ABSTRACT

Detailed kinetic studies of the formation of the di-μ-hydroxo-μ-sulfito bis[triamminecobalt(III)] ion and the μ-hydroxo-μ- sulfito bis[ethylenediaminecobalt(III)] ion from tri-μ-hydroxo-bis [triamminecobalt(III)] perchlorate (triol) and di-μ-hydroxo bis [ethylenediaminecobalt(III)] perchlorate (diol) respectively in aqueous buffered sulfite have been done. In the former reaction, the results were interpreted by a mechanism involving the reaction of triol and its ring-opened hydroxo-aqua species with HSO_3^- and SO_2 respectively to form the μ-sulfito product. The corresponding rate constants at 25 °C are k_1=1.33 ± 0.02 $M^{-1}s^{-1}$ ($\Delta H^{\neq}$=12.21 ± 0.31 kcal mol^{-1}, $\Delta S^{\neq}$= -17.22 ±6.14 cal K^{-1} mol^{-1}) and k_2 = (1.27 ±0.12) x 10^6 M^{-1} s^{-1} ($\Delta H^{\neq}$ = 18.01 ±0.03 kcal mol^{-1}, $\Delta S^{\neq}$ = 29.83 ±0.35 cal K^{-1} mol^{-1}) The latter reaction was interpreted by a mechanism involving the formation of an adduct between diol and SO_2 with a rate constant of k_1(25 °C) = 10.0 ±1.0 s^{-1} ($\Delta H^{\neq}$ = 10.2 ±0.6 kcal mol^{-1}, $\Delta S^{\neq}$ = -20.0 ±0.05 cal K^{-1} mol^{-1}).

The tri-bridged complex, di-μ-hydroxo-μ-sulfito bis [triamminecobalt(III)] undergoes two types of slow reactions depending on the pH of the system. The first of these, taking place within the range 2 < pH < 3, is a redox process that produces cobalt(II) and sulfate in a ratio of 2:1. Rate constants, k_{obs}, for the process are of the form $k_{obs} = k_1 + k_2K[H^+]$ at these pH's and $0.04 < [S]_T < 0.10$ M. The values of k_1 and k_2 at 25 °C and I = 0.5 M ($LiClO_4$) are (5.13 ±0.04)x10^{-5} s^{-1} and (7.15 ±0.04)x10^{-3} s^{-1} with the corresponding temperature parameters being ($\Delta H_1^{\neq}$ = 28.1 ±1.4 kcal mol^{-1}, $\Delta S_1^{\neq}$ = 28.1 ±0.1 cal K^{-1} mol^{-1}) and $\Delta H^{\neq}$ = 18.4 ±0.7 kcal mol^{-1},

$\Delta S^{\neq}$ = -6.9 ± 0.1 cal K^{-1} mol^{-1}. However, over the range 6 < pH < 7 and 0.04 < $[S]_T$ < 0.10 M the redox reaction no longer occurs, the only observable reaction being addition of a second sulfite group to yield the complex, μ-dihydroxo-μ-sulfito bis (triamminecobalt(III))(diamminesulfitocobalt(III)). A mechanism consistent with the data involves the substitution of HSO_3^- and SO_3^{2-} for NH_3 which is apparently labilized due to the proximity of the bridging sulfito ligand.

The μ-hydroxo-μ-sulfito bis [ethylenediaminecobalt(III)] complex undergoes isomerisation in the ranges 2.6 < pH < 5.2 and 0.01 < $[S]_T$ <0.10 M and I = 0.5 M ($LiClO_4$) with a rate constant equal to (3.23 ± 0.08) x $10^{-5}s^{-1}$ at 25 °C. The reaction is believed to be base-catalysed but the detailed mechanism of the process appears to be complicated.

The acid hydrolysis of the di-μ-hydroxo-μ-sulfito bis (triamminecobalt(III)) and the μ-hydroxo-μ-sulfito bis (ethylenediaminecobalt(III)) complexes have been studied under the following conditions:

0.03 < $[H^+]$ < 1.0 M and 15 < T < 25 °C at I = 2.0 M ($LiClO_4$);

0.03 < $[H^+]$ < 0.09 M and 30 < T < 40 °C at I = 1.0 M ($LiClO_4$);

respectively. A water assisted path has been detected for the dibridged species only, with the rate constant, k_o = (1.06 ± 0.86) x 10^{-5} s^{-1} at 30 °C ($\Delta H^{\neq}$ = 27.4 ± 4.3 kcal mol^{-1}, $\Delta S^{\neq}$ = 8.5 ± 0.3 cal $K^{-1}mol^{-1}$). The values of the acid dependent paths for the two species at 25 and 30 °C are respectively ($\Delta H^{\neq}$ in kcal mol^{-1}, $\Delta S^{\neq}$ in cal K^{-1} mol^{-1}): (1.48 ± 0.28) x $10^{-2}s^{-1}$ (14.1 ± 0.1, -29.1 ± 0.1); (4.14 ± 0.12) x $10^{-4}s^{-1}$ (16.2 ± 2.1, 121.2 ± 0.1).