Kinetics and Mechanism of Metal Ion Catalysed Dissociation of Tris-biguanide Complexes of Chromium(III) and Cobalt(III)

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Dissociation of tris-biguanide complexes of Cr(III) and Co(III) catalysed by some bivalent metal ions in acid medium has been studied. Linearity of $\triangle H^{\neq}$ vs $\triangle S^{\neq}$ corresponding to k_M for the different catalysing metal ions and each of the substrate complexes as well as of k_M for Co(III) complex vs k_M for Cr(III) complex for the different catalysing metal ions indicate similar mechanism in all the cases. The catalytic activity of the different metal ions decreases in the sequence $Cu(II) > Ni(II) > Co(II) > Zn(II) > Mn(II)$, with log k_M varying linearly with $Z^*/(r_{M^{2+}})^2$ of the catalysing metal, i.e., its complexing ability. From the results it has been possible to evaluate the values of the formation constants of the monobiguanide complexes of the other catalysing metal ions from a knowledge of the corresponding value of the Cu(II) complex and the k_M values.

Experimental

Materials and Reagents

Tris-biguanidechromium(III) p e r c h l o r a t e, $[Cr(BigH)_3](ClO_4)_3$ and tris-biguanidecobalt(III) perchlorate, $[Co(BigH)_3](ClO_4)_3$ were prepared by known methods as described earlier[4,7] and their purity was checked by chemical analysis and absorption spectra[4].

All other reagents used were of reagent grade or else purified suitably before use.

Apparatus and Procedure

The rate of dissociation was followed spectrophotometrically at the λ_{max} of 480 and 490 nm respectively for the Co(III) and Cr(III) complexes using a Carl Zeiss(VSU-2P) Spectrophotometer. Absorption measurements were made against a reference blank which was identical in every respect to the experimental solution except that it did not contain the substrate complex. The reactions were carried out in low acid concentration where the tris-biguanide complexes are known[4] to dissociate to only the diaquo-bis-biguanide complexes of these metals. Observations were made in presence of different concentrations of catalysing metal ion in each case and under experimental conditions that pseudo-first-order rate law was valid. The pseudo-first-order rate constants (k_{obs}) were evaluated graphically as usual using Guggenheim's method[8].

Results

For both the Cr(III) and Co(III) complexes the

THE role of metal cations in catalysing the aquation of metal complexes is attributable to the ability of the catalysing metal ions to bind to a suitable site of the ligand in the substrate complex and its ability to withdraw electrons causing a reduction in the electron density at the substrate metal-ligand bond by inductive effect. The catalysing efficiency of a metal ion therefore depends among other factors on the magnitude of the association constant of the catalysing metal ion with the departing ligand. For a closely related series of metal ions such as Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) of the 3d series, this association constant varies significantly from Mn(II) to Zn(II) in the Irving-William's sequence, while other factors may reasonably be expected to be more or less the same along this series. For such a series of metal ions, therefore, a quantitative correlation between metal-ligand association constant (or some other physical quantity related to it) and catalytic power of the metal ion in facilitating the dissociation of the ligand from a substrate complex is expected, and indeed it has been found to be true in several systems that have been studied so far[1,2,3].

The acid catalysed dissociation of metal-biguanide complexes have been studied earlier in our laboratory[4,5]. In this communication, the results of investigations on the catalytic effect of several bivalent metal ions of the 3d series on the dissociation of tris-biguanide complexes of Cr(III) and Co(III) have been reported. From the results it has also been possible to indirectly ascertain the stability constants of the monobiguanide complexes of the other catalysing metal ions, from a knowledge of the value[6] for the Cu(II)-monobiguanide complex.

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observed variations in k_{obs} with catalysing metal ion concentration in acid solution is consistent with the relation :

$$k_{obs} = k_H[H^+] + k_M[M^{2+}] \qquad \dots \quad (1)$$

where k_H and k_M are the specific rate constants for the acid and metal catalysed paths respectively.

From the values of k_M obtained from the slope of the k_{obs} vs [M²⁺] plots at fixed acid concentration (intercept of such plots in all cases was in good agreement with k_H[H⁺] value[4]) at different temperatures under otherwise identical conditions, the values of the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been evaluated by the least squares method using Eyring equation. The values of k_M and the activation parameters are given in Tables 1 and 2 respectively.

Fig. 1. A : [Co(BigH)₃]³⁺ system ; B : [Cr(BigH)₃]³⁺ system
Temp., 35°C ; Ionic strength, 1M

Discussions

It is known that[10] as expected the formation constants (K_{ML}) of analogous complexes of a particular series of metal ions and a particular ligand varies linearly with the $Z^*/(r_M{}^{m+})^2$ value of the metal ion, which is a measure of its surface charge density, according to the relation :

$$\log K_{ML} = A + BZ^*/(r_M{}^{m+})^2 \qquad \dots \quad (3)$$

Hence, the linear correlation observed between $\log k_M$ and $Z^*/(r_M{}^{2+})^2$ (see Eqn. 2 and Fig. 1) for the different catalysing metal ions for both Cr(III) and Co(III) tris-biguanide complexes indicates that there is a corresponding linear correlation between the catalytic power of the metal ions and the formation constants of their monobiguanide complexes. Again, for both the systems $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ corresponding to k_M for the different catalysing metal ions is linear, the slope of which is nearly the same for both the substrate complexes (see Fig. 2). Also the plot of k_M for the cobalt complex vs k_M for the chromium complex for the different catalysing

TABLE 1—VALUES OF THE KINETIC PARAMETERS FOR Cr(BigH)₃³⁺. [Complex], 0.001M : [HClO₄], 0.01M IONIC STRENGTH, 1M (NaClO₄)

	k_M (M⁻¹ min⁻¹)			$\Delta H^{\neq}$ (k cal/mole)	$\Delta S^{\neq}$ (e.u.)
	25°	30°	35°		
(4)					
H⁺	4.34	5.88	7.88	10.1	−30.2
Cu²⁺	0.300	0.575	1.10	23.1±0.7	8.1±2.4
Ni²⁺	0.240	0.480	0.970	25.5±0.9	15.7±2.9
Co²⁺	0.176	0.375	0.780	26.6±0.4	18.8±1.4
Mn²⁺	0.137	0.300	0.630	28.1±1.0	23.2±3.2
Zn²⁺	0.150	0.350	0.690	28.0±1.3	23.1±4.4

TABLE 2—VALUES OF THE KINETIC PARAMETERS FOR Co(BigH)₃³⁺. [Complex], 0.001M : [HClO₄], 0.04M : IONIC STRENGTH 1M (NaClO₄)

	k_M (M⁻¹ min⁻¹)			$\Delta H^{\neq}$ (k cal/mole)	$\Delta S^{\neq}$ (e.u.)
	30°	35°	40°		
(4)					
H⁺	0.584	0.801	1.085	11.1	−31.5
Cu²⁺	0.057	0.110	0.197	23.7±0.6	5.4±2.2
Ni²⁺	0.048	0.091	0.190	26.3±1.0	13.6±3.4
Co²⁺	0.038	0.079	0.160	27.4±0.5	16.8±1.7
Mn²⁺	0.028	0.064	0.136	29.3±0.9	22.5±3.1
Zn²⁺	0.035	0.072	0.154	28.3±0.8	19.6±2.7

The k_M values follow the sequence Cu(II)>Ni(II)>Co(II)>Zn(II)>Mn(II). Log k_M values for different catalysing metal ions when plotted against $Z^*/(r_M{}^{2+})^2$ gives a good straight line (see Fig. 1) according to the following relationship :

$$\log k_M = bZ^*/(r_M{}^{2+})^2 + c \qquad \dots \quad (2)$$

where Z^* is the effective nuclear charge of the catalysing metal ion which can be evaluated using Slater's rule[9] and $(r_M{}^{2+})$ is its ionic radius.
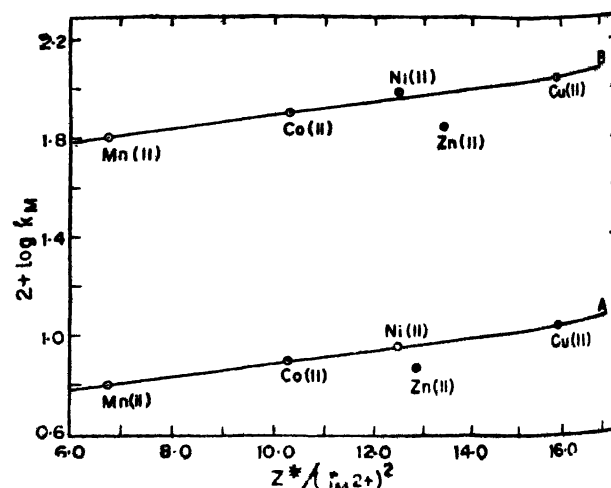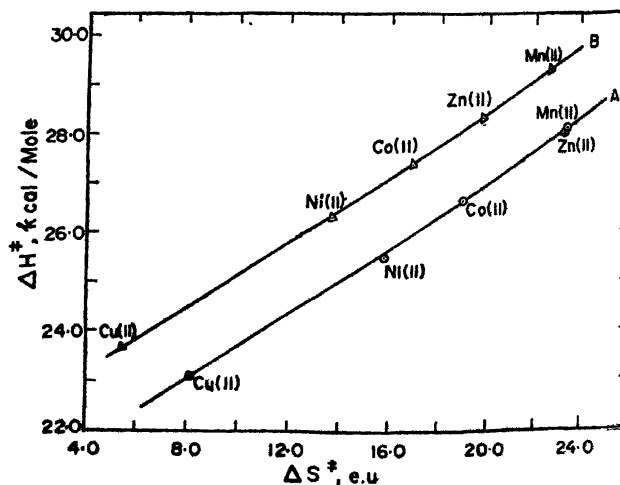

Fig. 2. A : [Cr(BigH)₃]³⁺ system ; B : [Co(BigH)₃]³⁺ system
Ionic strength, 1M

metal ions is also more or less linear (see Fig. 3). All these suggest the operation of identical mechanism in all these cases.
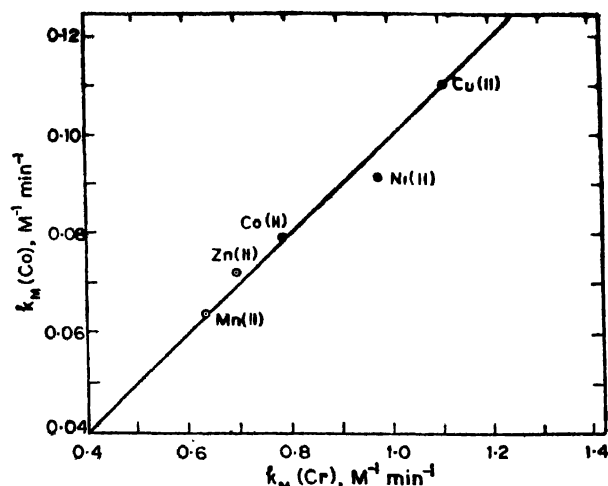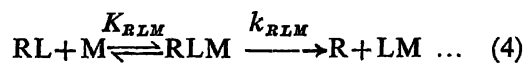

Fig. 8. Temp., 35°C, Ionic strength, 1M.

Taking all these facts into consideration, we can visualize the dissociation of the substrate complex, RL, in presence of the catalysing metal ion, M, as proceeding through the following sequence of changes :

$$RL + M \underset{}{\overset{K_{RLM}}{\rightleftharpoons}} RLM \xrightarrow{k_{RLM}} R + LM \ldots \quad (4)$$

Based on this,

$$k_M = K_{RLM} \cdot k_{RLM} \qquad \ldots \quad (5)$$

and this is similar to what has been observed for the metal ion catalysed dissociation of cis-$Cr(Ox)_2$-$(H_2O)_2^-$ ion[11]. Using the data reported earlier on the metal ion catalysed dissociation of cis-$Cr(Ox)_2(H_2O)_2^-$, it has now been found that the slope of the log k_M vs $Z^*/(r_{M^{2+}})^2$ plot for the system is 0.27 (at 25°, $\mu = 1M$) which is almost identical to the observed slope (0.26) (at 25°, $\mu = 0.1M$) of log K_{MOX} vs $Z^*/(r_{M^{2+}})^2$ plot. This clearly shows that k_M is proportional to K_{ML}, and the same is expected in the case of metal ion catalysed dissociation of tris-biguanide complexes also. This, therefore, affords a method for evaluating the value of K_{ML} for the monobiguanide complexes of the catalysing metal ions Mn(II), Co(II), Ni(II) and Zn(II) from a knowledge of the corresponding value for the Cu(II) complex reported in literature[6] and the experimental k_M values, from the following relation :

$$K_{ML}/K_{CuL} = k_M/k_{Cu} \qquad \ldots \quad (6)$$

$$\text{or,} \quad K_{ML} = K_{CuL} \cdot k_M/k_{Cu} \qquad \ldots \quad (7)$$

The K_{ML} values thus obtained from the study of Cr(III) and Co(III) biguanide systems are reported in Table 3. The fact that virtually identical values are obtained for any metal ion from both the systems further proves the correctness of this approach.

In the case of metal catalysed dissociation of cis-$Cr(Ox)_2(OH_2)_2^-$ it has been found that both Cu(II) and Ni(II) are much more effective than H$^+$ in weakening the Cr $-$ O bond as indicated by a con-

TABLE 3—VALUES OF K_{ML}

$K_{ML}(32° ; \mu, 1M)$

Metal ion[a]	From Cr(BigH)$_3^{3+}$ system	From Co(BigH)$_3^{3+}$ system
Ni(II)	1.09×10^{10}	1.06×10^{10}
Co(II)	0.84×10^{10}	0.87×10^{10}
Zn(II)	0.73×10^{10}	0.78×10^{10}
Mn(II)	0.65×10^{10}	0.67×10^{10}

(a) Under comparable condition, $K_{CuL} = 1.26 \times 10^{10}$ (ref. 6)

siderable reduction in the enthalpy of activation of the metal ion catalysed path compared to that of the H$^+$ catalysed path. However, H$^+$ is a much better electrophile than the bivalent metal ions for catalysing the dissociation of tris-biguanide complexes ; the metal ion catalysed paths have higher enthalpy of activation than the proton catalysed path. This indicates significantly weaker binding of the catalysing metal ion to the chelated biguanide presumably in the following fashion :
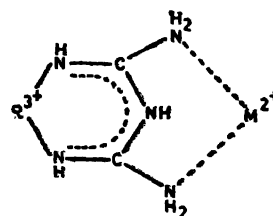
The weaker binding is obviously due to the electron densities on the nitrogen atoms of the chelated biguanide being much less than that on the free carbonyl oxygens of the oxalate chelate ring. Hence, a stronger bond is formed by the catalysing metal ions with the oxalate in the cis-$Cr(Ox)_2(H_2O)_2^-$.

Acknowledgement

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