Metal–Aminopolycarboxylic Acid Complexes. Part V.[1] Kinetic Study of the Dissociation of Cadmium Complexes of *N*-Carboxymethyliminobis(ethylenenitrilo-*N'N'*-diacetic acid) by a Polarographic Method

By **Peter Letkeman,** Department of Chemistry, Brandon University, Brandon, Manitoba R7A 6A9, Canada
John B. Westmore,* Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

The polarographic behaviour of Cd^{2+} in the presence of excess of *N*-carboxymethyliminobis(ethylenenitrilo-*N'N'*-diacetic acid) (H_5ceda) has been studied over the pH range 2—7. Three different polarographic waves can be distinguished. The wave occurring at the most negative potentials and highest pH values is assigned to an irreversible reduction of $[\mathrm{Cd(Hceda)}]^{2-}$ [equation (i)], where $k_C = 5{\cdot}4\times10^4$ l mol^{-1} s^{-1} and $k_{-C} = 3{\cdot}6$ s^{-1}. The wave occurring

$$[\mathrm{Cd(Hceda)}]^{2-} \underset{k_C}{\overset{k_{-C}}{\rightleftharpoons}} [\mathrm{Cd(ceda)}]^{3-} + \mathrm{H}^+ \qquad \text{(i)}$$

at intermediate potentials and pH values arises by irreversible reduction of $[\mathrm{Cd(H_2ceda)}]^-$ formed in reaction (ii)

$$[\mathrm{Cd(H_2ceda)}]^- \underset{k_B}{\overset{k_{-B}}{\rightleftharpoons}} [\mathrm{Cd(Hceda)}]_2 + \mathrm{H}^+ \qquad \text{(ii)}$$

where $k_B = (1{\cdot}1 \pm 0{\cdot}9) \times 10^4$ l mol^{-1} s^{-1} and $k_{-B} = 4 \pm 3$ s^{-1}. The reversible wave occurring at the most positive potentials and lowest pH values arises by reduction of aquated Cd^{2+} formed in reaction (iii), where

$$\mathrm{Cd}^{2+} + \mathrm{H_3ceda}^{2-} \underset{k_A}{\overset{k_{-A}}{\rightleftharpoons}} [\mathrm{Cd(H_2ceda)}]^- + \mathrm{H}^+ \qquad \text{(iii)}$$

$k_A = (2{\cdot}5 \pm 2{\cdot}0) \times 10^5$ and $k_{-A} = (2{\cdot}0 \pm 1{\cdot}6) \times 10^8$ l mol^{-1} s^{-1}. The stability constant log $K_{\mathrm{Cd(ceda)}} = 18{\cdot}8$; this and the rate constants are conditional constants obtained at an ionic strength of 0·2M and at 25° C. The proton-assisted dissociation of the complex is interpreted as stepwise unwrapping from one end of the molecule with cadmium–nitrogen fissions corresponding to the rate-determining steps.

INFORMATION on the thermodynamics and kinetics of equilibria between metal ions and aminopolycarboxylic acids in aqueous solution is of importance both from a theoretical viewpoint and because of the wide use of aminopolycarboxylic acids in analytical applications. In favourable circumstances the polarographic method can be used to obtain such information and, for Cd^{2+}, has been applied to the study of solutions of its complexes with glycine,[2] H_3nta,[3-5] H_4edta,[5-12] H_4cdta,[13] H_3hedta,[14]

---

[1] Part IV, P. Letkeman and J. B. Westmore, *Canad. J. Chem.*, 1972, **50**, 3821.

[2] J. Biernat and M. Baranowska-Zralko, *Roczniki Chem.*, 1964, **38**, 1703.

[3] J. Koryta, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2903.

[4] C. V. D'Alkaine and J. Koryta, *Coll. Czech. Chem. Comm.*, 1969, **34**, 2138.

[5] J. Koryta and I. Koessler, *Coll. Czech. Chem. Comm.*, 1950, **15**, 241.

[6] R. L. Pecsok, *J. Chem. Educ.*, 1952, **29**, 597.

[7] J. Heyrovsky and M. Matyas, *Coll. Czech. Chem. Comm.*, 1951, **16**, 455.

[8] N. Tanaka, I. T. Oiwa, and M. Kodama, *Analyt. Chem.*, 1956, **28**, 1555.

[9] R. W. Schmid and C. N. Reilley, *J. Amer. Chem. Soc.*, 1958, **80**, 2101.

[10] N. Tanaka, R. Tamamushi, and M. Kodama, *Z. phys. Chem.* (*Frankfurt*), 1958, **14**, 141.

[11] J. Koryta and Z. Zabransky, *Coll. Czech. Chem. Comm.*, 1960, **25**, 3153.

[12] G. H. Aylward and J. W. Hayes, *Analyt. Chem.*, 1965, **37**, 195.

[13] G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, 1954, **37**, 937.

[14] Y. Koike and H. Hamaguchi, *J. Inorg. Nuclear Chem.*, 1967, **29**, 473.

and H_6beda.[15,*] Koryta and Koessler [5] and Pecsok [6] (who used high concentrations of H_4edta) found no polarographic reduction wave for the cadmium–H_4edta complex, but Heyrovsky and Matyas [7] reported a doublet wave and Tanaka *et al.*[8] found a single wave. Schmid and Reilley [9] were able to resolve these contradictory observations by studying the kinetic character of the reduction waves. In this paper we describe a systematic study of solutions of Cd^{2+} with *N*-carboxymethyliminobis(ethylenenitrilo-*N'N'*-diacetic acid) (H_5ceda) by the polarographic method. The results complement and extend those obtained in our earlier ^{1}H n.m.r. study of this system [16] and are of value in the interpretation of mechanisms of proton-assisted dissociation of complexes formed from multidentate ligands.

EXPERIMENTAL

N-Carboxymethyliminobis(ethylenenitrilo-*N'N'*-diacetic acid) (H_5ceda) (J. T. Baker) was recrystallized from hot water, dried, weighed, and dissolved in distilled water containing sufficient sodium hydroxide to affect solution. This was then made up to a sufficient volume to give a 0·01M solution.[†] A stock solution of Cd^{2+} was prepared from cadmium(II) acetate (J. T. Baker). Chloroacetic acid–chloroacetate buffers were used for the pH range 2—4 and acetic acid–acetate buffers for the range 4—7. Sodium perchlorate was used to adjust the ionic strength of the test solution to 0·2M. Triton X-100 was obtained from Rohm and Hass, and gelatin from B.D.H. All solutions were stored in polyethylene bottles. Test solutions were prepared by taking appropriate aliquot portions of the stock, buffer, and sodium perchlorate solutions, then diluting to nearly the volume required. The pH was measured (Radiometer type PH28 pH meter calibrated at pH 2·00, 4·01, and 6·86 with Beckman buffers), then adjusted by addition of sodium hydroxide or perchloric acid as required. The solution was then made up to its final volume with distilled water.

The test solutions were placed in one arm of an H cell,[17] of resistance less than 100 Ω, immersed in a water thermostat, deoxygenated with nitrogen, and polarograms recorded with a Sargent model XXI polarograph. The potential of the dropping electrode was recorded against a saturated calomel electrode contained in the other arm of the H cell. When accurate potential measurements were required a Rubicon type B precision potentiometer was used. Capillary characteristics were measured at open circuit at a number of mercury heads (corrected for interfacial tension at the mercury drop). For the most frequently used conditions the characteristics were: h = 50 cm, $h_{corr.}$ = 48·4 cm, m = 1·733 mg s^{-1}, t = 5·02 s; h = 60 cm, $h_{corr.}$ = 58·4 cm, m = 2·071 mg s^{-1}, t = 4·20 s; and h = 70 cm, $h_{corr.}$ = 68·4 cm, m = 2·396 mg s^{-1}, t = 3·63 s, where the symbols have their conventional meanings. In analysis of the experimental data, t values at the potentials of the wave plateaux were used. To test the kinetic character of the waves, intermediate h values were also used and extended up to h = 80 cm.

RESULTS

In the pH range 2·5—3·5 polarograms of Cd^{2+} in the presence of H_5ceda exhibited maxima. These maxima could be suppressed by the addition of small amounts of gelatin or Triton X-100. Gelatin seemed to be the better of the two, a concentration of 0·001% being sufficient to suppress the maxima without distorting the polarographic waves.

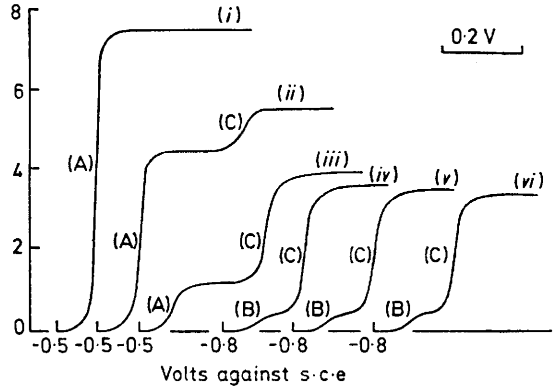


FIGURE 1 Effect of H_5ceda concentration on the polarograms at [Cd^{II}] = 1·0 × 10^{-3}M, pH 4·50 (acetate buffer), h = 60 cm, I = 0·2M, and 25 °C: [H_5ceda] = 0 (*i*), 4 × 10^{-4} (*ii*), 8 × 10^{-4} (*iii*), 1 × 10^{-3} (*iv*), 2 × 10^{-3} (*v*), and 1 × 10^{-2}M (*vi*)

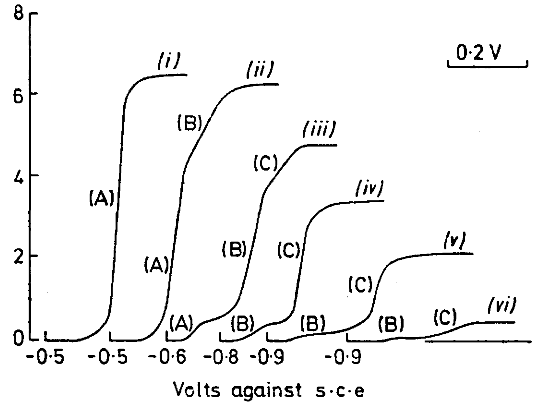


FIGURE 2 Effect of pH on the polarograms at [Cd^{II}] = 1·0 × 10^{-3}M, [H_5ceda] = 2·0 × 10^{-3}M, h = 60 cm, I = 0·2M, and 25 °C: pH = 2 (*i*), 2·5 (*ii*), 3·5 (*iii*), 4·5 (*iv*), 5 (*v*), and 6 (*vi*)

Figure 1 illustrates the addition of increasing amounts of H_5ceda to a given concentration of Cd^{2+} at pH 4·5. Figure 2 shows the effect of pH on solutions containing Cd^{2+} and H_5ceda in the ratio 1 : 2. In these figures three different polarographic waves can be distinguished which will subsequently be referred to as waves (A)—(C) and which appear at increasingly negative potentials respectively. The heights and positions of the three waves were strongly pH dependent, as verified by studies on solutions with metal : ligand concentration ratios of 1 : 1, 1 : 2, 1 : 4, 1 : 8, and 1 : 10. Results obtained for the 1 : 2 ratio are shown in Figures 3 and 4. The characteristics of the three waves are summarized in Table 1. Recalling the properties of reversible against

---

[*] H_3nta = Nitrilotriacetic acid, H_4edta = ethylenedinitrilo-*NNN'N'*-tetra-acetic acid, H_4cdta = cyclohexane-1,2-diyldinitrilo-*NNN'N'*-tetra-acetic acid, H_3hedta = *N*-(2-hydroxyethyl)-ethylenedinitrilo-*NN'N'*-triacetic acid, and H_6beda = *NN'*-biscarboxymethylethylenedi-iminobis(ethylenenitrilo-*N''N''*-diacetic acid).

[†] 1M = 1 mol dm^{-3}.

[15] G. Conradi, M. Kopanica, and J. Koryta, *Coll. Czech. Chem. Comm.*, 1965, **30**, 2029.

[16] P. Letkeman and J. B. Westmore, *Canad. J. Chem.*, 1971, **49**, 2073.

[17] L. Meites, 'Polarographic Techniques,' Interscience, New York, 1965, 2nd edn., p. 321.

irreversible, and of diffusion against kinetically controlled, waves listed in Part IV [1] the following conclusions about the waves can be drawn.

(*a*) Wave (A) changes from a diffusion-controlled to a kinetically controlled reduction wave as the pH increases and the wave height decreases. The electrochemical reduction step is reversible.

TABLE 1

Characteristics of the polarographic waves of Cd^{II}–H_5ceda solutions

Wave	Total metal-ion concentration/mM	Total ligand concentration/mM	*I*/M	pH	Suppressor (% gelatin)	Reciprocal gradient/mV	Dependence of i_l on mercury head	Temperature coefficient between 20 and 50 °C/ % per °C
(A)	1·0	2·0	0·2	3·5	0·002	31 ± 2	Partially dependent *	2·0
(A)	1·0	8·0	0·2	3·5	0·002		Partially dependent *	2·5
(B)	1·0	2·0	0·2	4·5	0	60 ± 2	Independent	1·8
(B)	1·0	8·0	0·2	4·5	0	40 ± 2	Independent	1·5
(C)	1·0	2·0	0·2	5·75	0	75 ± 2	Nearly independent †	1·9
(C)	1·0	8·0	0·2	5·75	0	70 ± 2	Nearly independent †	1·8

* i_l Increased, but by less than required for diffusion control. † i_l Increased slightly as *h* increased.

(*b*) At small wave heights, *e.g.* at pH 4·5 and 5·75 respectively, the properties of waves (B) and (C) are consistent with those of irreversible, kinetically controlled, waves. The fact that i_l is independent of *h* for each wave over-rides the observation that the temperature coefficients are unusually small for kinetically controlled reduction waves. It has also been reported that low temperature coefficients for kinetic currents are common when acid–base equilibria are involved.[18]

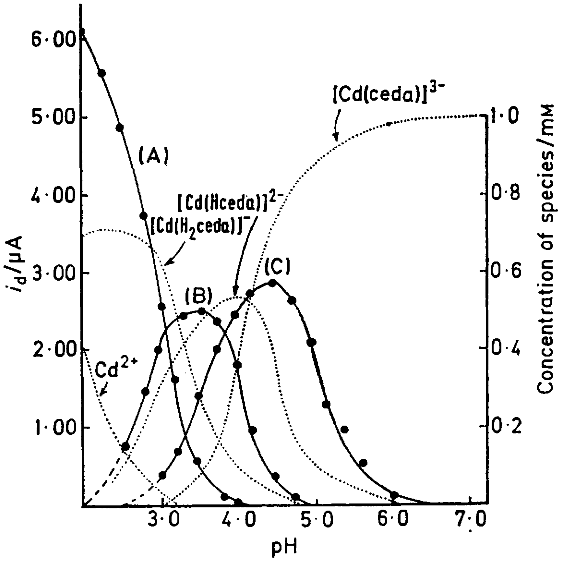


FIGURE 3 Limiting currents of waves (A)—(C) as a function of pH (——) and calculated concentrations of cadmium-containing species (····) at $[Cd^{II}]$ = 1·0 × 10^{-3}M, $[H_5ceda]$ = 2·0 × 10^{-3}M, *h* = 60 cm, *I* = 0·2M, and 25 °C

Supplementary Studies.—To supply data required for the mathematical interpretation of the characteristics of wave (A), the diffusion currents and half-wave potentials of Cd^{2+} were measured in solutions identical to those of the test solutions except that they did not contain H_5ceda. The values of the half-wave potentials in the buffer solutions are shown in Figure 4.

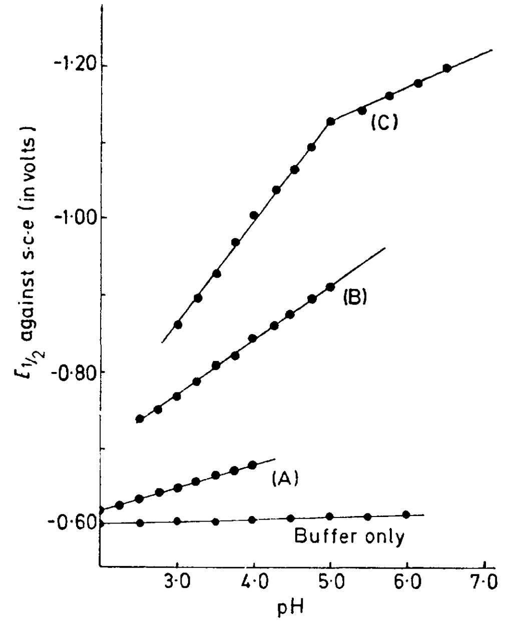


FIGURE 4 Half-wave potentials of waves (A)—(C) as a function of pH and of free cadmium ion in the same buffer at $[Cd^{II}]$ = 1·0 × 10^{-3}M, $[H_5ceda]$ = 2·0 × 10^{-3}M, *h* = 60 cm, *I* = 0·2M, and 25 °C

Treatment of Polarographic Data.—The three waves (A)—(C) can be analysed by the polarographic kinetic-current treatment to obtain data on the rates of chemical equilibria in the solutions. The equations arising from this treatment were presented in a form suitable for the present studies in Part IV.[1] Equilibrium constants are also required. Of the reported studies [19-24] on the Cd^{II}–

---

[18] P. Zuman in 'Methods in Enzymology,' ed. K. Kustin, Academic Press, New York, 1969, vol. 16, p. 135.

[19] E. Wanninen, *Suomen Kem.*, 1955, **B28**, 146.

[20] E. J. Durham and D. P. Ryskiewich, *J. Amer. Chem. Soc.*, 1958, **80**, 4812.

[21] G. Anderegg, P. Nageli, F. Müller, and G. Schwarzenbach, *Helv. Chim. Acta*, 1959, **42**, 827.

[22] S. Chabarek, A. E. Frost, M. A. Doran, and N. J. Bicknell, *J. Inorg. Nuclear Chem.*, 1959, **11**, 184.

[23] J. H. Holloway and C. N. Reilley, *Analyt. Chem.*, 1960, **32**, 249.

[24] V. T. Krumina, K. V. Astakhov, S. A. Barkov, and V. I. Kornev, *Russ. J. Phys. Chem.*, 1968, **42**, 1334 (2524).

H_5ceda system only one [22] includes data for formation of doubly protonated complexes, the values being $K_{Cd(ceda)} = [Cd(ceda)^{3-}]/[Cd^{2+}][ceda^{5-}] = 10^{18\cdot9}$, $K_{Cd(Hceda)}{}^{H} = [Cd(Hceda)^{2-}]/[H^+][Cd(ceda)^{3-}] = 10^{4\cdot17}$, and $K_{Cd(H_2ceda)}{}^{H} = [Cd(H_2ceda)^{-}]/[H^+][Cd(Hceda)^{2-}] = 10^{3\cdot32}$ l mol^{-1}. Our present results, and those reported earlier,[16] support the *existence* of $[Cd(H_2ceda)]^-$, but, because of difficulties associated with potentiometric determinations, the reported value of $K_{Cd(H_2ceda)}{}^{H}$ may be inaccurate. We have taken its value to be $10^{3\cdot3\pm0\cdot5}$ in this work. The concentrations of the complex ions, after correction for the complexing effect of the buffer, are compared with the heights of the polarographic waves in Figure 3. (Throughout this paper, published equilibrium constants are used without any attempt to correct for effects of ionic strength. We used a constant ionic strength of 0·2M throughout.) The waves are discussed in order of increasing complexity of interpretation, *i.e.* in reverse order.

Wave (C). The assumption that wave (C) is due to reduction of $[Cd(Hceda)]^{2-}$ resulted in a successful application of the kinetic-current treatment. In the pH range where wave (C) is a kinetic wave, $[Cd(Hceda)]^{2-}$ is produced by rate-determining protonation of $[Cd(ceda)]^{3-}$ [equation (1)]. Under kinetic-control conditions the relation of the

$$\underset{\text{reducible}}{[Cd(Hceda)]^{2-}} \underset{k_C}{\overset{k_{-C}}{\rightleftharpoons}} [Cd(ceda)]^{3-} + H^+ \text{ (rate determining)} \qquad (1)$$

mean limiting current, i_l, to the mean current, i_d, expected for a diffusion-controlled process is given by equation (2).[1]

$$i_l/(i_d - i_l) = 0\cdot886[H^+](k_C t K_{Cd(Hceda)}{}^{H})^{\frac{1}{2}} \qquad (2)$$

A plot of log $[i_l/(i_d - i_l)]$ against pH, shown in Figure 5, had a gradient of $-1\cdot14$, which is acceptably close to the required value of -1. Since the conditions required for kinetic control of this wave improve with increasing pH, data from the graph at pH 6·0 were used to calculate $k_C = 5\cdot4 \times 10^4$ l mol^{-1} s^{-1} and $k_{-C} = 3\cdot6$ s^{-1}.

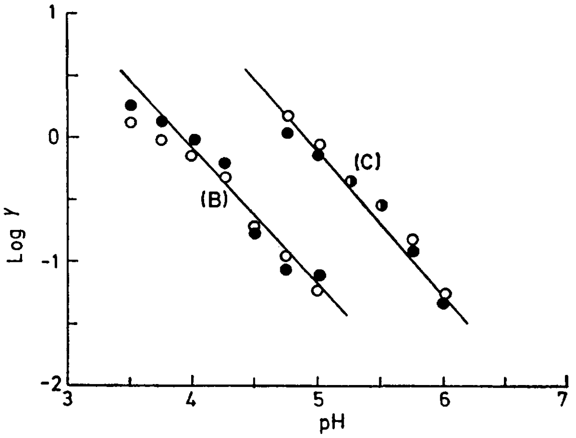


FIGURE 5 Test of the kinetic-current theory for waves (B) and (C). For (B), log $Y = [i_l/(i_d - i_l)] + \log \alpha_{Cd(Hceda)}$; for (C), log $Y = \log [i_l/(i_d - i_l)]$. Conditions: $[Cd^{II}] = 1\cdot0 \times 10^{-3}$M, $[H_5ceda] = 2\cdot0 \times 10^{-3}$ (●) and $8\cdot0 \times 10^{-3}$M (○), h = 60 cm, I = 0·2M, and 25 °C

An alternative interpretation of wave (C) which would give the observed pH dependence is as in equations (3)

$$\underset{\text{reducible}}{Cd^{2+}} + ceda^{5-} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [Cd(ceda)]^{3-} \text{ (rate determining)} \qquad (3)$$

$$ceda^{5-} + 2H^+ \rightleftharpoons H_2ceda^{3-} \quad \text{(fast)} \qquad (4)$$

and (4) for which the solution is (5), where the terms used

$$i_l/(i_d - i_l) = 0\cdot886[H^+](k_d t/K_{Cd(ceda)} c_L K_4 K_5)^{\frac{1}{2}} \qquad (5)$$

and their values are given in Part IV.[1] This interpretation can be rejected for the following reasons. (i) The quantity $i_l/(i_d - i_l)$ should be proportional to $c_L{}^{-\frac{1}{2}}$. In fact, it is independent of c_L, as can be verified by inspection of Figure 5 and was confirmed from unreported experiments at other values of c_L. (ii) The orders of magnitude of the rate constants required to satisfy this interpretation were evaluated assuming $[H^+] = 10^{-6}$M, $i_l/(i_d - i_l) = 0\cdot05$, t = 4 s, $K_{Cd(ceda)} = 10^{18\cdot9}$ l mol^{-1}, $c_L = 10^{-2}$M, $K_4 = 10^{-8\cdot7}$ mol l^{-1}, and $K_5 = 10^{-10\cdot5}$ mol l^{-1}. The values obtained were $k_d \simeq 6 \times 10^6$ s^{-1} and $k_f \simeq 6 \times 10^{25}$ l mol^{-1} s^{-1}. This value for k_f is obviously impossible for a diffusion-controlled bimolecular reaction.

Further interpretation of the mechanistic origin of this and other waves is deferred until the Discussion section when the behaviour of all the waves will have been described.

Wave (B). Under kinetic-control conditions this wave was found to correspond to equation (6) where $[Cd(H_2ceda)]^-$

$$\underset{\text{reducible}}{[Cd(H_2ceda)]^-} \underset{k_B}{\overset{k_{-B}}{\rightleftharpoons}} [Cd(Hceda)]^{2-} + H^+ \qquad (6)$$
(rate determining)

reduces more readily (*i.e.* at more-positive potentials) than $[Cd(Hceda)]^{2-}$, and where equation (7) holds.[1] A plot of

$$i_l/(i_d - i_l) = 0\cdot886[H^+](k_B t K_{Cd(H_2ceda)}{}^{H})^{1/2}/\alpha_{Cd(Hceda)} \qquad (7)$$

log $[i_l/(i_d - i_l)] + \log \alpha_{Cd(Hceda)}$ against pH, shown in Figure 5, had a gradient of $-1\cdot08$, which is acceptably close to the required value of -1. As for wave (C), data from the graph were selected near the high-pH limit. At pH 5·0 the values $k_B = (1\cdot1 \pm 0\cdot9) \times 10^4$ l mol^{-1} s^{-1} and $k_{-B} = 4 \pm 3$ s^{-1} were obtained. Equation (7) takes account of the pH dependence of $[Cd(Hceda)]^{2-}$ by means of the 'α' function.[1] Use of this function implies that $[Cd(Hceda)]^{2-}$ in solution can be formed much more rapidly by protonation of $[Cd(ceda)]^{3-}$ than it is consumed by conversion to $[Cd(H_2ceda)]^-$ and subsequent reduction (in much the same way that $[H^+]$ is maintained by a buffer). The fact that k_C is *ca.* five times as great as k_B means that this approximation is good at pH 5, where $[Cd(ceda)^{3-}] \gg [Cd(Hceda)^{2-}]$, but becomes poorer at lower pH.

An alternative approach was considered. The treatment of systems involving successive protonations has been given by Koutecky.[25,26] For the system (8), assuming

$$A^{2-} \overset{H^+}{\rightleftharpoons} HA^- \overset{H^+}{\rightleftharpoons} \underset{\text{reducible}}{H_2A} \qquad (8)$$

the diffusion coefficients of H_2A, HA^-, and A^{2-} to be equal, Koutecky's equation simplifies to (9) where K_{a1} and K_{a2}

$$i_l/(i_d - i_l) = 0\cdot866[H^+]^2(kt/K_{a1})^{1/2}/([H^+] + K_{a2}) \qquad (9)$$

have their usual meanings and k is the rate constant for

---

[25] J. Koutecky, *Coll. Czech. Chem. Comm.*, 1954, **19**, 1093.
[26] J. Koutecky, *Chem. listy*, 1954, **48**, 360.

protonation of HA^-. When $K_{a2} \gg [H^+]$, which is a common situation, then $i_l(i_d - i_l)$ is proportional to $[H^+]^2$. As the pH decreases the dependence of $i/i_l(i_d - i_l)$ on $[H^+]$ may decrease from second to first order. The experimental data for wave (B), assumed to be due to (10)

$$[Cd(ceda)]^{3-} \xrightleftharpoons{H^+} [Cd(Hceda)]^{2-} \xrightleftharpoons{H^+} \underset{\text{reducible}}{[Cd(H_2ceda)]^-} \quad (10)$$

and assuming equal diffusion coefficients for the complexes, agree with this analysis, which is, of course, equivalent to that given above. The argument is strengthened by estimating the rates of the four reactions in this last sequence. Using the values for k_C, k_{-C}, k_B, and k_{-B} obtained above and concentrations of $[Cd(ceda)]^{3-}$ and $[Cd(Hceda)]^{2-}$ from Figure 3 shows that at pH 5 the slow step in the sequence is $[Cd(Hceda)]^{2-} + H^+ \longrightarrow [Cd(H_2ceda)]^-$ as required for equations (6) and (7) to be applicable.

Wave (A). This wave is due to a reversible electrochemical reduction. Its height was much greater than expected from the equilibrium concentration of uncomplexed Cd^{2+} (see Figure 3). Wave (A) can be explained by the reduction of uncomplexed Cd^{2+} produced by rate-determining dissociation of its H_5ceda complex in the diffusion layer. Application of the kinetic-current treatment in the pH region where the equilibrium concentration of Cd^{2+} is insignificant, *i.e.* when pH >3 (Figure 3), shows that the major contribution to production of wave (A) under kinetic-control conditions comes from sequence (11)

$$\underset{\text{reducible}}{Cd^{2+}} + H_3ceda^{2-} \rightleftharpoons [Cd(H_3ceda)] \rightleftharpoons [Cd(H_2ceda)]^- + H^+ \quad (11)$$

where it is not possible to determine mathematically which reaction is rate determining. For reasons to be presented in the Discussion section, the preferred interpretation is that the major contribution to wave (A) involves rate-determining proton-assisted dissociation of $[Cd(H_2ceda)]^-$ to give free Cd^{2+} at the electrode surface, *i.e.* the contribution of $[Cd(H_3ceda)]$ to the reaction sequence is minor. In this case the reaction reduces to (12) and the dependence

$$\underset{\text{reducible}}{Cd^{2+}} + H_3ceda^{2-} \underset{k_A}{\overset{k_{-A}}{\rightleftharpoons}} [Cd(H_2ceda)]^- + H^+ \quad (12)$$

of i_l on pH is readily obtained by analogy from ref. (1) as (13). Values of $\alpha_{Cd(H_2ceda)}$ required to test this equation

$$\left(\frac{i_l}{i_d - i_l}\right)\left(1 + \frac{i_l}{i_d} \cdot \frac{c_M}{c_L} \cdot \frac{\alpha_{H_3ceda}}{\alpha_{Cd(H_2ceda)}}\right)^{1/2} = 0{\cdot}886[H^+](k_A t \alpha_{Cd(B)} \alpha_{H_3ceda}/K_{eq} c_L)^{1/2}/\alpha_{Cd(H_2ceda)} \quad (13)$$

are subject to errors in the value of $K_{Cd(Hceda)}{}^H$. Using the value of $10^{3{\cdot}3 \pm 0{\cdot}5}$ cited earlier a plot of the logarithm of the left-hand side of equation (13) against $\frac{1}{2}(\log \alpha_{H_3ceda} + \log \alpha_{Cd(B)}) - \log \alpha_{Cd(H_2ceda)} - pH$, shown in Figure 6, had a gradient of 1·25, rather higher than the required value of unity. The high value may arise, in part, from errors in equilibrium constants used in the treatment under these conditions, but could also arise from the presence of acetate complexes, or possibly a further proton-assisted dissociation competing with the indicated reaction, particularly at low pH. In addition, as for waves (B) and (C), conditions required for kinetic control of (A) improve with increasing pH. Thus, data from the graph for pH 4·0 were used to calculate $k_A = (2{\cdot}5 \pm 2{\cdot}0) \times 10^5$ and $k_{-A} = (2{\cdot}0 \pm 1{\cdot}6) \times 10^8$ l mol^{-1} s^{-1}. The value of $K_{eq} = 10^{2{\cdot}9 \pm 0{\cdot}5}$ was obtained from $K_{eq} = K_{Cd(ceda)} K_{Cd(H_2ceda)}{}^H K_{Cd(Hceda)}{}^H K_3 K_4 K_5$. Values of ionization constants for H_5ceda were given in Part IV.[1] Finally, we note that, although in equation (12) the concentration of $[Cd(H_2ceda)]^-$ may be quite small, Figure 3 shows that it is relatively large compared to the amount consumed in the production of wave (A) so that the rate of production of $[Cd(H_2ceda)]^-$ from $[Cd(Hceda)]^{2-}$ is not a factor in the theoretical treatment.

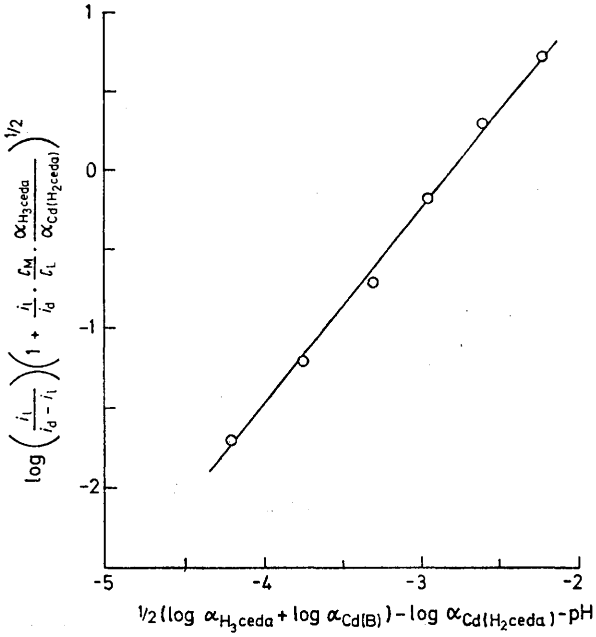


FIGURE 6 Test of kinetic-current theory for wave (A) at [Cd^{II}] = 1·0 × 10^{-3}M, [H_5ceda] = 8·0 × 10^{-3}M, h = 60 cm, I = 0·2M, and 25 °C

Calculation of Equilibrium Constants.—The polarographic method of determining formation constants from half-wave potentials requires a reversible electron-transfer electrode reaction. Hence, only wave (A) could yield information of this type. For a system where the complexes are in labile equilibrium except for *one* slow step governing the kinetic wave the apparent stability constant, $K_{app.}$, is given by equation (7) of ref. 1 as (14). Further-

$$\log K_{app.} = \frac{n}{0{\cdot}0591}(E_{\frac{1}{2}}{}^k - E_{\frac{1}{2}}{}^s) - \log \frac{i_l}{i_d} - \log c_L{}^0 \quad (14)$$

more,[1] it was shown that equation (15) holds. Equation

$$\log K_{app.} + \log \alpha_{ceda} = \log K_{Cd(ceda)} + \log \alpha_{Cd(ceda)} \quad (15)$$

(16) follows from the definition of the 'α' function [1] and

$$\alpha_{Cd(ceda)} = 1 + [H^+]K_{Cd(Hceda)}{}^H + [H^+]^2 K_{Cd(Hceda)}{}^H K_{Cd(H_2ceda)}{}^H + \ldots, \textit{etc.} \quad (16)$$

can be rewritten as (17). In Figure 7 the curve shown is

$$\alpha_{Cd(ceda)} = 1 + 10^{\log K_{Cd(Hceda)}{}^H - pH} + 10^{\log K_{Cd(Hceda)}{}^H + \log K_{Cd(H_2ceda)}{}^H - 2pH} + \ldots, \textit{etc.} \quad (17)$$

the best fit (least-squares method) to the experimental data using only two K^H type parameters as variables, and is given by (18) which gives $\log K_{Cd(ceda)} = 18{\cdot}8$, log $K_{Cd(Hceda)}^{H}$ = 3·58, and log $K_{Cd(H_2ceda)}^{H}$ = 3·30 which can be compared with the values of 18·9, 4·17, and 3·3

$$\log K_{app.} + \log \alpha_{ceda} = 18{\cdot}81 + \log(1 + 10^{3{\cdot}30-pH} + 10^{6{\cdot}88-2pH}) \quad (18)$$

respectively used earlier in the paper.[22] A better fit to the experimental points could have been obtained by including further terms in equation (18) but was not considered physically meaningful. The deviations from the behaviour required by equation (14) probably occur because at low pH more than one step governs the kinetic character of wave (A). On raising the pH it is to be anticipated that the reaction $[Cd(H_2ceda)]^- + H^+ \longrightarrow Cd^{2+} + H_3ceda^{2-}$ will eventually become the rate-determining step and the conditions required to satisfy equation (14) become more closely fulfilled. In support of this we note that with increasing pH the experimental results gave a limiting value of log $K_{app.}$ + log α_{ceda} which leads to a value for $K_{Cd(ceda)}$) in excellent agreement with the probably more reliable potentiometric determination.[22] More importantly, the close agreement between the values for $K_{Cd(ceda)}$ lends strong support to the interpretation that the origin of wave (A) is the reduction of free Cd^{2+} formed by dissociation of its H_5ceda complex.

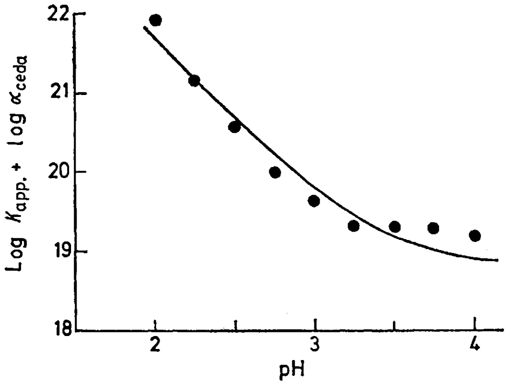
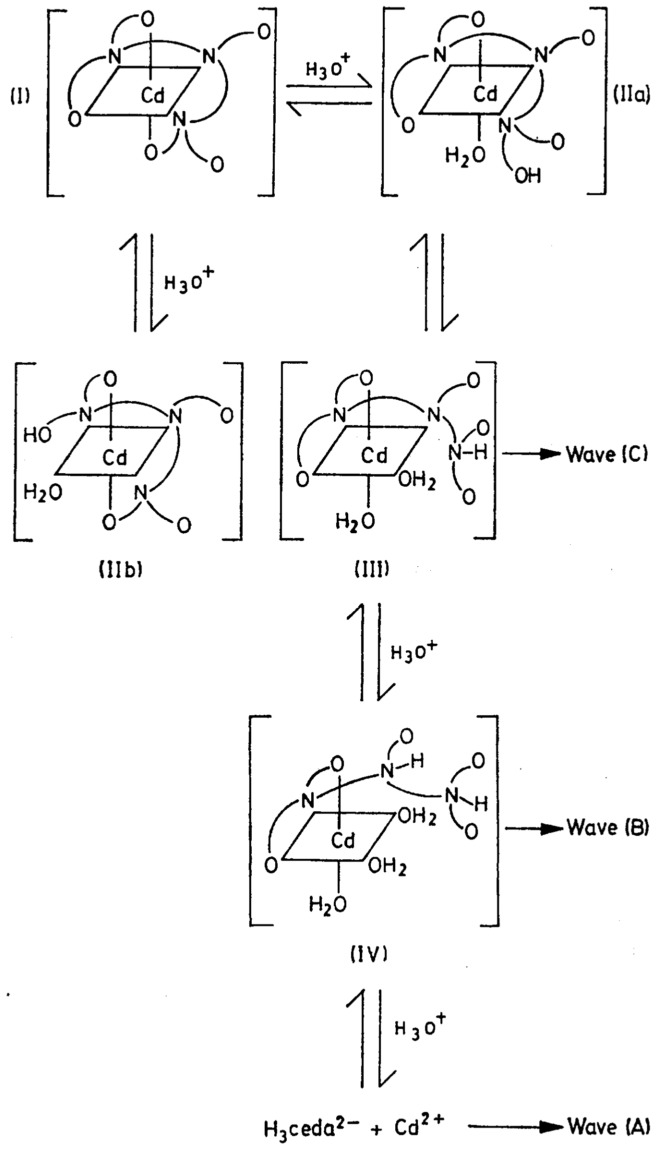


FIGURE 7 Values of log $K_{app.}$ + log α_{ceda} as a function of pH at [Cd^{II}] = 1·0 × 10^{-3}, [H_5ceda] = 2·0 × 10^{-3} and 8·0 × 10^{-3}M, h = 60 cm, I = 0·2M, and 25 °C

DISCUSSION

N.m.r.[16] and potentiometric [22] studies have shown that protonation of the $[Cd(ceda)]^{3-}$ complex starts to become appreciable when the pH is lowered to *ca.* 5 and furthermore the unbound centre carboxylate group and terminal nitrogen atoms both serve as sites for protonation. Thermodynamically, the nitrogen sites protonate slightly more readily than the centre carboxylate group. However, in addition to thermodynamic preferences for protonation, we must also consider whether a given site of protonation will lead to a more readily reducible complex. Proton attachment at a non-co-ordinated carboxylate group (such as one of the terminal ones, or the one at the centre) will not lead to a more easily reducible complex. Only when protonation occurs at a donor atom, accompanied or preceded by fission of that particular metal–ligand bond and entry of a water molecule into the primary co-ordination shell of the metal ion, will a more readily reducible species be formed. The highly labile metal–water bonds, with average lifetime *ca.* 10^{-8}—10^{-9} s for Cd^{2+},[27] provide an opportunity for electron transfer to occur at the electrode surface. The mechanisms of dissociation of multidentate ligands have been extensively investigated. Of particular significance to the present work are those studies related to the dissociation of labile aminopolycarboxylate complexes of diamagnetic metal ions.[28-36]



SCHEME Proposed dissociation pathways (for simplicity, charges are omitted and only mechanistically important protonations are shown).

---

[27] F. A. Cotton and G. Wilkinson in 'Advanced Inorganic Chemistry,' Interscience, New York, 1972, 3rd edn., p. 657.

[28] J. L. Sudmeier and C. N. Reilley, *Inorg. Chem.*, 1966, **5**, 1047.

[29] R. J. Kula and G. H. Reed, *Analyt. Chem.*, 1966, **38**, 697.

[30] J. D. Carr, K. Torrance, C. J. Cruz, and C. N. Reilley, *Analyt. Chem.*, 1967, **39**, 1358.

[31] R. J. Kula and D. L. Rabenstein, *J. Amer. Chem. Soc.*, 1967, **89**, 552.

[32] D. L. Rabenstein and R. J. Kula, *J. Amer. Chem. Soc.*, 1969, **91**, 2492.

[33] D. L. Rabenstein, *J. Amer. Chem. Soc.*, 1971, **93**, 2869.

[34] G. H. Reed and R. J. Kula, *Inorg. Chem.*, 1971, **10**, 2050.

[35] J. D. Carr and D. R. Baker, *Inorg. Chem.*, 1971, **10**, 2249.

[36] D. L. Rabenstein and B. J. Fuhr, *Inorg. Chem.*, 1972, **11**, 2430.

A sequence of proton-assisted dissociations of the Cd^{II}–H_5ceda complexes which could lead to the observed polarographic behaviour is shown in the Scheme. This scheme is consistent with earlier mechanistic principles of others [28,30-33,36] and leads to rates for specific bond-breaking and -making processes which fall within the range of typical values expected for those processes. Octahedral co-ordination has been assumed for the cadmium ion but this is not essential to the conclusions to be drawn. In fact, the co-ordination number may possibly differ from six.[16] Our earlier work [16] suggested a structure similar to (I) for the non-protonated complex. It is known that the rate of dissociation of a nitrilodiacetate group from a metal ion is greatly enhanced as the hydrogen-ion concentration is increased. This is evident from the data presented in Table 2 and will be discussed later. It is also known that the cadmium–oxygen bond lifetime in aminopolycarboxylate complexes is very short on the n.m.r. time scale.[15,32-34,36,37] Since protonation is electrophilic attack, possibly the first step in the proton-assisted dissociation of $[Cd(ceda)]^{3-}$ involves rapid protonation of a carboxylate group as it leaves the metal-ion co-ordination shell and is replaced by a water molecule to give species represented as (IIa) or (IIb). The lifetimes of these species are presumably very short since the n.m.r. spectra did not detect significant protonation of terminal carboxylate groups. It is difficult to predict which of the species (IIa) or (IIb) is formed more readily, but only for the former can dissociation of the nitrilodiacetate group occur readily. It is not necessary for (IIa) to have a long lifetime since the metal–oxygen bond may break and reform several times before metal–nitrogen bond fission occurs. The probability of metal–nitrogen bond fission will be proportional to the concentration of (IIa) and thus $[H^+]$. Once the metal–nitrogen bond is broken, protonation of the nitrogen atom occurs rapidly in the pH region at which wave (C) appears since this is the most basic site in a non-co-ordinated nitrilodiacetate group [38-40] and this promotes deprotonation of the carboxylate group. A movement of 'proton density' from the carboxylate groups to the nitrogen atom results, in accordance with the changes of chemical shifts on protonation of the complex, *i.e.* more extensive protonation at nitrogen rather than at terminal carboxylate groups. The protonation of the nitrogen atom would block its re-entry into the co-ordination shell, its place having been taken by a water molecule. The mechanisms and rates of proton-transfer reactions between tertiary amines in aqueous solution have been studied.[41-43] In the present situation, when the nitrogen atom is in a position where it can potentially bond to the metal ion, for steric reasons the only reasonable mechanism by which the proton can be removed from the nitrogen atom is by transfer to a water molecule. Pseudo-first-order rate constants for deprotonation of some bulky tertiary amines were found [41,42] to lie in the range 7·5—500 s^{-1}. Alternatively, if the rate of proton association with the nitrogen atom is assumed to be near the maximum value expected for a diffusion-

TABLE 2

Rate constants for reactions involving complexes of cadmium(II) and aminopolycarboxylic acids

Reaction	Rate constant Forward reaction	Reverse reaction	θ_c/°C	Ref.
(i) $[Cd(nta)]^- \rightleftharpoons Cd^{2+} + nta^{3-}$	$1{\cdot}03 \pm 0{\cdot}27\ s^{-1}$	$8{\cdot}7 \times 10^9\ l\ mol^{-1}\ s^{-1}$ *	25	4
	$<1\ s^{-1}$	$<2{\cdot}5 \times 10^9\ l\ mol^{-1}\ s^{-1}$	25	32
(ii) $[Cd(nta)]^- + H^+ \rightleftharpoons Cd^{2+} + Hnta^{2-}$	$(2{\cdot}9 \pm 0{\cdot}5) \times 10^5\ l\ mol^{-1}\ s^{-1}$	$(2{\cdot}1 \pm 0{\cdot}4) \times 10^5\ l\ mol^{-1}\ s^{-1}$	25	32
(iii) $[Cd(nta)_2]^{4-} \rightleftharpoons [Cd(nta)]^- + nta^{3-}$	$(2{\cdot}2 \pm 0{\cdot}4) \times 10^2\ s^{-1}$	$(1{\cdot}8 \pm 0{\cdot}3) \times 10^7\ l\ mol^{-1}\ s^{-1}$	25	32
(iv) $[Cd(nta)_2]^{4-} + H^+ \rightleftharpoons [Cd(nta)]^- + Hnta^{2-}$	$(1{\cdot}3 \pm 0{\cdot}4) \times 10^7\ l\ mol^{-1}\ s^{-1}$	$(2{\cdot}9 \pm 1{\cdot}0) \times 10^2\ l\ mol^{-1}\ s^{-1}$	25	32
			25	9
(v) $[Cd(Hedta)]^- \rightleftharpoons Cd^{2+} + Hedta^{3-}$	$12\ s^{-1}$	$1 \times 10^9\ l\ mol^{-1}\ s^{-1}$	28	28
	$2{\cdot}0\ s^{-1}$		25	†
	$10{\cdot}8\ s^{-1}$	$3{\cdot}7 \times 10^9\ l\ mol^{-1}\ s^{-1}$	25	10
		$8{\cdot}5 \times 10^8\ l\ mol^{-1}\ s^{-1}$	25	11
		$(5{\cdot}3—64) \times 10^8\ l\ mol^{-1}\ s^{-1}$	25	12
(vi) $[Cd(edta)]^{2-} + H^+ \rightleftharpoons [Cd(Hedta)]^-$	$4{\cdot}3 \times 10^4\ l\ mol^{-1}\ s^{-1}$	$54\ s^{-1}$ *	25	9
(vii) $[Cd(Heota)]^- \rightleftharpoons Cd^{2+} + Heota^{3-}$	$\leqslant 5 \times 10^{-2}\ s^{-1}$	$\leqslant 1 \times 10^9\ l\ mol^{-1}\ s^{-1}$	25	34
(viii) $[Cd(Heota)]^- + H^+ \rightleftharpoons Cd^{2+} + H_2eota^{2-}$	$(2 \pm 1) \times 10^4\ l\ mol^{-1}\ s^{-1}$	$1{\cdot}5 \times 10^6\ l\ mol^{-1}\ s^{-1}$	25	34
(ix) $[Cd(hedta)]^- + H^+ \rightleftharpoons Cd^2 + Hhedta^{2-}$ ‡	$3 \times 10^5\ l\ mol^{-1}\ s^{-1}$	$2 \times 10^9\ l\ mol^{-1}\ s^{-1}$	25	14
(x) $[Cd(H_2beda)]^{2-} \rightleftharpoons Cd^{2+} + H_2beda^{4-}$	$98\ s^{-1}$	$2{\cdot}3 \times 10^8\ l\ mol^{-1}\ s^{-1}$ *	25	15
(xi) $[Cd(H_2beda)]^{2-} + H^+ \rightleftharpoons Cd^{2+} + H_3beda^{3-}$	$2{\cdot}9 \times 10^4\ l\ mol^{-1}\ s^{-1}$	$6{\cdot}9 \times 10^8\ l\ mol^{-1}\ s^{-1}$ *	25	15

H_4eota = Ethylenebis(oxyethylenenitrilo)tetra-acetic acid.

* Calculated. † B. Bosnich, Ph.D. Thesis, Australian National University, Canberra, 1962. ‡ See text.

---

[37] R. J. Day and C. N. Reilley, *Analyt. Chem.*, 1964, **36**, 1073.

[38] J. L. Sudmeier and C. N. Reilley, *Analyt. Chem.*, 1964, **36**, 1968.

[39] R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Amer. Chem. Soc.*, 1963, **85**, 2930.

[40] R. J. Kula and D. T. Sawyer, *Inorg. Chem.*, 1964, **3**, 458.

[41] D. E. Leyden and W. R. Morgan, *J. Phys. Chem.*, 1969, **73**, 2924.

[42] W. R. Morgan and D. E. Leyden, *J. Amer. Chem. Soc.*, 1970, **92**, 4527.

[43] D. E. Leyden and W. R. Morgan, *J. Phys. Chem.*, 1971, **75**, 3190.

controlled bimolecular reaction,[44-46] *i.e.* the rate constant is *ca.* 10^{10} l mol^{-1} s^{-1}, then a deprotonation rate can be estimated from an appropriate pK value for a suitable model compound. Thus, using p$K_2 = 9{\cdot}65$ for *N*-methylnitrilodiacetic acid,[47] we estimate a pseudo-first-order deprotonation rate constant equal to *ca.* 2 s^{-1}. It is therefore assumed that metal–nitrogen bond reformation can only occur when a non-protonated nitrogen atom presents itself to the metal ion in a conformationally favourable position. Although such excellent agreement with the measured rate constant of 3·6 s^{-1} is probably fortuitous, it appears that the rate of nitrogen deprotonation is the dominant factor in the rate of metal–nitrogen bond formation.

Whatever the mechanism of the proton-assisted dissociation of the nitrilodiacetate group, the value of the rate constant obtained in the present case can be compared with the data presented in Table 2 for a number of cadmium–aminopolycarboxylate complexes. In reaction (ii) of the Table the proposed dissociation sequence [32,33] most closely parallels that for the proton-assisted dissociation of the first nitrilodiacetate group of the Cd^{II}–H_5ceda complex. Reactions (iv) and (viii) also involve proton-assisted dissociation of cadmium–nitrogen bonds. The value of $k_C = 5{\cdot}4 \times 10^4$ l mol^{-1} s^{-1} compares well with rate constants for reactions (ii) and (viii). The higher value for reaction (iv) is reasonable in view of the proposed structure of the $[Cd(nta)_2]^{4-}$ complex.[32] Typical rates for first-order dissociation of cadmium–nitrogen bonds in aminopolycarboxylate complexes can be obtained from reactions (i), (iii), (v), and (vii). Except for the higher value for the $[Cd(nta)_2]^{4-}$ complex, the rate constants fall approximately in the range $<5 \times 10^{-2}$—10 s^{-1}.

Further dissociation of the complex would occur more readily by fission of the centre nitrogen–cadmium bond to give species (IV) than by dissociation of the other terminal nitrilodiacetate group. Protonation of the nitrogen atom would block its re-entry into the co-ordination shell of the cadmium ion and its place would be taken by a water molecule. The rate constant for this proton-assisted dissociation, $k_B = (1{\cdot}1 \pm 0{\cdot}9) \times 10^4$ l mol^{-1} s^{-1}, is of comparable magnitude to those for k_C and for reaction (viii) of Table 2. Furthermore, the rate constants $k_{-B} = 4 \pm 3$ and $k_{-C} = 3{\cdot}6$ s^{-1}, both of which correspond to cadmium–nitrogen bond reformations, are very similar in magnitude. Since a similar value, namely 0·79 s^{-1}, was obtained for metal–nitrogen bond formation in the Pb^{II}–H_5ceda complex,[15] it is likely that the rate-determining step mainly involves rates of conformational changes and nitrogen deprotonation in the ligand.

Proton-assisted dissociation of (IV) would give the free Cd^{2+} ion. The rate constant $k_A = (2{\cdot}5 \pm 2{\cdot}0) \times 10^5$ l mol^{-1} s^{-1} compares well with k_B and k_C and with those for reactions (ii) and (viii) of Table 2, all of which represent comparable dissociations. The value $k_{-A} = (2{\cdot}0 \pm 1{\cdot}6) \times 10^8$ l mol^{-1} s^{-1} is also readily rationalized by this interpretation of wave (A). Rabenstein and Kula [32] have predicted the rate constant for formation of $[Cd(nta)]^-$ from aquated Cd^{2+} and $Hnta^{2-}$ as $1{\cdot}2 \times 10^{10}$ l mol^{-1} s^{-1}, which is 5×10^4 times greater than the measured value [reaction (ii)]. This ratio is almost identical to the ratio of nitrogen- to carboxylate-protonated $Hnta^{2-}$, and therefore the reactive species was assumed to be carboxylate-protonated $Hnta^{2-}$. In a similar way the maximum value for the rate constants for formation of other cadmium–aminopolycarboxylate complexes from Cd^{2+} and the ligand should be *ca.* 10^{10} l mol^{-1} s^{-1}. In Table 2, rate constants for reactions involving ligands having at least one non-protonated nitrogen atom approach this value [reactions (i), (v), and (vii)]. The slightly low values for reactions (v) and (vii) could be due to steric effects. It has been shown that the H_3ceda^{2-} is largely protonated on the three nitrogen atoms,[38] whereas the reactive species would be expected to have at least one non-protonated nitrogen atom. Similarly, the rate constant for reaction (viii) is *ca.* 10^4 times smaller than the maximum possible value, again reflecting the effects of nitrogen protonation.

The rate constants obtained in this work may be subject to significant errors. In the analysis of wave (C) a value of $K_{Cd(Hceda)}{}^H$ determined by potentiometric titration was used. In fact, since different sites compete for the proton, a slightly smaller value for $K_{Cd(Hceda)}{}^H$ for protonation at a terminal nitrogen atom should be used. This, in turn, means that our values for k_C and k_{-C} are too low. For the analysis of wave (B) the difficulties are compounded since there are uncertainties both in the correct value of $K_{Cd(H_2ceda)}{}^H$ to use, and in the values of $\alpha_{Cd(Hceda)}$ [which strictly should be defined with respect to species (III)]. Our values of k_B and k_{-B} are also expected to be lower than they should be. Similar remarks can be applied to the analysis of wave (A) and additionally the effect of formation of cadmium(II) acetate complexes on the reaction rates was not considered. Since the effects of ionic strength have also been ignored, the rate constants obtained should be regarded as conditional. These considerations do not, however, discredit the mechanistic interpretation of the proton-assisted dissociations.

The dissociation rates and mechanisms discussed in this paper may be helpful in the interpretation of the dissociation of related cadmium complexes. Thus, for the H_4edta complex the data for reaction (vi) (Table 2) correspond well to values expected for proton-assisted breaking and reformation of the cadmium–nitrogen bond of the nitrilodiacetate group. For reaction (ix), a rate constant for $[Cd(hedta)]^- \longrightarrow Cd^{2+} + hedta^{3-}$ equal to 30·5 s^{-1} was originally proposed.[14] However, this leads to a rate constant of *ca.* 10^{15} l mol^{-1} s^{-1} for the reverse reaction, *ca.* 10^5 times larger than the

---

[44] E. K. Ralph and E. Grunwald, *J. Amer. Chem. Soc.*, 1967, **89**, 2963.

[45] M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. Reaction Kinetics*, 1964, **2**, 308.

[46] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' John Wiley, New York, 1968, 2nd edn., p. 154.

[47] 'Stability Constants of Metal–Ion Complexes,' The Chemical Society, London, 1964, Special Publication no. 17.

maximum value expected for a diffusion-controlled bimolecular reaction. The reaction shown in the Table is suggested as an alternative, using the data given in the original paper. It appears that the reaction is more complex than originally suspected and further study is required. Finally, rate constants for reactions (x) and (xi) were estimated using data in the original paper and can apparently be identified with mechanisms described in this paper.

We thank the National Research Council of Canada for support.

[4/1195 *Received*, 18*th June*, 1974]