similar reaction according to the literature, and in the sense that the same stoicheiometry 2 $\mathrm{M^{II}}$ + peracid $\rightarrow$ 2 $\mathrm{M^{III}}$ has been found to apply, the corresponding peracid oxidation of manganese(II) acetate provides some surprises.

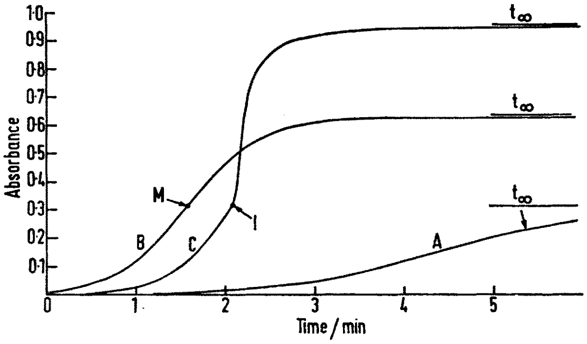

FIGURE 2. *m*-Chloroperbenzoic acid oxidation of manganese(II) acetate in 95% acetic acid. Conditions: 95% HOAc–5% $\mathrm{H_2O}$; 18 °C; Unicam SP8000 spectrophotometer; path length 10 mm; λ = 460 nm; zero chart time = *ca.* 10 s after mixing. A = 2·5 × 10^{-3} M $\mathrm{Mn(OAc)_2}$, 6·25 × 10^{-4} M $\mathrm{ClC_6H_4COOOH}$ (excess $\mathrm{Mn^{II}}$); B = 5 × 10^{-3} M $\mathrm{Mn(OAc)_2}$, 1·25 × 10^{-3} M $\mathrm{ClC_6H_4COOOH}$ (excess $\mathrm{Mn^{II}}$); C = 1·25 × 10^{-3} M $\mathrm{Mn(OAc)_2}$, 1·55 × 10^{-3} M $\mathrm{ClC_6H_4COOOH}$ (excess peracid).

Figure 2 shows examples of reactions followed at fixed wavelength for the oxidation of manganese(II) acetate in 95% HOAc at 18 °C. Sigmoid curve B (excess $\mathrm{Mn^{II}}$) is symmetric about its mid point M, is typical of an autocatalytic reaction,[7] and appears consistent with equation (11). Curve C (excess peracid) exhibits a change of slope at point I, precisely the point at which all the manganese(II) has been converted into manganese(III). Up to this time the spectrophotometer is recording an increase in manganese(III) concentration, whilst beyond this point manganese (IV), which has a larger molar extinction coefficient, is being detected. Curve C, beyond I, is also first order in manganese(III).

A mechanism which appears to account for these observations‡ assumes rate-determining attack upon $\mathrm{Mn^{III}_2}$ by peracid [reaction (8)], followed by rapid synproportionation [reaction (9)]. A direct reaction of manganese(II) with peracid [reaction (10)], which appears unfavourable in comparison with its indirect oxidation *via* reactions (8) + (9), may provide for the slow initiation of the autocatalytic sequence.

$$\mathrm{Mn^{III}_2 + ClC_6H_4COOOH \rightarrow 2\,Mn^{IV} + ClC_6H_4COOH} \tag{8}$$

$$\mathrm{Mn^{IV} + Mn^{II} \rightarrow Mn^{III}_2} \tag{9}$$

$$\mathrm{Mn^{II} + ClC_6H_4COOOH \rightarrow Mn^{IV} + ClC_6H_4COOH} \tag{10}$$

$$\frac{\mathrm{d[Mn^{III}]}}{\mathrm{dt}} \propto \mathrm{[peracid][Mn^{III}_2]} \tag{11}$$

Peracid oxidation of both cobalt and manganese acetates thus appears to proceed preferentially *via* metal dimers, whether they be present in trace equilibrium amount, as in the case of $\mathrm{Co^{II}_2}$, or as the major species, as in the case of $\mathrm{Mn^{III}_2}$.

Observations outlined in this communication provide important clues towards an understanding of the synergistic effects which are a feature of many catalysed autoxidations.[8] Model reactions which exhibit such synergistic effects will be included in the full paper.

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Added in proof: Recent reports highlight continuing uncertainties in this field, as regards both the structures of cobalt(II) and cobalt(III) acetates and the mechanisms of the reactions they catalyse (C. F. Hendriks, H. C. A. van Beek, and P. M. Heertjes, *Ind. and Eng. Chem. (Product and Res. Development)*, 1979, **18**, 38 and following paper).

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‡ Final spectra of solutions from reactions A—C are essentially superimposable upon those due to manganese(III) and manganese(IV) solutions prepared by dissolving calculated amounts of finely powdered $\mathrm{KMnO_3}$ in solutions of $\mathrm{Mn(OAc)_2}$ in 95% HOAc at room temperature. Compare reported methods for the preparation of $\mathrm{Mn(OAc)_4}$ (P. J. Andrulis, M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 5473; R. E. van der Ploeg, R. W. de Korte, and E. C. Kooyman, *J. Catalysis*, 1968, **10**, 52).

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