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Oxidation of Pyruvic Acid by Cobalt(III)

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The kinetics of oxidation of pyruvic acid and sodium pyruvate by Co^{3+} in sulphuric and nitric acid media, and the effects of $[Co^{2+}]$, $[SO_4^{2-}]$ and temperature on the reaction rates have been studied. The reaction is bimolecular, the order with reference to [substrate] and $[Co^{3+}]$ being unity. The reaction rates vary inversely with $[H^+]$. Increase in ionic strength and $[HSO_4^-]$ retards the rates. From the results of kinetic studies it is inferred that $CoOH^{2+}$ ions are active in HNO_3 medium while in H_2SO_4 medium Co^{3+} ions also are active along with $CoOH^{2+}$ ions. The stoichiometry of the reaction has been found to be $2Co^{3+}$ per mole of organic substrate; acetic acid and carbon dioxide are the products. A free radical reaction mechanism involving fission at carbonyl group followed by subsequent oxidation of carbonyl free radical to acetic acid has been proposed and the rate laws derived. The various reaction rate parameters have been evaluated and discussed.

THE kinetics and mechanism of oxidation of pyruvic acid by Mn^{3+}, Co^{4+} and H_2O_2 have been reported[1-4]. In the present communication, the kinetics and mechanism of oxidation of pyruvic acid and sodium pyruvate by Co^{3+} in aqueous and sulphuric acid media have been investigated and the results are presented.

Experimental Procedure

Pyruvic acid (pure, Ingelheim, Germany) was used without further purification. Sodium pyruvate was prepared by neutralization of the acid with AnalaR sodium hydroxide. Cobaltic sulphate, cobaltic nitrate and sodium perchlorate were prepared as described earlier[5]. Other reagents such as bisulphates of sodium or potassium, sodium nitrate, sodium thiosulphate, etc., were all of AnalaR grade. Water, doubly distilled and deionized with Biodeminrolit mixed bed ion exchange resin, was used for the preparation of solutions and all kinetic measurements. Concentrations of Co^{3+}, initial and during the course of the reaction, were determined by addition of excess potassium iodide followed by immediate titration of the liberated iodine with standard thiosulphate using starch as the indicator. The direct reaction between iodine and pyruvic acid was negligible within short intervals of time and hence reducing the error of using iodimetry for the evaluation of rates of disappearance of cobaltic ion ($-R_{Co}$). Cerimetry in conjunction with Fe^{2+} for determination of $[Co^{3+}]$

could not be used since pyruvic acid reacted instantaneously with Ce^{4+}. Kinetic measurements were carried out in 6×1 in. pyrex tubes in the temperature range 0-10°C. using a large Dewar flask as a thermostat.

Results and Discussion

The reaction between Co^{3+} and pyruvic acid was very fast at 0-10°C.; $[Co^{3+}]$; ($1{\cdot}25\times10^{-3}M$); and $[H^+]$; 0·5-2·0*M* in H_2SO_4 and HNO_3 media, though the reaction rates were comparatively less in the former.

The reaction was strictly of the first order with reference to $[Co^{3+}]$ even up to 80-90 per cent conversion of $[Co^{3+}]$. Plots of $-R_{Co}$ versus $[Co^{3+}]$ (Fig. 1, A and B) as well as log $a/a-x$ versus time were linear in both media. The pseudo unimolecular rate constant, k' sec^{-1}, also varied as [pyruvic acid] (HPy) or [sodium pyruvate] (NaPy) (Fig. 1, C-F) in both media, indicating the order with reference to [substrate] also as unity.

An inverse dependence of the reaction rates on $[H^+]$ was observed in both media. Plots of k' sec^{-1} versus $1/[H^+]$ were linear with intercepts in H_2SO_4 medium (Fig. 2, A and B) and without intercepts in HNO_3 medium (Fig. 2, C and D). The acid dependent reaction may be due to predominant $CoOH^{2+}$ plus substrate reaction in HNO_3 medium and $CoOH^{2+}$ or $CoSO_4^+$ plus substrate in H_2SO_4 medium. In view of the acidity range (0·5-2·0*M*) employed it is unlikely that the acid dependence is due to Co^{3+} plus substrate anion reaction. However, it is quite possible that a small percentage of the ionized organic acid also is active as indicated by the difference in the rates of oxidation of HPy and NaPy and also the retarding effect of ionic strength on the reaction rates. The acid independent reaction in H_2SO_4 medium is evidently due to the direct reaction between Co^{3+} and pyruvic acid or its sodium salt.

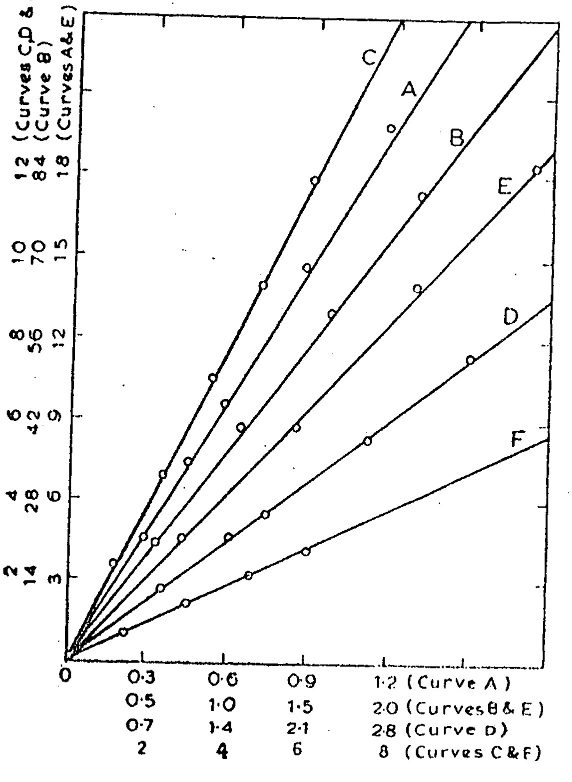

Fig. 1 — Variation of k' sec^{-1} with substrate and $-R_{Co}$ with $[Co^{3+}]$ [A and B: $-R_{Co}$ versus $[Co^{3+}]$ at $\mu = 2{\cdot}2M$ and temp. = 5°C.; A—$[H_2SO_4] = 2{\cdot}0M$; $[HPy] = 1{\cdot}944\times10^{-2}M$; B—$[HNO_3] = 2{\cdot}0M$ and $[HPy] = 3{\cdot}409\times10^{-2}M$. C and E: k' sec^{-1} versus [HPy] at $\mu = 2{\cdot}1M$ and temp. = 10°C.; C—$[H_2SO_4] = 2{\cdot}0M$; $[Co^{3+}] = 3{\cdot}477\times10^{-3}M$; E—$[HNO_3] = 1{\cdot}0M$ and $[Co^{3+}] = 3{\cdot}363\times10^{-3}M$. D and F: k' sec^{-1} versus [NaPy] at $\mu = 2{\cdot}1M$; D—$[HNO_3] = 1{\cdot}0M$, $[Co^{3+}] = 4{\cdot}32\times10^{-3}M$ and temp. = 10°C.; F—$[H_2SO_4] = 2{\cdot}0M$, $[Co^{3+}] = 3{\cdot}513\times10^{-3}M$ and temp. = 5°C.]

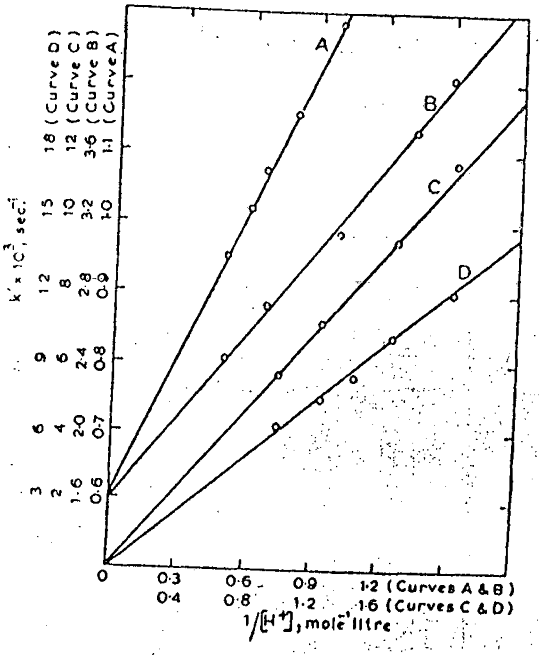

Fig. 2 — Variation of k' sec^{-1} with $[H^+]$ at $\mu = 2{\cdot}1M$ and temp. = 5°C. [A: $[NaPy] = 2{\cdot}1\times10^{-2}M$ and $[Co^{3+}] = 1{\cdot}82\times10^{-3}M$. B: $[HPy] = 3{\cdot}125\times10^{-2}M$ and $[Co^{3+}] = 3{\cdot}480\times10^{3}M$. C: $[NaPy] = 2{\cdot}625\times10^{-2}M$ and $[Co^{3+}] = 3{\cdot}086\times10^{-3}M$. D: $[HPy] = 2{\cdot}13\times10^{-2}M$ and $[Co^{3+}] = 3{\cdot}086\times10^{-3}M$. A and B, H_2SO_4 medium; and C and D, HNO_3 medium]

For a six-fold increase in μ (0·5-3·2*M*), the reaction rates decreased by about 20 per cent in HNO_3 medium. In H_2SO_4 medium for a four-fold increase in μ (0·5-2·1*M*), the rates were reduced to half of the initial reaction rate. From this it may be inferred that probably the ionized form of the organic acid is also active here, since the lowest acidity possible (0·45*M*) was used in the experiments on variation of μ.

The reaction rates were unaffected by increasing $[SO_4]$ at constant μ. This excludes the possibility of $CoSO_4^+$ being the active species. Further support for such conclusion was evident by the decrease in reaction rates observed with increasing $[HSO_4]$ at constant μ — a four-fold increase in $[HSO_4^-]$ reduced the rates by 30 per cent (equilibrium 2 below). The observed inverse dependence on acidity of the rates is also due to $CoOH^{2+}$ being the active species. Also it can be easily shown that if

$$k_{obs} = k_a[CoOH^{2+}]$$

and $[Co^{3+}]_{total} = [Co^{3+}]+[CoOH^{2+}]+[CoSO_4^+]$ then

$$1/k_{obs} = 1/k_a+[H^+]/k_aK_1+K_2[HSO_4^-]/K_1/k_a \quad ...(1)$$

where k_{obs} = observed rate constant, k_a = actual rate constant, K_1 is the hydrolytic equilibrium constant for the formation of $CoOH^{2+}$ and K_2 is the formation constant for $CoSO_4^+$, viz.

$$Co^{3+}+HSO_4^- \overset{K_2}{\rightleftharpoons} CoSO^+_4+H^+ \quad ...(2)$$

The reaction rates were unaffected by $[Co^{2+}]$ in HNO_3 medium while in H_2SO_4 medium, for a ten-fold increase in $[Co^{2+}]$, the reaction rates were doubled. No rational explanation can be offered for this anomalous increase in reaction rates with $[Co^{2+}]$ in H_2SO_4 medium.

Mechanism and rate laws — The reaction was found to be free radical in nature because Co^{3+}-pyruvic acid system enhanced the reaction rates of polymerization of acrylonitrile. It has been well established that in the oxidation of pyruvic acid by H_2O_2[3,4] the fission occurs at the carbonyl group and the COOH in the former is completely converted to CO_2. Enolization is also shown to be not involved[1]. In our system also, the rate of enolization (measured by bromination of pyruvic acid) was about 1/5 of the rate of oxidation under identical conditions and much less with increasing [HPy]. The following mechanism, therefore, is suggested:

$$\left.\begin{aligned} &CH_3COCOOH+CoOH^{2+} \xrightarrow[slow]{k_1} CH_3CO\cdot \\ &\qquad +Co^{2+}+H_2O+CO_2 \quad ...(a) \\ &CH_3CO\cdot+CoOH^{2+} \xrightarrow{fast} CH_3COOH \\ &\qquad +Co^{2+} \quad ...(b) \end{aligned}\right\} \begin{matrix} HNO_3 \\ medium \end{matrix}$$

$$\left.\begin{aligned} &CH_3COCOOH+CoOH^{2+} \xrightarrow[slow]{k_2} CH_3CO\cdot \\ &\qquad +Co^{2+}+H_2O+CO_2 \quad ...(c) \\ &CH_3COCOOH+Co^{3+} \xrightarrow[slow]{k_3} CH_3CO\cdot \\ &\qquad +Co^{2+}+H^++CO_2 \quad ...(d) \\ &CH_3CO\cdot+Co^{3+}+H_2O \xrightarrow{fast} CH_3COOH^{3+} \\ &\qquad +Co^{2+}+H^+ \quad ...(e) \\ &CH_3CO\cdot+CoOH^{2+} \xrightarrow{fast} CH_3COOH+Co^{2+} \ (f) \end{aligned}\right\} \begin{matrix} H_2SO_4 \\ medium \end{matrix}$$

The relevant rate expressions are

$$\begin{aligned} -R_{Co} &= k_1[CH_3COCOOH][CoOH^{2+}] \text{ in } HNO_3 \\ &= K_1k_1[CH_3COCOOH][Co^{3+}]/[H^+] \quad ...(3) \\ -R_{Co} &= [CH_3COCOOH]\{k_2[CoOH^{2+}]+k_3[Co^{3+}]\} \text{ in } H_2SO_4 \\ &= [Co^{3+}][CH_3COCOOH]\{K_1k_2/[H^+]+k_3\} \quad ...(4) \end{aligned}$$

Stoichiometry and product analysis — On addition of Co^{3+} to pyruvic acid, a vigorous evolution of carbon dioxide was noticed. Acetic acid, the other product was identified as ethylacetate and also by lanthanum nitrate and iodine test[6] after removing cobalt as the basic carbonate. The nickel dialkyl glyoxime test[7] for the presence of any 1,2-diketone arising out of enolized species was also found to be negative. The stoichiometry was found to be 2 moles of Co^{3+} per mole of pyruvic acid in HNO_3 medium and 1 mole of Co^{3+} or 2 equivalents of Co^{3+} per mole of pyruvic acid in H_2SO_4 medium. The mechanism suggested in both acid media is in conformity with the observed stoichiometry of the reaction.

TABLE 1 — RATE PARAMETERS FOR THE OXIDATION OF PYRUVIC ACID AND SODIUM PYRUVATE BY COBLT(III) AT μ = 2·1*M*

Substrate	HNO_3 medium		H_2SO_4 medium	
	HPy	NaPy	HPy	NaPy
Overall bimolecular rate constant*	0·2974 (5°C.) 0·2880 (5°C.)† 0·6408 (10°C.)	0·2144 (5°C.) 0·2159 (5°C.)† 0·4853 (10°C.)	0·0775 (5°C.) 0·1945 (10°C.)	0·0462 (5°C.) 0·1091 (10°C.)
$K_1k_2 \times 10^2$	—	—	5·119 (5°C.)	2·857 (5°C.)
$k_3 \times 10^2$ 1 m.$^{-1}$ sec.$^{-1}$			5·181 (5°C.)	3·333 (5°C.)
ΔE, kcal./mole	24·03	25·59	28·82	26·93

*Evaluated at $[H^+]$ = 1·0*M* in HNO_3 and $[H^+]$ = 2·0*M* in H_2SO_4.

†Evaluated from *k'* sec^{-1} versus $1/H^+$ plots.

Evaluation of rate constants — The overall bimolecular rate constants K_1k_2 in HNO_3 medium and K_1k_2 plus k_3 in H_2SO_4 medium were evaluated from *k'* sec.$^{-1}$ versus [HPy] or [NaPy] plots and also from *k'* sec.$^{-1}$ versus $1/[H^+]$ plots in HNO_3 medium. The individual values of K_1k_2 and k_3 in H_2SO_4 medium were evaluated from the slopes and intercepts of *k'* sec.$^{-1}$ versus $1/[H^+]$ plots. The sum of K_1k_2 plus k_3 at 2·0*M* $[H^+]$ is seen to be in good agreement with the overall rate constant at 2·0*M* $[H^+]$ evaluated from *k'* versus [HPy] plots (Table 1). The activation energy values in both media are also recorded in Table 1. The *E* values in HNO_3 medium are less than those in H_2SO_4 medium. This is understandable in view of the high spin and more reactive $CoOH^{2+}$ being the only active species in HNO_3 medium. Another significant observation is that the rate constants for sodium pyruvate are less than those of the free acid in both media. This is probably due to the occurrence of Co^{3+} or $CoOH^{2+}$ plus pyruvate ion reaction to some extent and the electrophilic nature of the carbonyl group in pyruvate ion, preventing the ease of electron transfer to Co^{3+}.

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