865. *Stages in Oxidations of Organic Compounds by Potassium Permanganate. Part VIII.* The Mechanism of Oxidation of Acraldehyde by Manganic Pyrophosphate.*

By Haring Land and William A. Waters.

The initial, rate-determining, stage in the oxidation of acraldehyde by manganic pyrophosphate is acid-catalysed and does not involve oxidant. It is suggested that this is the formation of the enol of β-hydroxypropionaldehyde:

$$H_2O + CH_2{:}CH{\cdot}CHO \xrightarrow{H^+} HO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}OH$$

The faster oxidation of crotonaldehyde and the slower oxidation of α-methylacraldehyde appear to take a similar course, though with crotonaldehyde the oxidation step is rate-determining at low concentrations of the oxidant. The first oxidation product of acraldehyde appears to be glyceraldehyde and later a chelated manganic complex of glyceric acid seems to be formed. Further oxidative degradation occurs by glycol fission, formaldehyde and carbon dioxide being the eventual products, 10 equivalents of Mn^{III} in all being consumed.

In Part II [1] it was shown that the oxidations of propionaldehyde and *n*-butyraldehyde by manganic pyrophosphate occurred at rates which were of zero order with respect to tervalent manganese, and first order with respect to both aldehyde and hydrogen-ion concentrations, and continued far beyond the stage of oxidation of the aldehyde to the corresponding acid. It was suggested therefore that the one-electron oxidation followed rapidly upon a rate-controlling acid-catalysed enolisation. The study (Part VI [2]) of the oxidations of *cyclo*hexanone and of diethyl ketone supported this mechanism, for again oxidation followed an acid-catalysed enolisation and from *cyclo*hexanone the successive formation of 2-hydroxy*cyclo*hexanone and then of *cyclo*hexane-1 : 2-dione was established. Related investigations of oxidations of aldehydes and ketones by alkaline ferricyanide [3] and by the free radical $\cdot ON(SO_3K)_2$ [4] supported the conclusion that oxidations of aldehydes and ketones by one-electron-abstracting reagents require the prior formation of an anion, $R'{\cdot}CH{:}CR{\cdot}O^-$, from which the removal of an electron is easy because it leads to production of a resonance-stabilised radical, $R'{\cdot}CH{:}CR{\cdot}O\bullet \longrightarrow R'{\cdot}\dot{C}H{\cdot}CR{:}O$. Removal of more electrons from this radical then occurs at the α-carbon atom so that α-hydroxy-aldehydes or -ketones are the primary products.

We have extended this work to the oxidation by manganic pyrophosphate of the αβ-unsaturated aldehyde acraldehyde, with which enolisation to give hydroxyallene, $CH_2{:}CH{\cdot}CHO \rightleftharpoons CH_2{:}C{:}CH{\cdot}OH$, must be regarded as very improbable, and in the course of the investigation we have made a more cursory examination of the corresponding oxidations of crotonaldehyde and α-methylacraldehyde. The latter compound cannot enolise by ionisation of an α-hydrogen atom yet all three aldehydes are easily oxidised.

Though manganic pyrophosphate does not attack olefinic double bonds, as in acrylic and crotonic acids, iodometric estimation of tervalent manganese during the oxidations of the unsaturated aldehydes was vitiated by the rapidity of addition of iodine to the olefinic groups. Fortunately, however, secondary reactions due to atmospheric oxygen, as encountered in several other cases with tervalent manganese,[2, 5] were not significant

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* Part VII, *J.*, 1956, 717.

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

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

[3] Speakman and Waters, *J.*, 1955, 40.

[4] Allen and Waters, *J.*, 1956, 1132.

[5] Drummond and Waters, *J.*, 1954, 2456.

enough to cause difficulty in spectrographic measurements with a Hilger "Spekker" photo-absorptiometer and the reactions were sufficiently fast to allow of simple but adequate temperature control.

Initial Stage of the Oxidation.—Table 1 shows that the oxidation of acraldehyde is a first-order reaction with respect to aldehyde, and Tables 2 and 3 show that the rate is of zero order with respect to tervalent manganese except at very low concentrations of the oxidant. Fig. 1 shows that, in solutions of sufficient acidity for the successive ionisation of the complex, $Mn(H_3P_2O_7)_3$, to be insignificant,[6] the reaction shows a first-order hydrogen-ion catalysis. Table 4 shows that the initial rate of oxidation is not affected by production of manganous ions. In all these kinetic features the oxidation of acraldehyde resembles that of propionaldehyde. In Tables 1—4 the temperature is 17·5°.

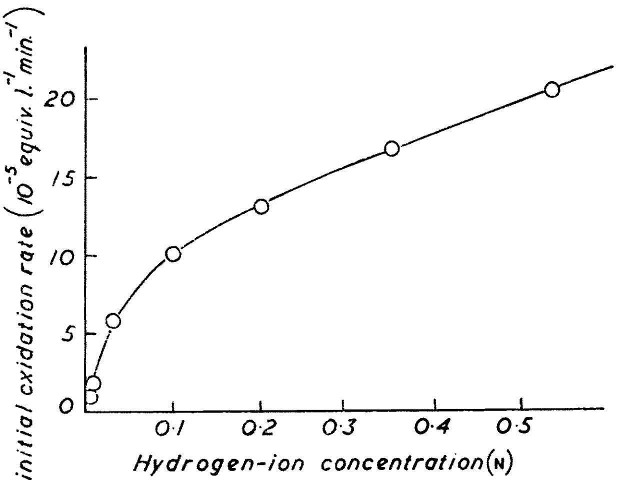

FIG. 1. *Initial rate of oxidation of acraldehyde by manganic pyrophosphate at various acidities.*

Initial [Acraldehyde], 9·0 × 10^{-3}M; initial [Mn^{III}], 2·32 × 10^{-3}M; total pyrophosphate, 0·050M; temp. 17·5° ± 0·1°.

TABLE 1. *Dependence of rate on initial acraldehyde concentration.*

Initial [Mn^{III}], 7·60 × 10^{-3}M; total pyrophosphate, 4·54 × 10^{-2}M; pH, 1·20

Initial [Acraldehyde] (× 10^{-2}M)	6·53	5·44	3·81	2·72	2·04	1·36	0·68
Initial rate, $-d[Mn^{III}]/dt$ (× 10^{-4} mole l.$^{-1}$ min.$^{-1}$)	6·3	4·9	3·5	2·5	1·8	1·2	0·7
Rate/[Acraldehyde]	0·96	0·90	0·92	0·92	0·88	0·88	1·03

TABLE 2. *Rate of consumption of* Mn.^{III}

Initial [Acraldehyde], 2·72 × 10^{-2}M; initial [Mn^{III}], 7·60 × 10^{-3}M; total pyrophosphate 4·54 × 10^{-2}M; pH, 1·20

Time (min.)	2	3	4	5	6	7	8	9	10	11
[Mn^{III}] (10^{-3}M)	7·18	6·90	6·60	6·32	6·08	5·82	5·57	5·32	5·07	4·57
$\Delta[Mn^{III}]$ Δt	0·21	0·23	0·25	0·25	0·25	0·25	0·25	0·25	0·25	0·25

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

Total pyrophosphate, 0·150M; pH, 1·62

	(*A*) Initial [Acraldehyde], 3·14 × 10^{-2}M.				(*B*) Initial [Acraldehyde], 9·0 × 10^{-3}M.				
Initial [Mn^{III}] (10^{-3}M)	27·9	18·6	9·3	7·0	4·6	2·3	1·7	1·2	0·6
Initial rate (10^{-5} mole l.$^{-1}$ min.$^{-1}$)	13	13	13	12	13	3·4	3·4	3·2	3·0
Initial rate (10^{-5} mole l.$^{-1}$ min.$^{-1}$) calc. for acraldehyde (*A*)					12	12	11	10	—

Comparative experiments with crotonaldehyde and with α-methylacraldehyde indicate that the former is oxidised somewhat more rapidly, and the latter much more

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[6] Kolthoff and Watters, *J. Amer. Chem. Soc.*, 1948, **70**, 2455.

slowly, than is acraldehyde, both oxidations being substantially of first order with respect to aldehyde concentration (Table 5). Over the concentration and acidity range chosen for all these measurements the initial rate of oxidation of crotonaldehyde is still dependent upon manganic salt concentration (Fig. 2) though there is an evident trend towards a limiting zero-order rate at high manganic concentration. With α-methylacraldehyde the zero-order rate with respect to oxidant has again been found, though further critical testing of this over a wide concentration range may be of interest.

The kinetic measurements thus indicate that with each aldehyde the one-electron oxidation by manganic pyrophosphate is preceded by an acid-catalysed reaction. With acraldehyde, and probably with α-methylacraldehyde, the actual oxidation step is so fast that the acid-catalysed reaction is rate-controlling: with crotonaldehyde this initial process is apparently rapid enough to make the oxidation step the rate-controlling one unless high concentrations of manganic salt are used. In the presence of vinyl cyanide the oxidation of acraldehyde by manganic pyrophosphate induced the separation of a

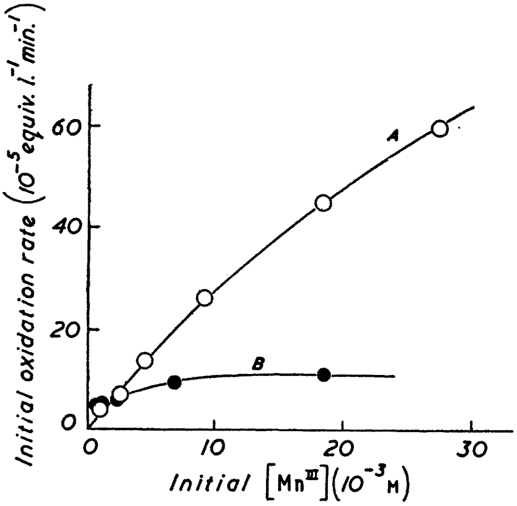

Fig. 2. *Initial rates of oxidation of crotonaldehyde and of α-methylacraldehyde.*

A, Initial [Crotonaldehyde], 9·68 × 10^{-3}M; *B*, initial [α-Methylacraldehyde], 2·22 × 10^{-2}M; temp., 17·5°; pH, 1·00; total pyrophosphate, 0·150M.

Table 4. *Oxidation in presence of manganous ions.*

Initial [Mn^{III}], 1·16 × 10^{-3}M; initial [Acraldehyde], 1·07 × 10^{-2}M; total pyrophosphate, 0·042M; pH, 1·67

[The ionic strength of the solution was kept constant by replacing $MnSO_4$ with the requisite amount of $(NH_4)_2SO_4$.]

[$MnSO_4$] (10^{-3}M) …………………………………	0·0	30·1	51·6	258
Initial rate (10^{-5} mole l.$^{-1}$ min.$^{-1}$) ……………	4·9	4·7	4·6	4·7

Table 5. *Oxidations of crotonaldehyde and of α-methylacraldehyde at* 17·5°: *dependence of initial rate on aldehyde concentration.*

Initial [Mn^{III}], 4·64 × 10^{-3}M; pyrophosphate, 0·050M; pH, 1·10

Crotonaldehyde oxidation			α-Methylacraldehyde oxidation		
Initial [Aldehyde] (10^{-3}M)	Initial rate (10^{-5} mole l.$^{-1}$ min.$^{-1}$)	$\frac{\text{Rate} - 3\cdot3}{[\text{Aldehyde}]}$	Initial [Aldehyde] (10^{-3}M)	Initial rate (10^{-5} mole l.$^{-1}$ min.$^{-1}$)	$\frac{\text{Rate}}{[\text{Aldehyde}]}$
77	85	1·06	90	14·5	0·16
52	59	1·07	60	9·6	0·16
26	32·4	1·12	30	5·3	0·18
14	17·6	1·02	15·1	3·2	0·21
6·5	11·6	1·28	7·5	1·3	0·17
2·8	6·4	1·11			

polymer that had an infrared absorption indicating the presence of both OH and CO groups. This indicates that an active free radical had been formed from the acraldehyde. However, the formation of the polymer did not affect the rate of consumption of Mn^{III}. This is to be expected, since the oxidation process which yields the free radical is much faster than the rate-controlling initial reaction.

It is currently agreed that in all acid-catalysed reactions of aliphatic aldehydes and ketones the actual process of proton addition to the oxygen atom of a carbonyl group is an instantaneous equilibrium and that the rate-controlling step is the following slow addition of an anion to this primary cation from a solvent molecule such as water. In the case of acraldehyde the initially formed cation is a mesomeric system:

$$CH_2{:}CH{\cdot}CHO + H^+ \rightleftharpoons CH_2{:}CH{\cdot}\overset{+}{C}H{\cdot}OH \longleftrightarrow \overset{+}{C}H_2{\cdot}CH{:}CH{\cdot}OH$$

so that, in water, the formation of two isomeric hydrates of acraldehyde can be envisaged:

$$CH_2{:}CH{\cdot}\overset{+}{C}H{\cdot}OH + H_2O \longrightarrow CH_2{:}CH{\cdot}CH(OH)_2 \qquad (I)$$

$$\overset{+}{C}H_2{\cdot}CH{:}CH{\cdot}OH + H_2O \longrightarrow HO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}OH \qquad (II)$$

Studies of the rates of hydration of saturated aldehydes [7, 8] have shown that the velocity of hydration of an aldehyde to products structurally resembling (I) is very much more rapid than the enolisation velocity as indicated by studies of one-electron oxidations, and hence oxidation of acraldehyde *via* compound (I) is unlikely. Again, chloral hydrate is not oxidised by manganic pyrophosphate.[1] Compound (II) however is the enol of β-hydroxypropionaldehyde; it could oxidise to the mesomeric radical, (III):

$$HO{\cdot}CH_2{\cdot}CH{:}CHO{\cdot} \longleftrightarrow HO{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CHO \qquad (III)$$

and thence to glyceraldehyde, $HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CHO$, just as the enol of propionaldehyde would oxidise to α-hydroxypropionaldehyde. Consequently, we suggest that the formation of the enol (II) is the rate-determining step in the one-electron oxidation of acraldehyde. Similarly, α-methylacraldehyde can be envisaged as giving $HO{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}OH$, then $HO{\cdot}CH_2{\cdot}CMe(OH){\cdot}CHO$.

The acid-catalysed addition of water to acraldehyde has already been studied kinetically, first by Lucas and Pressman [9] and later by Hall and Stern.[10] These workers, however, have dealt with the reversible addition of a water molecule to the olefinic bond of acraldehyde to give the aldehydic form of β-hydroxypropionaldehyde and not the enol (II):

$$CH_2{:}CH{\cdot}CHO + H_2O \rightleftharpoons HO{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$$

The earlier workers give the activation energy of the forward reaction as 18 kcal., whilst the later workers give 15·7 kcal. Both these values are much higher than the value of 12·9 ± 0·4 kcal. which we deduce from our oxidation-rate measurements over the temperature range 17·5—44° (Table 6) and undoubtedly we have not been concerned with this hydration of the olefinic bond. To confirm this we have demonstrated that if aqueous acraldehyde is left, under nitrogen, in contact with mineral acid for several hours before

TABLE 6. *Rates of oxidation of acraldehyde at different temperatures.*

Initial [Acraldehyde], 0·01M; total pyrophosphate, 0·125M; initial [Mn^{III}], $1{\cdot}55 \times 10^{-3}$M.

Temp.	44°	38°	32°	25°	17·5°
pH	1·05	1·00	1·02	1·04	1·05
Rate (10^{-5} mole l.$^{-1}$ min.$^{-1}$)	58	43	28	17	10
Rate corrected to pH 1·05	58	41	27	17	10

Activation energy (from graph): 12·9 ± 0·4 kcal.

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[7] Bell and Clunie, *Proc. Roy. Soc.*, 1952, *A*, **212**, 33.

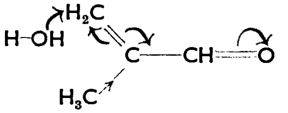
[8] Bell and Darwent, *Trans. Faraday Soc.*, 1950, **46**, 34.

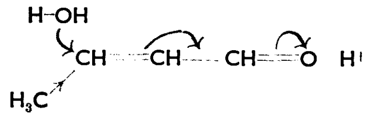
[9] Lucas and Pressmann, *J. Amer. Chem. Soc.*, 1942, **64**, 1953.

[10] Hall and Stern, *J.*, 1950, 490.

it is oxidised with manganic pyrophosphate then the initial rate of oxidation decreases considerably (Table 7). We infer that β-hydroxypropionaldehyde yields the enol (II) much less rapidly that does acraldehyde. α-Methylacraldehyde behaves similarly, though the effect of pre-treatment with acid is proportionally much less.

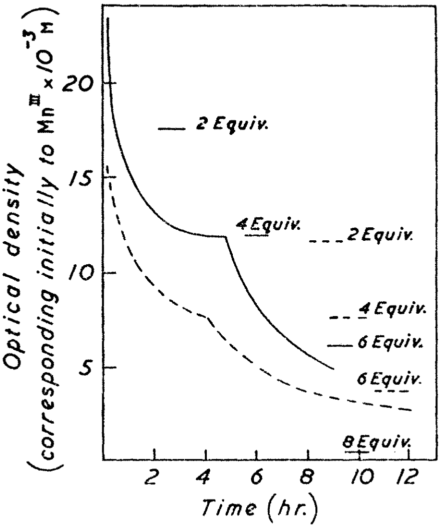
The relative reactivities of acraldehyde, crotonaldehyde, and α-methylacraldehyde are explicable if the preceding reaction mechanism is correct:





The inductive effect of a methyl group at an α-carbon atom would decrease the ease of catalysed hydroxylation at the double bond by compensating, in part, for the electro-

FIG. 3. *Complex formation in prolonged oxidation of acraldehyde with manganic pyrophosphate.*

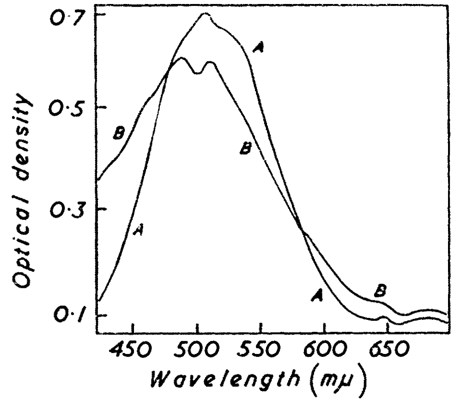


Upper curve: Initial [Mn^{III}], 2·33 × 10^{-2}M; [Acraldehyde], 5·75 × 10^{-3}M.

Lower curve: Initial [Mn^{III}], 1·55 × 10^{-2}M; [Acraldehyde], 3·93 × 10^{-3}M.

Temp., 50°; pH, 0·12.

FIG. 4. *Absorptions of manganic complexes in a 1-cm. cell.*



(*A*) Manganic pyrophosphate; [Mn^{III}], 11·5 × 10^{-3}M.

(*B*) Solution after oxidation of acraldehyde by 4 equiv. of Mn^{III} (Fig. 3, upper curve); residual [Mn^{III} *ca.* 8 × 10^{-3}M.

TABLE 7. *Effect of acid catalysis of hydration of acraldehyde on its rate of oxidation by* Mn^{III}.

(*A*) Initial [Mn^{III}], 2·32 × 10^{-3}M; total pyrophosphate, 0·15M; pH, 1·66; temp., 17·5°; [Acraldehyde], 1·38 × 10^{-2}M in oxygen-free distilled water. (Rates in 10^{-5} mole l.$^{-1}$ min.$^{-1}$.)

Initial rate, freshly prepared solution	4·7
Initial rate for solution stored for 18 hr. at room temp.	4·5

(*B*) The following solutions were stored in absence of oxygen for 24 hr. at 25°, then mixed with pyrophosphate, Mn^{III}, and sulphuric acid to give in each case [Acraldehyde], 1·93 × 10^{-2}M; [Mn^{III}], 4·64 × 10^{-3}M; pyrophosphate, 0·15M; pH, 1·65, and the rate of consumption of Mn^{III} was measured at 17·5°.

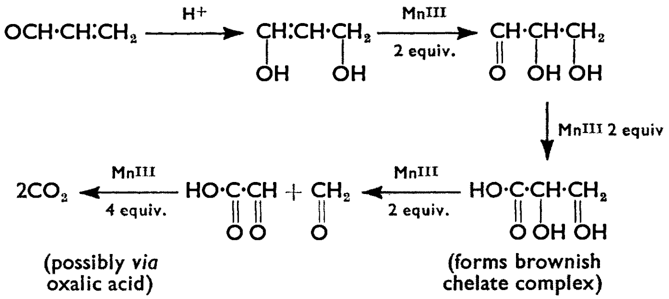
Solution	Oxidation rate (10^{-5} mole l.$^{-1}$ min.$^{-1}$)
(*a*) Acraldehyde in distilled water	7·8
(*b*) ,, 0·125M-pyrophosphate	4·4
(*c*) ,, 0·083M-pyrophosphate plus 0·57N-sulphuric acid	1·8
(*d*) ,, 0·85N-sulphuric acid	0·9

α-Methylacraldehyde (6 × 10^{-2}M), when stored as in (*a*) above, gave an initial rate of 9·6 × 10^{-5} mole l.$^{-1}$ min.$^{-1}$: after storage as in (*d*) the rate was 7·9 × 10^{-5} mole l.$^{-1}$ min.$^{-1}$.

meric effect of the carbonyl group; in the β-position the methyl group would enhance this electromeric polarisation of the double bond.

Later Stages of the Oxidation.—To investigate the prolonged oxidation of acraldehyde, sealed ampoules containing oxygen-free solutions of acidified manganic pyrophosphate and acraldehyde were stored at 50° and after suitable intervals cooled to 10° and emptied into absorptiometer cells. Fig. 3 shows typical optical-density measurements made with a blue-green filter (No. 603). The discontinuities in the curves are due to the presence of a brownish-red intermediate having a broader absorption band than the cherry-red manganic pyrophosphate in the 450—600 mμ region (Fig. 4). This intermediate substance, which evidently reaches its maximum concentration when 4 equiv. of Mn^{III} have been consumed per mole of acraldehyde, is probably a chelated manganic complex of an α-hydroxy-acid, similar to those noted as being formed during the oxidations of lactic and tartaric acids.[11] Solutions containing as many as 6 equiv. of Mn^{III} were decolorised in a few days, one containing 8 equiv. became colourless in about a week, whilst one containing 10 equiv. remained slightly pink after 4 weeks. Titration of this solution indicated an overall consumption of 9·96 equiv. of Mn^{III} per mole of acraldehyde. A test with chromotropic acid showed that this final solution contained formaldehyde. Carbon dioxide was present but formic acid could not be detected. After consumption of 2 equiv. of Mn^{III} formaldehyde could not be detected in the solution; after consumption of 6 or more equiv. however it was present. At no stage was it possible to detect 1 : 2-dioxo-compounds, R·CO·CO·R′, by treating solutions with hydroxylamine and then with a nickel salt. Hence oxidation *via* $HO{\cdot}CH_2{\cdot}CO{\cdot}CHO$ is unlikely.

The evidence presented above indicates that the course of oxidation of acraldehyde can probably be represented as follows:



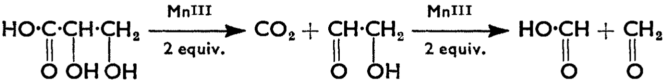
$$OCH{\cdot}CH{:}CH_2 \xrightarrow{H^+} \underset{OH}{CH}{:}CH{\cdot}\underset{OH}{CH_2} \xrightarrow[2\text{ equiv.}]{Mn^{III}} \underset{O}{\overset{}{CH}}{\cdot}\underset{OH}{CH}{\cdot}\underset{OH}{CH_2} \xrightarrow{Mn^{III}\ 2\text{ equiv}} HO{\cdot}\underset{O}{C}{\cdot}\underset{OH}{CH}{\cdot}\underset{OH}{CH_2}$$

$$2CO_2 \xleftarrow[4\text{ equiv.}]{Mn^{III}} HO{\cdot}\underset{O}{C}{\cdot}\underset{O}{CH} + \underset{O}{CH_2} \xleftarrow[2\text{ equiv.}]{Mn^{III}} HO{\cdot}\underset{O}{C}{\cdot}\underset{OH}{CH}{\cdot}\underset{OH}{CH_2}$$

(possibly *via* oxalic acid)

(forms brownish chelate complex)

According to this scheme, glyceraldehyde yields glyceric acid which is then oxidised as a 1 : 2-glycol,[12] giving formaldehyde when 6 equiv. of Mn^{III} have been consumed. The glyoxylic acid must oxidise completely, *via* oxalic acid, and not undergo fission to formic acid since this is resistant to manganic pyrophosphate.[1] An alternative path from glyceric acid would be that suggested for α-hydroxy-acids in Part V,[11] but this is much less likely because it should end with the consumption of only 8 equiv. of tervalent manganese and should yield a mixture of formaldehyde and formic acid:



$$HO{\cdot}\underset{O}{C}{\cdot}\underset{OH}{CH}{\cdot}\underset{OH}{CH_2} \xrightarrow[2\text{ equiv.}]{Mn^{III}} CO_2 + \underset{O}{CH}{\cdot}\underset{OH}{CH_2} \xrightarrow[2\text{ equiv.}]{Mn^{III}} HO{\cdot}\underset{O}{CH} + \underset{O}{CH_2}$$

Further evidence that the oxidation of acraldehyde involves the successive formation of glyceraldehyde and of glyceric acid has been obtained by oxidising it with known amounts of manganic pyrophosphate and, when destruction of Mn^{III} was complete, adding standard periodate solution and estimating the further oxidation effected thereby

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[11] Levesley and Waters, *J.*, 1955, 217.

[12] Drummond and Waters, *J.*, 1953, 3119.

in 4 hr. at 6°. Table 8 shows that the periodate consumption, appreciable after oxidation by 2 equiv. of Mn^{III}, rises to a maximum at the 4 equiv. stage (that of production of glyceric acid) and has almost disappeared when 6 equiv. of Mn^{III} have been consumed. Since cold periodic acid rapidly oxidises both 1 : 2-glycols and glycollaldehyde,[13] but oxidises glyoxylic acid very slowly,[14] these observations favour the view that manganic pyrophosphate oxidises glyceric acid by glycol fission rather than by decarboxylation.

EXPERIMENTAL

Materials.—Acraldehyde was twice fractionated in oxygen-free nitrogen through a short Vigreux column, the middle fraction only being collected. Immediately after distillation, quantities of about 1 g. were sealed in thin-walled glass bulbs and weighed. Solutions were prepared by breaking bulbs in boiled-out distilled water in standard flasks and immediately making them up to volume. In this way polymerisation of the acraldehyde was avoided. Crotonaldehyde and α-methylacraldehyde were purified similarly, but some slight polymerisation of the latter could not be prevented.

Manganic pyrophosphate solutions were prepared as described in Part II.[1]

Procedure for Kinetic Measurements.—Analyses were carried out with a Hilger " Spekker " photoabsorptiometer using blue-green filter No. 603. With 4-cm. cells the calibration curve was nearly linear over the concentration range 4—7 × 10^{-3}M-Mn^{III}; higher concentrations were measured in 1-cm. cells. The colour change due to the transient product (Fig. 3) does not affect the accuracy of the initial rate measurements.

Standard solutions of the components were prepared in oxygen-free distilled water and brought to 17·5°. Aliquot parts were then mixed inside the thermostat in a flask that was being continually flushed with oxygen-free nitrogen; the acraldehyde solution was added last and the instant of half admixture taken as the zero time of reaction. The mixture was then poured into an absorptiometer cell that had been brought to 17·5° inside the thermostat and flushed thoroughly with nitrogen. The full cell was then closed with a glass plate to exclude air, transferred to the absorptiometer, covered with a black cloth, and kept at 17·5° ± 0·1° by a current of warm or cold air from an electric hair-dryer, a thermometer in a second water cell under the cloth being used to check the temperature control. Measurements were made at 1—2 min. intervals and no kinetic experiment was continued for more than 30 min.

Studies of Prolonged Reaction (see Fig. 3).—These were carried out by mixing oxygen-free solutions of acraldehyde and manganic pyrophosphate, acidified with sulphuric acid to pH 0·12, sealing them in ampoules of about 8 ml. capacity so as to leave only about 0·2 ml. of gas space, and placing these in a thermostat at 50°. At intervals ampoules were cooled to 10°, and the contents poured into absorptiometer cells and compared with a freshly-prepared manganic pyrophosphate solution at the same pH.

The data of Fig. 4 were obtained by rapid use of a Unicam spectrophotometer with a solution that showed maximum colour deviation.

Completion of reaction was tested by sealing similar ampoules of acraldehyde with 2, 4, 6, 8, and 10 equiv. of manganic pyrophosphate and storing them at 50°. Solutions containing up to 6 equiv. of Mn^{III} were decolorised completely in 1—2 days, that with 8 equiv. became colourless after a week, and that with 10 equiv. remained slightly pink after 4 weeks and had deposited a trace of manganese dioxide. Colour tests [15] for possible reaction products, *i.e.*, CH_2O, $H{\cdot}CO_2H$, $\cdot CO{\cdot}CO\cdot$, were made with each of these decolorised solutions.

Consumption of periodate after completion of reaction with tervalent manganese was examined in similar solutions. To aliquot parts of each, cooled to 6°, an excess of standard periodate solution was added, and after 4 hr. the iodine liberated on treatment with potassium iodide was titrated with thiosulphate.

Induced Polymerisation of Vinyl Cyanide.—This was examined in evacuated Thunberg tubes containing in each case 0·3 ml. of vinyl cyanide in 15 ml. of solution. A solution containing acraldehyde (0·03M) in acid pyrophosphate was not turbid after 18 hr., solutions containing acid manganic pyrophosphate (4 × 10^{-3}M) and neutral manganic pyrophosphate

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[13] Fleury and Courtois, *Bull. Soc. chim. France*, 1941, **8**, 75; 1945, **12**, 548.

[14] Fleury and Lange, *J. Pharm. Chim.*, 1933, **17**, 196, 313, 409.

[15] F. Feigl, " Spot Tests," 4th English Edition, Elsevier Publ. Co., Amsterdam, 1954.

(4×10^{-3}M) plus acraldehyde (0·03M) contained only a minute amount of polymer after 18 hr., but a solution containing the same concentrations of acraldehyde and manganic pyrophosphate in approx. N-sulphuric acid gave an immediate separation of polymer. Decoloration of this solution was complete in 9·60 min.; a similar solution not containing vinyl cyanide was decolorised in 9·67 min. The collected polymer had infrared absorption bands at 1720 (CO) and 3450 cm.$^{-1}$ (OH).

TABLE 8. *Formation of a* 1 : 2-*glycol by oxidation of acraldehyde with manganic pyrophosphate.*

Initial [Acraldehyde] (10^{-3}M)	Mn^{III} reduced (equiv.)	Periodate reduced (10^{-3}M)	Molar fraction of glycol present
1·21	2	0·145	0·12
0·97	4	0·355	0·37
0·85	6	0·024	0·03
0·79	8	nil	0·00

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

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