436. *Stages in Oxidations of Organic Compounds by Potassium Permanganate. Part IX.* Oxidation of Allyl Alcohol by Manganic Pyrophosphate.*

By HARING LAND and WILLIAM A. WATERS.

Allyl and crotyl alcohol are very slowly oxidised by manganic pyrophosphate. The reaction order with respect to Mn^{III} is complex, becoming of first order at high Mn^{III} concentrations. Manganous ions retard the oxidation but this retardation reaches a limiting value. Peroxidic impurities have a noticeable immediate effect. Suggestions concerning the reaction mechanism are advanced.

ALTHOUGH acid manganic pyrophosphate does not oxidise either monohydric alcohols or olefins [1] it slowly attacks allyl alcohol and we have studied this reaction kinetically. The slow oxidation cannot be followed titrimetrically by adding portions to aqueous potassium iodide since the combination of iodine with allyl alcohol has a significant velocity at room temperature. However, though manganic pyrophosphate does not react directly with

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* Part VIII, *J.*, 1957, 4312.

[1] Drummond and Waters, *J.*, 1953, 440.

arsenite a trace of iodide causes immediate reduction of Mn^{III} and, in a bicarbonate buffer, arsenite can be titrated with iodine under conditions in which there is negligible addition of iodine to allyl alcohol provided that air-free conditions are maintained and the arsenite solutions are neutralised immediately the reduction of Mn^{III} is visibly complete.

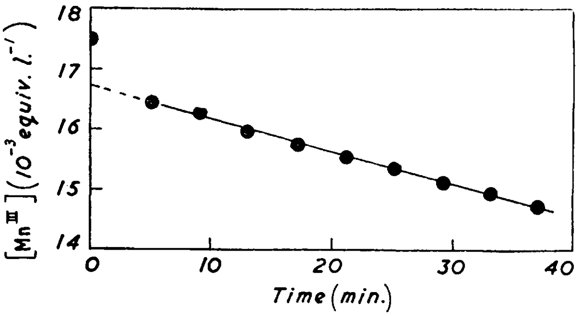


FIG. 1. *Typical initial stage of an oxidation of allyl alcohol by manganic pyrophosphate.*

Initial concns.: $[Mn^{III}]$ 1·75 × 10^{-2}M; $[C_3H_5{\cdot}OH]$ 0·20M; [pyrophosphate] 0·086M; pH 0·1.

At 45°, with allyl alcohol in large excess, excellent initial rate constants could be obtained though a slight immediate drop of titre was always noted (see Fig. 1). When this small drop is neglected the initial rate measurements show that the consumption of Mn^{III} is a first-order process with respect to allyl alcohol in absence of oxygen (Table 1) but becomes of higher order in its presence (Fig. 2). The rate constants themselves were independent of the source or method of purification of the allyl alcohol, so that the main oxidation, though slow, does not depend on the presence of an impurity.

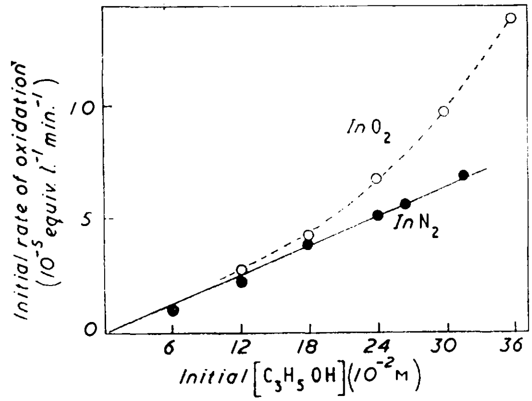


FIG. 2. *Dependence of initial rate on allyl alcohol concentration.*

Initial concns.: $[Mn^{III}]$ 1·75 × 10^{-2}M; [pyrophosphate] 0·086M; pH 0·10.

The order with respect to $[Mn^{III}]$ is complex and appears to be the sum of a first-order process and one that approaches a limiting value (Fig. 3). Manganous ions specifically affect this rate; at low $[Mn^{II}]/[Mn^{III}]$ ratios the oxidation is retarded by them but a lower limit, at which the reaction velocity is about halved, is soon reached, and at high $[Mn^{II}]/[Mn^{III}]$ ratios the rate of oxidation shows a slight upward trend (Fig. 4). Since high concentrations of zinc ions produce a corresponding effect the gradual increase in rate may possibly be due to the formation of sufficient manganous or zinc pyrophosphate to diminish significantly the concentration of free pyrophosphate anions in the solution. This change

TABLE 1. *Oxidation of allyl alcohol under nitrogen at* 45°.

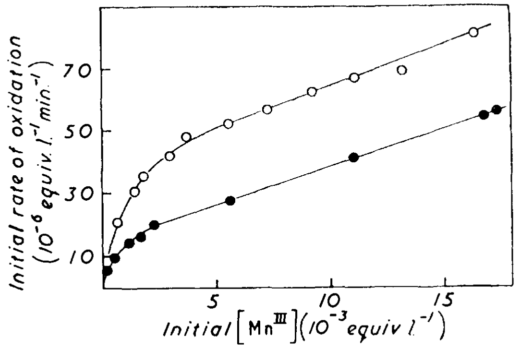
Initial $[Mn^{III}]$ 1·75 × 10^{-2}N. Total pyrophosphate 0·086M. pH 0·2.

Initial $[C_3H_5{\cdot}OH]$ (10^{-2}M)	20·0	16·7	13·3	11·1	8·3	5·6	2·8
Initial $-d[Mn^{III}]/dt$ (10^{-5} mole l.$^{-1}$ min.$^{-1}$)	5·7	4·9	3·8	3·2	2·6	1·6	1·0
Initial rate/$[C_3H_5{\cdot}OH]$	2·85	2·93	2·85	2·88	3·13	2·86	2·8

would increase the oxidation potential of the reagent for, as in other cases of oxidation by manganic pyrophosphate, the rate of oxidation of allyl alcohol is decreased by increasing the pyrophosphate concentration and increased by increasing the acidity. A more cursory examination of the oxidation of crotyl alcohol showed that it was somewhat faster but had similar kinetic features.

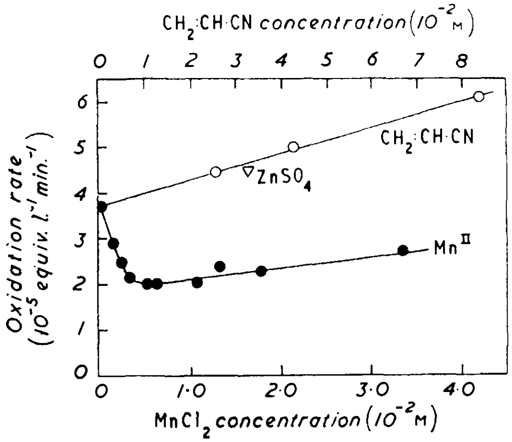
The oxidation of allyl alcohol by manganic pyrophosphate must generate free radicals, for the oxidising mixture can absorb oxygen and catalyse the polymerisation of vinyl cyanide (which is not attacked by manganic pyrophosphate alone [2]). Addition of this monomer to the oxidising allyl alcohol increases the consumption of Mn^{III} (Fig. 4, top line). A more marked effect of the same character had been found in the oxidation of malonic acid.[3] Again the oxidising system can induce the reduction of mercuric chloride,[2] but it does not promote the oxidation of propan-2-ol.[3]

FIG. 3. *Dependence of initial rate on* $[Mn^{III}]$.



Initial concns.: [pyrophosphate] 0·086M; Upper curve: $[C_3H_5{\cdot}OH]$, 0·30M; pH 0·35; Lower curve: $[C_3H_5{\cdot}OH]$ 0·20M; pH 0·20.

FIG. 4. *Dependence of initial rate on* $[Mn^{II}]$ *and on* $[CH_2{:}CH{\cdot}CN]$.



Initial concns.: $[Mn^{III}]$ $1{\cdot}53 \times 10^{-2}$M; [pyrophosphate] 0·078M; $[C_3H_5{\cdot}OH]$ 0·133M; pH 0·20.

The Reaction Mechanism.—For the straight portion of the graphs of Fig. 3 the limiting rate equation becomes:

$$-d[Mn^{III}]/dt = \text{Const.}\ [Mn^{III}]\ .\ [C_3H_5{\cdot}OH]\ .\ [H^+]$$

The dependence of the rate on acidity may well be due to the effect of acidity on the redox potential of complexed manganic pyrophosphate [4] and it has not been studied in detail. The strict first-order dependence on $[C_3H_5{\cdot}OH]$ shows that the formation of a ternary (manganic–allyl alcohol–pyrophosphate) complex is not a prerequisite of the oxidation as it is for a 1 : 2-glycol [5] or an α-hydroxy-acid.[6] Again spectrographic examination of reacting mixtures over the wave-band 200—500 μ gave no indication of the formation of transient manganic complexes. The initial reaction can therefore be visualised as a one-electron abstraction from the allyl alcohol (possibly coupled with proton loss), but the effects of both manganous and manganic ions at low concentrations show that reactions subsequent to the formation of the primary organic free radical can, in certain circumstances, be kinetically significant.

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[2] Drummond and Waters, *J.*, 1953, 2836.
[3] *Idem, J.*, 1954, 2456.
[4] Kolthoff and Watters, *J. Amer. Chem. Soc.*, 1948, **70**, 2455.
[5] Drummond and Waters, *J.*, 1953, 3119.
[6] Levesley and Waters, *J.*, 1955, 217.

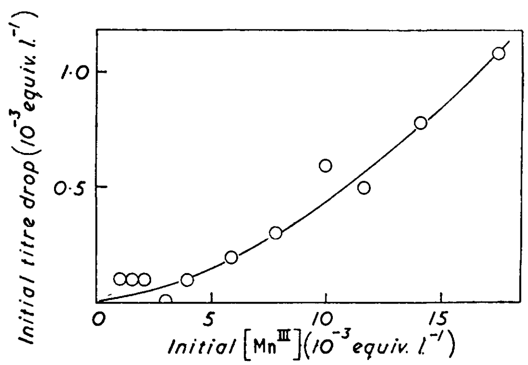
In Part IV[3] retardation of the oxidation of malonic acid by manganous ions was ascribed to the formation of an oxidising radical, *i.e.*:

$$\text{Substrate} + \text{Mn}^{\text{III}} \rightleftharpoons \text{Radical} + \text{Mn}^{\text{II}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{Radical} + \text{Mn}^{\text{III}} \longrightarrow \text{Product} + \text{Mn}^{\text{II}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

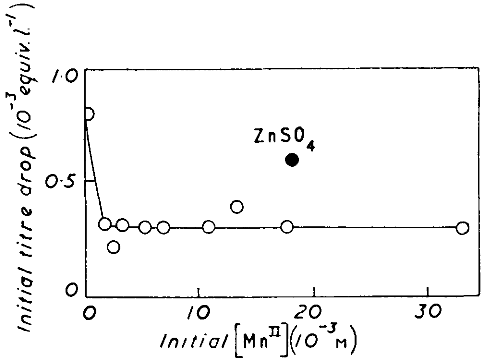
but equations of this type do not indicate how the retarding effect of manganous ions could reach a limiting value (cf. Fig. 4). One possibility that cannot altogether be excluded is that the reversible reaction (1) involves a molecular oxidation product of allyl alcohol, but it is difficult to reconcile such a reaction sequence with the rate-dependence on [Mn^{III}] at low concentrations. It is more probable that the initial radical is removed by oxidation and reduction, as in equations (1) and (2), and partly by the bimolecular processes of dimerisation or disproportionation that give inert products for, as Part VI[7] exemplifies, such reactions may be very fast. According to the scheme:

FIG. 5. *Dependence of initial titre drop on initial* [Mn^{III}].



Concns.: [$C_3H_5\cdot OH$] 0·30M; [pyrophosphate] 0·086M; pH 0·35.

FIG. 6. *Dependence of initial titre drop on initial* [Mn^{II}].



Concns.: [$C_3H_5\cdot OH$] 0·133M; [Mn^{III}] 1·53 × 10^{-2}M; [pyrophosphate] 0·078M; pH 0·20.

$$C_3H_5\cdot OH + \text{Mn}^{\text{III}} \rightleftharpoons R\cdot + \text{Mn}^{\text{II}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$R\cdot + \text{Mn}^{\text{III}} \longrightarrow \text{Product I} + \text{Mn}^{\text{II}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$2R\cdot \longrightarrow \text{Products II} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the reversibility of reaction (3) would cause manganous ions to depress the initial reaction velocity and at high Mn^{III} concentrations a sufficient radical concentration would build up to allow reaction (5) to predominate over (4), the forward reaction (3) then becoming rate-determining. However, though equations (3)—(5) accord with the observed rate-dependence on [Mn^{III}] they do not indicate strict first-order dependence on [$C_3H_5\cdot OH$] at low Mn^{III} concentrations. Though Table 1 does not indicate any departure from first-order reactivity it relates to the linear portion of the curves of Fig. 3; the oxidation was far too slow to be tested at low concentrations of both allyl alcohol and manganic pyrophosphate.

The acceleration of the oxidation by vinyl cyanide corresponds to a fast reaction (6), giving a radical that is more easily oxidised than the primary radical R·:

$$R\cdot + CH_2{:}CH\cdot CN \longrightarrow R\cdot CH_2\cdot CH(CN)\cdot \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This again was inferred in the investigation of the oxidation of malonic acid.[3]

Product investigation has not been practicable for the overall extent of the oxidation

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[7] Drummond and Waters, *J.*, 1955, 497.

is slight and, as Part VIII [8] has shown, all the simple oxidation products of allyl alcohol are easily attacked by manganic pyrophosphate. Traces of formaldehyde and of formic acid which do resist the oxidative degradation have in fact been detected. Without definite evidence of the nature of the first oxidation product it is not possible to decide whether attack on allyl alcohol occurs initially at the $CH_2{\cdot}OH$ group or at the double bond.

The initial titre drop. This effect (see Fig. 1) was most evident in stored samples of allyl alcohol that gave a slight positive peroxide reaction (ferrous thiocyanate test), and was very greatly reduced, though not completely eliminated, by repeated fractionation of the allyl alcohol in purified nitrogen through a column packed with glass helices; metal gauze packings had an adverse effect. With any one batch of allyl alcohol the titre drop were proportional to the allyl alcohol concentration (Table 2); it increased with increasing concentration of Mn^{III} (Fig. 5), but manganous ions in quite low concentration specifically depressed it to a small but limited extent (Fig. 6). These effects are consistent with the presence in the allyl alcohol of a very small amount of a hydroperoxide capable both of reducing Mn^{III} and of oxidising Mn^{II}, *i.e.*:

TABLE 2. *Initial drop in titre on oxidation of allyl alcohol with manganic pyrophosphate.*

$[C_3H_5{\cdot}OH]$ (10^{-2}M)	0·0	2·8	5·6	8·3	11·1	13·3	16·7	20
Initial $[Mn^{III}]$ extrapolated (10^{-2}M)	1·75	1·75	1·74	1·72	1·71	1·69	1·69	1·68

$$RO_2H + 2Mn^{3+} + H_2O = ROH + O_2 + 2Mn^{2+} + 2H^+$$

$$RO_2H + 2Mn^{2+} + 2H^+ = ROH + 2Mn^{3+} + H_2O$$

Reactions of these types have frequently been described.[9] These equations also explain why oxygen, which would yield $RO_2{\cdot}$ radicals, enhances the rate of reduction of Mn^{III} (Fig. 2). Indeed the initial titre drop may in part be due to a rapid removal by radicals, R·, of residual dissolved oxygen in the aqueous solution of the oxidant.

EXPERIMENTAL

Kinetic experiments were carried out with stirring in a three-necked flask immersed in a thermostat at 45° ± 0·3°. Purified nitrogen was continually passed through the reacting solutions and aliquot parts were removed by suction at a rate much less than that of the nitrogen flow. About 1 g. of sodium hydrogen carbonate was placed in each of a series of 250 ml. stoppered bottles together with enough dilute sulphuric acid to bring about the displacement of all air. To each bottle was added slightly more standard arsenite solution than that expected for complete reduction of the Mn^{III}, then 0·1 ml. of a 0·5% solution of potassium iodide, and finally the aliquot part of the reaction mixture. Immediately decolorisation was complete excess of sodium hydrogen carbonate was added and the remaining arsenite was titrated with standard iodine with starch as indicator.

Allyl alcohol, dried by azeotropic distillation with benzene, was repeatedly distilled in purified nitrogen through a column filled with Fenske helices, the fraction of b. p. 96·5° being collected and stored in the dark under nitrogen. When required, weighed sample were dissolved in boiled-out distilled water. To avoid contamination, smallish samples were stored in sealed ampoules, unused material from opened ampoules being returned for refractionation.

Neither commercial samples of allyl alcohol, nor material prepared in the laboratory from glycerol, could be freed completely from peroxides. However, all samples after purification as described above were oxidised at the same rate after the first few minutes.

Material fractionated through a column packed with nickel gauze had a high peroxide content and tended to polymerise.

Manganic pyrophosphate solutions were prepared by the method described in earlier parts of this series.

Results are recorded in Tables 1 and 2 and Figs. 1—6.

One of us (H. L.) thanks the British Council for a Scholarship.

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[8] Land and Waters, *J.*, 1957, 4312.

[9] Kharasch, Fono, Nudenberg, and Bischoff, *J. Org. Chem.*, 1952, **17**, 207.