SHORT PAPER

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Oxidation of vicinal diketones with manganese(III) fluoride

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Vicinal diketones were oxidised, at room temperature, to carboxylic acids by manganese(III) fluoride with 90% yield. Investigation of the kinetics suggested that the reaction proceeded via a cyclic intermediate.

Keywords: vicinal, diketone, manganese(III)

Although it has been known for a long time that manganese(III) compounds were involved in the oxidation of ethanedioic acid (oxalic acid) with acidified potassium manganate(VII) (potassium permanganate),[1,2] this is the first report of the use of a manganese(III) compound to oxidise other substances containing adjacent carbonyl groups. The importance of manganese(III) compounds was noticed when it was observed that vicinal diketones were only slowly oxidised by hot, acidified potassium manganate(VII), but were readily oxidised when manganese(II) ions had first been added,

$$MnO_4^- + 8H^+ + 4Mn^{2+} \rightarrow 5Mn^{3+} + 4H_2O,\ E^\ominus = -0.014\ V.$$

This formation of manganese(III) ions explained why the double bond in alkenes can be ruptured by potassium manganate(VII) to yield carboxylic acids. During the oxidation of the alkene to the diol or dione, sufficient manganese(II) ions were generated to form the manganese(III) ions necessary to complete the oxidation. Although manganese(III) ions and potassium manganate(VII) were comparable oxidising agents, manganese(III) compounds did not react directly with alkenes in the cold; the exception was manganese(III) ethanoate (acetate) that produced a cyclic ester by free radical addition.[3] To minimise the possibility of such a reaction, manganese(III) fluoride was the preferred oxidant to manganese(III) ethanoate.

Water soluble diketones were readily oxidised by Mn(III) ions in aqueous solution, though care had to be taken to prevent disproportionation

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+;\ E^\ominus = +0.576\ V.$$

The Mn(III) ions were stabilised under acid conditions and by complexing agents, such as phosphate or sulfate ions.[4] Under these conditions, the oxidation of the diketone by MnF_3 was carried out in aqueous solution without disproportionation taking place. This solution had an absorption spectrum identical to that produced by $MnSO_4$ and $KMnO_4$ in H_2SO_4, indicating that the Mn(III) species present was probably $[Mn(H_2O)_6]^{3+}$ or $[Mn(H_2O)_5(HSO_4)]^{2+}$.

Two methods were used to estimate the yield of the reaction. The first method was by titration. An aqueous solution of hexane-3,4-dione was treated with an excess of MnF_3 in 5.0 mol dm^{-3} H_2SO_4. After allowing the mixture to stand for 10 minutes, the excess MnF_3 was back-titrated with standardised iron(II) sulfate solution. Under these conditions, each mole of hexane-3,4-dione, reacted with 1.96 mol of MnF_3. This corresponded to nearly quantitative oxidation according to the following equation

$$RCOCOR + 2H_2O + 2Mn(III) \rightarrow 2RCO_2H + 2H^+ + 2Mn(II)$$

that required 1 mol of the hexane-3,4-dione to react with 2 mol of MnF_3.

Table 1 Results for the oxidation of butane-2,3-dione with MnF_3 in phosphoric acid at 25 °C. The values of k_1 are the first order rate constants obtained when the diketone was in large excess. The second order rate constants, k_2, are obtained by dividing k_1 by the diketone concentration

Initial [butane-2,3-dione]/mol dm^{-3}	k_1/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
0.040	0.027	0.62
0.054	0.030	0.56
0.080	0.047	0.59
0.11	0.057	0.52
0.12	0.070	0.58
0.21	0.11	0.52
0.23	0.13	0.57
0.36	0.17	0.47
0.40	0.20	0.50
		Mean 0.54±0.02

The second method involved treating hexane-3,4-dione with MnF_3 in 5.0 mol dm^{-3} H_2SO_4, in a one to two molar ratio, and analysing the products by gas chromatography. After the reactants had been allowed to stand for 10 minutes, analysis of the product showed that for each mole of the diketone used 1.76 mol of propanoic acid were produced. This was an 88% conversion to the carboxylic acid.

The rate of the reaction of diketones with MnF_3 was followed using a spectrophotometer. Preliminary work showed that absorption of Mn(III) ions, at 510 nm, was proportional to concentration. There was no significant difference in the absorption of MnF_3 in phosphoric acid from that in sulfuric acid.

The rate of reaction of MnF_3 with butane-2,3-dione was too fast to be conveniently followed when the reaction was carried out in sulphuric acid but it could be followed in phosphoric acid. When an excess of the diketone was used, the reaction was first order with respect to Mn(III) ions as their concentration decreased exponentially with time. The absorption was measured with a spectrophotometer attached to computer. A curve fitting program was used to evaluate the pseudo first order rate constant. The concentration of butane-2,3-dione was also varied. The results are shown in Table 1. They showed that the reaction was first order with respect to the diketone as well as being first order with respect to Mn(III) ions. As two moles of Mn(III) ions were used for each mole of diketone, one of the Mn(III) oxidation stages must be a rapid

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reaction after the rate determining step. A possible mechanism involves the formation of an intermediate DMn(III), where D represents the diketone.

$$\text{D} + \text{Mn(III)} \rightleftarrows \text{DMn(III), equilibrium, constant } K \qquad (1)$$

$$\text{DMn(III)} \rightarrow \text{Intermediate} + \text{Mn(II), rate constant } k \qquad (2)$$

$$\text{Intermediate} + \text{Mn(III)} \rightarrow \text{Products} + \text{Mn(II), fast step} \qquad (3)$$

We have $[\text{Mn(III)}]_{\text{initial}} = [\text{Mn(III)}] + [\text{DMn(III)}] + [\text{Mn(II)}]$. On differentiation and using the substitutions $[\text{Mn(II)}] = k[\text{DMn(III)}]$ and $[\text{DMn(III)}] = K[\text{Mn(III)}]$, this leads to

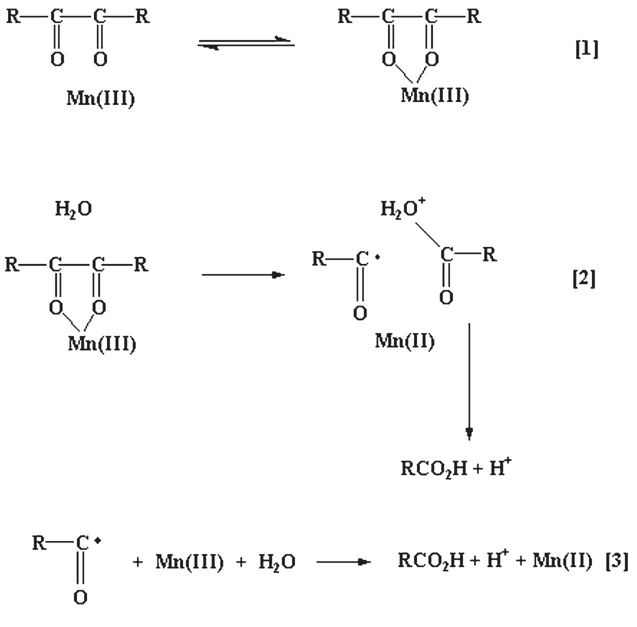
$$0 = d/dt[\text{Mn(III)}] + Kd/dt[\text{Mn(III)}][\text{D}] + kK[\text{Mn(III)}][\text{D}].$$

As [D] is in large excess, it may be considered as constant,

and the measured rate $= -d/dt[\text{Mn(III)}] = \dfrac{kK[\text{D}][\text{Mn(III)}]}{1 + K[\text{D}]}$

As the rate varied with [D], K[D] must be very small which suggests that step 1 in the above reaction scheme was rate determining.

It is possible that a 5-membered ring complex was initially formed between Mn(III) and the diketone, similar to that postulated between Mn(III) ions and ethanedioic acid.[5,6] This could undergo hydrolysis yielding one carboxylic acid molecule and a free radical that would be rapidly oxidised by further Mn(III) ions to give the other carboxylic acid molecule.



Scheme

In the above reaction scheme, the manganese(III) species was likely to be in the form of a complex with hydrogen sulfate or hydrogen phosphate ions. This mechanism suggested that the reduction of the two Mn(III) ions took place in separate steps (2 and 3). An alternative mechanism in which two carboxylic acid molecules and a Mn(I) complex were formed in a single stage, followed by oxidation of Mn(I) by Mn(III) to Mn(II), was extremely unlikely as compounds containing Mn(I) are formed only under strongly reducing conditions.[7]

A comparison of the rates of reaction of different dicarbonyl compounds in ethanoic acid (Table 2) suggested that Step 1, the formation of the 5-membered complex was rate determining, although the kinetics suggested that both Step 1 and Step 2 were important. The solvent was ethanoic acid as this enabled diketones that were insoluble in water (for example benzil) to be studied. Under these conditions, manganese(III) ethanoate might have been formed, but a visual check on the colour of the reactants made this unlikely. In anhydrous ethanoic acid, both MnF_3 and manganese(III) ethanoate formed a brown solution; when ten parts (by volume) of this solution were mixed with one part of 5.0 mol dm^{-3} sulfuric acid, the brown solution turned red. This red solution was the same composition as that used in the rates experiments. Moreover, this red solution had an absorption spectrum identical to that of MnF_3 dissolved in 5.0 mol dm^{-3} sulfuric acid, without any ethanoic acid being present, so that we may infer that the ethanoate was not the principal species present.

Table 2 Rates of reaction of diketones relative to ethanedioic acid, using ethanoic acid/sulfuric acid as solvent

Diketone	Relative rate of reaction
Cyclohexane-1,2-dione	2.2
Ethanedioic acid	1
Butane-2,3-dione	0.39
Hexane-3,4-dione	0.35
Benzil	6.0×10^{-3}

Cyclohexane-1, 2-dione: It was difficult to interpret the rate of reaction of this compound, as it existed predominately in the *enol* form.[8] If only the *keto* form reacted, the actual reaction rate would be much larger, but there is also the possibility that a complex could be formed with the enol form as well. In either case, the high rate could be due to the oxygen atoms being held in a *s-cis* configuration, favouring the formation of the cyclic complex.

Ethanedioic acid: This compound reacted readily as the presence of two oxygen atoms on each carbon atom increased the probability of forming a cyclic complex.

Butane-2,3-dione and hexane-3,4-dione: These both reacted at comparable rates. It is known that the two carbonyl groups are nearly coplanar, predominately in the *s-trans* conformation.[9] However, rotation about the central carbon to carbon bond could bring the oxygen atoms into a planar *s-cis* conformation which would then have been favourable orientated for reaction.

Benzil (diphenylethanedione): This substance reacted very slowly with manganese(III) ions. A study of its UV spectrum showed conjugation between the carbonyl groups and the benzene rings[10] and in solution, the two carbonyl groups were nearly perpendicular to each other.[9,11] Such a structure would reduce the likelihood of forming a cyclic ring with manganese(III) ions.

Experimental

All the chemicals were obtained from Sigma-Aldrich.

To confirm the 2:1stoichiometry for MnF_3/hexane-2,3-dione reaction, a slight excess of 0.0200 mol dm^{-3} MnF_3 in 5.0 mol dm^{-3} H_2SO_4 was added to a known amount of the dione. After stirring for 10 minutes at room temperature, the excess MnF_3 was found by adding 0.100 mol dm^{-3} $FeSO_4$ from a dropping pipette until the red colour was just discharged.

The spectrophotometer was a CamSpec M302 instrument with the output fed to a computer using a pico ADC-100 converter. A scan showed maximum absorption of MnF_3 in sulfuric acid at 510 nm and the same position of the maximum was observed for solutions in phosphoric acid. For the kinetic experiments, the results were processed either using an exponential curve fitting program or by using a logarithmic plot.

In the kinetic experiments, the diketone was in large excess, typically between 0.04 and 0.4 mol dm^{-3}. Usually, 2.0 cm^3 of diketone was placed in the cell and 50 _l of 0.03 mol dm^{-3} of MnF_3 in 5.0 mol dm^{-3} phosphoric acid added, using a syringe. After shaking, up to 200 readings were then recorded by the computer. The reactants were first placed in a thermostatic water bath and then the reaction carried out in a glass cell mounted in a temperature controlled water circulator. The water bath was kept at 25.0 ±0.04 ^{o}C. For the comparison of rates experiments, 0.01 mol dm^{-3} solutions of the dicarbonyl compounds in ethanoic acid were prepared. To 2.0 cm^3 of these solutions, 0.2 cm^3 of a 0.03 mol dm^{-3} solution of MnF_3 in 5.0 mol dm^{-3} H_2SO_4 were added and the absorbance followed at 510 nm.

The gas chromatogram was a Perkin-Elmer AutoSystem XL with a column temperature of 100 ^{o}C. Analysis of the reaction products from the oxidation of hexane-3,4-dione with MnF_3 was carried out by shaking the aqueous solution with pentane; the pentane layer was separated, dried with silica gel, and 1.0 µl samples injected into the GC. The amounts of propanoic acid and hexane-3,4-dione were determined by comparison with standard solutions of these substances in 5.0 mol dm^{-3} H_2SO_4 which had been similarly extracted with pentane.

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