Cacodylic Acid Catalysed Metal-complex Formation Reactions

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The catalytic effect of cacodylic acid (dimethylarsinic acid) on the complex formation reaction of zinc(II) with pentane-2,4-dione is demonstrated; cacodylic acid also catalyses the acid dissociation of the nickel(II) triglycine complex.

In aqueous solution many reactions involving the formation and hydrolysis of metal complexes also involve acid–base equilibria. This may arise from the use of protonated ligands or from hydrolysis of the metal ions themselves. This necessitates that during the course of kinetic studies, the pH must be carefully controlled. At high acidities, the hydrogen ion concentration is usually in pseudo-first-order excess thus maintaining a constant acidity. However, at lower acidities (higher pH values) the use of buffers is required to maintain a constant hydrogen ion concentration. Where metal ions are present, ideally, the buffer used should not form complexes with the metal ions present. Elias *et al.*[1] have described a range of suitable buffers which can be used in the pH range 3–8. However, they are not suitable for studies requiring spectrophotometric monitoring below 350–400 nm. An alternative buffer which has been very widely used both in chemical and biological studies involving metal ions is cacodylic acid (dimethylarsinic acid), $Me_2As(O)OH$ which has a pK of 6.27.[2]

During the course of recent stopped-flow investigations of the complex formation and hydrolysis reactions of zinc(II) complexes of β-diketones, we have found that varying the total cacodylic acid concentration present in the reactant solutions has a considerable effect on the pseudo-first-order rate constants obtained. Fig. 1 shows a plot of k_{obs} against cacodylic acid concentration for reaction of Zn^{2+} ion with pentane-2,4-dione (Hpd) at three different concentrations of total zinc (pH = 6.5). Although the overall rate-law is quite complex and is not included in this communication, the data in Fig. 1 clearly demonstrate the catalytic effect of cacodylic acid on the complex formation reactions of Zn^{2+} with this ligand.

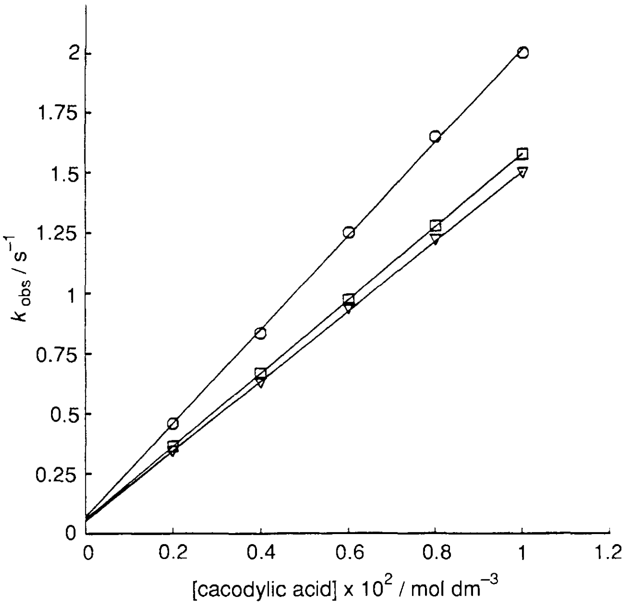

Fig. 1 Plot of k_{obs} against total cacodylic acid concentration for reaction of Zn^{2+} with pentane-2,4-dione in aqueous solution at 25 °C and I = 0.5 mol dm^{-3} $NaClO_4$; pH = 6.5; $[Hpd]_{total}$ = 0.0001, $[zinc(II)]_{total}$ = 0.001 (○), 0.002 (□) 0.003 (▽) mol dm^{-3}

The well characterised acid dissociation of the nickel(II) triglycine complex has previously been used as a model to investigate the catalytic activity of buffers and their conjugate bases.[3,4] A preliminary investigation of the effect of cacodylic acid on this reaction has also been carried out. Previous studies of this[3,4] and similar systems[5] have shown that k_{obs} has the general form of eqn. (1). In eqn. (1), k_w is the acid-independent pathway, k_H is the H^+ catalysed pathway, k_{HB} represents the general acid catalysis pathway and k_B is the general base catalysis pathway. In terms of the dissociation constant of cacodylic acid, eqn. (1) may be written as eqn. (2) where $[HB]_T$ is the total cacodylic acid concentration and K_a is the dissociation constant.

$$k_{obs} = k_w + k_H[H^+] + k_{HB}[HB] + k_B[B^-] \qquad (1)$$

$$k_{obs} = k_w + k_H[H^+] + k_{HB}[HB]_T\{1 + K_a/[H^+]\}^{-1} + k_B[HB]_T\{1 + [H^+]/K_a\} \qquad (2)$$

For the nickel(II) triglycine system, the values of k_w and k_H have been previously reported to be 0.088 s^{-1} and 9.5 × 10^4 dm^3 mol^{-1} s^{-1} respectively.[5] In the present investigation which has been carried out at pH = 6.5, the contribution of both of these terms to the k_{obs} values, which are in the range of 2–10 s^{-1}, is quite small.

A number of experiments were carried out in which both the hydrogen ion and cacodylic acid concentrations were varied. Fitting the kinetic data to eqn. (2) gives the following values for the unknown constants k_{HB} and k_B respectively: 180 (±23) and 3.31(±13) dm^3 mol^{-1} s^{-1}. While the value of k_B is not significantly different from zero, the magnitude of the k_{HB} term demonstrates that the protonated form of cacodylic acid is quite an effective general acid catalyst, comparable to 4-chloropyridine.[1]

The results presented here clearly demonstrate the inherent dangers of using cacodylic acid as a buffer to control the hydrogen ion concentration in kinetic and equilibrium investigations of the reactions of metal ions and their complexes. In each investigation, experiments should be carried out in order to determine if the cacodylic acid or its conjugate base exert a catalytic effect.

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