

## Kinetics & Mechanism of Dissociation of Heterochelate Complexes: Acid-catalyzed Aquation of Oxinatobisbiguanidecobalt(III) Perchlorate

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Kinetics of acid-catalysed aquation of heterochelate complex, oxinatobisbiguanidecobalt(III) perchlorate has been investigated in the temperature range 30°-40°C in the presence of 0.05-0.3 mol dm<sup>-3</sup> perchloric acid. Under these conditions both the biguanide moieties undergo substitution by the aquo ligand simultaneously and the rates of substitution have been evaluated from the graphical biphasic plots. Release of both the biguanide moieties is acid-dependent, and bond-breaking is important in the transition state. Activation parameters for both the stages of aquation have been evaluated using Eyring's equation.

Substitution reactions, such as aquation of coordination complexes have mostly been investigated with those complexes in which the leaving groups are usually monodentate ligands<sup>1</sup> because of relatively simple mode of aquation. Non-leaving groups may comprise both unidentate as well as multidentate groups. Because of the chelate effect<sup>2</sup>, multidentate groups are more strongly bonded and in the presence of unidentate groups these do not act as the leaving groups and consequently complexities arise in the study of their substitution mechanisms. Such complexities are somewhat overcome if in mixed chelate complexes multidentate groups are chosen in such a way that while one acts as a non-leaving group, the other acts as a leaving group. The correctness of this approach has been demonstrated in some earlier works on the kinetics of aquation of several such complexes reported from our laboratory<sup>3-6</sup>. In continuation of the earlier work<sup>3-6</sup>, we present in this paper the results of the investigation on the kinetics of aquation of oxinatobisbiguanidecobalt(III) perchlorate. Biguanide having nitrogen donors at both ends forms a symmetrical chelate ring but the oxinate with nitrogen and oxygen donors forms an unsymmetrical chelate ring. This complex provides an interesting example for the study of the aquation mechanism because of the presence of a multidentate group as a leaving group, and an unsymmetrical chelating ligand.

### Materials and Methods

All the chemicals used were of AR grade and solutions were prepared in doubly distilled water.

#### *Oxinatobisbiguanidecobalt(III) perchlorate:*

The corresponding complex sulphate was prepared following the method of Dutta *et al.*<sup>7</sup>, and the complex perchlorate was obtained in solution by triturating an aqueous suspension of the complex sulphate with an

equivalent amount of barium perchlorate in a mortar each time before a kinetic run and filtering the precipitated barium sulphate formed.

#### *Rate measurements*

Aliquots (3 to 4 ml) were withdrawn at regular time intervals from thermally equilibrated ( $\pm 0.1^\circ\text{C}$ ) reaction mixture, quenched by cooling in ice-cold water and the absorbances were measured immediately in stoppered quartz cells using a ECIL spectrophotometer. The absorption spectra of the complex ion with various amounts of perchloric acid (0.05 mol dm<sup>-3</sup>) change with time at 30°C and above. Isosbestic points were not observed at any stage of the reaction.

#### *Stoichiometry of the reaction and identification of reaction products*

The absorption spectra of a 0.001 mol dm<sup>-3</sup> solution of the complex in the presence of 0.2 mol dm<sup>-3</sup> perchloric acid at different time intervals are given in Fig. 1. None of the spectra matches that of the diaquo complex,  $[\text{Co}(\text{BigH})_2(\text{H}_2\text{O})_2]^{3+}$ , indicating that the diaquo complex was not formed throughout the reaction course and that the oxinate did not act as a leaving group.

In order to identify the products of aquation, the reaction was carried out at 40°C in the presence of 0.1 mol dm<sup>-3</sup> acid for 6 hr, the reaction mixture neutralized with potassium bicarbonate, cooled, filtered to remove potassium perchlorate, the filtrate concentrated on a rotary evaporator and the residue analysed. It was found to contain cobalt(II) ion, biguanide as perchlorate and oxine. Cobaltous ion was identified by  $\alpha$ -nitroso- $\beta$ -naphthol spot test and biguanide was isolated as its copper complex from ammoniacal medium<sup>8</sup> and estimated gravimetrically.

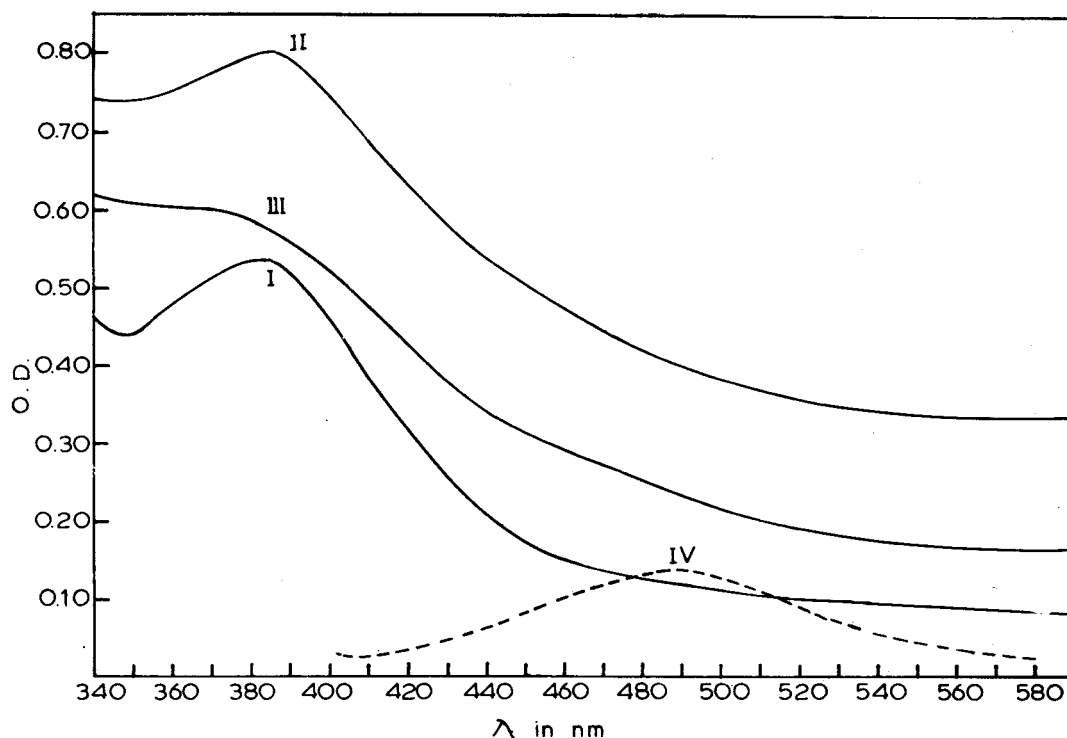
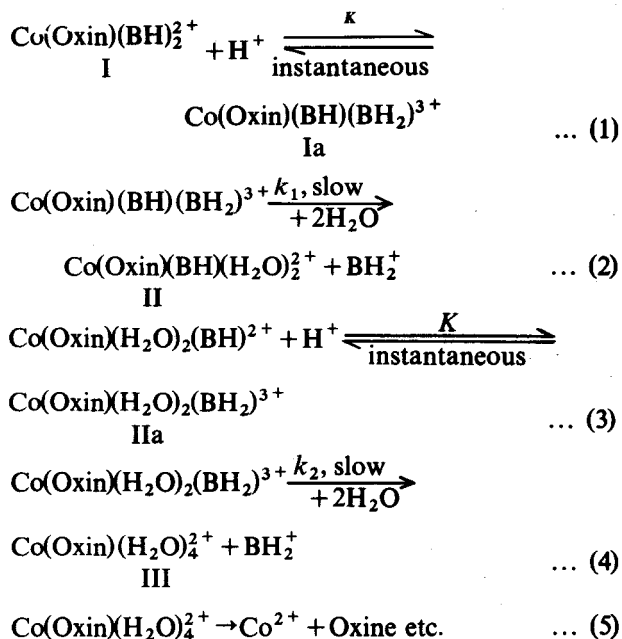


Fig. 1—Time-dependent spectra of  $1 \times 10^{-3} \text{ mol dm}^{-3}$  solution of the complex ion  $\text{Co}(\text{BH})_2(\text{Oxin})^{2+}$  in the presence of  $0.2 \text{ mol dm}^{-3}$   $\text{HClO}_4$  at room temperature ( $30^\circ$ ) [(I) Fresh solution (II) after 3 hr, (III) after 24 hr and (IV) spectrum of a  $1 \times 10^{-3} \text{ mol dm}^{-3}$  solution of  $\text{Co}(\text{BH})_2(\text{H}_2\text{O})_2^{3+}$  under similar conditions]

The colour of the solution at the initial stages of aquation was yellowish pink. As the reaction progressed the colour became deep pink with higher absorbance values, and only after a few hours, the colour intensity decreased along with the absorbance values. During the first 3-4 hr although absorbance values changed with time the solution remained clear. During this period dissociation of two biguanide groups had taken place. The biguanides thus released formed perchlorate salts which remained in water to give a clear solution. After the release of the two biguanide residues, the remaining tetraaquo complex decomposed spontaneously giving cobalt(II) ion and oxine. Oxine being insoluble in water, formed a colloidal suspension. Only above  $60^\circ$  coagulation of the colloidal suspension occurred. Since in the experimental acidic solution, oxine did not combine with cobalt(II) ion, it was extracted with chloroform and estimated titrimetrically<sup>9</sup>.

### Results and Discussion

Biguanide is more basic ( $pK_1 = 12.5$  at  $25^\circ$ )<sup>10</sup> than oxinate ion ( $pK_1 = 9.81$  at  $25^\circ$ )<sup>11</sup> and so in acid solution the former protonates before the latter. On the basis of the reaction products and stoichiometry, the various reactions (1-5) taking place during the aquation process are shown in Scheme 1

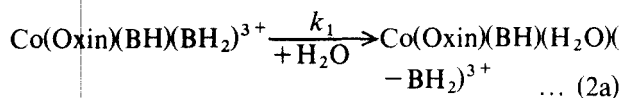


(Dissociation and reduction products)

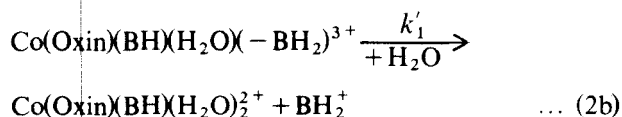
(BH = biguanide, Oxin = Oxinate radical)

### Scheme I

Equations (2) and (4) in Scheme 1 represent two separate rate-determining steps. However, each of these steps may comprise two steps (2a and 2b)



and



The step (2a) indicates ring-opening with the formation of a monodentate biguanide complex and the step (2b) indicates loss of the biguanide. Nevertheless, ring-opened complex species with monodentate biguanide has not been observed at any stage of the reaction and till to date no monodentate biguanide complex is known. So  $k_1$ , the rate constant for step (2b) cannot be slow. Only step (2a) is slow while step (2b) is fast and the loss of each biguanide moiety apparently takes place stepwise in the reaction steps (2) and (4) of Scheme 1.

Unimolecular plots are not linear indicating that more than one reaction takes place during the aqutation of the complex ion. This further indicates that the rate-determining steps (2) and (4) take place simultaneously. The values of  $k_1$  and  $k_2$  have been derived from the observed variation in absorbance of the solution with time, by a method similar to that used in the determination of rate of decay of two radioactive parent-daughter components when there is no equilibrium<sup>12</sup>. Absorbance of the complex species in aqueous solution remains unaltered immediately after the addition of acid suggesting that the original complex species (I) and its protonated form have similar absorbances. The absorbance of the diaquo species (II) could not be determined with certainty, however, it was assumed that its protonated form (IIa) also has similar absorbance value.

The observed rates for the first and the second stages of dissociation as obtained from the biphasic plots<sup>13</sup>

are given in Table 1. The observed rates do not depend on [complex] but linearly vary with [acid]. The plots of [acid] versus  $k_{\text{obs}}$  for both the stages pass through origin showing that there is no acid-independent path. From the slopes of these linear plots second-order rate constants for both the stages were evaluated and are also given in Table 1. The rates are reproducible within  $\pm 3\%$ .

On the basis of the reactions (1) to (4), the rate of dissociation of the complex for each stage in acid medium may be given by Eq. (6),

$$\text{Rate} = k[\text{conjugate acid}] = kK[\text{complex}][\text{H}^+] \dots (6) \\ = k^*[\text{complex}][\text{H}^+]$$

where  $k^*$  is the second order rate constant,  $K$  is the equilibrium constant for the formation of the protonated species (conjugate acid, CA) and  $k$  (either  $k_1$  or  $k_2$ ) is the rate constant for the rate-determining step.  $K$  is assumed to be very small, so that  $[\text{I}] \gg [\text{Ia}]$  and  $[\text{II}] \gg [\text{IIa}]$ .

Activation parameters for the acid-catalyzed aqutation of the bisbiguanide and the monobiguanide complexes (first and second stages of aqutation) in the experimental temperature range have been evaluated using the Eyring equation<sup>14</sup>. These values are also given in Table 1. These activation parameter values are smaller than those of other bisbiguanide and monobiguanide complexes respectively<sup>3-6</sup> and are comparable to those of diaquobisbiguanide complex<sup>15</sup>. The smaller enthalpy value of the present complex indicates a much greater rate of aqutation in comparison to that of other complexes under similar conditions. Moreover, upto now it has been observed<sup>5</sup> that all the monobiguanide complexes are very stable, show a very high value of enthalpy and correspondingly a smaller rate of aqutation than the bisbiguanide complexes, and the conditions required for the dissociation of the two biguanide moieties are wide

Table 1—Rate Data for Acid-catalyzed Dissociation of Oxinatobisbiguanidecobalt(III) Complex at Different Acidity and Temperature [Complex] =  $2 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $I = 1.0 \text{ mol dm}^{-3}$

| Temp.<br>(°C) |                     | Obs. rates $\times 10^4 (\text{s}^{-1})$<br>at $[\text{HClO}_4]$ (mol<br>$\text{dm}^{-3})$ |      |       |      |      | $10^3 k_1^*$<br>( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) | $10^3 k_2^*$<br>( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) |
|---------------|---------------------|--------------------------------------------------------------------------------------------|------|-------|------|------|-----------------------------------------------------------------|-----------------------------------------------------------------|
|               |                     | 0.05                                                                                       | 0.10 | 0.15  | 0.20 | 0.30 |                                                                 |                                                                 |
| 30            | First stage, $k_1$  |                                                                                            | 2.0  | 3.2   | 4.21 | 6.24 | 2.05                                                            | 5.2                                                             |
|               | Second stage, $k_2$ |                                                                                            | 5.0  | 8.3   | 9.8  | 15.8 |                                                                 |                                                                 |
| 35            | First stage, $k_1$  | 0.59                                                                                       | 2.5  | 4.22  | 5.28 | 8.01 | 2.71                                                            | 6.65                                                            |
|               | Second stage, $k_2$ | 3.14                                                                                       | 6.5  | 10.20 | 13.0 | 19.5 |                                                                 |                                                                 |
| 40            | First stage, $k_1$  | 2.71                                                                                       |      | 6.54  | 8.1  |      | 4.80                                                            | 9.32                                                            |
|               | Second stage, $k_2$ | 4.22                                                                                       |      | 14    | 19.2 |      |                                                                 |                                                                 |

$\Delta H^\ddagger (\text{kJ mol}^{-1})$ : First stage ( $k_1$ ) =  $56 \pm 3.2$ ; and second stage ( $k_2$ ) =  $42 \pm 3$

$\Delta S^\ddagger (\text{JK}^{-1} \text{mol}^{-1})$ : First stage ( $k_1$ ) =  $113 \pm 12$ ; and second stage ( $k_2$ ) =  $134 \pm 14$

apart in acidity and temperature. Nevertheless, in the present case there is no such distinction in conditions and both the biguanides are released under the same experimental conditions with some differences in rates. For this reason their activation parameters are also similar. As the monodentate complex could not be isolated, the rate of its aquation has been determined *in situ* from the biphasic plot. Oxinate, which is a bulky substituent on a five-membered chelate ring, may not form thermodynamically more stable complex with cobalt(III) than that formed by biguanide; but due to a basic site on the biguanide, which helps protonation, kinetically the latter becomes less stable. So, under the present circumstances biguanide acts as a more labile leaving group than the oxinate.

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