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Kinetics and Mechanism of the Oxidation of Ethyl Acetoacetate and Diethyl Malonate by Dodecatungstocobaltate(III)

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The reactions of dodecatungstocobaltate(III) with ethyl acetoacetate (EAA) and diethyl malonate (DEM) have been studied in aqueous acidic medium at 60 °C. A first-order dependence of rate on both the concentrations of oxidant and reductant is obtained and the reactions are catalyzed by alkali metal ions. The general rate law for the reactions is expressed as $k_{obs}=2(k_0+k[M^+])[R]$ where k_0 and k denote the spontaneous and catalyzed paths respectively and [R], the reductant concentration. For EAA oxidation the values of $k_0=(1.82\pm0.10)\times10^{-4}$ dm^3 mol^{-1} s^{-1} and $k_{Li^+}=(2.23\pm0.09)\times10^{-3}$ dm^6 mol^{-2} s^{-1}, $k_{Na^+}=(1.19\pm0.07)\times10^{-3}$ dm^6 mol^{-2} s^{-1}, $k_{K^+}=(1.01\times0.02)\times10^{-3}$ dm^6 mol^{-2} s^{-1}. The corresponding values for DEM are $k_0=(2.63\pm0.07)\times10^{-5}$ dm^3 mol^{-1} s^{-1} and $k_{Li^+}=(2.11\pm0.07)\times10^{-4}$ dm^6 mol^{-2} s^{-1}, $k_{Na^+}=(9.13\pm0.25)\times10^{-5}$ dm^6 mol^{-2} s^{-1}, $k_{K^+}=(8.25\pm0.06)\times10^{-5}$ dm^6 mol^{-2} s^{-1}. The less resonance stabilization of the protonated free radical species compared to the free radical obtained from the ester itself in the rate-determining step would cause a lowering in rate and this seems to explain the $[H^+]^{-1}$ dependence for the ester oxidations. A plausible mechanism considering an outer-sphere association between the complex and reductant has been suggested. The phenomenon of catalysis is explained by assuming an intermediate bridge formation via alkali metal ions between the reactants.

The redox reactions of dodecatungstocobaltate(III) have been the subject of continuing interest as witnessed by the recent publications related to the interaction of this polyanion with carboxylic acids,[1–3] sugars,[4] alcohols,[5] thiols,[6,7] iodide,[8] hydroxylammonium ion[9] etc. This paper reports the reactions of two esters namely ethyl acetoacetate and diethyl malonate with this polyanion. Compounds with an α-CH to a carbonyl function are known to undergo keto-enol tautomerism[10] and in the redox reactions of these compounds either the keto or the enol form has been found to be reactive.[11–21] The complex under investigation possesses high negative charge and specific metal ion catalysis has been obtained in its reactions with both neutral[4] and anionic[1–3] species. The present study therefore aims at the exploration of the reactivities of the tautomeric forms of the esters and their behavior towards metal ion catalysis during the oxidation process.

Experimental

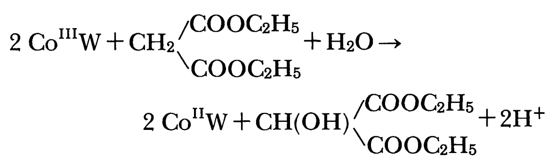
Materials and Reagents. The methods of preparation and standardization[22,23] of the potassium salts of dodecatungstocobaltate(III) $[CoW_{12}O_{40}]^{5-}$ and dodecatungstocobaltate(II), $[CoW_{12}O_{40}]^{6-}$, (hereafter designated as $Co^{III}W$ and $Co^{II}W$ respectively) are the same as reported earlier. Ethyl acetoacetate (E. Merck) is purified by usual procedure.[24] Diethyl malonate (E. Merck) has been distilled thrice before use. Analytical grade perchloric and acetic acid are used to maintain the pH of the solutions. Doubly recrystallized sodium acetate, sodium perchlorate, potassium nitrate, and lithium nitrate have been used for studying the metal ion dependence on rates of the reactions.

Kinetic Studies. The rates of the reactions have been followed in a Pye-Unicam SP8-150 UV/VIS spectrophotometer equipped with thermostated cell compartments. The reactions have been monitored at 388 nm, the absorption maximum of the complex. A few kinetic studies have also been carried out at 625 nm, the absorption maximum of $Co^{II}W$. The results obtained at both the wavelengths are identical. The kinetic results are not affected by dissolved oxygen or the buffer used to adjust the pH. The pH measurements have been performed with Systronics digital pH meter (model 335, India).

Polymerization Studies. Generation of free radicals during the course of reaction has been confirmed by the polymerization of acrylonitrile in aqueous solution. The reactant solutions are degassed separately with dinitrogen and mixed together and acrylonitrile (5% v/v) is then added to the reaction mixture containing $Co^{III}W$ and the esters. The appearance of a white precipitate within five minutes of reaction at 60 °C indicates that the reaction proceeds through free-radical formation. Blank tests performed by adding acrylonitrile separately to the reactant solutions do not show any polymerization.

Stoicheiometry and Reaction Products. The overall stoicheiometry of the reactions of ethyl acetoacetate and diethyl malonate with $Co^{III}W$ corresponds to the following equations established through spectral measurement.

$$2\,Co^{III}W + CH_3COCH_2COOC_2H_5 + H_2O \rightarrow 2\,Co^{II}W + CH_3COCH(OH)COOC_2H_5 + 2H^+ \quad (1a)$$



$$2\,Co^{III}W + CH_2\!\begin{matrix}\diagup COOC_2H_5\\ \diagdown COOC_2H_5\end{matrix} + H_2O \rightarrow 2\,Co^{II}W + CH(OH)\!\begin{matrix}\diagup COOC_2H_5\\ \diagdown COOC_2H_5\end{matrix} + 2H^+ \quad (1b)$$

The reaction products are characterized as the corresponding hydroxy keto esters[25] in a 1 : 1 ([complex] : [ester]) reaction mixture. A drop of the aqueous test solution is mixed with one drop each of 25% Na_2CO_3 solution and 5% *o*-dinitrobenzene (in benzene). The mixture is kept on a water-bath and shaken from time to time. A light violet color appears within five minutes, confirming the formation of hydroxy keto ester. It has been observed that after prolonged heating at 80—90 °C of stoicheiometric mixtures containing excess $Co^{III}W$ ($[Co^{III}W]:[ester]=6:1$), the absorbance due to $Co^{II}W$ increases and both the reaction show a 4 : 1 ([complex] : [ester]) stoicheiometry. The reaction solutions are then tested by the same procedure as described above but adding 4% HCHO solution. A light violet coloration confirms the presence of 1,2-diketones.

Results and Discussion

The reactions of EAA and DEM with $Co^{III}W$ have been investigated in mild acidic conditions. A first-order dependence of rate on complex concentration is obtained from the linearity of the plot of $-\log(A_t-A_\infty)$ vs. t over 80% of the reaction. The dependences on reductant concentration have been carried out under the following conditions: for EAA, at pH=1.0, $[Na^+]=1.00$ mol dm^{-3} and temperature 60 °C, and for DEM at pH=2.5, $[Na^+]=1.0$ mol dm^{-3} and temperature 60 °C. In either case a first-order dependence of rate on reductant concentration is obtained and the results are summarized in Table 1. The corresponding rate law may be formulated as

$$-\frac{d[Co^{III}W]}{dt}=2k_{ox}[Co^{III}W][R]=k_{obs}[Co^{III}W] \qquad (2)$$

where [R] represents the concentration of ester and the factor 2 accounts for the stoicheiometric ratio.

To determine the effect of hydrogen ion on the reaction rates, pH variation experiments have been carried out. NaOAc-HOAc buffer has been used to adjust the high pH range (3.2—4.3) and at lower region no change in pH is observed during the reaction. A decrease in rate with the increase in $[H^+]$ is obtained for these reactions and a plot of $k_{ox}(=k_{obs}/2[R])$ vs. $[H^+]^{-1}$ yields a straight line without any intercept on the rate axis. This has been depicted in Fig. 1.

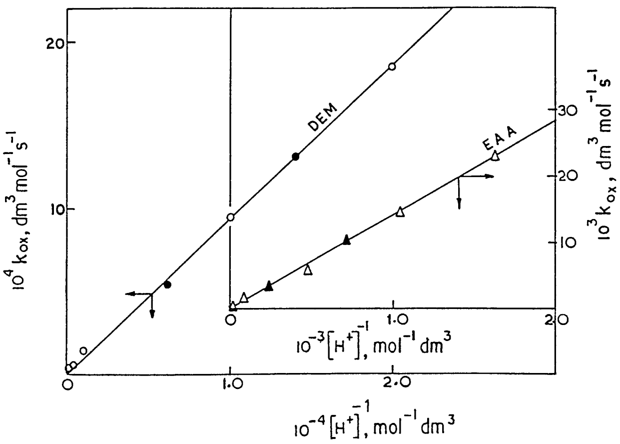


Fig. 1. A plot of k_{ox} $(=k_{obs}/2[ester])$ vs. $[H^+]^{-1}$ for the reactions of $Co^{III}W$ with 1) diethyl malonate at [DEM]=0.08 mol dm^{-3}, $[Na^+]=0.50$ mol dm^{-3}, $[Co^{III}W]=2\times10^{-4}$ mol dm^{-3} and temperature 60 °C, 2) ethyl acetoacetate at [EAA]=0.10 mol dm^{-3} $[Na^+]=1.0$ mol dm^{-3}, $[Co^{III}W]=2\times10^{-4}$ mol dm^{-3} and temperature 60 °C. Dark points indicate $[Co^{III}W]=5\times10^{-3}$ mol dm^{-3}.

The effect of alkali metal ions added as supporting electrolytes have been investigated for these systems. The reactions are found to be influenced by both the nature and concentration of alkali cations. Such behavior has been encountered in our previous studies.[1—4] An increase in rate is obtained with the increase in alkali metal ion concentration. But a reactivity order $Li^+>Na^+>K^+$ has been observed here in contrast to the order $K^+>Na^+>Li^+$ obtained by us[1—4] and also by other workers[26—28] previously. Consequently an attempt to correlate the rate constants with polarizability fails here. To discriminate the phenomenon of catalysis and ionic strength effect, the results have been subjected to the extended Brönsted-Christiansen-Scatchard relation[3] given by Eqs. 3—5

Table 1. Kinetic Data for the Variation of Ester Concentration in the Reaction of $Co^{III}W$ with Ethyl Acetoacetate and Diethyl Malonate at $[Co^{III}W]=2\times10^{-4}$ mol dm^{-3}, $[Na^+]=1.0$ mol dm^{-3} and Temperature=60 °C

[Reductant] mol dm^{-3}	EAA[a] 10^5k_{obs} s^{-1}	DEM[b] 10^5k_{obs} s^{-1}
0.01	0.40	0.22
0.03		0.71
0.05	1.84	1.08
0.06		1.42
0.07	2.53	
0.08		1.80
0.10	3.85	2.24
0.13	4.79	
0.16	5.68	

a) pH=1.0. b) pH=2.5.

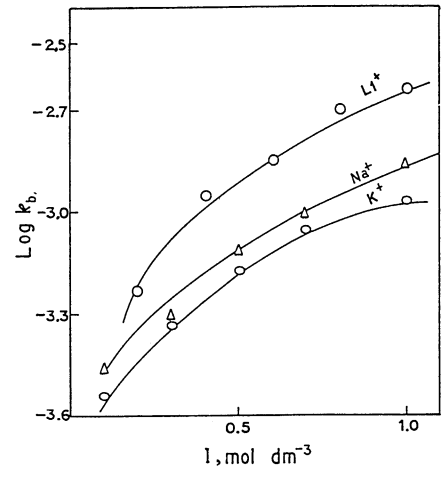


Fig. 2a. Brönsted-Christiansen-Scatchard plot showing the dependence of log k_b on ionic strength for the electron-transfer reaction between $Co^{III}W$ and ethyl acetoacetate (EAA) in $LiNO_3$ (O), $NaClO_4$ (△), and KNO_3 (⊖) media; pH=2.0, $[Co^{III}W]=2\times10^{-4}$ mol dm^{-3}, [EAA]=0.10 mol dm^{-3} and temperature=60 °C.

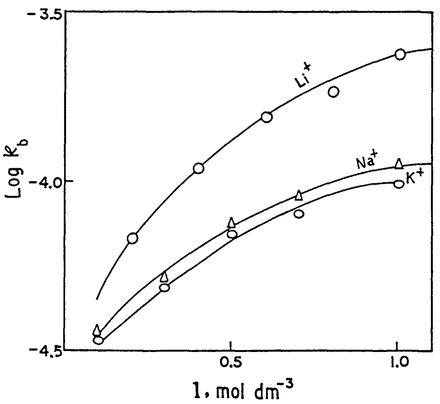


Fig. 2b. Brönsted-Christiansen-Scatchard plot, log k_b vs. I for the reaction of Co^{III}W with diethyl malonate (DEM) in $LiNO_3$ (O), $NaClO_4$ (△), and KNO_3 (⊖) media at pH=2.5, [Co^{III}W]=2×10^{-4} mol dm^{-3}, [DEM]=0.08 mol dm^{-3}, temperature=60 °C.

$$\log k_{ox}=\log k_a+2Az_Az_B\frac{\sqrt{I}}{1+\sqrt{I}}+BI, \tag{3}$$

$$\log k_b=\log k_{ox}-2Az_Az_B\frac{\sqrt{I}}{1+\sqrt{I}}. \tag{4}$$

Conbining the Eqs. 3 and 4

$$\log k_b=\log k_a+BI. \tag{5}$$

Since one of the reacting species is neutral $z_Az_B=0$, so that $\log k_b=\log k_{ox}$. Plots of $\log k_b$ vs. I (which is equivalent to the concentration of metal ions) as shown in Figs. 2a and 2b deviates from linearity. This indicates the presence of some nonelectrostatic interaction in addition to the electrostatic forces and is reminiscent of specific metal ion catalysis. The specific effect of metal ions has been further checked in the following way. Different ratios of Na_2SO_4 and $NaClO_4$ have been used to adjust the total metal ion concentration of the solutions so that the ionic strength varies but $[Na^+]_{total}$ remains constant. Table 2 contains such data. No rate enhancement due to the increased ionic strength supports the occurence of specific metal ion catalysis.

The individual effect of cations on the reactions is shown by the plot of k_{ox} vs. [M$^+$] (where M=Li, Na, or K) which is linear with a positive intercept on the rate axis. For each of the esters, (R) a common intercept is obtained for all the cations and the results are listed in Table 2. The above results may be explained by Eq. 6 as

$$k_{ox}=k_0+k[M^+] \tag{6}$$

Table 2. Kinetic Data for the Variation of Metal Ions in the Reaction of Co^{III}W with Ethyl Acetoacetate and Diethyl Malonate at 60 °C [Co^{III}W]=2×10^{-4} mol dm^{-3}. Other Conditions are EAA : pH=2.0, [EAA]=0.10 mol dm^{-3}; DEM : pH=2.5, [DEM]=0.08 mol dm^{-3}

[M$^+$]/mol dm^{-3}	10^3k_{ox}(EAA)/dm^{3}mol^{-1}s^{-1}			10^4k_{ox}(DEM)/dm^{3}mol^{-1}s^{-1}		
	[Li$^+$]	[Na$^+$]	[K$^+$]	[Li$^+$]	[Na$^+$]	[K$^+$]
0.10		0.35	0.29		0.36	0.34
0.20	0.59			0.67		
0.30		0.50	0.47		0.53	0.49
0.40	1.11			1.10		
0.50$^{a)}$		0.77 (0.79)	0.67		0.75 (0.72)	0.70
0.60	1.46			1.54		
0.70$^{b)}$		1.00 (0.98)	0.89		0.91 (0.92)	0.82
0.80	2.02			1.87		
0.90			1.09			1.00
1.00$^{c)}$	2.36	1.41 (1.42)		2.38	1.17 (1.18)	

	EAA	DEM
Li$^+$	k_0=(1.72±0.61)×10^{-4} dm^{3}mol^{-1}s^{-1} k=(2.23±0.09)×10^{-3} dm^{6}mol^{-2}s^{-1}	k_0=(2.61±0.41)×10^{-5} dm^{3}mol^{-1}s^{-1} k=(2.11±0.07)×10^{-4} dm^{6}mol^{-2}s^{-1}
Na$^+$	k_0=(1.92±0.40)×10^{-4} dm^{3}mol^{-1}s^{-1} k=(1.19±0.07)×10^{-3} dm^{6}mol^{-2}s^{-1}	k_0=(2.70±0.15)×10^{-5} dm^{3}mol^{-1}s^{-1} k=(9.13±0.25)×10^{-5} dm^{6}mol^{-2}s^{-1}
K$^+$	k_0=(1.81±0.10)×10^{-4} dm^{3}mol^{-1}s^{-1} k=(1.01±0.02)×10^{-3} dm^{6}mol^{-2}s^{-1}	k_0=(2.58±0.11)×10^{-5} dm^{3}mol^{-1}s^{-1} k=(8.25±0.06)×10^{-5} dm^{6}mol^{-2}s^{-1}
	k_0(av)=(1.82±0.10)×10^{-4} dm^{3}mol^{-1}s^{-1}	k_0(av)=(2.63±0.07)×10^{-5} dm^{3}mol^{-1}s^{-1}

The parenthetical values are obtained at constant [Na$^+$] but different ionic strength using a mixture of Na_2SO_4 and $NaClO_4$. The contribution of [H$^+$] and [Co^{III}W] towards ionic strength is ≤0.023 mol dm^{-3} and constant for all the experiments done. Their contribution has been neglected.

a) 0.2 mol dm^{-3} Na_2SO_4+0.1 mol dm^{-3} $NaClO_4$; I (Na_2SO_4+$NaClO_4$)=0.7 mol dm^{-3}. For experiments with $NaClO_4$ alone, I=0.5 mol dm^{-3}. b) 0.3 mol dm^{-3} Na_2SO_4+0.1 mol dm^{-3} $NaClO_4$; I (Na_2SO_4+$NaClO_4$)=1.0 mol dm^{-3}. For experiments with $NaClO_4$ alone, I=0.7 mol dm^{-3}. c) 0.2 mol dm^{-3} Na_2SO_4+0.1 mol dm^{-3} $NaClO_4$; I (Na_2SO_4+$NaClO_4$)=1.40 mol dm^{-3}. For experiments with $NaClO_4$ alone, I=1.0 mol dm^{-3}.

where k_0 represents the spontaneous reaction and k the catalyzed path. The corresponding rate parameters are shown in Table 2.

On the basis of above discussion, the plausible mechanism for the spontaneous and catalyzed paths may be expressed as,

(a) Spontaneous path

$$Co^{III}W+R \overset{K_1}{\rightleftarrows} \underset{(A)}{\{Co^{III}W, R\}} \xrightarrow{k_1} Co^{II}W+R^{\cdot} \quad (7)$$

(b) Catalyzed path

$$Co^{III}W+M^{+}+R \overset{K_2}{\rightleftarrows} \{Co^{III}W\cdots M^{+}\cdots R\} \xrightarrow{k_2} Co^{II}W+M^{+}+R^{\cdot} \quad (8)$$

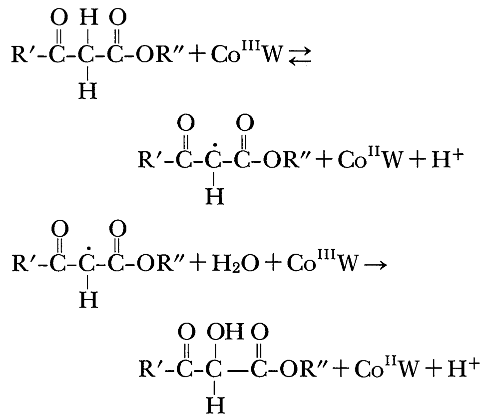
where K_1 and K_2 represent the formation constants of the species (A) and (B) respectively and k_1 and k_2 are their corresponding decomposition rates. The overall rate thus turns to

$$k_{obs}=2\{k_1K_1+k_2K_2[M^+]\}[R] \quad (9)$$

$$k_{ox}=k_1K_1+k_2K_2[M^+] \quad (10)$$

which is similar to Eq. 6 with $k_0=k_1K_1$ and $k=k_2K_2$.

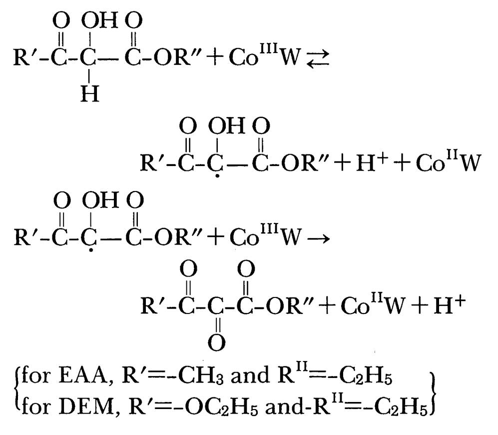
Here $R^{\cdot}$ represents the corresponding free radical produced in the rate-determining step for the oxidation of EAA and DEM. The reaction scheme accounting for the stoicheiometry and oxidation product may be presented as,



$$R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR''+Co^{III}W \rightleftarrows R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{\dot{C}}\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR''+Co^{II}W+H^+ \quad (11)$$

$$R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{\dot{C}}\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR''+H_2O+Co^{III}W \rightarrow R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}\text{—}\overset{\overset{O}{\|}}{C}\text{-}OR''+Co^{II}W+H^+ \quad (12)$$

However, in presence of excess complex over the ester, further decomposition of the hydroxy keto ester takes place (vide supra) and the formation of 1,2-diketones may be given by the following scheme,



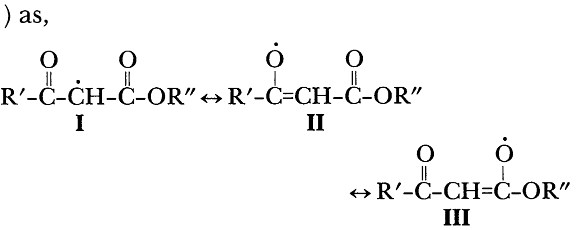
$$R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}\text{—}\overset{\overset{O}{\|}}{C}\text{-}OR''+Co^{III}W \rightleftarrows R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\cdot}{\overset{\overset{OH}{|}}{C}}\text{—}\overset{\overset{O}{\|}}{C}\text{-}OR''+H^++Co^{II}W \quad (13)$$

$$R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\cdot}{\overset{\overset{OH}{|}}{C}}\text{—}\overset{\overset{O}{\|}}{C}\text{-}OR''+Co^{III}W \rightarrow R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{O}{\|}}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR''+Co^{II}W+H^+ \quad (14)$$

$\left\{\begin{array}{l}\text{for EAA, } R'=\text{-}CH_3 \text{ and } R^{II}=\text{-}C_2H_5 \\ \text{for DEM, } R'=\text{-}OC_2H_5 \text{ and-} R^{II}=\text{-}C_2H_5\end{array}\right\}$

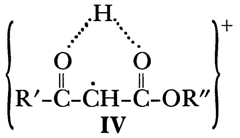
It is apparent from the above results that the reactions of the esters with $Co^{III}W$ is of outer-sphere type. The complex is a substitution inert one[1—4] and formation of a single isosbestic point at 510 nm during spectral scanning also indicates that no stable intermediate is formed during the reaction. The alkali metal ion catalysis may be explained by considering an outer-sphere bridge formation between the oxidant and reductant via alkali metal ions. The reversal of catalytic order is however difficult to explain. A consideration of the size of the hydration sphere of these metal ions gives a order $K^+<Na^+<Li^+$ and therefore the catalysis is expected to follow the opposite sequence $K^+>Na^+>Li^+$. A possible interpretation would therefore involve the true ionic sizes which seems to be somewhat unlikely at $[H^+]\leq 0.01$ mol dm^{-3}. Unfortunately no other explanation is befitting here. It is however noteworthy that at $[H^+]\geq 1.0$ mol dm^{-3}, no metal ion catalysis is observed. This may arise from excess H^+ in the solution, thus causing disfavor in the bridge formation. Conforming to our earlier studies, variation of anionic counterpart of the alkali metal salt (ClO_4^-, NO_3^-, OAc^-, SO_4^{2-}) has no effect on the reaction rates.

The relevance of $[H^+]^{-1}$ dependence to mechanistic pathways seems interesting in this study. An explanation for such dependence may be offered by considering the resonance stabilization of the free radical species (**I**—**III**) generated in the rate-determining step (11) as,



$$\underset{\textbf{I}}{R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}\dot{C}H\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR''} \leftrightarrow \underset{\textbf{II}}{R'\text{-}\overset{\overset{\dot{O}}{|}}{C}\text{=}CH\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR''} \leftrightarrow \underset{\textbf{III}}{R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH\text{=}\overset{\overset{\dot{O}}{|}}{C}\text{-}OR''}$$

For a protonated species such stabilization would be disfavored due to the protonation (**IV**) and this in turn would increase the reverse path in the rate-determining step (11) and thus cause a lowering in rate than the free ester.



IV

$$\left\{R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}\dot{C}H\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR''\right\}^{+}$$

Temperature variation experiments have been carried out for both the EAA and DEM oxidations. The second-order rate constants (k_{ox}) for these esters at different temperatures are presented in Table 3, alongwith the corresponding activation parameters evaluated using Eyring equation. These parameters however should be treated as composite since they take into account the contribution of both catalyzed and uncatalyzed paths. The negative value of $\Delta S^{\neq}$ is consistent with the proposed mechanism whereby a crowded intermediate may be conceived to be formed

Table 3. The Rate Constants and Activation Parameters for the Reaction of $Co^{III}W$ with Ethyl Acetoacetate at pH=1.0 and Diethyl Malonate at pH=2.5, $[Co^{III}W]=2\times10^{-4}$ mol dm^{-3}, $[Na^+]=1.0$ mol dm^{-3}

Temperature /°C	10^4k_{ox}(EAA)/ dm^{3}mol^{-1}s^{-1}	10^4k_{ox}(DEM)/ dm^{3}mol^{-1}s^{-1}
50	1.24	0.57
60	1.83	1.14
70	3.36	3.78

EAA: $\Delta H^{\neq}=(43\pm7)$ kJ mol^{-1}; $\Delta S^{\neq}=(-188\pm20)$ J K^{-1} mol^{-1}. DEM: $\Delta H^{\neq}=(83\pm6)$ kJ mol^{-1}; $\Delta S^{\neq}=(-71\pm47)$ J K^{-1}mol^{-1}.

prior to its rate-determining decomposition.

As it has been mentioned in the introductory part of this paper, one of the objectives of this study is to verify whether the keto or enol form of these esters is reactive towards the heteropolyacid. It is important to mention here that in the oxidations of cyclohexanone, 2-butanone, and 1,3-dihydroxyacetone with the same heteropolyanion,[29] we have obtained a zero-order rate in complex at high oxidant and low acid concentrations, and a first-order rate in complex at high acid and low oxidant concentrations. These results have been explained by considering the enol form of the carbonyl compounds as the reactive species. Similar results are obtained by Ng and Henry[17] in the oxidation of cyclohexanone by a number of tris(polypyridyl) iron(III) complexes. However, for the present system no such behavior is observed over a wide range of acidity and oxidant concentration (Fig. 1). Thus it is evident that for the oxidation of ethylacetoacetate and diethyl malonate, the keto form of the esters is the reactive species. This is also supported by the $[H^+]$ and $[M^+]$ variation results of this system. The alkali metal ion dependence also sites one of the rare examples[4,30] where the reaction between a neutral and a negatively charged species is catalyzed by alkali metal ions. In such cases possibly the bridging by alkali cations is mediated via ion-induced-dipole interaction exerted by M^+ on the neutral reductant.

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