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TABLE 1 — EFFECT OF VARYING [ACID] ON THE REACTION RATE

{$[MnO_4^-] = 13.33 \times 10^{-4}$; temp. $= 28°C$}

| [Acid] $\times M$ | $10^5 \times k_1$, sec$^{-1}$ | |
|---|---|---|
| | (H$_2$SO$_4$) | (HClO$_4$) |
| [MONOCHLOROACETIC ACID] = 0.25M | | |
| 2.0 | 4.75 | — |
| 2.5 | 6.95 | — |
| 3.0 | 8.14 | 4.32 |
| 3.5 | 12.80 | 8.12 |
| 4.0 | 21.92 | 12.04 |
| 4.5 | 40.03 | 24.17 |
| 5.0 | 83.52 | 46.51 |
| 6.0 | — | — |
| [DICHLOROACETIC ACID] = 0.33M | | |
| 2.0 | 4.51 | — |
| 2.5 | 5.70 | — |
| 3.0 | 7.48 | 5.11 |
| 3.5 | 10.52 | 7.13 |
| 4.0 | 16.47 | 10.26 |
| 4.5 | 23.28 | 15.26 |
| 5.0 | 34.67 | 24.01 |
| 6.0 | 93.36 | 73.79 |
| [TRICHLOROACETIC ACID] = 0.33M | | |
| 2.0 | — | — |
| 2.5 | — | — |
| 3.0 | 4.96 | 3.52 |
| 3.5 | 6.37 | 4.18 |
| 4.0 | 9.19 | 5.32 |
| 4.5 | 12.61 | 7.32 |
| 5.0 | 16.73 | 10.27 |
| 6.0 | 30.62 | 16.06 |

reaction has been determined[3(c)] and thus the stoichiometry of the reactions is studied.

$$3Cl-CXX'COOH + 2MnO_4^- + 2H^+ \longrightarrow 3Cl-CXX'OH + 2MnO_2 + 3CO_2 + H_2O$$
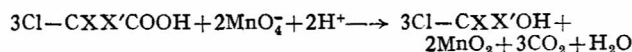
The dissolution of MnO$_2$ is helped by moderately concentrated acid media. The proposed mechanism and stoichiometry is further supported by the identification of the products. Chloro alcohols were detected by their colour reactions given by Feigl[10].

The rates of oxidation of chloroacetic acids in the case of moderately conc. sulphuric and perchloric acid media by potassium permanganate are in the order trichloroacetic acid < dichloroacetic acid < monochloroacetic acid.

The order of reactivity is also in accordance with the *pK* values of the respective chloroacetic acids.

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# (Ag$^+$+Mn$^{2+}$)-catalysed Oxidation of Isopropanol by Ceric Sulphate

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The catalytic activity of mixed (Ag$^+$+Mn$^{2+}$) ions in the oxidation of isopropyl alcohol by Ce$^{4+}$ has been found to be higher than the sum total effect due to the two catalysts taken separately. This is explained by assuming that Mn$^{3+}$ reacts with Ag$^+$-isopropanol adduct in the rate determining step to give the products.

HAVING studied the catalytic activity of Ag$^+$ (ref. 1) and Mn$^{2+}$ (ref. 2) ions separately on the oxidation of isopropanol, it was thought worthwhile to find whether McCurdy and Guibault's contention[3] that a mixture of two metal ions acts as a better catalyst is applicable in the oxidation of isopropanol by Ce(IV). In fact, the results presented in this note show that the catalytic effect of the mixture (Ag$^+$+Mn$^{2+}$) is greater than the sum of the effects due to the two catalysts taken separately. The methods employed to follow the reaction rates were the same as described in our earlier paper[4].

As observed earlier[1,2] the order of reaction with respect to [Ce(IV)] in the presence of (Ag$^+$+Mn$^{2+}$) was one as revealed by the linear plots between log $(a/a-x)$ versus time (Fig. 1, curve A). The pseudo first order rate constants ($k_{obs}$) were calculated from the slopes of these linear plots. The $k_{obs}$ values increased with increasing [Ag$^+$+Mn$^{2+}$]. However, the magnitude of $k_{obs}$ values in the presence of the mixed catalyst was greater than the sum of the $k_{obs}$ values in the presence of Ag$^+$ and Mn$^{2+}$ ions, when taken separately under similar conditions (Table 1).

TABLE 1 — EFFECT OF VARIOUS CATALYSTS ON $k_{obs}$ IN THE OXIDATION OF ISOPROPANOL BY CERIC SULPHATE

{$[Ce^{4+}] = 0.004M$; $[H_2SO_4] = 2.5M$; [isopropanol] = $1.0M$; temp. $= 50°C$; $\mu = 8.0M$}

| [Catalyst] mole litre$^{-1}$ | $k_{obs} \times 10^3$ (min$^{-1}$) in the presence of | | |
|---|---|---|---|
| | Ag$^+$ | Mn$^{2+}$ | Ag$^+$-Mn$^{2+}$ |
| 0.000 | 1.31 | 1.31 | 1.31 |
| 0.002 | 2.76 | 4.60 | 8.51 |
| 0.006 | 5.50 | 5.29 | 12.40 |
| 0.010 | 8.05 | 5.75 | 16.10 |

The order with respect to [isopropanol] was found to be fractional (0·63) as revealed by the plot of log $k_{obs}$ versus log [isopropanol] (Fig. 1, curve B) in the presence of the mixed catalyst. Keeping [Mn²⁺] and ionic strength ($\mu$) constant, an increase in [Ag⁺] increased the rate (Table 2), and the order with respect to [Ag⁺] at constant [Mn²⁺] was found to be nearly one. However, when [Ag⁺] and $\mu$ were constant, the increase in [Mn²⁺] did not affect the $k_{obs}$ values (Table 3).

TABLE 2 — EFFECT OF [Ag⁺] ON $k_{obs}$ AT CONSTANT [Mn²⁺]

{[Ce⁴⁺]=0·004$M$; [H₂SO₄]=2·5$M$; [isopropanol]=0·5$M$; [Mn²⁺]=0·002$M$; $\mu$=8·0$M$; temp.=50°}

| [Ag⁺] mole litre⁻¹ | $k_{obs} \times 10^3$ min⁻¹ |
|---|---|
| 0·002 | 4·69 |
| 0·003 | 5·75 |
| 0·004 | 7·73 |
| 0·005 | 9·34 |
| 0·006 | 11·04 |
| 0·008 | 14·52 |

TABLE 3 — EFFECT OF [Mn²⁺] ON $k_{obs}$ AT CONSTANT [Ag⁺]

{[Ce⁴⁺]=0·004$M$; [H₂SO₄]=2·5$M$; [isopropanol]=0·5$M$; [Ag⁺]=0·002$M$; $\mu$=8·0$M$; temp.=50°}

| [Mn²⁺] mole litre⁻¹ | $k_{obs} \times 10^3$ min⁻¹ |
|---|---|
| 0·001 | 4·68 |
| 0·002 | 4·69 |
| 0·005 | 4·68 |
| 0·010 | 4·70 |



Fig. 1(A)— Plot of log $a/(a-x)$ versus time {[Ce⁴⁺]=0·004$M$; [H₂SO₄]=2·50$M$; [Ag⁺]=[Mn²⁺]=0·02$M$; [isopropanol]= 1·00$M$; temp.=40°C; $\mu$=8·00$M$}; (B) plot of log $k_{obs}$+3 versus log [isopropanol]+1 at 45°, other conditions same as in (A); (C) plot of $1/k_{obs}$ versus 1/[isopropanol] under the same conditions as in (B)

The kinetic data for the oxidation of isopropanol by Ce⁴⁺ in the presence of (Ag⁺+Mn²⁺) ions are similar to those obtained using Ag⁺ ions alone in so far as the fractional order with respect to [isopropanol] and first order dependence on [Ag⁺] are concerned. The catalysis due to Ag⁺ ions alone was explained[1] by assuming that the first step of reaction involves the formation of a Ag⁺-isopropanol adduct which later reacts with Ce⁴⁺ in the rate determining step. The formation of Ag⁺-isopropanol adduct was supported by the NMR spectrum[5] which exhibited a decrease in the line width of the hydroxyl proton due to its enhanced rate of inter-molecular exchange in the presence of Ag⁺ ions. This also accounted for the fractional order with respect to [isopropanol) in the presence of Ag⁺ ions[1]. In the absence of the catalyst the order with respect to [isopropanol] was one[4] and also with respect to [Ag⁺] in the low concentration region was unity.

The catalytic effect of Mn²⁺ was explained by a different mechanism[2], involving the formation of Mn³⁺ species in the reaction between Ce⁴⁺ and Mn²⁺ in a fast step. Mn³⁺ being a better oxidant was assumed to react later with the substrate in the rate determing step. It is quite likely that Mn³⁺ could be the reactive species in the presence of (Ag⁺+Mn²⁺) also. This contention was supported by the fact that the observed rate constant was not affected by increasing [Mn²⁺] ten-fold at a constant [Ag⁺] (Table 3). However, increasing [Ag⁺] at constant [Mn²⁺] increased the reaction rate. Since, the effect of [Ag⁺] in the presence as well as in the absence of Mn²⁺ is the same, the mechanism of oxidation of isopropanol by Ce⁴⁺ in the presence of (Ag⁺+Mn²⁺) could be written as shown in Scheme 1.

$$Ce^{4+}+Mn^{2+} \xrightarrow{fast} Ce^{3+}+Mn^{3+} \quad \text{...(i)}$$

$$Ag^{+}+R_2CHOH \rightleftharpoons \left[Ag{\leftarrow}O{-}\overset{\overset{H}{|}}{C}{-}R_2\right]^{+} \quad \text{...(ii)}$$
colourless adduct

$$Mn^{3+}+\left[Ag{\leftarrow}O{-}\overset{H}{C}{-}R_2\right]^{+} \xrightarrow[slow]{k} Mn^{2+}$$

$$+\left[Ag{\leftarrow}O{-}\overset{H}{C}{-}R_2\right]^{2+} \quad \text{...(iii)}$$

$$\left[Ag{\leftarrow}O{-}\overset{H}{C}{-}R_2\right]^{2+} \xrightarrow{fast} Ag^{+}+H^{+}+R_2\dot{C}OH \quad \text{...(iv)}$$

$$Mn^{3+}+R_2\dot{C}OH \xrightarrow{fast} Mn^{2+}+R_2C{=}O+H^{+} \quad \text{...(v)}$$
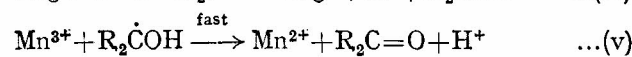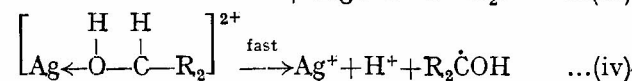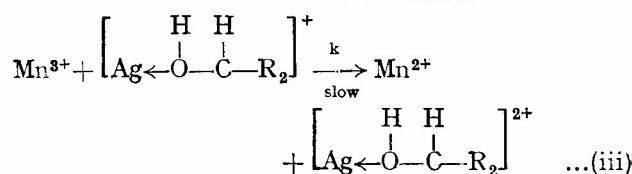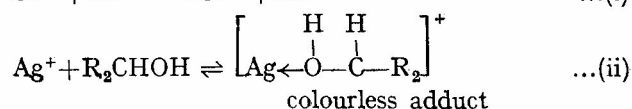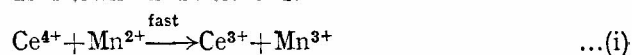
Scheme — 1 Probable mechanisam for the (Ag⁺+Mn²⁺) -catalysed oxidation of isopropanol

Considering Scheme 1, and since [Mn³⁺]=[Ce⁴⁺] when [Mn²⁺]≫[Ce⁴⁺], the rate law comes out to be:

$$\frac{-d[Ce^{4+}]}{dt} = \frac{kK[Ce^{4+}][Ag^{+}][R_2CHOH]}{1+K(R_2CHOH)+K[Ag^{+}]} \quad \text{...(1)}$$

Since [Ag⁺]≪[R₂CHOH], the $K[Ag^+]$ term in the denominator of Eq. (1) could be neglected to give Eq. (2) which accounts for the first order

$$\frac{-d \ln [Ce^{4+}]}{dt} = k_{obs} = \frac{kK[R_2CHOH][Ag^{+}]}{1+K[R_2CHOH]} \quad \text{...(2)}$$

dependence on $[Ce^{4+}]$ and $[Ag^+]$ and a fractional order on $[R_2CHOH]$.

Taking the reciprocals of Eq. (1), we get Eq. (3).

$$\frac{1}{k_{obs}} = \frac{1}{[R_2CHOH]}\left\{\frac{1}{k} + \frac{1}{kK[Ag^+]}\right\} + \frac{1}{k[Ag^+]} \quad ...(3)$$

From Eq. (3) it is evident that the plot of $1/k_{obs}$ versus $1/[R_2CHOH]$ at constant $[Ag^+]$ should be linear with an intercept. This was found to be the case in the present study (Fig. 1, curve C). From the intercept and slope values of the above linear plot, the formation constant $(K)$ of the $Ag^+$-isopropanol adduct was evaluated to be 0·781 litre mole$^{-1}$ which is in agreement with the value (0·728 litre mole$^{-1}$) obtained in the $Ag^+$-catalysed Ce(IV) oxidation of isopropanol. The value of $k$ for step (iii) in Scheme 1 was found to be $2·08 \times 10^{-2}$ litre mole$^{-1}$ sec$^{-1}$ at 45°C which is higher than the value $(1·45 \times 10^{-2}$ litre mole$^{-1}$ sec$^{-1})$ of $k$ obtained using $Ag^+$ alone as the catalyst under otherwise identical conditions, indicating that in the rate determining step $Ag^+$-substrate adduct is oxidized by $Mn^{3+}$ and not by $Ce^{4+}$. This is understandable as $Mn^{3+}$ is a better oxidant than $Ce^{4+}$ in $H_2SO_4$ medium.

In the $Ag^+$-catalysed reaction[1], the formation of $Ag^+$-substrate adduct accounted for the enhanced reaction rate while in $Mn^{2+}$-catalysed reaction[2], the change in the reactive species from $Ce^{4+}$ to $Mn^{3+}$ was assumed to increase the reaction rate. In the mixed catalyst $(Ag^+ + Mn^{2+})$ system the observed catalytic effect was found to be greater than the sum of the effects due to the two catalysts taken separately owing to the participation in the rate limiting step two different reactive species, viz. $Ag^+$-isopropanol adduct and $Mn^{3+}$.

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## Adducts of Oxovanadium(IV) Chloroacetates with Pyridine & Quinoline

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**Pyridine and quinoline adducts of oxovanadium-(IV) chloroacetates have been prepared. The adducts are moisture-sensitive and insoluble in common organic solvents. The adducts have been characterized on the basis of analytical, infrared and electronic spectral data.**

IN continuation of our earlier work on oxovanadium-(IV) carboxylates[1], in this note we now report the preparation and characterization of the adducts of oxovanadium(IV) acetate and chloroacetates with pyridine and quinoline.

All manipulations were carried out in a dry box as far as possible.

Oxovanadium(IV) dichloride was prepared by the method already reported[1]. Acetic acid and acetic anhydride were purified by the procedure outlined in the literature[2,3]. Monochloroacetic acid (BDH, LR) and trichloroacetic acid (E. Merck) were first crystallized from benzene and ether respectively and then distilled collecting the fractions distilling at 189°/750 mm and 194°/750 mm respectively. Dichloroacetic acid was distilled under reduced pressure, b.p. 105-7°/26 mm. Carbon tetrachloride was distilled over $P_2O_5$. Pyridine (BDH, b.p. 114°/750 mm) and quinoline (BDH, b.p. 235°/750 mm) were purified by distillation after keeping them overnight over potassium hydroxide beads.

*Preparation of carboxylates* — Bis(acetato)oxovanadium(IV) was prepared by refluxing oxovanadium(IV) dichloride with excess of acetic acid. When no more HCl gas was evolved the reaction was taken as complete. The light grey solid formed was filtered under reduced pressure, washed with dry $CCl_4$ and dried *in vacuo*. Oxovanadium(IV)chloroacetates were prepared by acid interchange method developed in our laboratory[4,5] i.e. refluxing bis(acetato) oxovanadium(IV) with excess of respective chloroacetic acid. The compounds thus obtained were filtered, washed with dry $CCl_4$ and dried *in vacuo*.

*Preparation of adducts* — A known weight of the respective bis(chloroacetato)oxovandium(IV) was refluxed with excess of pyridine or quinoline in dry $CCl_4$. The adducts thus formed were filtered, washed with dry $CCl_4$ and dried *in vacuo*. The 1:1 adducts of bis(acetato)oxovanadium(IV) with pyridine and bis(monochloroacetato)oxovandium(IV) with pyridine and quinoline were prepared by refluxing the two components in dry $CCl_4$ in stoichiometric ratios.

Analytical data of these adducts are given in Table 1.

The infrared spectra of the compounds were taken in nujol using sodium chloride/silver chloride plates on a Perkin Elmer 337 spectrophotometer. Far IR

TABLE 1 — ANALYTICAL DATA OF OXOVANADIUM(IV) CHLOROACETATE ADDUCTS WITH PYRIDINE AND QUINOLINE

| Formula | Colour | Found (%) (calc.)* | | |
|---|---|---|---|---|
| | | V | Cl | N |
| $VO(CH_2ClCOO)_2.Py$ | Brown | 15·65 (15·31) | 20·66 (21·32) | 4·13 (4·20) |
| $VO(CH_2ClCOO)_2.2Py$ | Light green | 12·25 (12·37) | 16·94 (17·23) | 6·13 (6·79) |
| $VO(CH_2ClCOO)_2.Q$ | do | 13·50 (13·31) | 18·15 (18·53) | 3·46 (3·65) |
| $VO(CHCl_2COO)_2.2Py$ | Black | 11·11 (10·60) | 28·99 (29·52) | 6·00 (5·82) |
| $VO(CHCl_2COO)_2.2Q$ | Greenish black | 9·23 (8·78) | 25·14 (24·44) | 5·03 (4·81) |
| $VO(CCl_3COO)_2.2Py$ | Light blue | 9·03 (9·27) | 37·69 (37·72) | 4·87 (5·09) |
| $VO(CCl_3COO)_2.2Q$ | Dark green | 8·12 (7·84) | 33·49 (32·76) | 4·93 (4·30) |

*Vanadium was estimated gravimetrically; chlorine by Volhard's method; and nitrogen by Duma's method.