CHAPTER VI

SUMMARY
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The work embodied in this dissertation deals with the study of the acid hydrolysis reaction of bromopentaammine cobalt(III) ion in aqueous medium. The objectives of the present investigation may be briefly stated as follows.

The mechanism of the equation reactions of haloamine cobalt(III) complexes is fairly well understood at present. Haloamine cobalt(III) complex cations are known to form ion-pairs with polyvalent anions. The mechanism of the reactions of such ion-pairs in aqueous solution has not been looked into in an unequivocal manner. The present investigation, therefore, has been undertaken to elucidate the mechanism of the reactions of the ion-pairs of bromopentaammine cobalt(III) perchlorate with certain bivalent anions.

The kinetic method has been utilised throughout this work to throw light on the mechanism of the reaction. The reaction rates were mostly followed by potentiometric titration of the bromide ion released by aquation with silver nitrate solution. The spectrophotometric method has also been used for following reaction rates. On the basis of the objectives mentioned above, the results obtained have been collected and discussed in the following paragraphs.
The present investigation pertains to the determination of the acid hydrolysis rate constants of the complex, \([\text{Co(NH}_3\text{)}_5\text{Br}]^{2+}\), in the presence of the bivalent anions: Sulphate, oxalate, malonate, succinate, maleate and phthalate. It was observed that the rate of aquation of the complex was significantly accelerated in the presence of the added anions. Such catalytic effect of anions has been ascribed to the formation of more labile ion-pairs. The \(k_{\text{obs}}\) vs concentration of the anion plots were found to be asymptotic to the anion axis at higher concentration of the anion, signifying complete conversion of the complex ion into its ion-pairs, and thus giving a limiting value to the observed rate constants.

The rate data were analysed in terms of Wyatt-Davies treatment. The ion-pair rate constants and the association constants of the ion-pairs were calculated to explore the reactivity pattern of the ion-pairs. The results revealed that the rate accelerating influence followed the sequence: sulphate < oxalate < malonate < succinate < maleate < phthalate. Comparison of the rate constants of the ion-pairs with their respective stability constants show that the reactivity of the ion-pairs is not governed by their stability. A specific anion effect in the reactivity of the ion-pairs was perceptible, but all attempts to correlate the same with known parameters of the ion-pairing ligands proved futile. The greater
reactivity of the ion-pairs compared to that of the free complex ion has, therefore, been attributed solely to the charge effect. This points to a dissociative mechanism for the aquation reaction of the ion-pairs. The magnitude of the activation entropies and a reasonably good linear free energy correlation led support to such a postulate. However, product analysis experiments revealed that sulphato or carbaxylatopentaammine cobalt(III) ion was one of the reaction products.

In order to describe different path-ways for the reaction of the ion-pairs, the observed rate constant which was a measure of the bromide ion released upon aquation was considered to be a composite term consisting of the following processes:

(a) Aquation of the bromopentaammine cobalt(III) ion leading to the production of aquo-complex by a pseudo-unimolecular process.

(b) Aquation of the bromopentaammine cobalt(III) ligand ion-pairs leading to the formation of aquo-pentaammine cobalt(III)-ligand ion-pairs by a pseudo-unimolecular process.

(c) Interchange reaction involving exchange between the inner sphere bromide ion and the outer sphere associating ligand of the ion-pair, leading to the formation of the sulphato or carbaxylato pentaammine
The formation of the sulphato or carbaxylato complex could also result from the anation of the aquo-pentaammine complex ligand ion-pair (reverse reaction of path 'b').

The product analysis experiment was performed spectrophotometrically. The rate constants for each of the reaction paths were evaluated and their significance has been discussed. The results reveal that only about 5 per cent of the total bromide release results from the direct entry of the associating ligand into the bromo complex. Further, it was found that nearly 80 per cent of the sulphato or carbaxylato complex formed results via the anation of the aquopentaammine complex-ligand ion-pair. These results have been substantiated by the excellent agreement between the experimental optical density and the optical density calculated on the basis of the complete reaction scheme suggested above.

Thermodynamic parameters for the ion-association process were also calculated. The negative enthalpy changes indicated exothermic association.