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),

$$Cr(NH_3)_5OH^{2+} + H_2Y^{2-} + 4H^+ \rightarrow CrY(H_2O^-) + 5\,NH_4^+ \qquad (1)$$

where Y^{4-} 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 CO_2. Beck[5] has reported CO_2 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 $[CO_2]_t$ 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

$$\text{Rate} = k_{obs}[Cr(NH_3)_5OH_2^{3+}]_t[CO_2]_t \cdot f[H^+].$$

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 $Cr(NH_3)_5$]:

$$CO_2 + H_2O \overset{K_1}{\rightleftharpoons} H^+ + HCO_3^- \overset{K_2}{\rightleftharpoons} H^+ + CO_3^{2-}$$

$$ROH_2^{3+} \overset{K_s}{\rightleftharpoons} ROH^{2+} + H^+$$

$$ROH_2^+ + CO_2 \overset{K_c}{\rightleftharpoons} ROCO_2{\cdot}H^{2+}$$

$$ROCO_2{\cdot}H^{2+} \overset{K_d}{\rightleftharpoons} ROCO_2^+ + H^+$$

$$ROCO_2H^{2+} \xrightarrow{k'} \text{products}$$

$$ROCO_2^+ \xrightarrow{k''} \text{products}$$

K_s is[7] $1{\cdot}42 \times 10^{-5}$ M, K_d is taken as 4×10^{-7} M, by analogy with Co^{III},[8] K_1[9] is 9×10^{-7} M. Using a value of $3{\cdot}5 \times 10^{-8}$ M for K_2,† the values $k'K_c = 2{\cdot}55 \times 10^{-2}$ M^{-1} s^{-1} and $k''K_c = 2{\cdot}70$ M^{-1} s^{-1} are obtained. The major pathway for the reaction is that involving k''. These values may be compared with the rate of CO_2-catalysed ^{18}O exchange of ROH^{2+} (7 M^{-1} s^{-1}).[7]

A reaction like (1) but involving $Cr(NH_3)_6^{3+}$ as substrate is about 10^3 times slower than reaction (1). Rates of reaction of *cis*- and *trans*-$Cr(NH_3)_4(H_2O)(OH)^{2+}$ are similar and close to that of $Cr(NH_3)_5OH^{2+}$. The aquation of the substrate

$$2\,Cr(NH_3)_5OH^{2+} + H_2O + 6H^+ \rightarrow \text{“}Cr_2O_3\text{”} + 10NH_4^+$$

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† 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 $[CO_2]_t$ (*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 $[CO_2]$ and complex dependence on $[H^+]$.

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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