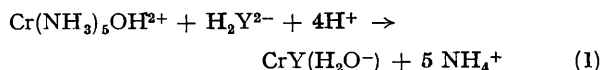


Carbon Dioxide Catalysis of Formation of Carboxylato-chromium(III) Complexes

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Summary Carbon dioxide, in low concentration, acts as an efficient (base dependent) catalyst for formation of amino acid complexes of Cr^{III}, probably through formation of a chelated carbonato-complex.

PREVIOUS reports clearly show that reactions of Cr^{III} aquoions with carboxylate ligands do not follow the simple dissociative mechanism usual for anation reactions of Cr^{III}.² We have used a pH-stat to study the kinetics of reaction (1),



where Y⁴⁻ represents ethylenedinitrilotetra-acetate ion.

Although it has not been noted in previous kinetic studies of this or related reactions,^{3,4} we report that reaction (1) proceeds exclusively through catalytic paths involving CO₂. Beck⁵ has reported CO₂ catalysis of Cr^{III} substitution and Rao *et al*⁶ have used this effect for an analytical method involving rapid formation of the Cr^{III}-EDTA complex. Unless the total carbonate concentration [CO₂]_t is carefully controlled, induction periods and other irregularities occur in kinetic runs. However, if this concentration is controlled, the reaction follows pseudo-first-order kinetics for several half times and reproducible rate constants are obtained.

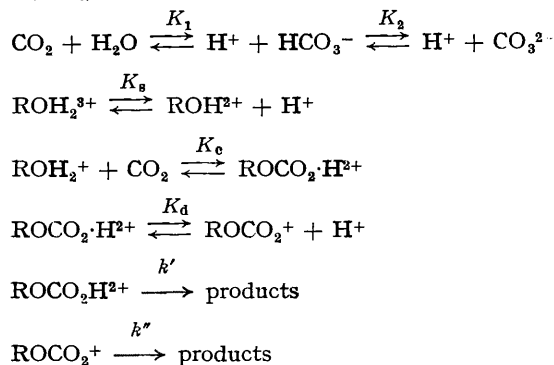
Reaction (1) follows the rate law

$$\text{Rate} = k_{\text{obs}}[\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}]_t[\text{CO}_2]_t f[\text{H}^+].$$

Change in the concentration of the ligand does not change

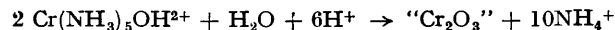
the rate. The rate increases with increasing pH to a maximum near pH 6.8 and then decreases.

The variation of rate with pH is fitted by the mechanism [R is Cr(NH₃)₅]:



K_3 is 7.142×10^{-5} M, K_d is taken as 4×10^{-7} M, by analogy with Co^{III},⁸ K_1 is 9×10^{-7} M. Using a value of 3.5×10^{-8} M for K_2 ,[†] the values $k'K_6 = 2.55 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ and $k''K_6 = 2.70 \text{ M}^{-1} \text{ s}^{-1}$ are obtained. The major pathway for the reaction is that involving k'' . These values may be compared with the rate of CO₂-catalysed ¹⁸O exchange of ROH²⁺ ($7 \text{ M}^{-1} \text{ s}^{-1}$).⁷

A reaction like (1) but involving Cr(NH₃)₆³⁺ as substrate is about 10³ times slower than reaction (1). Rates of reaction of *cis*- and *trans*-Cr(NH₃)₄(H₂O)(OH)²⁺ are similar and close to that of Cr(NH₃)₅OH²⁺. The aquation of the substrate



[†] This value is somewhat larger than the value given by direct measurement (3×10^{-9} M).⁹ The larger value is required by the shape of the rate-pH profile at pH values greater than 8, and other effects may complicate the reaction here. No other simple variation (*e.g.* variation of K_d) will give a satisfactory fit for the data.

also followed pseudo-first-order kinetics, well at low $[\text{CO}_2]_t$ (ca 10^{-6} M) and less well at higher concentrations. The initial rate of this reaction was close to that of reaction (1) and also exhibited a linear dependence on $[\text{CO}_2]$ and complex dependence on $[\text{H}^+]$.

These results indicate that the "spin" of a co-ordinated CO_2 , especially when coupled with deprotonation, can lead

to reaction at other co-ordination sites on Cr^{III} . Formation of a chelated intermediate seems likely.

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