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KINETICS OF THE CHROMIC ACID OXIDATION OF GLYOXYLIC AND PYRUVIC ACIDS

K. K. SEN GUPTA and T. SARKAR
Department of Chemistry, Jadavpur University, Calcutta-32, India

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Abstract—The reactions of glyoxylic and pyruvic acids by chromium (VI) have been studied in the presence of perchloric acid. Each reaction is first order with respect to chromium (VI), α-keto acid and hydrogen ion concentrations. The addition of sodium perchlorate to the reaction mixture had no effect on the rates but sodium chloride and sodium dihydrogen phosphate have retarding influences. Manganous ions increase the rate of reaction. The activation parameters are evaluated and tentative mechanisms for the oxidation reactions are discussed.

INTRODUCTION

The oxidation of a variety of organic compounds like aldehydes, ketones, alcohols, fatty acids and α-hydroxy acids by chromium (VI) have been reported.[1-3] The oxidation of α-keto acids by different oxidants like iodine,[4] cerium (IV)[5], manganese (III)[6] and vanadium (V)[7] have been studied. We report the results for the oxidation of both glyoxylic and pyruvic acids by chromium (VI) in detail, although a preliminary account of the oxidation of glyoxylic acid by chromium (VI) has been reported earlier.[8]

EXPERIMENTAL

Reagents. All inorganic materials including potassium dichromate were of Merck (G. R.) grade. Glyoxylic and pyruvic acids were used without further purification. Pyridine was purified twice by distillation.

Kinetic measurements. The rate of decrease of chromium (VI) was followed from the measurements of optical densities at 350 nm in a Beckman DU model spectrophotometer. The spectrophotometer had its cell compartment and the cell temp was kept constant by circulating water into the thermostat. Requisite volumes of the reactants previously equilibriated to bath temperature were mixed externally and the mixture was immediately transferred to a cell of path length 1 cm. The ionic strength and hydrogen ion concentrations were much higher than that of the oxidant. The rate of decrease of chromium (VI) was followed for at least 60% conversion of initial chromium (VI) concentration. The pseudo first order rate constants were then calculated which were reproducible to within ±2%. The experiments were performed at 35°C unless otherwise mentioned.

RESULTS

The products in excess substrate concentrations were formic and acetic acids respectively. The substrates were quantitatively oxidised to the same product by allowing mixtures containing substrate with the large excess of oxidant to stand for 24 h at 30°. The unreacted oxidant was then estimated. The reactions may be represented stoichiometrically by the general equation:

$$3\,RCOCOOH + Cr_2O_7^{=} + 8\,H^+ \rightarrow 3\,RCOOH + 2Cr(III) + 4H_2O + 3CO_2$$

where, R = H for glyoxylic and R = CH_3 for pyruvic acids respectively.

Effect of reactant concentrations. The reactions were studied under pseudo first order conditions, i.e. when substrate is nearly 10 times excess than that of the oxidant. The rate is decreased with the increase in initial concentration of chromium (VI) (Table 1). This is possibly because a progressively smaller portion of total amount remains in the form of $HCrO_4^-$, as the concentration of initial chromium is increased. Ionic strength was held constant in each run to $\mu = 1{\cdot}0$ M. The values of k_{cor} at various initial chromium (VI) concentrations have been calculated from the relation, $k_{cor} = k_1\,[Cr\,(VI)]/[HCrO_4^-]$ and are reported in the same table. The equation, $K_d = \{[Cr\,(VI)] - ([HCrO_4^-/2]\}/[HCrO_4^{\ }]^2$ was used to calculate the concentration of $HCrO_4^-$ using the reported value[9] of 'K_d' which is 76·0, at $\mu = 1{\cdot}0$ M. The subsidiary equilibrium, $HCrO_4^- \overset{K_d'}{\rightleftharpoons} H^+ + CrO_4^{=}$ was neglected since, $K_d' = 1{\cdot}75 \times 10^{-6}$ and $[H^+] \gg K_d'$ in each case. The results, however, indicate that $HCrO_4^-$ is the reacting species.

The rate of oxidation increased with the increase in substrate concentrations. The initial concentrations of both chromium (VI) as well as of hydrogen ions were held constant in each run. The plots of $1/k_1$ against $1/[\alpha\text{-keto}]$ are straight lines passing through the origin showing the absence of intermediate compound in each case (Fig. 1). The results further indicate that the order with respect to substrate is unity.

Effect of acids on the reaction. The acidity was varied by the addition of perchloric acid. The ionic strength of each mixture was maintained constant by the addition of sodium perchlorate. The reactions are acid catalysed and the values of $k_1/[H^+]$ at various acidities have been computed (Table 2). The results indicate that the rate is proportional to the first power of hydrogen ion concentration. Although the reactions could not be studied under comparable conditions, it is apparent from the results obtained that the reaction is faster with glyoxylic acid. The rate of oxidation also increased with the increase in the proportion of acetic

Table 1. Effect of oxidant on the reaction rate at μ = 1·0 M

(a) [Glyoxylic] = 2·077 × 10^{-3} M, [H^+] = 0·2 M
(b) [Pyruvic] = 5·233 × 10^{-3} M, [H^+] = 1·0 M

		a		b	
[Cr(VI)] × 10^4 M	[$HCrO_4^-$] × 10^4 M	$k_1 \times 10^4$ (s^{-1})	$k_{cor} \times 10^4$ (s^{-1})	$k_1 \times 10^4$ (s^{-1})	$k_{cor} \times 10^4$ (s^{-1})
1·036	2·013	5·59	2·88	3·64	1·87
2·072	3·914	5·52	2·92	3·38	1·79
3·108	5·718	5·29	2·88	3·24	1·76
4·144	7·447	5·18	2·88	3·06	1·70
5·180	9·105	—	—	2·88	1·64

Table 2. Variation of rate with change in hydrogen ion concentration

(a) [Glyoxylic] = 2·077 × 10^{-3} M, [Cr(VI)] = 2·073 × 10^{-4} M, μ = 0·3 M.
(b) [Pyruvic] = 5·233 × 10^{-3} M, [Cr(VI)] = 2·073 × 10^{-4} M, μ = 1·8 M.

a			b		
[H^+] M	$k_1 \times 10^4$ (s^{-1})	$\frac{k_1}{[H^+]} \times 10^3$ (lit. $mole^{-1}$ s^{-1})	[H^+] M	$k_1 \times 10^4$ (s^{-1})	$\frac{k_1}{[H^+]}$ (lit. $mole^{-1}$ s^{-1})
0·10	2·80	2·80	1·0	3·15	3·15
0·15	3·99	2·66	1·2	4·77	3·97
0·20	5·22	2·61	1·4	5·59	3·99
0·25	6·45	2·57	1·6	5·99	3·74
0·30	7·67	2·55	1·8	6·52	3·62

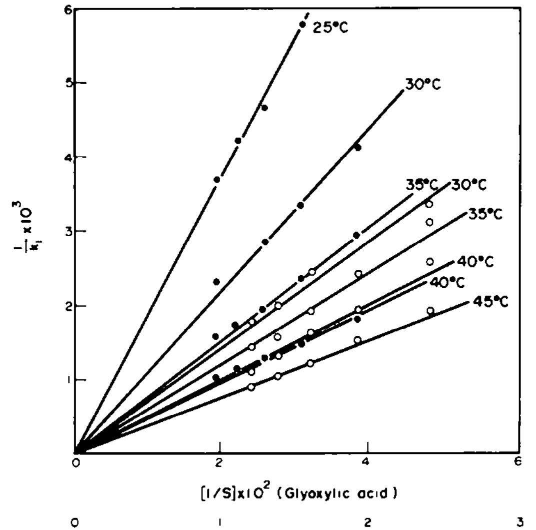


Fig 1. Influence of substrate concentrations on the pseudo first order rate at different temperatures. Curves showing the absence of complex formation between α-keto acids and chromium (VI) (open circles for glyoxylic and closed circles for pyruvic acids).

1, [Cr(VI)] = 2·073 × 10^{-4} M, [H^+] = 0·1 M.

2, [Cr(VI)] = 2·073 × 10^{-4} M, [H^+] = 1·0 M.

acid (Table 3). This increase was either due to the increase in the protonation of $HCrO_4^-$, since dielectric constant decreased with the increase in acetic acid,[10] or due to the production of stronger oxidants[11] like $CH_3COOCrO_2OH$ or $CH_3COOCrO_2OH_2^+$.

Effect of salts on the rate. The rate decreased considerably with the increase in the concentration of added salts (Fig 2) except perchlorate which does not seem to have any influence in the range 0·1–1·5 M. The observed rate constants in 4·0 × 10^{-2} M concentration of the salts are found to be 3·18 × 10^{-4} and 1·60 × 10^{-4} (s^{-1}) for chloride and dihydrogen phosphate respectively during the oxidation of glyoxylic acid whereas the respective values of 3·12 × 10^{-4} and 2·0 × 10^{-4} (s^{-1}) have been obtained for the other reaction at the same concentration of the salts. The rate decrease, therefore, followed the order, dihydrogen phosphate > chloride. The above order has been explained earlier[12] as due to the tendency of anions to react with the acid chromate ion, $HCrO_4^-$ to form complexes of decreasing stabilities, although the interaction of perchlorate with $HCrO_4^-$ would be small since perchlorate is a least complex forming anion and hence the rate had no effect even in swamping concentration of perchlorate (~ 1·5 M). Moreover, $H_2PO_4^-$ is basic in character and on addition of salt of this anion to 0·1 or 1·0 M $HClO_4$ there would be a sizeable change in the value of [H^+] because the basic anions would take up protons from perchloric acid. As the reactions are acid catalysed, this must effect the rate and cause it to be reduced.

Influence of manganous ions on the rate. The effect of addition of manganous ions which usually inhibit the rate of chromic acid oxidation of organic compounds,[13–17] has been studied. In contrast to the observations made earlier, we have noticed that manganous ions increase the rate of reaction (Table 4). The first order constants which increased linearly with the increase in manganous ion concentration, can be expressed by the empirical equations, k_1 = 2·75 × 10^{-4} + 0·041 [Mn^{++}] and k_1 = 3·25 × 10^{-4} + 0·043 [Mn^{++}] for the respective cases of oxidations. It is to be

Table 3. Variation of acetic acid on the rate of the reaction at 50°

(a) [Glyoxylic] = $2{\cdot}077 \times 10^{-3}$ M, [Cr(VI)] = $2{\cdot}073 \times 10^{-4}$ M, [H^+] = 0·1 M.
(b) [Pyruvic] = $5{\cdot}233 \times 10^{-3}$ M, [Cr(VI)] = $2{\cdot}073 \times 10^{-4}$ M, [H^+] = 1·0 M.

←a→		←b→	
% acetic acid (v/v)	$k_1 \times 10^4$ (s^{-1})	% acetic acid (v/v)	$k_1 \times 10^4$ (s^{-1})
0	6·45	0	10·29
5	6·91	10	12·43
10	7·14	15	12·89
15	7·52	20	13·51
20	7·83	25	14·02
25	8·75	—	—

Table 4. Effect of manganous sulphate on the rate

(a) [Glyoxylic] = $2{\cdot}077 \times 10^{-3}$ M, [Cr(VI)] = $2{\cdot}073 \times 10^{-4}$ M, [H^+] = 0·1 M.
(b) [Pyruvic] = $5{\cdot}233 \times 10^{-3}$ M, [Cr(VI)] = $2{\cdot}073 \times 10^{-4}$ M, [H^+] = 1·0 M.

[$MnSO_4, 4H_2O$] $\times 10^3$ M	0	2·5	5·0	7·5	10·0
(a) $k_1 \times 10^4$ (s^{-1})	2·80	4·07	4·61	—	6·86
(b) $k_1 \times 10^4$ (s^{-1})	3·15	4·26	5·29	6·60	7·76

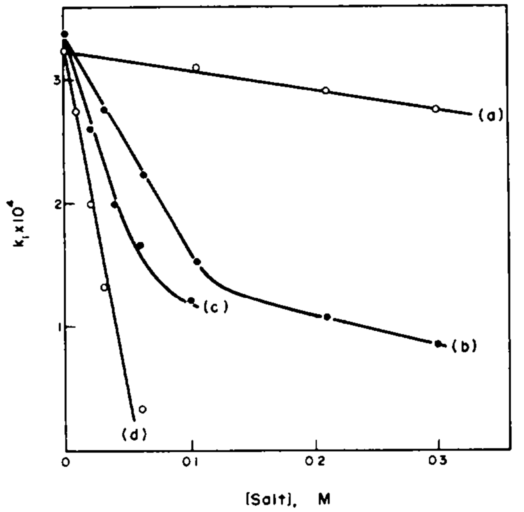


Fig 2. Influence of sodium chloride and sodium dihydrogen phosphate on the pseudo first order rate constant (open circles for glyoxylic and closed circles for pyruvic acids).

1, [Glyoxylic] = $2{\cdot}077 \times 10^{-3}$ M, [Cr(VI)] = $2{\cdot}073 \times 10^{-4}$ M, [H^+] = 0·1 M.
2, [Pyruvic] = $5{\cdot}233 \times 10^{-3}$ M, [Cr(VI)] = $2{\cdot}073 \times 10^{-4}$ M, [H^+] = 1·0 M.

a, b → sodium chloride and c, d → sodium dihydrogen phosphate.

mentioned that the experimental values of k_1 in the absence of manganous ions are $2{\cdot}8 \times 10^{-4}$ and $3{\cdot}15 \times 10^{-4}$ (s^{-1}) as against the values of $2{\cdot}75 \times 10^{-4}$ and $3{\cdot}25 \times 10^{-4}$ (s^{-1}) obtained graphically for the respective cases of oxidation. However, the agreement between the experimental and extrapolated values is reasonably good.

Effect of pyridine on the rate. The observed rate constant in the presence of pyridine decreased with the increase in pyridine concentration (Table 5). the dissociation constant of pyridinium ion,[18] $pyH^+ \rightleftharpoons py + H^+$ was of the order of 10^{-6} at 35°. Since pyridine removes hydrogen ions, the effective hydrogen ion concentrations would correspond to {[H^+] − [py]}. The values of $k_1/\{[H^+]-[py]\}$ will increase with increase in pyridine concentration, if pyridine catalyses[13] the reaction. The results indicate that pyridine does not catalyse the reaction.

Activation parameters of the reactions. The specific rates at various temperatures were calculated from the relation, $k_{sp} = k_1/[\alpha\text{-keto acid}][H^+]$. The values have been computed to be 1·37, 1·6, 2·06, and 2·60 at 30, 35, 40 and 45° for glyoxylic and $2{\cdot}63 \times 10^{-2}$, $4{\cdot}44 \times 10^{-2}$, $6{\cdot}34 \times 10^{-2}$ and $9{\cdot}84 \times 10^{-2}$ ($lit^2 mole^{-2} s^{-1}$) at 25, 30, 35 and 40° respectively for the other reaction. The plots of log k_{sp} against 1/T are linear. The energy of activations were calculated to be 9·5 ± 0·5 and 15·2 ± 1·0 kcals/mole from the slopes of the above plots, for the glyoxylic and pyruvic acids respectively. The details of the calculations of different thermodynamic parameters have been reported elsewhere.[17] The values of ΔS‡ and ΔG‡ (at 308°K) for the chromic acid oxidation of glyoxylic acid have been computed to be −30·1 ± 1·6 (e.u.) and 17·8 ± 0·1 kcals/mole respectively. The corresponding values for the other reaction are −14·8 ± 3·0 (e.u.) and 19·8 ± 0·24 kcals/mole. The results indicate that more activation energy is needed to rupture C–C bond of pyruvic acid than glyoxylic acid. This is expected since with the substitution of carbonyl hydrogen atom of glyoxylic acid by an electron donating methyl radical, the electron density of carbonyl carbon atom is increased, thus making C–C bond of pyruvic acid more stable. Again, free energy of activations of two reactions are not widely different unlike energy and entropy of activations which differ appreciably. This is possibly because ΔH‡ and TΔS‡ compensate each other so that ΔG‡ values do not differ by an appreciable amount.

DISCUSSION

The uncatalysed oxidations take place by the rupture of C–C bond of α-keto acids. However, there are other possibilities also for the oxidations of α-keto acids.

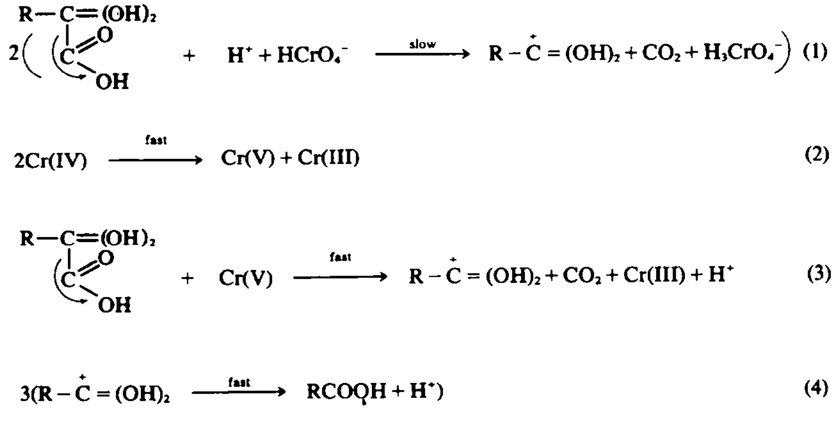
Table 5. Influence of pyridine on the first order rate

(a) [Glyoxylic] = 2·077 × 10^{-3} M, [Cr(VI)] = 2·073 × 10^{-4} M, [H$^+$] = 0·1 M.
(b) [Pyruvic] = 5·233 × 10^{-3} M, [Cr(VI)] = 2·073 × 10^{-4} M, [H$^+$] = 1·0 M.

a			b		
[Pyridine] × 10^2 M	$k_1 \times 10^4$ (s^{-1})	$\frac{k_1 \times 10^3}{\{[H^+]-[Py]\}}$ (lit. mole^{-1} s^{-1})	[Pyridine] × 10^2 M	$k_1 \times 10^4$ (s^{-1})	$\frac{k_1 \times 10^4}{\{[H^+]-[Py]\}}$ (lit. mole^{-1} s^{-1})
1·769	2·92	3·55	0·296	3·57	3·58
3·538	2·30	3·55	1·186	3·52	3·56
4·720	1·83	3·48	2·372	3·38	3·46

Glyoxylic acid may be oxidized initially to give oxalic acid followed by the rupture of C–C bond of oxalic acid to CO$_2$. The stoichiometry as well as formation of formic acid in solution rule out the possibility of oxidation via oxalic acid. Alternatively, both the substrates may be oxidized by way of their decarboxylations followed by the oxidation of hydrated aldehyde molecules to give fatty acids. The oxidation of formaldehyde by chromic acid has been studied by Kemp and Waters[20] and in an attempt to compare their results with the oxidation of glyoxylic acid, several kinetic differences between these two reactions have been observed. Unlike the oxidation of glyoxylic acid, the rate is not proportional to the first power of formaldehyde and hydrogen ion concentrations. The evidence for the formation of protonated intermediate complex has also been noted during the oxidation of formaldehyde. Moreover, Chatterjee and Mukherjee[19] have observed retardations by manganese (II) during the chromic acid oxidation of formaldehyde, unlike present reactions. All these lend further support to the fact that chromic acid oxidation of glyoxylic acid does not proceed via decarboxylation and subsequently by the oxidation of hydrated formaldehyde molecule. The striking resemblems between the reactions of α-keto acids and chromium (VI) have been noticed. These facts suggest that the mechanism of the oxidation of pyruvic acid is similar to that for the oxidation of glyoxylic acid. The dissociation constants (K$_a$) of glyoxylic and pyruvic acids are 4·7 × 10^{-4} and 3·2 × 10^{-3} at 25° respectively. Moreover, α-keto acids are partially hydrated,[21,22] in aqueous solution, and the hydrated forms would remain as undissociated molecules (since, [H$^+$] ≫ K$_a$). Again since the order with respect to hydrogen ion is unity, the proton may add on to the substrate molecule only (since H$_2$CrO$_4$ is a highly ionised species) forming a protonated species by a fast step. This protonated substrate molecule would subsequently react with the reactive species of chromium (VI) to give a carbonium ion in the slow rate determining step. However, in view of the absence of evidence for the formation of intermediate protonated species (since water is more basic than α-keto acid) we have considered Eq (1) as the rate determining step for the reactions where $R-\overset{+}{C}=(OH)_2$ and chromium (IV) are formed by the rupture of C–C bond of α-keto acids. Chromium (IV) on the other hand, from step (1) either disproportionates or reacts rapidly with chromium (VI). It has recently been shown[23] that the disproportionation of chromium (IV) is more probable than its reaction with chromium (VI) to give chromium (V). However, chromium (V) would further react with substrate to give carbonium ion by fast step (3). The carbonium ion would get converted to the stable product fatty acids according to step (4). The intermediate chromium species like chromium (IV) and chromium (V) have been designated as HCrO$_4^{3-}$ and HCrO$_4^{2-}$ respectively in the steps (1, 5 and 6) in order to balance the equations.

A one electron transfer mechanism, on the other hand, will lead to the formation of unstable chromium (V) and an organic free radical in the first stage. The formation of free radical in the slow rate determining step followed by a number of rapid steps can be explained by the Scheme II.



$$2\left(\text{hydrate}\right) + H^+ + HCrO_4^- \xrightarrow{\text{slow}} R-\overset{+}{C}=(OH)_2 + CO_2 + H_3CrO_4^- \quad (1)$$

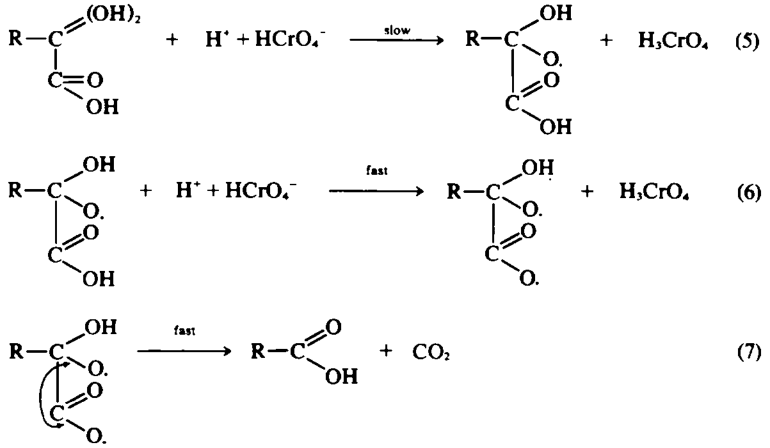
$$2Cr(IV) \xrightarrow{\text{fast}} Cr(V) + Cr(III) \quad (2)$$

$$\text{hydrate} + Cr(V) \xrightarrow{\text{fast}} R-\overset{+}{C}=(OH)_2 + CO_2 + Cr(III) + H^+ \quad (3)$$

$$3(R-\overset{+}{C}=(OH)_2 \xrightarrow{\text{fast}} RCOOH + H^+) \quad (4)$$

SCHEME I

The two chromium (V) molecules which are generated in steps (5) and (6) might get converted to chromium (III) by reacting rapidly with two substrate molecules according to step (3), the latter will be followed as usual by step (4) to give two molecules of fatty acids. The addition of acrylamide to the reaction mixture failed to polymerise the solution and therefore the Scheme II appears less favourable.



SCHEME II

followed by steps (3) and (4).

The prompt oxidation of α-keto acids on the addition of manganese (II) can be explained in the following manner. Since manganese (II) prefers co-ordination with oxy anions,[24] it is suggested that manganese (II) reacts initially with the substrates to give five membered metal chelates which are oxidised by chromium (VI) to give chelates of higher valence states of manganese. The strong electron pull of higher valent manganese (III) is so great that an electron is donated to the metal with simultaneous breaking of C–C bond, as a result, the concentration of manganese (II) would remain unaltered during the whole course of a run. Again, the oxidation potential of chromium (VI)–chromium (III) couple is 1·36 volts in comparison with the same for manganese (II)-manganese (III) couple which is 1·45 volts, the reaction between manganese (II) and chromium (VI) according to step (8) followed by the reactions of manganese (III) with α-keto acids to give metal chelate seem unlikely.

$$\mathrm{Cr(VI)} + \mathrm{Mn\,(II)} \rightarrow \mathrm{Cr(V)} + \mathrm{Mn(III)} \ldots \qquad (8)$$

The manganese (III) solution is stable at higher acidity i.e. >5 M and it is expected that it would undergo auto oxidation and reduction by step (9) at very low concentrations of acid, <1 M.

$$2\,\mathrm{Mn(III)} \rightarrow \mathrm{Mn(II)} + \mathrm{Mn(IV)} \ldots \qquad (9)$$

However, we have not observed any precipitation of manganese dioxide in solution. It is to be mentioned that the oxidation of pyruvic acid by manganic pyrophosphate proceeded via intermediate complex formation[6] and the kintetics of the reaction was studied at 10° since the reaction was very fast. Consequently, the manganese (III)-pyruvic chelate is expected to be more unstable at 35°, the temperature at which the present reactions were carried out.

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