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Electron exchange and transfer reactions of heteropoly oxometalates

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CONTENTS

ABBREVIATIONS

$Ce^{IV}Mo$	dodecamolybdocerate(IV)
$Co^{III}W[Co^{III}W]^{5-}$	dodecatungstocobaltate(III)
$Co^{II}W[Co^{II}W]^{6-}$	dodecatungstocobaltate(II)
$Cu^{I}W$	dodecatungstocuprate(I)
$Mn^{IV}Mo$	nonamolybdomanganate(IV)
$Ni^{IV}Mo$	nonamolybdonickelate(IV)

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HOAc	acetic acid
$ArCH_2COOH$	arylacetic acid
ArR	alkyl aromatic compounds
but	2-butanone
chxn	cyclohexanone
DEM	diethylmalonate
dhp	1,3-dihydroxy-2-propanone
EAA	ethylacetoacetate
EDTA, H_4edta	ethylenediamine-*NNN'N'*-tetraacetic acid
Fru	D-fructose
Glu	D-glucose
GSH	glutathione
IDA, H_2ida	iminodiacetic acid
Nu	nucleophile
PMT	*p*-methoxytoluene
PNT	*p*-nitrotoluene
NTA, H_3nta	nitrilotriacetic acid
ox	oxalate
RSH	thiols

A. INTRODUCTION

Heteropoly oxometalates are receiving increased attention with respect to their catalytic activities, specialized redox behaviour [1] and electron exchange characteristics. Many of these heteropoly oxometalates are fairly soluble and stable in water and oxygen-containing organic solvents. The thermal stability in the solid state is also pronounced. This makes them useful as homogeneous and heterogeneous oxidation catalysts and also as bifunctional catalysts [2]. The structures of heteropoly oxometalates (Fig. 1(a)–(e)) bear a strong resemblance to metal oxide lattice fragments.

Although the heteropoly acids and their salts have been known for a long time [3–9], relatively little is known of the mechanism of their reactions in solution, which is very important for the understanding of their catalytic action. In recent years, the number of electron exchange and electron transfer studies of these heteropoly oxometalates has increased significantly, and a review of these reactions would be of topical interest. We attempt to categorize the reactions primarily with respect to the type of hetero atom and the class of substrate chosen for such studies.

B. ELECTRON EXCHANGE IN DODECATUNGSTOCOBALTATE(II/III) AND DODECATUNGSTOCUPRATE(I/II)

The kinetics of electron exchange between dodecatungstocobaltate(II) and dodecatungstocobaltate(III) ions was studied in aqueous solution by Rasmussen and

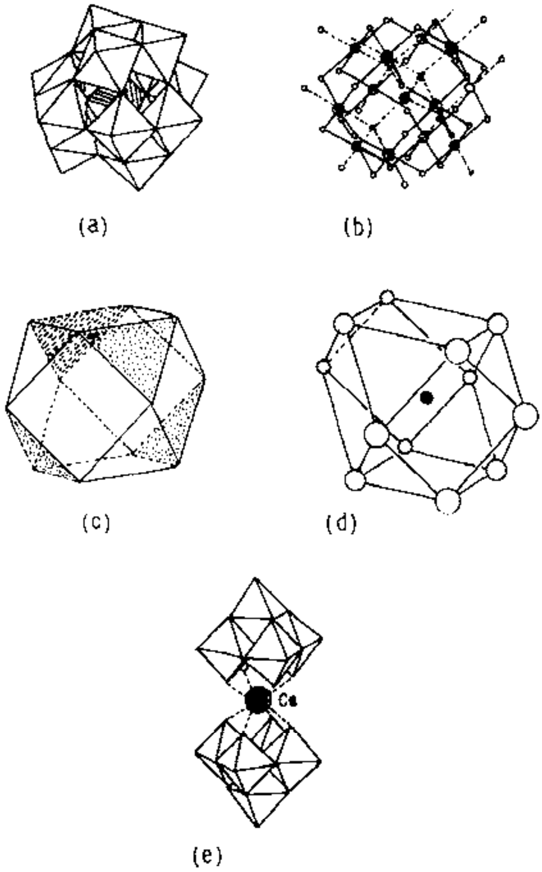


Fig. 1. (a), (b), (c), (d), Four representations of the Keggin structure for heteropoly tungstates; (e) the $[CeW_{10}O_{36}H_2]^{6-}$ anion. (Reproduced with permission from ref. 47.)

Brubaker [10]. The reaction is first-order in each ion and independent of hydrogen ion concentration, but shows a marked dependence on ionic strength. At 25°C and $I = 0.21$ M (LiCl), the second-order rate constant for the exchange reaction is $0.72\ \mathrm{M^{-1}\ s^{-1}}$. Rates determined experimentally are about 10^{-5} or 10^{-6} of that calculated from the Marcus theory of outer-sphere reactions with several simplifying assumptions. This large discrepancy is supported by the fact that the central ions are surrounded by WO_4 octahedra rather than by simple oxygen atoms, and hence the transfer of electrons across the octahedra may not be equivalent to the transfer in a simple oxoanion molecule. Substitution of the lithium cations by potassium cations leads to large increases in the rate of electron exchange. This specific cation effect is due mostly to increased ion pairing by the larger K^+ which has been corroborated by later investigations (vide infra).

The study of the redox properties of $[CuW_{12}O_{40}]^{6-/7-}$ indicates the presence of a reversible couple, although the possible occurrence of intervalence charge transfer of the type $Cu^{I}–W^{VI} \leftrightarrow Cu^{II}–W^{V}$ cannot be totally ignored. A kinetic study [11] on the oxidation of $[CuW_{12}O_{40}]^{7-}$ by $[Fe(CN)_6]^{3-}$ shows that the pseudo-first-order rate constants under excess $[Fe(CN)_6]^{3-}$ exhibit a linear dependence on $[Fe(CN)_6]^{3-}$, yielding a second-order rate constant of 4.1×10^5 M^{-1} s^{-1} at 25 °C. On the basis of the self-exchange rate constant of $[Fe(CN)_6]^{3-/4-}$ and other parameters, the self-exchange rate for $[CuW_{12}O_{40}]^{6-/7-}$ has been calculated as 2.61 M^{-1} s^{-1}. This low value indicates that the nature of the polytungstate medium through which the electron moves has a controlling influence on the reaction. The close agreement between the exchange rates of $[CuW_{12}O_{40}]^{6-/7-}$ (2.61 M^{-1} s^{-1}) and $[CoW_{12}O_{40}]^{5-/6-}$ (0.45 M^{-1} s^{-1}, $I = 0.1$ M (LiCl) at 25 °C) suggests a common rate-limiting step. A hop mechanism for the rate-determining electron transfer with the tungstate shell is proposed.

C. ELECTRON TRANSFER REACTIONS OF DODECATUNGSTOCOBALTATE(III)

(i) Reactions with inorganic reagents

A number of studies appear on the redox reactions involving $[Co^{III}W]^{5-}$ and inorganic reagents. In the oxidation of thiocyanate and iodide ions (X^-) by $[Co^{III}W]^{5-}$, a one-electron transfer mechanism yielding the reactive intermediates $X^{\cdot}$ and $X_2^{\cdot -}$ has been proposed [12]. The outer-sphere reduction of $[Co^{III}W]^{5-}$ by HNO_2 [13]

$$2[Co^{III}W]^{5-} + HNO_2 + H_2O \rightarrow 2[Co^{II}W]^{6-} + 3H^+ + NO_3^- \tag{1}$$

is independent of $[H^+]$ in the range 0.1–1.0 M with a rate law

$$-\frac{d[[Co^{III}W]^{5-}]}{dt} = 2[[Co^{III}W]^{5-}][HNO_2] \tag{2}$$

The kinetic data are rationalised in electron transfer terms to yield $NO_2^{\cdot}$, a rapidly reacting radical whose fate is not directly examined. The authors assumed it reduced a second $[Co^{III}W]^{5-}$. Instead of reacting with a second $[Co^{III}W]^{5-}$, the $NO_2^{\cdot}$ generated might be lost via rapid disproportionation or hydrolysis:

$$2NO_2^{\cdot} + H_2O \rightarrow HNO_2 + NO_3^- + H^+ \tag{3}$$

with $k = 1.0 \times 10^8$ M^{-1} s^{-1} [14].

The oxidations of hydroxylammonium [15] and hydrazinium [16] ions by $[Co^{III}W]^{5-}$ in acidic medium are believed to occur simply by electron transfer between the reductants and $[Co^{III}W]^{5-}$ with the reversible generation of free radical intermediates ($NH_2\dot{O}$ or $\dot{N}_2H_4^+$). It is surprising that although the authors observed a specific cation catalysis ($K^+ > Na^+ > Li^+$), no account of the possible association between the cations and the multicharged anion in the reaction scheme was considered. The observed role of Cu^{2+} in the oxidation of the hydrazinium ion is twofold:

it shows pronounced redox catalysis and confirms the existence of a free radical intermediate. The dependence of the electron transfer rate vs. the reduction potential (E^0) of several metal complexes to establish a Marcus-type correlation should be accepted with reservations in view of the scanty data. Other factors, e.g. high charge of the polyanion, medium effect and ion-pairing of alkali metal ions, which are likely to complicate the situation, were ignored.

The reaction between $[\mathrm{Co^{III}W}]^{5-}$ and sulphite [17] has been studied in the range pH 1.5–3.5 at 25°C and $I = 0.5$ M ($\mathrm{NaClO_4}$). The work has been of a very careful nature in that stoichiometry and product studies were carried out under varying conditions. In the presence of excess sulphite ($\mathrm{S^{IV}}$), the reaction stoichiometry is 1 : 1, and the corresponding reaction product is dithionate. However, when the complex : sulphur(IV) mole ratio is $> 1.5 : 1$, sulphate is obtained together with dithionate and their amounts are dependent on the mole ratio of the reactants. The stoichiometry, $[\mathrm{S^{IV}}]_{\text{consumed}} : [\text{complex}]_{\text{consumed}}$ varies in the range 0.7–1.0 : 1, on a par with the [sulphate] : [dithionate] ratio. A mixed first- and second-order dependence on $[\mathrm{S^{IV}}]$ is a very interesting feature of this study. The corresponding rate law which gives a 1 : 1 stoichiometry is given by

$$-\frac{\mathrm{d}[\text{complex}]}{\mathrm{d}t} = (k_0 + k'_1[\mathrm{H^+}]^{-1} + k_2[\mathrm{HSO_3^-}])[\mathrm{HSO_3^-}][\text{complex}] \tag{4}$$

where k_0 and k'_1 represent the first-order paths corresponding to the reactions of $\mathrm{HSO_3^-}$ and $\mathrm{SO_3^{2-}}$, respectively. Excluding protonation and ion association, the first-order behaviour, in general, may be shown as

$$[\mathrm{Co^{III}W}]^{5-} + \mathrm{S^{IV}} \xrightarrow{\text{slow}} [\mathrm{Co^{II}W}]^{6-} + \mathrm{S^{V}} \tag{5}$$

The sulphur(V) species thus produced may reduce another molecule of $[\mathrm{Co^{III}W}]^{5-}$ giving $\mathrm{SO_4^{2-}}$ as the reaction product or it may recombine with a second radical

$$\mathrm{H\dot{S}O_3(SO_3^{\dot{-}})} + [\mathrm{Co^{III}W}]^{5-} + \mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{SO_4^{2-}} + [\mathrm{Co^{II}W}]^{6-} + 3(2)\mathrm{H^+} \tag{6}$$

or

$$2\mathrm{SO_3^{\dot{-}}}\,(2\mathrm{H\dot{S}O_3}) \xrightarrow{\text{fast}} \mathrm{S_2O_6^{2-}} + (2\mathrm{H^+}) \tag{7}$$

$\mathrm{H\dot{S}O_3}$ and $\mathrm{SO_3^{\dot{-}}}$ represent the free radicals produced in the k_0 and k'_1 paths, respectively. The k_2 path accounts for the second-order dependence in $[\mathrm{HSO_3^-}]$ and the rate-determining step is rationalised by either of the mechanisms (A) or (B)

$$\text{(A)}\ 2\mathrm{HSO_3^-} \xrightleftharpoons{K_1 < 1} \mathrm{S_2O_5^{2-}} + \mathrm{H_2O} \tag{8}$$

$$[\mathrm{Co^{III}W}]^{5-} + \mathrm{S_2O_5^{2-}} \xrightarrow{\text{slow}} [\mathrm{Co^{II}W}]^{6-} + \mathrm{S_2O_5^{\dot{-}}} \tag{9}$$

$$\mathrm{S_2O_5^{\dot{-}}} \xrightarrow[\mathrm{H_2O}]{\text{fast}} \text{products} \tag{10}$$

$$\text{(B) } [\text{Co}^{\text{III}}\text{W}]^{5-} + \text{HSO}_3^- \xrightleftharpoons{K_1} \{\text{Co}^{\text{III}}\text{W, HSO}_3\}^{6-} \tag{11}$$

$$\{\text{Co}^{\text{III}}\text{W, HSO}_3\}^{6-} + \text{HSO}_3^- \xrightarrow{\text{slow}} [\text{Co}^{\text{II}}\text{W}]^{6-} + \text{H}\dot{\text{S}}\text{O}_3 + \text{HSO}_3^- \tag{12}$$

$$\text{H}\dot{\text{S}}\text{O}_3 \xrightarrow[\text{H}_2\text{O}]{\text{fast}} \text{products} \tag{13}$$

The available data do not permit distinction between the two mechanisms. The alkali metal ion dependence ($\text{K}^+ > \text{Na}^+ > \text{Li}^+$) observed in the reaction was explained by assuming outer-sphere complex formation via the alkali metal ion where it acts as a bridge between the negatively charged species.

The study of the oxidation of thiosulphate by $[\text{Co}^{\text{III}}\text{W}]^{5-}$ [18] in the pH range 4.2–5.2 at 20°C reveals the stoichiometric equation

$$[\text{Co}^{\text{III}}\text{W}]^{5-} + \text{S}_2\text{O}_3^{2-} \rightarrow [\text{Co}^{\text{II}}\text{W}]^{6-} + \tfrac{1}{2}\text{S}_4\text{O}_6^{2-} \tag{14}$$

An appreciable alkali metal ion (M^+) catalysis is also observed in this reaction and the rate equation conforms to

$$-\frac{\text{d[complex]}}{\text{d}t} = (k_0 + k_1[\text{M}^+])[\text{S}_2\text{O}_3^{2-}]_{\text{T}}[\text{Co}^{\text{III}}\text{W}] \tag{15}$$

and is compatible with the set of reactions

$$[\text{Co}^{\text{III}}\text{W}]^{5-} + \text{S}_2\text{O}_3^{2-} \xrightarrow{k_0} [\text{Co}^{\text{II}}\text{W}]^{6-} + \text{S}_2\text{O}_3^- \tag{16}$$

$$[\text{Co}^{\text{III}}\text{W}]^{5-} + \text{M}^+ + \text{S}_2\text{O}_3^{2-} \xrightleftharpoons{K_2'} \{\text{Co}^{\text{II}}\text{W, M, S}_2\text{O}_3\}^{6-} \tag{17}$$

$$\{\text{Co}^{\text{II}}\text{W, M, S}_2\text{O}_3\}^{6-} \xrightarrow{k_1'} [\text{Co}^{\text{II}}\text{W}]^{6-} + \text{M}^+ + \text{S}_2\text{O}_3^- \tag{18}$$

$$\text{S}_2\text{O}_3^- + \text{S}_2\text{O}_3^- \xrightarrow{\text{fast}} \text{S}_4\text{O}_6^{2-} \tag{19}$$

with $k_1 = k_1' K_2'$. No saturation kinetics were observed in the experimental range of study.

The oxidation of arsenious acid by $[\text{Co}^{\text{III}}\text{W}]^{5-}$ in aqueous hydrochloric acid medium [19] is reported to follow the route

$$\text{H}_3\text{AsO}_3 + [\text{Co}^{\text{III}}\text{W}]^{5-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{Co}^{\text{II}}\text{W}]^{6-} + [\text{H}_2\text{AsO}_3]^{\cdot} + \text{H}^+ \tag{20}$$

$$[\text{Co}^{\text{III}}\text{W}]^{5-} + \text{H}_2\text{O} + [\text{H}_2\text{AsO}_3]^{\cdot} \xrightarrow{k_2} [\text{Co}^{\text{II}}\text{W}]^{6-} + \text{H}_3\text{AsO}_4 + \text{H}^+ \tag{21}$$

In the corresponding reaction with hypophosphorous acid (H_3PO_2), the active form of the reductant reacts with $[\text{Co}^{\text{III}}\text{W}]^{5-}$ generating the $[\text{H}_2\text{PO}_2]^{\cdot}$ radical in an identical route. The reversible tautomeric shift catalyzed by acid between the inactive ($\text{H}_2\text{PO(OH)}$) and active (HP(OH)_2) forms of hypophosphorous acid is already known and the active form is the predominant one in the range $[H^+] = 0.1$–1.0 M [20].

(ii) *Reactions with thiols and related species*

Ayoko and Olatunji have carried out a series of studies on the electron transfer reaction of $[Co^{III}W]^{5-}$ with thio ligands (RSH), e.g. L-cysteine, mercaptoacetic acid, β-mercaptoethylamine [21] and glutathione [22], in aqueous acidic medium at $[H^+] = 0.02$–0.1 M and temperature 25°C. The stoichiometry of the reactions corresponds to

$$2[Co^{III}W]^{5-} + 2RSH \rightarrow 2[Co^{II}W]^{6-} + RSSR + 2H^+ \tag{22}$$

The rates increase with decreasing acidity. For L-cysteine and mercaptoacetic acid, the rates are second-order dependent on [thiol] represented by

$$2RSH \xrightleftharpoons{K_a} 2RS^- + 2H^+ \tag{23}$$

$$Co^{III}W + RS^- \xrightleftharpoons{K_{os}} [Co^{III}W, RS^-] \tag{24}$$

$$[Co^{III}W, RS^-] + RS \xrightarrow{k_1} [Co^{II}W]^{5-} + RSSR^{\cdot} \tag{25}$$

$$[Co^{III}W]^{5-} + RSSR^{\cdot -} \xrightleftharpoons{\text{fast}} [Co^{II}W]^{6-} + RSSR \tag{26}$$

where k_{os} is the outer-sphere equilibrium constant. The reaction scheme is consistent with the rate law

$$-\frac{d[Co^{III}W]}{dt} = \frac{k_1 K_{os} K_a [RSH]^2 [Co^{III}W]}{[H^+]^2 + K_{os} K_a^{1/2} [H^+][RSH]} \tag{27}$$

Under the condition $[H^+]^2 \gg K_{os} K_a^{1/2} [H^+][RSH]$, the rate law becomes

$$k_{obs} = \frac{k_1 K_{os} K_a [RSH]^2}{[H^+]^2} \tag{28}$$

For mercaptoethylamine, both first- and second-order paths are concurrently operative. An outer-sphere mechanism has been postulated in each case. Methionine and thiourea react with $[Co^{III}W]^{5-}$ showing no acid-dependent path. This observation is quite likely since they do not have any sulphydryl group to show protic equilibrium.

(iii) *Reactions with carboxylates, α-hydroxycarboxylates and amine-N-polycarboxylates*

Banerjee and co-workers have carried out detailed kinetic investigations on the reactions involving the reduction of $[Co^{III}W]^{5-}$ by carboxylic acids, (e.g. oxalic [23], formic [24] and citric [25] acid), α-hydroxy acids [26], (e.g. mandelic, glycolic and lactic acid) and amine-*N*-polycarboxylates [27], (e.g. iminodiacetate, nitrilotriacetate and ethylenediaminetetraacetate) in the range pH 0–5.5. All the reactions have been found to follow an overall second-order rate, first-order with respect to both the oxidant and reductant, the corresponding formate oxidation showing a second-order dependence on $[Co^{III}W]^{5-}$ as an exception. The reaction scheme in the latter case has been postulated to involve the initial formation of a free radical bound activated species, $[Co^{II}W\ HCO_2^{\cdot}]^{\ddagger}$ which can react with another molecule of $[Co^{III}W]^{5-}$ and produce the reduced polyanion. The reactivity of all the reacting carboxylate species available in the experimental range of pH is evaluated. A representative case for oxidation of edta is

$$H_4edta \overset{K_1}{\rightleftharpoons} H_3edta^- + H^+ \quad pK_1 = 1.91 \tag{29}$$

$$H_3edta^- \overset{K_2}{\rightleftharpoons} H_2edta^{2-} + H^+ \quad pK_2 = 2.67 \tag{30}$$

$$H_2edta^{2-} \overset{K_3}{\rightleftharpoons} Hedta^{3-} + H^+ \quad pK_3 = 6.16 \tag{31}$$

$$[Co^{III}W]^{5-} + H_4edta \xrightarrow{k_0} [Co^{II}W]^{6-} + \text{radical} \tag{32}$$

$$[Co^{III}W]^{5-} + H_3edta^- \xrightarrow{k_1} [Co^{II}W]^{6-} + \text{radical} \tag{33}$$

$$[Co^{III}W]^{5-} + H_2edta^{2-} \xrightarrow{k_2} [Co^{II}W]^{6-} + \text{radical} \tag{34}$$

$$[Co^{III}W]^{5-} + Hedta^{3-} \xrightarrow{k_3} [Co^{II}W]^{6-} + \text{radical} \tag{35}$$

$$[Co^{III}W]^{5-} + \text{radical} \xrightarrow{\text{fast}} [Co^{II}W]^{6-} + \text{products} \tag{36}$$

and the corresponding rate equation is

$$k_{obs} = \frac{k_0[H^+]^3 + k_1K_1[H^+]^2 + k_2K_1K_2[H^+] + k_3K_1K_2K_3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3}[edta]_T \tag{37}$$

With the exception of the molecular form, H_4edta, all the steps involve another parallel path

$$[Co^{III}W]^{5-} + H_medta^{n-} + xM^+ \xrightarrow{k_m} [Co^{II}W]^{6-} + \text{radical} + xM^+ \tag{38}$$

and this metal ion dependence path is given by

$$k_{obs} = (k_n + k_{nc}[M^+]^x)[edta]_T \tag{39}$$

where $x = 1$ or 2 depending on the nature and type of reactive form of the reductant and alkali metal ion, e.g. for H_3edta^- oxidation, the order with respect to $[Na^+]$ is 2. The intrinsic effect of ionic strength alone on the reaction was, however, verified by using a mixture of $NaNO_3$ and Na_2SO_4 whereby the total $[Na^+]$ was kept constant but the ionic strength varied. The results show that the effect of ionic strength on the rates in these systems is negligibly small. It has been argued that for H_3edta^-, the mononegative charge may not be sufficient to compete with Na^+ in the ion pair. The bridge formation is facilitated by incorporation of another Na^+ in the ion-pair, i.e. by reducing the effective charge on the complex and it results in a second-order dependence. A report by Sulfab et al. [28] cites a second-order dependence of rate on $[Na^+]$ in the redox interaction of $[Fe(CN)_6]^{4-}$ and tris(malonato)-cobaltate(III).

(iv) *Reactions with carbonyl compounds and esters*

The kinetics of the oxidation of cyclohexanone (chxn), 2-butanone (but) and 1,3-dihydroxy-2-propanone (dhp) have been investigated in aqueous acid medium [29]. A first-order dependence in [complex] is obtained at high acid ($[H^+]$, 0.50–3.0 M) and low oxidant ($[Co^{III}W]$, $1.0–2.0 \times 10^{-4}$ M) concentrations for these ketones (A). However, a zero-order rate prevails at high oxidant ($[Co^{III}W]$, 5.0×10^{-3} M) and low acid ($[H^+]$, $6.0 \times 10^{-4}–2.0 \times 10^{-2}$ M) concentrations (B), and the rate (temperature 30–50°C) has been shown to be the acid-catalysed enolisation rate of the ketones. The mechanism which accounts for the kinetic data over the whole range of $[Co^{III}W]^{5-}$ and $[H^+]$ has been postulated as

$$\text{ketone} + H^+ \underset{k'_{H^+}}{\overset{k_{H^+}}{\rightleftharpoons}} \text{enol} + H^+ \tag{40}$$

$$\text{enol} + [Co^{III}W]^{5-} \xrightarrow{k} [Co^{II}W]^{6-} + H^+ + R' \tag{41}$$

where R′ is the free radical from the enol of the respective ketones.

A steady-state approximation for the formation of the enol leads to

$$-\frac{d[Co^{III}W]}{dt} = \frac{k_{H^+} \cdot k[\text{ketone}][Co^{III}W][H^+]}{k'_{H^+}[H^+] + k[Co^{III}W]} \tag{42}$$

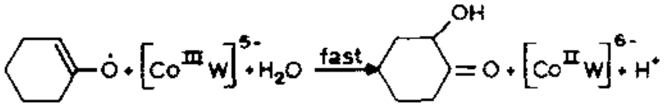
Under condition (A), the term $k'_{H^+}[H^+] \gg k[Co^{III}W]$ and the rate-law becomes

$$-\frac{d[Co^{III}W]}{dt} = \{k_{H^+}/k'_{H^+}\}k[\text{ketone}][Co^{III}W] = k'[\text{ketone}][Co^{III}W] \tag{43}$$

Under condition (B), the term $k[Co^{III}W] \gg k'_{H^+}[H^+]$ and the rate-law becomes

$$-\frac{d[Co^{III}W]}{dt} = k_{H^+}[\text{ketone}][H^+] \tag{44}$$

where k_{H^+} refers to the acid-catalysed enolisation of the ketones, k'_{H^+} is the ketonisation of the enol and k is the second-order rate constant for the oxidation of the enol. The overall reaction in the subsequent steps of the radicals for cyclohexanone (as a representative radical) may be formulated as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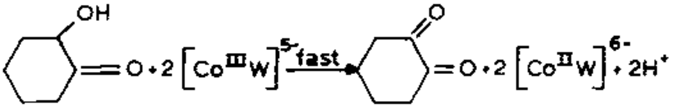
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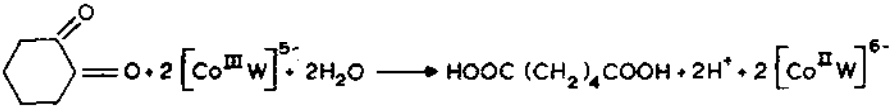
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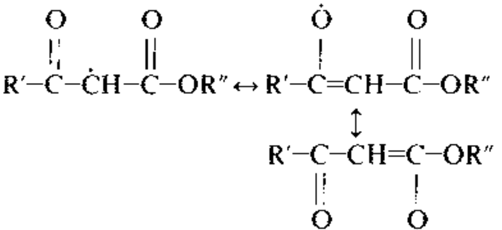
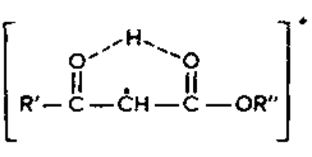
The interesting feature of this study seems to be that all three ketones under investigation, although structurally different from each other, are oxidised by the same mechanistic path, which is explained by a unified rate law.

The oxidation of ethylacetoacetate (EAA) and diethylmalonate (DEM) by $[Co^{III}W]^{5-}$ in aqueous acidic medium (pH 1.0–4.3) at 60°C follows simple second-order kinetics with respect to the oxidant and reductants [30]. The rates are found to be $[H^+]^{-1}$ dependent and are also influenced by the nature and concentration of alkali metal ions. The catalytic order is $Li^+ > Na^+ > K^+$ and this is just the reverse to that obtained in other studies. No satisfactory explanation to this has been offered. However, the relevance of $[H^+]^{-1}$ dependence to the mechanistic pathways seems interesting because of the resonance stabilisation of the free radical species generated in the rate-determining step



$$R'-\overset{\overset{O}{\|}}{C}-\dot{C}H-\overset{\overset{O}{\|}}{C}-OR'' \leftrightarrow R'-\overset{\overset{\dot{O}}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-OR'' \updownarrow R'-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{\dot{O}}{|}}{C}-OR''$$

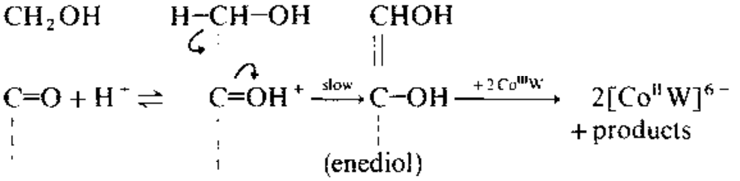
For the protonated species, such stabilisation would not be favoured because of protonation



This in turn would oppose the reverse path in the rate-determining step and cause a rate lower than the free ester. The keto form of these esters is believed to be the reactive species.

(v) Reactions with carbohydrates

The kinetics and mechanism of the oxidation of D-fructose, D-glucose and D-mannose by $[\mathrm{Co^{III}W}]^{5-}$ in aqueous acid medium have been reported [31]. A pseudo-zero-order rate is obtained with the ketose. However, pseudo-second-order rates are obtained for the aldose reactions. The oxidation of D-fructose is found to be acid catalysed with a first-order dependence on $[\mathrm{H^+}]$, but for aldosugars the rates are unaffected by acid in the region of $[\mathrm{H^+}] = 0.01$–1.0 M at $[\mathrm{Na^+}] = 1.0$ M and temperature 60°C. The kinetic results are compatible with a rate-determining acid-catalysed enolisation of D-fructose, followed by a fast reaction of the enediol thus formed with $[\mathrm{Co^{III}W}]^{5-}$ to give the redox products



$$\overset{\mathrm{CH_2OH}}{\mathrm{C{=}O}} + \mathrm{H^+} \rightleftharpoons \overset{\mathrm{H{-}CH{-}OH}}{\mathrm{C{=}OH^+}} \xrightarrow{\text{slow}} \underset{\text{(enediol)}}{\overset{\mathrm{CHOH}}{\mathrm{C{-}OH}}} \xrightarrow{+2\mathrm{Co^{III}W}} \begin{matrix} 2[\mathrm{Co^{II}W}]^{6-} \\ + \text{products} \end{matrix} \tag{48}$$

It has been assumed that the fast enediol reaction produces a free radical and the molecule of $[\mathrm{Co^{II}W}]^{6-}$. The free radical in turn reacts rapidly with another molecule of $[\mathrm{Co^{III}W}]^{5-}$ to give the products. In contrast the aldosugar oxidations are catalyzed by alkali metal ions and not by acid. The processes for D-glucose oxidation have been described as

spontaneous path:

$$[\mathrm{Co^{III}W}]^{5-} + \mathrm{Glu} \xrightleftharpoons{K_1} [\mathrm{Co^{III}W}]^{5-}, \mathrm{Glu} \tag{49}$$

$$[\mathrm{Co^{III}W}]^{5-}, \mathrm{Glu} \xrightleftharpoons{K_2} [[\mathrm{Co^{II}W}]^{6-}, \mathrm{Gl\dot{u}}]^{\ddagger} + \mathrm{H^+} \tag{50}$$

$$[[\mathrm{Co^{II}W}]^{6-}, \mathrm{Gl\dot{u}}]^{\ddagger} + [\mathrm{Co^{III}W}]^{5-} \xrightarrow{k_1} [\mathrm{Co^{II}W}]^{6-} + \mathrm{H^+} + \text{products} \tag{51}$$

The catalyzed path involves the incorporation of one alkali cation in the reversible outer-sphere association step prior to the electron transfer step. The interesting features of this study are (a) the difference in order of reaction between the keto- and aldosugars and (b) enediol formation in sugar oxidation in acid medium. Enediol formation in alkaline medium is, however, known [32]. The specific metal ion catalysis for aldosugar oxidation has been explained rationally by outer-sphere complex formation via an ion-induced dipole-type interaction.

(vi) Reactions with substituted alkyl aromatic compounds

Chester [33] carried out the oxidation of toluene and xylene (*o*-, *m*- and *p*-) by $[\mathrm{Co^{III}W}]^{5-}$ both in homogeneous and heterogeneous media. The products are the corresponding benzyl alcohol, benzaldehyde and diphenylmethane, the last being predominant.

An electron transfer initiated by a radical cation is assumed to take place in the first step. The author proposes an electron transfer from the π system of the aromatic ring via the tungsten framework to the cobalt atom (an idea based on earlier electrochemical observations of Pope and Varga [34] on the Keggin molecule). The reaction sequences are formulated as

$$ArCH_3 + [Co^{III}W]^{5-} \rightleftharpoons ArCH_3^{\cdot +} + [Co^{II}W]^{6-} \tag{52}$$

$$ArCH_3^{\cdot +} + B \rightleftharpoons ArCH_2^{\cdot} + BH^{+} \tag{53}$$

$$ArCH_2^{\cdot} + [Co^{III}W]^{5-} \rightarrow ArCH_2^{+} + [Co^{II}W]^{6-} \tag{54}$$

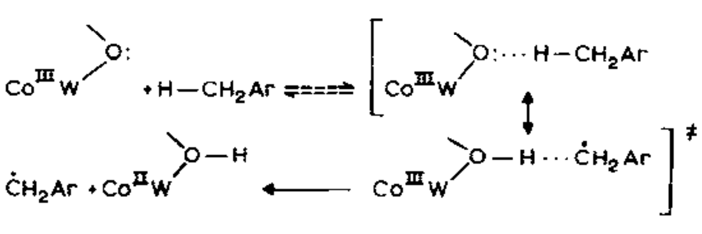
$$ArCH_2^{+} + HOAc \rightarrow ArCH_2OAc + H^{+} \tag{55}$$

$$ArCH_2^{+} + H_2O \rightarrow ArCH_2OH + H^{+} \tag{56}$$

An alternative path for generation of the benzyl radical is proposed via H atom transfer as

$$[Co^{III}W]^{5-} + ArCH_3 \rightleftharpoons [HCo^{II}W]^{5-} + ArCH_2^{\cdot} \tag{57}$$

This suggestion is important and has been highlighted in later studies. Eberson and Wistrand [35] have made an extensive study of analogous reactions under different conditions. In aqueous acetic acid medium, the corresponding α-acetate and alcohol are obtained as reaction products while acetoxymethylated compounds are also obtained in HOAc–Ac_2O–KOAc medium. Reactions carried out with compounds having no α-hydrogen atom and 4-fluoroanisole also show formation of products similar to that of Ag(II) and anodic oxidations. The authors thus designate the heteropoly anion in solution as the "soluble anode". Based on theoretical calculations, the reaction mechanism proposed by the authors considers a concerted proton-electron transfer in the rate-determining step. A ligand oxygen in the tungsten framework is supposed to act as acceptor of the H atom, and the transition state is thought to be a hybrid of identical energy (within the error limits of about 0.6 kcal mol^{-1}), differing only in the position of the electron to be transferred.



(58)

This mechanism, termed a special case of the non-bonded mechanism, has interesting repercussions in organic chemistry and is seemingly not in accordance with the Marcus theory or other electron transfer theories which predict an exceedingly slow reaction for such cases (E^0 for oxidant, 1.0 V vis-a-vis the E^0 for reductant $\geqslant 2.6$ V). The free radical produced in eqn. (59) is capable of undergoing further reactions according to eqns. (60) and (61). The formation of acetoxymethylated compounds is believed to proceed as

$$CH_3COOH \xrightarrow{[O]} \dot{C}H_2COOH \tag{59}$$

$$ArH + \dot{C}H_2COOH \rightarrow ArCH_2COOH \tag{60}$$

$$ArCH_2COOH \xrightarrow[HOAc]{[O]} ArCH_2OAc \tag{61}$$

Oxidation of *p*-methoxytoluene by $[Co^{III}W]^{5-}$ in $HOAc–OAc^-–H_2O$ [36] yields net two-electron oxidation to $ArCH_2OAc$ (36%) and $ArCH_2OH$ (47%), although the kinetic data, particularly the inverse dependence of rate on $[Co^{II}W]^{6-}$, suggest an electron transfer mechanism

$$[Co^{III}W]^{5-} + ArCH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co^{II}W]^{6-} + ArCH_3^{+\cdot} \tag{62}$$

$$ArCH_3^{+\cdot} + OAc^- \text{ (or } H_2O) \xrightarrow{k_2} \text{products} \tag{63}$$

Using the steady-state approximation of $[ArCH_3^{+\cdot}]$, one eventually obtains

$$-\frac{d[Co^{III}W]^{5-}}{dt} = \frac{k'[Co^{III}W]^{5-}}{C + [Co^{II}W]^{6-}} \tag{64}$$

$$k' = \frac{k_1 k_2}{k_{-1}}[OAc^-][ArCH_3] \tag{65}$$

$$C = (k_2/k_{-1})[OAc^-] \tag{66}$$

The composite rate constant shows a large kinetic effect for $ArCD_3$ ($k_H/k_D = 4.5–7.3$), strong salt effects, specific cation accelerations ($Sr^{2+} > Cs^+ > Ca^{2+} > Rb^+ > K^+ > Li^+ > Na^+ > Me_4N^+$) and inhibitions ($Bu_4N^+$) and a marked dependence on solvent ratio and dielectric constant. Marcus equation estimates of k_1 and k_{-1}, the latter diffusion controlled, yield $k_2 = 3.6 \times 10^{-6}$ (OAc^-) and 80 (H_2O) $M^{-1}\,s^{-1}$. It is noteworthy that in the treatment of the Marcus relation, the free energy change ($\Delta G^{0\prime}$) of the reaction has been corrected by a term involving the gain or loss of electrostatic energy upon transfer of an electron within the transition state. This is particularly important in view of the highly charged ions treated in this investigation. In addition, owing to the pronounced specific cation effect, it is more realistic to assume that ion-pairs such as $[Co^{III}W, M^+]^{4-}$ and $[Co^{III}W, M_2^{2+}]^{3-}$ are the kinetically active species. The authors admit that the kinetic data are not sufficient to evaluate all such parameters arising from the ion-pair formation scheme. The approximations necessary to obtain a manageable expression for mathematical analysis were probably not in the allowed range. These complications, however, do not invalidate the analysis in a qualitative way. Since the E^0 for $[\mathrm{Co^{III}W}]^{5-/6-}$ decreases by 0.25 V on going from 0.5 M KOAc to 0.5 M $\mathrm{Bu_4NOAc}$, the explanation that either the cation has a catalytic/inhibitory effect in the ion-pair by facilitating/inhibiting the electron-transfer, or that the cation has the more fundamental role of acting as an electron mediator between the two anions in the transition state is rather difficult to ascertain.

The oxidative decarboxylation of substituted arylacetic acids by $\mathrm{Co^{III}W}$ in refluxing acetic acid containing 0.5 M KOAc and acetic anhydride resulted in the formation of benzyl acetates, which accounted for more than 80% of all products observed [37]. The results of these studies are interpreted by two different outer-sphere mechanisms. The first mechanism is assumed to involve an electron transfer from the aromatic ring in arylacetic acid (having electron-rich substituents)

$$\mathrm{ArCH_2COOH} \xrightarrow{\mathrm{M^{n+}}} \overset{\cdot+}{\mathrm{Ar}}\mathrm{CH_2COOH} \xrightarrow{\text{fast}} \mathrm{ArCH_2^{\cdot}} + \mathrm{CO_2} + \mathrm{H^+} \tag{67}$$

$$\mathrm{ArCH_2^{\cdot}} \xrightarrow{\mathrm{M^{n+}}} \mathrm{ArCH_2^+} \xrightarrow{\mathrm{Nu}} \mathrm{ArCH_2Nu} \tag{68}$$

The other pathway (for less electron-releasing substituents) considers an electron transfer from the carboxylic group, possibly with concerted loss of carbon dioxide

$$\mathrm{ArCH_2COOH} \xrightarrow{\mathrm{M^{n+}}} \mathrm{ArCH_2COO^{\cdot}} \xrightarrow{\text{slow}} \mathrm{ArCH_2^{\cdot}} + \mathrm{CO_2} \tag{69}$$

$$\mathrm{ArCH_2^{\cdot}} \xrightarrow{\mathrm{M^{n+}}} \mathrm{ArCH_2^+} \xrightarrow{\mathrm{Nu}} \mathrm{ArCH_2Nu} \tag{70}$$

where M^{n+} = oxidant and $\mathrm{Nu^-}$ = water or acetate base. The logarithms of the relative rates (determined from the relative amounts of the corresponding benzyl acetates produced) were plotted against the substituent constant σ, and gave a ρ value of -1.71. The ρ values lie in the range -0.3 to -1.5 for processes where a benzyl radical is generated in the rate-determining step. This indirectly supports the second mechanism. The deviation of *p*- and *m*-methoxy compounds from such a plot indicates that they follow a route with electron transfer from the aromatic ring. A relatively good agreement between observed and calculated rate constants from the Marcus theory lends support for the overall outer-sphere route. In the application of the theory, the free-energy change of the reaction has been reasonably corrected by an electrostatic energy term with due consideration for the effect of ionic strength.

(vii) *Miscellaneous reactions*

The oxidation of several organic substrates having dihydroxy groups, e.g. ascorbic acid, hydroquinone and catechol, with $[\mathrm{Co^{III}W}]^{5-}$ has been carried out by

McAuley et al. [38]. In the reaction with ascorbic acid (H_2A), the rate law

$$-\frac{d[Co^{III}W]}{dt} = 2(k_1 + k_2[H^+]^{-1})[H_2A][Co^{III}W] \tag{71}$$

observed is consistent with reactions of both ascorbic acid and its anion. The absence of any dissociable proton in hydroquinone and catechol makes the reactions pH independent. The applicability of the general Marcus format for reactions of this type is also questionable (vide supra), although such processes almost certainly follow the outer-sphere route. The oxidation of butane-1,4-diol and pentane-1,5-diol by $[Co^{III}W]^{5-}$ in aqueous perchloric acid [39] has been claimed to follow an inner-sphere route in which two hydroxyl groups of butane-1,4-diol or one hydroxyl group of two pentane-1,5-diol molecules are attached to the surface tungsten atom in the transition state. There are no supporting data to justify this view. The transfer of electrons to the $[Co^{III}W]^{5-}$ centre by a hop mechanism involving the tungsten atoms as described can also be treated as an outer-sphere path. The oxidation of iodide and hydroxide ions (L^-) by $[Co^{III}W]^{5-}$ in water and binary aqueous solvents at 25°C, as described by Blandamer et al. [40], follows a rate law

$$\text{rate} = (k_1 + k_2)[L^-][Co^{III}W]^{5-} \tag{72}$$

A decrease in rate on going from aqueous to mixed aqueous media has been apportioned between chemical potential changes consequent on solvation for each reactant and the transition state. The results with hydroxide ion provide the base hydrolytic decomposition rate of $[Co^{III}W]^{5-}$ which may be useful for further studies.

D. ELECTRON TRANSFER REACTIONS OF DODECATUNGSTOCOBALTATE(II)

(i) *Reactions of* $[Co^{II}W_{12}O_{40}]^{6-}$ *with peroxodisulphate and periodate*

Dodecatungstocobaltate(II), $[Co^{II}W_{12}O_{40}]^{6-}$ (abbreviated as $[Co^{II}W]^{6-}$), can be generated from $[Co^{III}W_{12}O_{40}]^{6-}$ either by chemical or electrochemical reduction. Ali, Saha and Banerjee [41] have reported the reactions of $[Co^{II}W]^{6-}$ with peroxodisulphate and periodate. In the peroxodisulphate reaction, the reaction is zero-order in the complex and follows a rate law, $-d[Co^{II}W]^{6-}/dt = 2k_s[S_2O_8]^{2-}$. However, with periodate the reaction is first-order in $[Co^{II}W]^{6-}$ and a limiting dependence of rate both in [periodate] and $[H^+]$ is obtained. An interesting stoichiometric result has been observed in this study. At high [complex]:[periodate] ratio (>6), the stoichiometry is 2, but under pseudo-first-order conditions with excess of periodate, the stoichiometry is less than 1. The possible consumption of periodate in the latter case has been explained by the generation of the free radical $H_3IO_5^{\cdot-}$ which decomposes thermally in a number of steps. An inhibition of the rate by alkali metal salts has also been noted. The kinetic results have been explained by considering the mechanism

$$\begin{array}{l} H_5IO_6 + [Co^{II}W]^{6-} \underset{}{\overset{Q}{\rightleftharpoons}} \{[Co^{II}W]^{6-}.H_5IO_6\} \\ \qquad\qquad\qquad\qquad\qquad \downarrow k_r \\ \qquad\qquad\qquad\qquad [Co^{III}W]^{5-} + H_3IO_5^{\cdot} + H_2O \end{array} \tag{73}$$

The value obtained for Q is large (391 M^{-1}); this is not absolute but could well incorporate the ion-pairing constant between the alkali metal ion and $[CoW_{12}O_{40}]^{6-}$.

(ii) Reactions of $[Co^{II}W_{12}O_{40}]^{7-}$ and $[Co^{II}W_{12}O_{40}]^{8-}$ with polyhalogenated alkanes

Eberson and Ekström [42,43] have described electron transfer reactions of the heteropoly "blues", $[Co^{II}W_{12}O_{40}]^{7-}$ and $[Co^{II}W_{12}O_{40}]^{8-}$ (abbreviated as $[Co^{II}W]^{7-}$ and $[Co^{II}W]^{8-}$, respectively). These species are not well-known [4] and are obtained at high pH by controlled potential reduction of the heteropoly ions beyond the normal oxidation states of the central ion. The electrons are, however, spread over the whole tungstate shell by hopping between the metal atoms. The substitution inert nature of each tungsten atom is still retained. These heteropoly blues have been generated from $K_5HCo^{II}W_{12}O_{40}$ (abbreviated as $[Co^{II}W]^{6-}$), which is a common heteropoly tungstate [4]. The reaction between carbon tetrabromide and $[Co^{II}W]^{7-}$ (/$[Co^{II}W]^{8-}$) was followed at 20°C in CH_3CN/H_2O (64/36 v/v) buffered at pH ≈ 7. The kinetics were followed spectrophotometrically by monitoring the disappearance of the heteropoly blue at 640 nm (620 nm for $[CoW]^{8-}$) under pseudo-first-order conditions, keeping $[CBr_4]$ in excess. The reaction was found to be first-order in both substrate and reagent, the rate-determining step being an outer-sphere electron-transfer path. A decrease in rate with increase in acidity has been noted and attributed to the decrease in the reduction potential of the heteropoly blue with increasing acidity. Tetraalkylammonium salts are found to increase the reaction rate, while the alkali cation has a negative effect on the rate. The kinetic and product studies indicate the mechanism for the reaction between CBr_4 and $[Co^{II}W]^{7-}$ as in the scheme

$$CBr_4 + [Co^{II}W]^{7-} \underset{k_{-1}}{\overset{\text{slow}}{\overset{k_1}{\rightleftharpoons}}} [CBr_4^{\cdot -}.[Co^{II}W]^{6-}] \xrightarrow[\text{fast}]{k_2} Br_3\dot{C} + Br^- + [Co^{II}W]^{6-} \tag{74}$$

$$2Br_3\dot{C} \xrightarrow{k_3} C_2Br_6 \tag{75}$$

$$Br_3\dot{C} + CH_3CN \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} CHBr_3 + \dot{C}H_2CN \tag{76}$$

$$Br_3\dot{C} + [Co^{II}W]^{7-} \xrightarrow{k_5} Br_3C^- + [Co^{II}W]^{6-} \tag{77}$$

$$Br_3C^- + H_2O \xrightarrow{k_6} Br_3CH + OH^- \tag{78}$$

The product distribution ratio also shows that eqns. (75) and (76) can be neglected when deriving the rate law. Using the steady-state assumption for $[Br_3\dot{C}]$, the rate equation becomes

$$\text{Rate} = 2k_{ET}[CBr_4][Co^{II}W]^{7-} \qquad (79)$$

The calculated value of k_{ET} is $1.10 \pm 0.30\ M^{-1}\ s^{-1}$ and estimates for $k_3 \approx 5.0 \times 10^7\ M^{-1}\ s^{-1}$, $k_4 \leqslant 10^{-1}\ M^{-1}\ s^{-1}$ and $k_s = 10^6\ M^{-1}\ s^{-1}$ were made.

The reaction between $[Co^{II}W]^{8-}$ and CBr_4 [42] is found to be similar to that of $[Co^{II}W]^{7-}$. Two plausible schemes of reaction have been proposed.

Scheme A.

$$[Co^{II}W]^{8-} + CBr_4 \rightarrow [[Co^{II}W]^{7-}, Br_3\dot{C}, Br^-] \rightarrow [Co^{II}W]^{6-} + Br_3C^- + Br^- \qquad (80)$$

This would give pseudo-first-order kinetics according to

$$\text{Rate} = k_{ET}[CBr_4][Co^{II}W]^{8-} \qquad (81)$$

with $k_{ET} = 4.3\ M^{-1}\ s^{-1}$.

Scheme B.

$$[Co^{II}W]^{8-} + CBr_4 \rightarrow [Co^{II}W]^{7-} + Br_3\dot{C} + Br^- \qquad (82)$$

$$[Co^{II}W]^{8-} + Br_3\dot{C} \rightarrow [Co^{II}W]^{7-} + Br_3C^- \qquad (83)$$

$$[Co^{II}W]^{7-} + CBr_4 \rightarrow [Co^{II}W]^{6-} + Br_3\dot{C} + Br^- \qquad (84)$$

$$[Co^{II}W]^{7-} + Br_3\dot{C} \rightarrow [Co^{II}W]^{6-} + Br_3C^- \qquad (85)$$

The expected biphasic behaviour for Scheme B is absent, probably because of the lack of a large difference in the reaction rates between $[Co^{II}W]^{8-}$ and $[Co^{II}W]^{7-}$, and the small difference in absorbance for these two heteropoly blues at a particular wavelength. The decrease in rate with the addition of alkali cations and the increase with the addition of tetraalkylammonium salts is explained partly by the decrease in the redox potential value on going from 0.1 M $NaClO_4$ to 0.1 M Me_4NClO_4 as electrolyte. In the reaction of CBr_4 with $[Co^{II}W]^{7-}$, the charge change upon electron transfer is $-7+0 \rightarrow -6+(-1)$, while that for alkylaromatics reacting with $[Co^{III}W]^{5-}$ is $-5+0 \rightarrow -6+1$. Thus, a repulsive electrostatic force operates in the former, while an attractive force develops upon electron transfer in the latter case. This would impart quite large differences in the electrostatic correction term for $\Delta G^{0\prime}$ in the Marcus theory, and as a consequence of the added salts tending to alter the importance of this term, possibly through ion-pairing, opposite behaviour may be expected for the heteropoly ions when acting as oxidants or reductants. The observations seem to support this view.

The reactions of $[Co^{II}W]^{7-}$ with other polyhaloalkanes have been investigated [43] and a reactivity order $CBr_4 > (CBrCl_2)_2 > CBr_2Cl_2 > C_2Cl_6 > CBrCl_3 >$

$CF_3CHClBr > CHBr_3 > CCl_4$ has been noted. Qualitative product studies indicate that the halomethanes undergo loss of the heaviest halogen during the reaction to yield haloforms, while the haloethanes lead to ethylene derivatives. The reactions with polyhalomethanes probably take place by a mechanism described earlier [40], whereas the polyhaloethanes are assumed to follow the scheme

$$\begin{aligned} &X_3C{-}CX_3 + [Co^{II}W]^{7-} \xrightarrow{\text{rds}} ([X_3C{-}CX_3^{\cdot-}] + [Co^{II}W]^{6-}) \\ &\qquad\qquad\qquad\qquad\qquad \downarrow \\ &\qquad\qquad\qquad C_2X_5^{\cdot} + [Co^{II}W]^{6-} + X \end{aligned} \tag{86}$$

$$C_2X_5 + [Co^{II}W]^{7-} \rightarrow C_2X_5^- + [Co^{II}W]^{6-} \tag{87}$$

$$C_2X_5 \rightarrow X_2C{=}CX_2 + X \tag{88}$$

$$C_2X_5^- + H_2O \rightarrow X_3C{-}CHX_2 + OH^- \tag{89}$$

Spin-trap studies confirmed the generation of the radical in the rate-determining step. A difference in reaction rates between CBr_4 and $CBrCl_3$ is also considered as support for the formation of a short-lived intermediate anion-radical. The studies gained some special stature in that they deal with heteropoly blues rather than the more usually employed heteropoly ions.

E. ELECTRON TRANSFER REACTIONS OF DODECAMOLYBDOCERATE(IV)

The oxidation of alkylaromatic hydrocarbons, e.g. ethylbenzene, toluene, *o*-, *m*- and *p*-xylene, 1,2,3-trimethylbenzene and mesitylene by $[Ce^{IV}Mo_{12}O_{42}]^{8-}$ [44] in acetic acid/water (50/50 v/v) at 50°C has been carried out by Eberson and Jönsson [45]. For the model species *p*-xylene, the rate of oxidation is first-order in each of $[Ce^{IV}Mo]$ and $[ArCH_3]$. The following kinetic scheme is proposed.

$$ArCH_3 + M^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArCH_3^{+\cdot} + M \tag{90}$$

$$ArCH_3^{+\cdot} + B: \xrightarrow[\text{slow}]{k_2} ArCH_2^{\cdot} + BH^+ \tag{91}$$

$$ArCH_2^{\cdot} + M^+ \xrightarrow{\text{fast}} ArCH_2^+ + M \tag{92}$$

where M^+/M symbolizes a general $1e^-$ redox couple and B: is the base added as acetate ion. Application of steady-state treatment to $[ArCH_3^{+\cdot}]$ of eqns. (90) and (91) gives

$$-\frac{d[M^+]}{dt} = \frac{k_1k_2[M^+][B:][ArCH_3]}{k_{-1}[M] + k_2[B:]} \tag{93}$$

If k_2 is rate-determining ($k_{-1}[\mathrm{M}] \gg k_2[\mathrm{B:}]$), the expression

$$P = k_1 k_2[\mathrm{ArCH_3}][\mathrm{B:}]/k_{-1}[\mathrm{M}^+] + k_2[\mathrm{B:}] \tag{94}$$

is obtained.

If k_1 is rate-determining ($k_{-1}[\mathrm{M}] \ll k_2[\mathrm{B:}]$), eqn. (93) reduces to

$$-\frac{\mathrm{d}[\mathrm{M}^+]}{\mathrm{d}t} = k_1[\mathrm{ArCH_3}][\mathrm{M}^+] \tag{95}$$

It is then possible to evaluate k_1 under pseudo-first-order conditions. Application of the Marcus theory after corrections for large electrostatic factors shows serious complications arising out of back electron transfer within the successor complex competing with its dissociation into free ions, and this excludes the operation of a rate-determining outer-sphere pathway. The mechanism is probably best modelled as a synchronous electron–proton transfer reaction.

F. ELECTRON TRANSFER REACTIONS OF NONAMOLYBDONICKELATE(IV) AND NONAMOLYBDOMANGANATE(IV)

The isostructural nonamolybdonickelate(IV) and nonamolybdomanganate(IV), represented by the general formula $[\mathrm{MMo_9O_{32}}]^{6-}$, are reduced by iodide, arsenite, oxalate and sulfite in neutral or slightly acidic medium [46]. The reduced products are Mn^{2+} and $[\mathrm{NiMo_6O_{24}H_6}]^{4-}$ ions. The latter is precipitated as the ammonium salt and characterised by its X-ray powder pattern. $\mathrm{Ni^{IV}Mo}$ also oxidizes $\mathrm{H_2O_2}$ and (in acid medium) water. No detailed kinetic study is reported.

Both $\mathrm{Ni^{IV}Mo}$ and $\mathrm{Mn^{IV}Mo}$ oxidize aromatic hydrocarbons and arylacetic acids in acetic acid and acetic acid–water media yielding acetates and alcohols [37].

The substituted arylacetic acids are decarboxylated when treated with $\mathrm{Ni^{IV}Mo}$. The results of oxidation of aromatic hydrocarbons by these oxidants show that the product and isomer distributions are in conformity with those obtained in the acetoxylation of the same compounds by established electron transfer agents, (e.g. $\mathrm{Ce^{IV}}$, $\mathrm{Ag^{II}}$ and $\mathrm{Co^{III}}$), as shown below.

$$\mathrm{ArCH_3} \xrightarrow[\mathrm{Mn^{IV}Mo,\ OAc}]{\mathrm{Ni^{IV}Mo}} \mathrm{ArCH_2OAc} \tag{96}$$

$$\mathrm{ArH} \xrightarrow[\mathrm{OAc}]{\mathrm{Ni^{IV}Mo}} \mathrm{ArOAc} \tag{97}$$

$$\mathrm{ArCH_2COOH} \xrightarrow[\mathrm{OAc}]{\mathrm{Ni^{IV}Mo}} \mathrm{ArCH_2OAc} \tag{98}$$

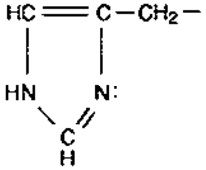
A mechanism analogous to that for $\mathrm{Co^{III}W}$ acetoxylation [37] has been proposed. However, since $\mathrm{Ni^{IV}Mo}$ and $\mathrm{Mn^{IV}Mo}$ are two-electron reagents, an intermediate $\mathrm{M^{III}Mo}$ species can act as oxidant ion in both steps (96) and (98) in competition with $\mathrm{M^{IV}Mo}$. For the substituted arylacetic acids, two different mechanisms of the types represented in eqns. (67)–(68) and (69)–(70) seem to operate. These reactions assume significance and an extensive study with $\mathrm{Ni^{IV}Mo}$ and $\mathrm{Mn^{IV}Mo}$ as oxidants is possible.

G. CONCLUSIONS

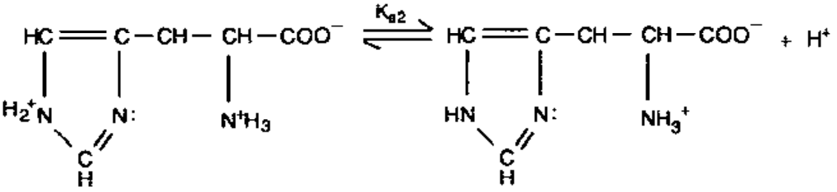
The majority of work described in this review has only appeared in the last decade. The electron transfer reactions of heteropoly oxometalates show interesting and varying mechanistic routes and dodecatungstocobaltate(III) is the major species studied in these reactions. The heteropoly oxometalates are basically outer-sphere electron transfer agents having moderate reduction potential, and the reaction rates are strongly guided by the reduction potential values of the substrates [32–35]. Species having higher reduction potentials are also oxidized by $[\mathrm{Co^{III}W}]^{5}$ via a path whereby a radical cation is formed either with a concerted proton transfer or a subsequent proton release. The results exemplify the applicability of $[\mathrm{Co^{III}W}]^{5}$ as a soluble anode [33]. The use of polyoxometalates in synthetic organic chemistry is sure to expand in the coming years and developments in this area should provide further interesting chemistry.

NOTE ADDED IN PROOF

An important piece of work has appeared on the oxidation of histidine by $\mathrm{Co^{III}W}$ in the pH range 3.0–5.5 at 60°C [48]. The reaction proceeds through the generation of free radical, $\mathrm{R\dot{C}(NH_2)COO^-}$ or $\mathrm{RCH(NH_2)CO\dot{O}}$ where R is represented as



and this has been confirmed through EPR study. Analysis of the reaction products (β-imidazolyl pyruvic acid and NH_3) definitely suggests the formation of $\mathrm{R\dot{C}(NH_2)COO^-}$ rather than $\mathrm{RCH(NH_2)CO\dot{O}}$ as the radical intermediate. A comparison of the reactivity of different reacting species of histidine (H_2L^+ and HL shown in eqn. (99)) available in the experimental pH region shows that HL reacts 173 times faster than H_2L^+.



(99)

(H_2L^+) (HL)

The availability of an electron from the C−H bond is less in H_2L^+ owing to the negative inductive (−I) effect of both the protonated imidazole ring and NH_2 group. But in HL, the deprotonated imidazole ring imparts a +I effect along with the −I effect of the NH_3^+ group. This combined effect is the likely cause of the greater availability of electron, leading to the higher reactivity of HL.

The electron transfer between $Co^{III}W$ and vanadyl ion (VO^{2+}) proceeds with a rate law

$$\text{rate} = k[\text{Co}^{\text{III}}\text{W}][\text{VO}^{2+}]$$

having $k = 129 \pm 5\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ at 25°C [49]. The rates for ^{18}O solvent exchange in VO^{2+} become $9.1\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ (for $V{-}OH_2$ equatorial) and ca. $10^7\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ (for $V{-}OH_2$ axial) upon consideration of solvent water concentration [50]. In a reacting pair, when the rate constant is greater than the rate constant for substitution on the most labile complex, the reaction must necessarily be of the outer-sphere type. The electron transfer rate here is in between the two limits, and thereby difficult to be assigned. Keeping in view the substitution inert nature of $Co^{III}W$, it may follow the outer-sphere route, though certain deviations from the general Marcus treatment are quite apparent in the results.

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