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Kinetics and Mechanism of Bromination of Tris(Acetylacetates) of Co(III), Cr(III) and Bis(Acetylacetonato) Co(II) by Pyridinium Bromochromate in Aqueous Acetic Acid Medium

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The kinetics of bromination of $Cr(acac)_3$, $Co(acac)_3$ and $Co(acac)_2$ by pyridinium bromochromate (PBC) in aqueous acetic acid have been studied under pseudo-first order conditions Co(III), Cr(III) acetylacetonates undergo electrophilic γ-substitution yielding $M(Bracac)_3$ whereas Co(II) acetylacetonate undergoes nucleophilic bromination, yielding $[CoBr_4][PyH]_2$. The rate for the tris-chelates is dependent on the concentration of the reagent (PBC) and not the substrate. For the bis-chelate, the rate is dependent on both the substrate and the reagent. Probable mechanistic pathways for the bromination of the two cases are presented. A rate law is derived for the electrophilic γ-substitutions in metal(III) chelates.

INTRODUCTION

The compound pyridinium bromochromate (PBC) was recently synthesised and has since been employed as a reagent for brominating organic substrates like anisole, acetanilide, benzanilide, anthracene, fluorene and acetophenone[1]. We have earlier introduced PBC as a brominating agent for the first time for brominating β-diketonates both under thermal and photochemical conditions[2]. Investigation of kinetic and mechanistic aspects of such substitution reactions by PBC have not been reported though the kinetics of oxidation reaction brought about by analogous pyridium fluorochromate (PFC) and pyridinium chlorochromate (PCC)[3–6] are available aplenty. This paper reports the results of kinetics and mechanistic study on Co(III), Cr(III) and Co(II) acetylacetonates in aqueous acetic acid medium.

EXPERIMENTAL

AnalaR acetic acid was purified according to the literature. Doubly distilled water was used for all purposes. Sodium acetate, sodium thiosulphate, perchloric acid, concentrated sulphuric acid, sodium sulphate, sodium nitrate and starch were of AR grade and used as such. The reagent PBC and the title substrates were prepared according to the literature[7, 8].

The reactions were carried out at constant temperature under pseudo-first order

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conditions followed by estimating the unreacted reagent iodometrically at regular time intervals. The medium was acetic acid-water mixture (50% v/v).

RESULTS AND DISCUSSION

The kinetic experiments have been run keeping the acetylacetonate substrate concentration constant and maintaining the concentration of PBC reagent nearly ten times that of the chelate substrate. It has been found that variation in the concentration of the chelate substrate under these conditions upto 4 times its initial value does not bring about a change in the reaction rate. This means that within this concentration range the reaction rate is independent of the substrate concentration.. However, varying the PBC concentration in the limit 0.00635 M to 0.02538 M shows a marked change in the observed rate of the reaction by about 27.5%. Thus, under the pseudo-first order experimental conditions, the reaction is first order with respect to the PBC. This argument pertains to the kinetically inert Co(III) and Cr(III) acetylacetonate triscomplexes and not to the Co(II) bischelate. The product analyses and spectral identifications (Tables 1–5) clearly show that the type of bromination reaction that takes place is electrophilic substitution in all the three chelate rings, the rings of course remaining intact without suffering cleavage. However, Co(II) acetylacetonate kinetically behaves differently from the Co(III) and the Cr(III) counterparts upon bromination. The pseudo-first order dependence of the observed rate in respect of both the reactants is just the reverse of what is observed for the trischelates. Thus, the k_{obs} values vary considerably upon a change in the concentration of the chelate substrate keeping the concentration of PBC constant. For example, it has been found that for a two-fold variation in the concentration of the $Co(acac)_2$, the k_{obs} value nearly gets trebled whose change is dramatic. Likewise for the same bischelate on keeping the concentration of the acetylacetonate substrate constant (0.00127 M) and varying the concentration of PBC just by 50% (from 0.0124 M to 0.0185 M), the observed rate constant markedly varies from 5.14 to 11.57. One is therefore tempted to think that the trischelates behave differently from the bischelates probably following an entirely different reaction route. Analyses of the products of the reactions in the two cases confirm this.

TABLE-1
ANALYTICAL DATA OF THE PRODUCTS

Complex	Colour	Yield %	% Found (Calcd.)					μ_{eff} B.M.
			M	C	H	Br	N	
1. $Co(Bracac)_3$	Green	44	9.7 (9.9)	30.5 (30.4)	3.2 (3.1)	40.7 (40.5)	—	—
2. $Cr(Bracac)_3$	Brownish green	35	8.6 (8.9)	30.82 (30.75)	3.21 (3.07)	41.2 (40.9)	—	3.8
3. $[CoBr_4][PyH]_2$	Blue	38	11.4 (10.9)	22.4 (22.2)	2.5 (2.3)	60.1 (59.5)	5.5 (5.2)	5.1

TABLE-2
IMPORTANT IR DATA OF $M(acac)_3$ AND $M(Bracac)_3$

Complex	IR frequency (cm^{-1})			
	ν(C=O)	ν(C—H$^{+)}$ ν(C=O)	δ(C—H)	π(C—H)
$Co(Hacac)_3$	1590	1525	1195	780
$Cr(Hacac)_3$	1590	1525	1195	780
$Co(Hacac)_2$	1570	1525	1190	775
$Co(Bracac)_3$	1585	—	—	—
$Cr(Bracac)_3$	1585	—	—	—

TABLE-3
IMPORTANT IR DATA (cm^{-1}) of $[CoBr_4][PyH]_2$

Complex	ν(N—H)	δ(N—H)	ν(C=N)	Pyridine ring def.	ν(C—H), CH_2, CH_3
$[CoBr_4][PyH]_2$	3070	1620	1595	755	—

TABLE-4
UV DATA OF BROMINATED PRODUCTS

Complex	Absorption Maxima (cm^{-1})		
$[CoBr_4][PyH]_2$	16100	19600	21970
$Co(Bracac)_3$	29850	33890	38460
$Cr(Bracac)_3$	29400	33300	37040

TABLE-5
^1H NMR DATA OF BROMINATED PRODUCTS

Complex	Solvent	Pyridinium protons			Methyl protons	ν(C—H)
		NH	Ring	CH		
$Co(acac)_3$	$CDCl_3$	—	—	—	2.18	5.52
$Co(Bracac)_3$	$CDCl_3$	—	—	—	2.17	—

Analyses would also show that the bromo product isolated in the kinetic study of the trischelates is a γ-bromo substituted trischelate, $M(Bracac)_3$. This means that the type of reaction undergone by the substrate under the said experimental condition is an electrophilic substitution reaction at the 3-carbon positions of the chelate ring. However, the analytical results of the bischelate substrate reaction product shows no appreciable γ-substituted bromo product, but a totally ring cleaved nucleophilic product bearing the composition $[MBr_4][PyH]_2$. This shows that essentially a nucleophilic reaction has taken place in the bischelate studies as opposed to an electrophilic reaction for trischelates.

Product Analysis and Stoichiometry: Microanalytical and metal analysis show that bromo product has a metal to bromine ratios of 1:3 for trischelates and a totally ring cleaved product for the bischelate (Table-1). IR and NMR data for Co(III) complex confirm that the bromine has substituted each of the γ-hydrogen of the ring.

UV-Vis spectra of the products derived by the bromination of cobalt(II) acetylacetonate exhibit three characteristic absorption bands. In the case of Co(II) product the bands occurring at the higher wavelength region are assignable to $^4A_2(F) \rightarrow {}^4T_1(P)$ and $^4A_2(F) \rightarrow {}^4T_1(F)$ transition. This implies a $^4A_2$ ground state for the metal ion and a tetrahedral environment around it.

Based on the above discussion and observed product analysis, the mechanism for the reaction can be written as shown in Scheme-1.

Scheme-1

$$\mathrm{PyHCrO_3Br} \rightleftarrows \mathrm{PyH^+} + [\mathrm{CrO_3Br}]^- \tag{1}$$

$$[\mathrm{CrO_3Br}]^- + \mathrm{H^+} \underset{\mathrm{HOAc}}{\rightleftarrows} [\mathrm{HCrO_3}]^+ + \mathrm{Br^-} \tag{2}$$

$$\mathrm{Br^-} + \mathrm{M(acac)_2} \rightarrow [\mathrm{MBr_4}][\mathrm{PyH}]_2$$

The formation of $\mathrm{M(Bracac)_3}$ *i.e.* the formation of the electrophilic γ-substituted bromochelate involves $\mathrm{Br^+}$ cationic species. This can be accounted for by the probable *in situ* oxidation of $\mathrm{Br^-}$ to $\mathrm{Br^+}$ by $[\mathrm{HCrO_3}]^+$ species of the PBC reagent in acid medium. The compatible reaction steps involving oxidant Cr(VI) of species $[\mathrm{HCrO_3}]^+$ could be written as:

$$4\mathrm{Cr(VI)} + 2\mathrm{Br^-} \xrightarrow{\mathrm{H^+}} 2\mathrm{Br^+} + 2\mathrm{Cr(IV)} + 2\mathrm{Cr(VI)} \tag{3}$$

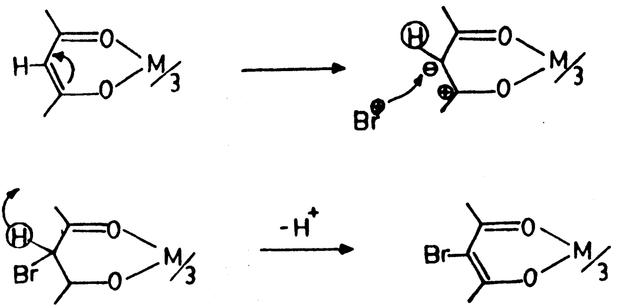
$$2\mathrm{Cr(IV)} \rightarrow \mathrm{Cr(III)} + \mathrm{Cr(V)} \tag{4}$$

$$\mathrm{Cr(V)} + \mathrm{Br^-} \rightarrow \mathrm{Cr(III)} + \mathrm{Br^+} \tag{5}$$

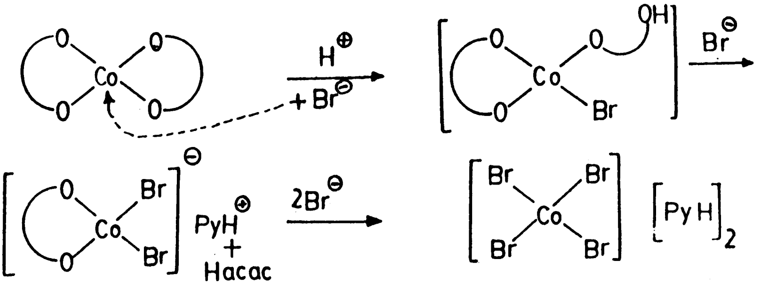
$$2\mathrm{Cr(VI)} + 3\mathrm{Br^-} \rightarrow 2\mathrm{Cr(III)} + 3\mathrm{Br^+} \tag{6}$$

It appears that two competing reactions involving the species $\mathrm{Br^-}$ and/or $\mathrm{Br^+}$ are possible and the actual reaction probably depends on the nature of the central metal ion of the chelate and its oxidation state.

Formation of Electrophilic Substituted Product



Formation of Nucleophilic Substituted Product



Derivation of Rate Law: The salient kinetic results obtained are summarised below:

1. The reaction exhibits first-order dependence in the reagent, PBC and independence in the substrate.
2. Added salts like Na_2SO_4 and $NaNO_3$ have no effect on rate, but sodium acetate increases the rate of the reaction.
3. The rate is decreased by increasing the concentration of the solvent namely acetic acid.
4. There is a linear increase in the reaction rate with acidity.
5. The rate of the reaction is unaffected by changing the concentration of acrylonitrile.

The rate law can be derived as follows:

$$PyHCrO_3Br + H^+ \xrightarrow{k_1} PyH^+ + HCrO_3^+ + Br^- \qquad (1)$$

$$3Br^- + 2Cr(VI) \xrightarrow{k_2} 3Br^+ + 2Cr(III) \qquad (2)$$

$$3Br^+ + M(acac)_3 \xrightarrow{k_3} M(Bracac)_3 + 3H^+ \qquad (3)$$

$$-\frac{d}{dt}[M(Bracac)_3] = k_3[M(acac)_3[Br^+]^3 \qquad (4)$$

$$-\frac{d}{dt}[Br^+] = k_2[Cr(VI)]^2[Br^-]^3 - k_3[M(acac)_3][Br^+]^3$$

Applying steady-state principle, the rate of formation is equal to the rate of dissociation, *i.e.*,

$$-\frac{d}{dt}[Br^+] = 0$$

$$k_2[Cr(VI)]^2[Br^-]^3 - k_3[M(acac)_3][Br^+]^3 = 0$$

$$k_2[Cr(VI)]^2[Br^-]^3 = k_3[Br^+]^3[M(acac)_3]$$

$$[Br^+]^3 = \frac{k_2[Cr(VI)]^2[Br^-]^3}{k_3[M(acac)_3]} \qquad (5)$$

$$-\frac{d}{dt}[Br^-] = k_1[H^+][PyHCrO_3Br] - k_2[Br^-]^3[Cr(VI)]^2$$

Applying steady-state principle,

$$k_1[H^+][PyHCrO_3Br] = k_2[Br^-]^3[Cr(VI)]^2$$

$$[Br^-]^3 = \frac{k_1[H^+][PyHCrO_3Br]}{k_2[Cr(VI)]^2} \qquad (6)$$

Substituting the value of $[Br^-]^3$ in Eq. (5),

$$[Br^+]^3 = \frac{k_2[Cr(VI)]^2 k_1[H^+][PyHCrO_3Br]}{k_3[M(acac)_3]k_2[Cr(VI)]^2}$$

$$= \frac{k_1[H^+][PyHCrO_3Br]}{k_3[M(acac)_3]} \qquad (7)$$

Substituting Eq. (7) in Eq. (4),

$$-\frac{d}{dt}[M(Bracac)_3] = \frac{k_3[M(acac)_3]k_1[H^+][PyHCrO_3Br]}{k_3[M(acac)_3]}$$

$$= k_1[H^+][PyHCrO_3Br]$$

$$-\frac{d}{dt}[M(Bracac)_3] = k_1[H^+][PyHCrO_3Br]$$

Thus, the above mechanism leads to the above rate law. This explains the above experimental observations. This is only applicable for M = Cr(III) and Co(III).

The experimental observations can be explained as follows, following the mechanism:

1. The linear increase in the reaction rate with acidity suggests involvement of a protonated Cr(VI) species in the rate determining step. Involvement of such species are well known in chromic acid oxidation[9].

2. The rate constant studied as a function of the composition of the acetic acid-water medium, is found to decrease as the proportion of the acetic acid and hence the over all dielectric constant increases.

3. A hydrogen abstraction mechanism is unlikely, though not ruled out, in view of the failure to induce polymerization of acrylonitrile.

4. The rate is dependent on the concentration of the reagent, PBC only and not the substrate. This is confirmed from the rate law, in which there is no substrate concentration and it suggests a multistep reaction sequence *via* the formation of an intermediate between the substrate and PBC.

5. The kinetic parameters E_a, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been calculated. A near constancy of the free energy of activation of the trischelate shows that the same mechanism is operative.

6. The rate of the reaction increases with the increase of $[H^+]$. This suggests an interaction between a dipole and positive ion. This is in accord with the observation that the rate determining step, in the presence of acid, involves a protonated Cr(VI) species.

For Bis(acetylacetonato) Co(II): The salient results obtained from the foregoing studies are:

1. The stoichiometry (substrate : reagent) of the reaction was found to be 1:2 and the product was found to the $[CoBr_4][PyH]_2$. The rate depends on both the substrate and reagent.
2. The rate is independent of the concentration of H^+ and decreased when the concentration of acetic acid is increased.
3. The reaction rate is not significantly altered by the addition of salts like Na_2SO_4 and $NaNO_3$. But the rate increases with the increase of the concentration of sodium acetate.
4. The rate of the reaction is unaffected by changing the concentration of acrylonitrile.

The probable mechanistic pathway is given in vide infra (6).

The rate law for this bischelate is given by

$$-\frac{d}{dt}[(CoBr_4)(PyH)_2] = k[Co(acac)_2][PyHCrO_3Br]$$

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