Kinetic Studies of Fast Reactions: Electron Transfer between Hexaaquocobalt(III) Ion & 2-Mercaptoisobutyric Acid*

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MUCH of the current interest in electron transfer reactions between metal ions and organic compounds containing sulphydryl and polarizable hydroxyl groups is due to the expectation that these may serve as model systems for studying biochemical redox reactions since many active sites of redox enzymes are thought to involve both, a sulphur atom and a metal ion.

In reactions of hexaaquocobalt(III) with organic compounds containing thiol groups (thiouric acid and cysteine) formation of precursor complexes as transient intermediates has been reported. The intermediates have been characterized for both Co^3+aq. and CoOH^2+aq. ions using stopped-flow technique. However, in reactions with thiourea and N-substituted thioureas, no such complex formation could be detected either kinetically or spectrophotometrically.

The electron transfer reactions of 2-mercaptoisobutyric acid (2MIBA) with Fe(III) and V(V), like those of thiomalic acid, proceed via intermediate complex formation. This led us to investigate the Co(III)-2MIBA system with a view to exploring the effect of gem-dimethyl group on the nature and reactivity of the transient intermediates, if these are formed.

Materials and Methods

The preparation, standardization and storage of stock solutions of hexaaquocobalt(III) ion were carried out as described earlier. 2MIBA (Koch-Light) was used as such. Solutions were prepared and used the same day after checking their strength spectrophotometrically. The stoichiometry of the reaction was determined by spectrophotometric titration of the substrate with the oxidant at 400 and 600 nm and it was found to be 1.00±0.05 in accord with the equation:

2 RSH + 2 Co^3+aq. → RSSR + 2 Co^2+aq. + 2H+

Rate data were obtained using a stopped-flow apparatus which was a modification of the apparatus described previously.

Ionic strength (μ) was maintained at a constant value of 1.5M using sodium perchlorate (Fluka). Hydrogen ion concentration was varied from 0.2 to 1.4M using a stock solution made up from AR grade material.

The solutions were prepared in distilled water obtained using an all glass assembly. Solutions were allowed to equilibrate at each temperature (constant to ±0.01°C) for at least 30 min before the start of an experiment.

The organic compound (0.2 g) was titrated with Co(III) perchlorate until Co(III) was in slight excess. A precipitate was obtained under these conditions. This was filtered, washed with cold water and dried in vacuo over anhydrous CaCl_2. Elemental analyses and IR studies indicated the product to be a disulphide. This was confirmed by obtaining the same compound by oxidation of 2MIBA using iodine and comparing its IR spectrum and elemental analyses with those of the above mentioned product. Presence of S-S bond was also confirmed by laser Raman spectroscopy.

Results and Discussion

The rate data are consistent with second order kinetics, first order with respect to each reactant, over the concentration range studied (Tables 1-4). Under second order conditions also the values of k_2 are fairly constant up to 80% completion of the reaction. Optical densities of hexaaquocobalt(III) ion obtained from extrapolation of rate plots to t=0 were identical with those for similar concentrations of the oxidant alone. No kinetic or spectrophotometric evidence was found for the existence of
any transient intermediates like those observed previously for the reactions of Co(H2O)63+ with chloride4, thiomalic acid5, malic acid5 and cysteine5. Ligand variation at two different [H+] (Tables 1 and 2) also failed to indicate kinetically any complex formation5. In case where complex formation is not indicated Eq. (1) holds:

\[ k_{\text{obs}} = [L][k_1 + k_2 K_{\text{H}^+}]/(1 + K_{\text{H}^+}) \]  

... (1)

This is in keeping with the following sequences of reactions:

1. \[ \text{Co}^{3+} \text{aq.} + \text{H}_2\text{O} \rightarrow \text{CoOH}^{2+} + \text{H}^+ \]  
2. \[ \text{CoO}^{2+} \text{aq.} + \text{L} \rightarrow \text{Co}^{2+} + \text{L}^2- \]  

CoOH2+ + L \rightarrow Co2+ + L. \[ k_{\text{obs}} \] values (Table 5) suggest that the rate-controlling step is substitution-controlled, the electron transfer being fast. The slower reaction of 2MIBA than that of thiomalic acid may be due to the presence of gem-dimethyl group which keeps SH and COOH groups of 2MIBA in more or less a rigid conformation. Coordination of SH to COOH2+ is thus hindered by the non-bonded interaction between COOH and the neighbouring coordinated H2O molecule.

A comparison of the rate of electron transfer between CoOH2+ and 2MIBA with the rate of complex formation of CoOH2+ with thiomalic acid (Table 5) suggests that the rate-controlling step is substitution-controlled, the electron transfer being fast. The slower reaction of 2MIBA than that of thiomalic acid may be due to the presence of gem-dimethyl group which keeps SH and COOH groups of 2MIBA in more or less a rigid conformation. Coordination of SH to COOH2+ is thus hindered by the non-bonded interaction between COOH and the neighbouring coordinated H2O molecule.

A comparison of \[ k_{2}K_{\text{H}^+} \] values (Table 5) suggests a dissociative interchange type of mechanism with the exception of reactions with hydroquinone and iodide ion where unusually high rate of electron transfer precludes inner-sphere mechanism. The changes in the observed rate constants are explained on the basis of (i) ligand effects on the forward rate constant7, (ii) effect of solvent structure11 and (iii) solvating effect of coordinated OH- ions3. However, positive entropies are indicative of a high electronic transition probability.
between the two reactants 12 which arises due to
greater reorganization of the hydration spheres
resulting in "unfrozen" water molecules in the
formation of each activated complex. For the
present system there is no unambiguous proof to
suggest a dissociative interchange type of mechanism
except the basis of analogy.

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