

The growing polymer chains get terminated by the mutual annihilation of polymer radicals as evidenced by the dependence of rate of polymerization over square roots of  $[Ce(IV)]$  and  $[BA]$ .



Mutual type of termination proposed by us seems to be a rate occurrence since in most cases termination of polymer radical by  $Ce(IV)$  was reported to be predominant<sup>1, 2, 8</sup>. Similar mutual type combination of polymer chains was observed in the case of  $Ce(IV)$ -malonic acid initiated polymerization of methyl acrylate<sup>4</sup> and also  $Ce(IV)$ -acetaldehyde initiated polymerization of acrylonitrile<sup>3</sup>. Termination by  $Ce(IV)$  in our case would give a kinetic dependence of  $[AN]^2$ ,  $[BA]$  and  $[Ce(IV)]^{-1}$  on  $R_p$  and hence inconsistent with our observed results.

Assuming the stationary state kinetics for free radicals and under the conditions  $k_t [AN] \gg k_0 [Ce(IV)]$ , the following rate expressions are derived:

$$R_p = k_p/k_t^{1/2} [AN] [Ce(IV)]^{1/2} [BA]^{1/2} \quad (I)$$

$$-R_{Ce(IV)} = k_r [Ce(IV)] [BA] \quad (II)$$

The overall activation energy was evaluated as 13.25 K.cals mole<sup>-1</sup>, which is of the same order as that obtained for  $Ce(IV)$ -acetaldehyde initiated polymerization of acrylonitrile<sup>3</sup>. The second order rate constant  $k_p$ , evaluated from plots of  $-R_{Ce(IV)}$  against  $[Ce(IV)]$  and  $[BA]$  agreed well and was equal to 7.5 lit. mole<sup>-1</sup> sec<sup>-1</sup>. The value of the rate constant  $k_p/k_t^{1/2}$  was evaluated as 0.0113 lit<sup>-1/2</sup>. mole<sup>1/2</sup>. sec<sup>-1/2</sup> which compares well with that reported in the literature for acrylonitrile polymerization<sup>3, 8-10</sup>.

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### HEXAAQUOCOBLTIC ION AS THE ACTIVE SPECIES OF Co(III)

STUDIES involving  $Co(III)$ <sup>1,2</sup> indicate that the hydroxopentaaquocobaltic ion is more active than the hexaaquocobaltic ion. The general explanation<sup>1</sup> offered to this point, is the greater ease of conversion of  $Co(III)$  from the low spin form ( $t_{2g}^5 e_g^1$ ) in the case of  $[Co(OH)(H_2O)_5]^{2+}$  since a preliminary or subsequent step involving purely a multiplicity change should be considered in reactions involving  $Co(III)$  besides the normal rate-determining step in any oxidation reaction. Actually, evidence for spin-state conversion has been provided in a very fast reaction, namely the oxidation of  $Fe^{2+}(aq.)$  by  $Co(III)$ <sup>3</sup>. But a careful analysis of oxidations by  $Co(III)$  indicates that there are certain reactions wherein  $Co(H_2O)_6^{3+}$  is the only active species of  $Co(III)$ . A striking feature of these reactions is that all of them occur by bonded mechanism.

Even though  $Co(III)$  has a very high redox potential<sup>4</sup> capable of oxidising the substrate by non-bonded mechanism, the lability of the complex,  $Co(H_2O)_6^{3+}$  is in favour of a bonded mechanism. But the chemistry of  $Co(III)$  is not rich in evidence for complex formation preceding electron transfer from substrate to  $Co(III)$  unlike the other one-electron oxidants,  $V(V)$ <sup>1</sup> and  $Ce(IV)$ <sup>5</sup>. Of the very large number of oxidations investigated with  $Co(III)$ , only a few reactions exhibited evidence for complex formation and it is indeed surprising that  $Co(H_2O)_6^{3+}$  is the active oxidant in all these instances. These reactions are summarised in Table I.

In all the reactions summarized in Table I, only  $Co(H_2O)_6^{3+}$  has been the active species and the rate laws correspond to

$$\frac{1}{k} = \frac{1}{k_t} + \frac{(H^+)}{k_t K (\text{substrate})} \quad (1)$$

and/or

$$\frac{1}{k} = \frac{1}{k_t} + \frac{1}{k_t K (\text{substrate})} \quad (2)$$

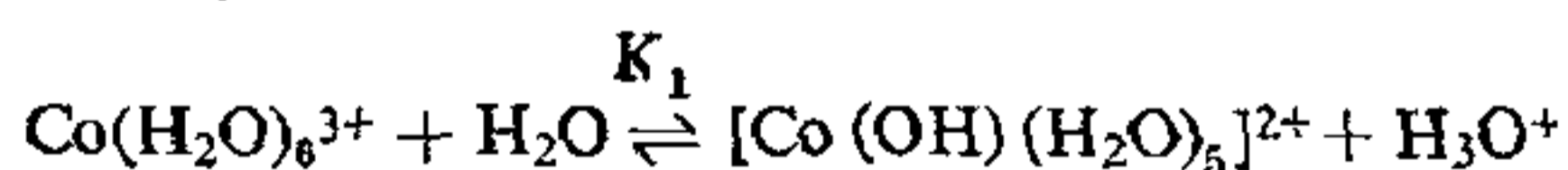
where  $k$  is the pseudo-first-order rate constant,  $k_t$  is the rate constant for the disproportionation of the complex and  $K$  is equilibrium constant for complex formation. On the contrary,  $[Co(OH)(H_2O)_5]^{2+}$  as the active oxidant yielding the rate law,

$$\frac{1}{k} = \frac{(H^+)}{k_t K_1} + \frac{(H^+)}{k_t K_1 K (\text{substrate})} \quad (3)$$

TABLE I  
Oxidations by bonded mechanism with  $\text{Co}(\text{H}_2\text{O})_6^{3+}$   
as the active species

Substrate	Medium	K	Reference
Propionic acid	$\text{HClO}_4$ (39% $\text{CH}_3\text{CN}$ ) (15° C)	0.72	6
Phenylacetic acid	$\text{HClO}_4$ (39% $\text{CH}_3\text{CN}$ ) (15° C)	27.7	6
Ph $(\text{CH}_2)_3\text{COOH}$	$\text{HClO}_4$ (50% $\text{CH}_3\text{CN}$ ) (20° C)	4.7	7
Ph $(\text{CH}_2)_4\text{COOH}$	$\text{HClO}_4$ (50% $\text{CH}_3\text{CN}$ ) (20° C)	17.0	7
Ph $(\text{CH}_2)_5\text{COOH}$	$\text{HClO}_4$ (60% $\text{CH}_3\text{CN}$ ) (20° C)	14.0	7
Glutaric acid	$\text{HClO}_4$ (15° C)	12.37	2
Glutaric acid	$\text{H}_2\text{SO}_4$ (15° C)	1.65	2
4-Hydroxy-4-methylpentan-2-one	$\text{HClO}_4$ (20° C)	7.8	8

has not been realized in any of the oxidations by  $\text{Co}(\text{III})$  where  $K_1$  is the hydrolytic equilibrium constant,



The general characteristic of all the oxidations by  $\text{Co}(\text{III})$  occurring *via* bonded mechanism with  $\text{Co}(\text{H}_2\text{O})_6^{3+}$  as the active oxidant cannot be a mere coincidence of the experimental facts. This may point to a common reason as to why the hexa-aquo cobaltic ion is the active species in oxidations proceeding *via* complex formation between  $\text{Co}(\text{III})$  and substrate. Probably, in reactions occurring *via* inner sphere oxidative path or bonded mechanism, the deciding factor is the lability of the active species of  $\text{Co}(\text{III})$ . The change in spin multiplicity of  $\text{Co}(\text{III})$  is inevitable whether the oxidation occurs by bonded or non-bonded mechanism. But the ruling factor in oxidations by bonded mechanism appears to be the lability of the cobaltic species. Since  $\text{Co}(\text{H}_2\text{O})_6^{3+}$  is more labile than  $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  the former is found to be the active species in all the oxidations proceeding *via* complex formation.

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#### SIMPLE PHOTOMETRIC ESTIMATION OF METHYLDOPA

METHYLDOPA, L-3-(3,4-Dihydroxyphenyl)-2-methylalanine is a widely used antihypertensive agent. The reported methods of micro estimation of methyldopa include colour formation with iron salts<sup>1,2</sup>, complex formation with molybdenum<sup>3</sup>, colour formation with *p*-dimethylaminobenzaldehyde<sup>4</sup> and with thiosemicarbazide<sup>5</sup>. The methods are either not specific or they require long time and critical reaction conditions.

In the present paper a simple and quick photometric estimation of methyldopa has been described with: (i) *p*-phenylenediamine dihydrochloride (PPDA), (ii) aqueous ammonia, (iii) *p*-aminophenol (PAP) and (iv) resorcinol.

A comparative data of estimation of methyldopa with the four reagents are given in Table I.

#### Experimental

Methyldopa standard was prepared in 0.1 M HCl. All the reagents used were of analytical grade.

#### Assay Procedures

(i) By PPDA—Aliquots of standard and samples containing 100  $\mu\text{g}$  were mixed with 1 ml of reagent and 2 ml of NaOH and diluted to mark (10 ml) with water. The absorbance of the colour at 494 nm against a reagent blank was measured after 5 minutes.

(ii) By  $\text{NH}_4\text{OH}$ —In 10 ml graduated test tubes, aliquots containing 200  $\mu\text{g}$  of standard and sample