Oxidation of Nickel(II) Ethylenediaminetetraacetate by Carbonate Radical

Parikshit C. Mandal, Debaki K. Bardhan, Samir Sarkar and Sudhindra N. Bhattacharyya *
Nuclear Chemistry Division, Saha Institute of Nuclear Physics, I/AF, Bidhan nagar, Calcutta 700 064, India

Reactions of the carbonate radical ($CO_3^{\bullet -}$), generated by photolysis or by radiolysis of a carbonate solution, with nickel(II) ethylenediaminetetraacetate $[Ni^{II}(edta)]^{2-}$ were studied at pH 11.4 and ionic strength (I) = 0.2 mol dm^{-3}. Time-resolved spectroscopy and kinetics for the transients were studied using flash photolysis whereas the stable products arising from ligand degradation of the complex were ascertained by steady-state radiolysis experiments. From the kinetic data it is suggested that $CO_3^{\bullet -}$ reacts initially with $[Ni^{II}(edta)]^{2-}$ to form a five-co-ordinated Ni^{III} species [$k = (4.5 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1}] which undergoes aquation with a first-order rate constant of $(1.1 \pm 0.3) \times 10^3$ s^{-1} to give $[Ni^{III}(edta)(H_2O)]^-$. The latter reacts with iodide with a rate constant of $(5.5 \pm 0.4) \times 10^5$ dm^3 mol^{-1} s^{-1}. At the alkaline pH used $[Ni^{III}(edta)(H_2O)]^-$ undergoes transformation to give a radical intermediate which reacts with $[Ni^{II}(edta)]^{2-}$ to give ligand degradation products of which glyoxylic acid and formaldehyde were detected.

The radiolysis of transition-metal complexes of aminopolycarboxylic acids has been studied extensively by γ-radiation [1–4] as well as by pulse radiolysis [5–7] techniques. For nickel(II) aminopolycarboxylates, however, steady-state γ-radiolysis results indicated that the $OH^\bullet$ radical reacts with the metal complex by hydrogen abstraction from the ligand [1b] whereas the pulse-radiolysis study indicated oxidation of the central metal atom to Ni^{III}.[7] Formation of the Ni^{III} species has also been reported [8,9] in the oxidation of nickel(II) complexes of macrocyclic ligands with various oxidizing species, *viz.* $OH^\bullet$, $Cl_2^{\bullet -}$, $Br_2^{\bullet -}$ or $(SCN)_2^{\bullet -}$. The hydroxyl radical reacts with Ni^{II}–glycine (1:1) complex by hydrogen abstraction while the $Br_2^{\bullet -}$ radical anion, which has much lower redox potential ($E^\circ = 1.7$ V) than that of $OH^\bullet$ ($E^\circ = 2.8$ V),[10] is found to oxidize [11] the metal centre to Ni^{III}. The redox potential of the carbonate radical $CO_3^{\bullet -}$ ($E^\circ = 2.1$ V) [12] is higher than that of $Br_2^{\bullet -}$ and hence it was of interest to study its reaction with nickel(II) aminopolycarboxylates to ascertain its mode of reactivity. Herein we report the oxidation of $[Ni^{II}(edta)]^{2-}$ (H_4edta = ethylenediaminetetraacetic acid) by $CO_3^{\bullet -}$ using steady-state γ-radiolysis and flash photolysis techniques.

Experimental

Materials.—All chemicals were of analytical reagent grade and used without further purification. Solutions for irradiation were made up in triply distilled water. The gases N_2O and Ar used for degassing were of high purity. pH Values of the solutions were adjusted by adding appropriate amounts of NaOH and ionic strength was maintained by using sodium perchlorate solution.

The complex $[Ni^{II}(edta)(H_2O)]^{2-}$ was prepared by adding Na_2H_2edta to freshly prepared alkali-free nickel hydroxide such that a slight excess of $Ni(OH)_2$ remained. The solution was filtered, evaporated to dryness to obtain the solid complex and finally recrystallized.[13]

Generation of the Carbonate Radical.—Under steady-state radiolysis conditions, the $CO_3^{\bullet -}$ radical was generated by γ-radiolysis of N_2O-saturated aqueous solution of Na_2CO_3 (5×10^{-2} mol dm^{-3}, pH ≈ 11.4; $I \approx 0.2$ mol dm^{-3}). Radiolysis of an aqueous solution generates e_{aq}^-, $OH^\bullet$ radicals and $H^\bullet$ atoms according to equation (1) where the G values for the

$$H_2O \xrightarrow{\gamma} e_{aq}^- \,(2.63) + OH^\bullet \,(2.72) + H^\bullet \,(0.55) + H_2 \,(0.45) + H_2O_2 \,(0.68) \qquad (1)$$

individual species are given in parentheses [number of molecules formed per 100 eV (1.60×10^{-17} J) of energy absorbed].[14] In N_2O-saturated solution (2.5×10^{-2} mol dm^{-3}),[15] e_{aq}^- is converted to $OH^\bullet$ according to reaction (2) ($k_2 = 8.7 \times 10^9$

$$e_{aq}^- + N_2O \xrightarrow[H_2O]{k_2} N_2 + OH^- + OH^\bullet \qquad (2)$$

dm^3 mol^{-1} s^{-1}).[16] In the presence of Na_2CO_3 at alkaline pH ≈ 11.4, reaction (3) then takes place ($k_3 \approx 4.2 \times 10^8$ dm^3

$$OH^\bullet + CO_3^{2-} \xrightarrow{k_3} CO_3^{\bullet -} + OH^- \qquad (3)$$

mol^{-1} s^{-1}).[17,18] Thus in N_2O-saturated solutions containing Na_2CO_3 at alkaline pH, the reactive species is the $CO_3^{\bullet -}$ radical [$G(CO_3^{\bullet -}) \approx 5.4$].

Under flash photolysis conditions $CO_3^{\bullet -}$ is produced by photolysing the N_2O-saturated Na_2CO_3 solution using high-energy light,[19,20] where the following sequence of reactions occurs.

$$CO_3^{2-} \xrightarrow{h\nu} CO_3^{2-*} \longrightarrow CO_3^{\bullet -} + e_{aq}^- \qquad (4)$$

$$e_{aq}^- + N_2O \longrightarrow N_2 + OH^- + OH^\bullet \qquad (2)$$

$$OH^\bullet + CO_3^{2-} \longrightarrow CO_3^{\bullet -} + OH^- \qquad (3)$$

It should be noted that in studying the reactions of $CO_3^{\bullet -}$ with $[Ni^{II}(edta)]^{2-}$, the experimental solutions contained sufficiently large amounts of Na_2CO_3 (*e.g.*, 5×10^{-2} mol dm^{-3}) to minimize direct reaction of $OH^\bullet$ with the complex.

γ-Irradiation.—A ^{60}Co source was used for γ-irradiation. The absorbed dose (dose rate = 10.4 Gy min^{-1}) was measured using a Fricke dosimeter taking $G(Fe^{3+}) = 15.6$.[21] Solutions for recording the difference spectra were irradiated in stoppered spectrophotometer cells.

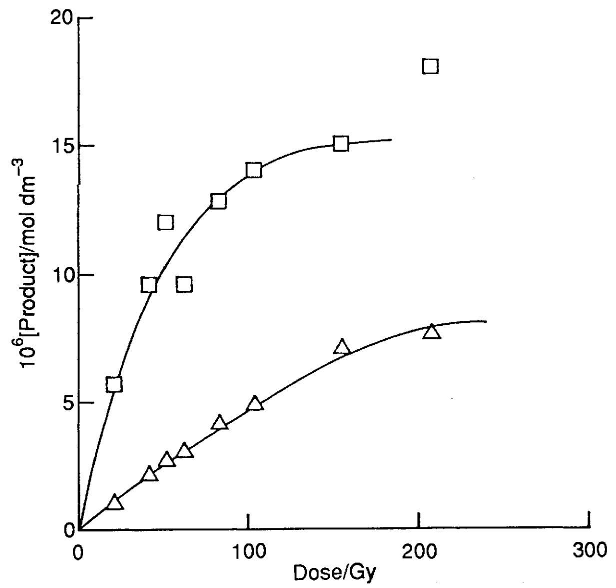

Fig. 1 Plots of yield *vs.* dose for the formation of glyoxylic acid (□) and formaldehyde (△) in the steady-state radiolysis of a N_2O-saturated solution of $[Ni^{II}(edta)]^{2-}$ (5×10^{-4} mol dm^{-3}) in the presence of Na_2CO_3 (5×10^{-2} mol dm^{-3}) at pH ≈ 11.4 and $I \approx 0.2$ mol dm^{-3}

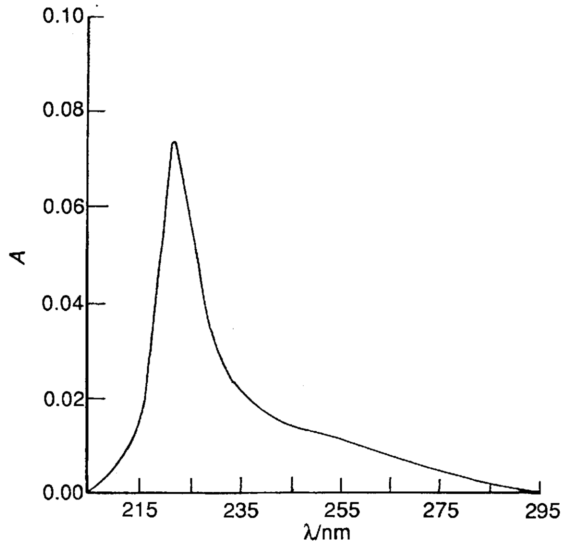

Fig. 2 Difference spectra of the products formed by the reaction of $CO_3^{\bullet-}$ with $[Ni^{II}(edta)]^{2-}$ under conditions as for Fig. 1; absorbed dose ≈104 Gy. The spectra were taken immediately after irradiation and the duration of the total scan was *ca.* 5 min

Analysis of the Products of Radiolysis.—Products of the reaction of $CO_3^{\bullet-}$ with $[Ni^{II}(edta)]^{2-}$ consist of mainly glyoxylic acid and formaldehyde. Glyoxylic acid was determined as follows.[22]

An aliquot of the γ-irradiated sample was treated with an excess of 2,4-dinitrophenylhydrazine. The resulting hydrazone of glyoxylic acid was extracted into ethyl acetate and back extracted into 10% aqueous sodium carbonate solution. The aqueous extract was treated further with 2 mol dm^{-3} sodium hydroxide solution and the absorbance of the resulting solution at 425 nm measured immediately.

Formaldehyde was determined by measuring the absorbance at 570 nm of its derivative with chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulphonic acid.[23]

Spectrophotometric measurements were made on a Perkin-Elmer 554 spectrophotometer.

Flash Photolysis.—Kinetics of the formation and decay of the transient intermediates of the reaction of $CO_3^{\bullet-}$ with $[Ni^{II}(edta)]^{2-}$ were studied using the flash photolysis technique. The apparatus consisted of a conventional flash photolysis system (Applied Photophysics, model KN-020) with photolysis cell of pathlength 10 cm. Two flash lamps (LR 16) connected in series were operated at 15 kV which gave a flash of light of 10 μs duration (full-width at half measure). The digitized transient signal from the oscilloscope (Iwatsu TS-8123) was fed into a PC through a GPIB-interface and the absorbance (A) *vs.* time (t) data were analysed for first- and second-order fits by least-square methods.

Results and Discussion

Steady-state γ-Radiolysis.—When a N_2O-saturated aqueous solution, 5×10^{-2} mol dm^{-3} in Na_2CO_3 and 5×10^{-4} mol dm^{-3} in $[Ni^{II}(edta)]^{2-}$ at pH ≈ 11.4 and ionic strength ≈0.2 mol dm^{-3} was irradiated by γ-rays the radiolytic products arising from the degradation of the ligand consisted mainly of glyoxylic acid. A small amount of formaldehyde was also detected using chromotropic acid.[23] The nitrogen-containing fraction, ethylenediaminetriacetic acid, could not be measured in the presence of a large excess of $[Ni^{II}(edta)]^{2-}$. Fig. 1 shows the resulting concentration of both of the detected organic products *vs.* the absorbed dose. The G values for the formation of the products were calculated from the initial slopes of the respective curves and found to be ≈2.6 and ≈0.5 for glyoxylic acid and formaldehyde respectively. The spectra of irradiated and non-irradiated solutions also indicated the presence of a product absorbing in the UV region (220–250 nm) as shown in Fig. 2.

As stated earlier under N_2O-saturated conditions the only reactive species present is $CO_3^{\bullet-}$. Hence the products observed after radiolysis must have arisen from the reaction of $CO_3^{\bullet-}$ with $[Ni^{II}(edta)]^{2-}$ [equation (5)].

$$CO_3^{\bullet-} + [Ni^{II}(edta)]^{2-} \longrightarrow \text{Products} \qquad (5)$$

As $CO_3^{\bullet-}$ is a one-electron oxidant, it is presumed that it oxidizes the complex. This oxidation could occur either at the central metal atom to produce $[Ni^{III}(edta)]^-$ or by hydrogen abstraction from the ligand to give $[Ni^{II}(RR'N\dot{C}HCO_2)]^{2-}$ [$R = -(CH_2)_2N(CH_2CO_2^-)_2$, $R' = -CH_2CO_2^-$]. Both intermediates then undergo reactions to give the observed products. It is to be noted here that the yields of the products arising from the ligand degradation are less than that of the oxidizing $CO_3^{\bullet-}$ ($G = 5.4$) according to the stoichiometry of equation (5). In order to determine which of the intermediates was responsible for the product formation, a kinetic study of the decay of the intermediate products was undertaken using the flash photolysis technique.

Kinetics.—Flash photolysis of a N_2O-saturated aqueous solution of Na_2CO_3 at pH ≈ 11.4 generates $CO_3^{\bullet-}$ as the only reactive species, which undergoes bimolecular decay with a measured rate constant, $2k$, of $(1.1 \pm 0.2) \times 10^8$ dm^3 mol^{-1} s^{-1} in close agreement with the reported literature data.[19,20] In the presence of $[Ni^{II}(edta)]^{2-}$, however, the decay of $CO_3^{\bullet-}$ (as monitored by the decrease in absorption at 600 nm) accelerates but cannot be fitted to a single first- or second-order rate law; however, its decay can be adequately described by concurrent (pseudo) first- and second-order processes (in $CO_3^{\bullet-}$). A profile of the decay kinetics is shown in Fig. 3. An apparent second-order rate constant, k', was determined by plotting $1/A$ *vs.* t. Subtraction of the slow second-order component from the observed change in absorbance showed a fast exponential decay of $CO_3^{\bullet-}$ in the presence of $[Ni^{II}(edta)]^{2-}$. The second-order rate constant, k, for the reaction of $CO_3^{\bullet-}$ with $[Ni^{II}(edta)]^{2-}$ was determined to be $(4.5 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1} from the observed dependence of the pseudo-first-order rate constant on $[Ni^{II}(edta)^{2-}]$.

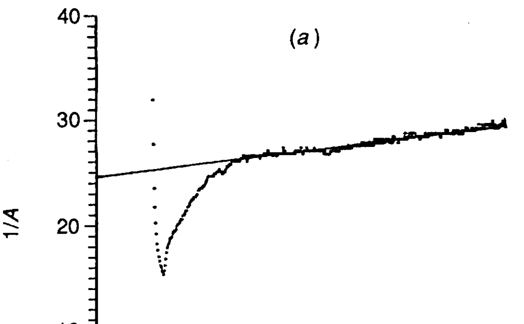

Fig. 3 (*a*) Second-order kinetic fitting of absorbance (*A*) *vs.* time (*t*) data for the decay of $CO_3^{\bullet -}$ formed by the photolysis of a N_2O-saturated solution of $[\mathrm{Ni^{II}(edta)}]^{2-}$ (1×10^{-4} mol dm^{-3}) in the presence of Na_2CO_3 (5×10^{-2} mol dm^{-3}) at pH ≈ 11.4 and $I = 0.2$ mol dm^{-3}, monitored at 600 nm. (*b*) *A vs. t* curve for the decay of $CO_3^{\bullet -}$ at 600 nm after subtracting the contribution for the second-order component from the absorbance–time data. (*c*) Fitting of the data in (*b*) by an integrated equation based on first-order kinetics

It should be mentioned here that the reaction was studied in strongly alkaline medium (pH ≈ 11.4) where hydrolysis of the metal complex [reaction (6)] may take place.[24] In order to

$$[\mathrm{Ni^{II}(edta)(H_2O)}]^{2-} + \mathrm{OH^-} \longrightarrow [\mathrm{Ni^{II}(edta)(OH)}]^{3-} + \mathrm{H_2O} \qquad (6)$$

determine the importance of this reaction, its rate was measured for several values of ionic strength. It is expected that the reactions between the charged species will vary with ionic strength of the solution. Thus an increase in rate constant was observed upon increasing the ionic strength. When the rate data were plotted as a function of the ionic strength (I) according to the classical relationship (7), where k and k_0 are the second-order

$$\log k - \log k_0 = 1.02\, Z_aZ_bI^{\frac{1}{2}}(1 + I^{\frac{1}{2}})^{-1} \qquad (7)$$

rate constants at ionic strength I and 0 respectively and Z_aZ_b is the product of charges of the reacting species,[21] a straight line with a slope of 1.99 was obtained so giving a value for Z_aZ_b of 2. Since the charge of $CO_3^{\bullet -}$ is −1 the charge of the reacting $\mathrm{Ni^{II}}$–edta species must be −2. This clearly indicates that this species is $[\mathrm{Ni^{II}(edta)(H_2O)}]^{2-}$ and that hydrolysis of the complex is of no importance under our experimental conditions. A similar conclusion was made previously by Buitenhuis *et al.*[24] during their study on the reaction of e_{aq}^- with a variety of metal complexes of H_4edta at alkaline pH.

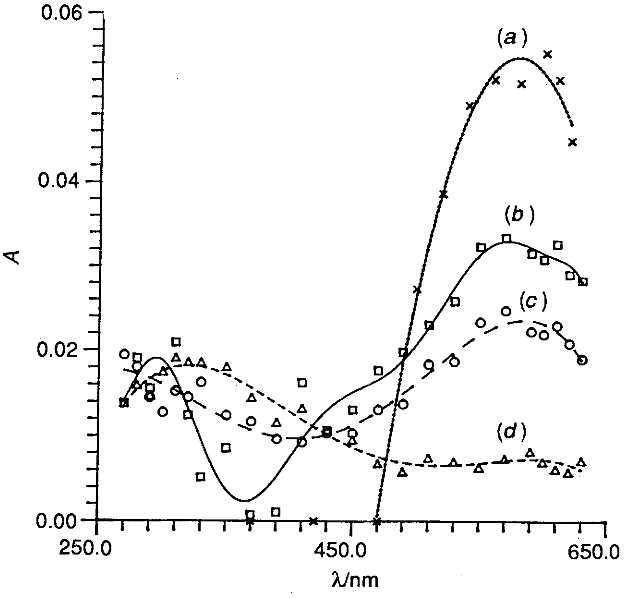

Fig. 4 Difference absorption spectra for the transient species observed in the flash photolysis of a N_2O-saturated solution of $[\mathrm{Ni^{II}(edta)}]^{2-}$ (3×10^{-4} mol dm^{-3}) in the presence of Na_2CO_3 (5×10^{-2} mol dm^{-3}) at pH ≈ 11.4 and $I = 0.2$ mol dm^{-3}: (*a*) 170 µs, (*b*) 420 µs, (*c*) 2 ms and (*d*) 15 ms after the flash. The spectra for the transients are assigned as: (*a*) $CO_3^{\bullet -}$, (*b*) $[\mathrm{Ni^{III}(edta)}]^-$ **I**, (*c*) $[\mathrm{Ni^{III}(edta)(H_2O)}]^-$ **II** and (*d*) $[\mathrm{Ni^{II}(RR'N\dot{C}HCO_2)}]^{2-}$ **III** [$R = -(CH_2)_2N(CH_2CO_2^-)_2$, $R' = -CH_2CO_2^-$]

The characteristics and decay of the intermediates formed in reaction (5) were also studied using absorption spectrophotometry. Fig. 4 shows the differential absorption spectra for the different transient intermediates formed in the reaction of $CO_3^{\bullet -}$ (*a*) with $[\mathrm{Ni^{II}(edta)}]^{2-}$. After 420 µs, a transient intermediate **I** having a strong absorption in the range 270–350 nm with a peak at *ca.* 300 nm and a broad absorption band in the range 370–450 nm was observed [Fig. 4(*b*)]. However, on monitoring the change in absorbance at 300 nm of this initially formed intermediate, three different reaction processes could be observed at different time scales. The first has a rate constant k'' of $(1.1 \pm 0.3) \times 10^3$ s^{-1} and causes a small decrease in absorbance in the region of λ_{max} to give the spectrum in Fig. 4(*c*) arising from an intermediate **II**. The rate constant for this reaction is independent of complex concentration and pH of the solution in the range 11.4–13.0.

Assuming that species **I** was formed from reaction with $CO_3^{\bullet -}$, the absorption coefficient (ε) for the product was determined to be 2600 ± 700 dm^3 mol^{-1} cm^{-1}. As the transient species **II** is obtained directly from **I**, the value ε for this species was calculated to be 2010 ± 50 dm^3 mol^{-1} cm^{-1}. As stated earlier the $CO_3^{\bullet -}$ radical might oxidize either the central metal atom or the ligand of $[\mathrm{Ni^{II}(edta)}]^{2-}$. The one-electron reduction potential of $CO_3^{\bullet -}$ is 2.1 V,[12] whereas those for $\mathrm{Ni^{III}}$ complexes are in the range 1.7–1.9 V.[25] Hence the product of reaction (5) may well be a $\mathrm{Ni^{III}}$ species. The water-exchange rate constant of $[\mathrm{Ni^{II}(edta)(H_2O)}]^{2-}$ is 7.2×10^5 s^{-1} [26] which is comparable to values found for most cobalt(II) complexes. It has been reported[6] that cobalt(II) complexes are oxidized by $OH^\bullet$ or dihalogen radicals to $\mathrm{Co^{III}}$ species by an inner-sphere electron-transfer process. In a similar way, $CO_3^{\bullet -}$ might oxidize $[\mathrm{Ni^{II}(edta)}]^{2-}$ to $[\mathrm{Ni^{III}(edta)}]^-$ [intermediate **I**, Fig. 4(*b*), equation (8)]. However, the five-co-ordinate $[\mathrm{Ni^{III}(edta)}]^-$

$$[\mathrm{Ni^{II}(edta)(H_2O)}]^{2-} + CO_3^{\bullet -} \longrightarrow [\mathrm{Ni^{II}(edta)(CO_3^{\bullet})}]^{3-} + \mathrm{H_2O} \xrightarrow{\text{electron transfer}} [\mathrm{Ni^{III}(edta)}]^- + CO_3^{2-} \qquad (8)$$

Table 1 Rate constants (k'') for the conversion of $[\mathrm{Ni^{III}(edta)(H_2O)}]^-$ **II** [Fig. 4(*c*)] into $[\mathrm{Ni^{II}(RR'N\dot{C}HCO_2)}]^{2-}$ **III** [Fig. 4(*d*)] [$\mathrm{R = -(CH_2)_2N(CH_2CO_2^-)_2}$, $\mathrm{R' = CH_2CO_2^-}$] in the pH range 11.4–13.0

pH	10^5 $[\mathrm{Ni^{II}(edta)^{2-}}]$/ mol dm^{-3}	10^{-2} k''/s^{-1}
11.4	5	1.4 ± 0.3
	10	1.4 ± 0.3
	20	1.7 ± 0.3
	30	1.7 ± 0.3
12.0	2	1.5 ± 0.2
	5	1.2 ± 0.1
	8	1.4 ± 0.1
	10	1.1 ± 0.1
13.0	5	1.6 ± 0.1

undergoes aquation with a rate constant of $(1.1 \pm 0.3) \times 10^3$ s^{-1} [change of spectrum from Fig. 4(*b*) to (*c*)] to fill its sixth co-ordination position and gives $[\mathrm{Ni^{III}(edta)(H_2O)}]^-$ (intermediate **II**). That the intermediate **II** is $[\mathrm{Ni^{III}(edta)(H_2O)}]^-$ is evident from the following. (*a*) Nickel(III) species should be highly oxidizing and should react with iodide ions at an appreciable rate. In fact in the presence of iodide ions, at concentrations well below the limit for direct reaction with $\mathrm{CO_3^{\bullet -}}$, decay of the transient **II**, monitored at 300 nm, was measured and the rate constant for its reaction with iodide was determined to be $(5.5 \pm 0.4) \times 10^5$ dm^3 mol^{-1} s^{-1}. (*b*) Further, if the reaction is carried out in an argon saturated solution, e_{aq}^- and $\mathrm{CO_3^{\bullet -}}$ should be produced in almost equal amounts [reaction (4)]. Hydrated electrons are known to reduce $\mathrm{Ni^{II}}$ to $\mathrm{Ni^{I}}$ which would be expected to transfer an electron rapidly to any $\mathrm{Ni^{III}}$ species [equation (9)]. In argon-saturated solution, at pH ≈ 11.4,

$$[\mathrm{Ni^{III}(edta)}]^- + [\mathrm{Ni^{I}(edta)}]^{3-} \longrightarrow 2[\mathrm{Ni^{II}(edta)}]^{2-} \quad (9)$$

species **II** was found to decay by second-order kinetics the rate constant of which remained unaltered on increasing the photon flash energy but increased with increasing ionic strength. A plot of measured rate constants *vs.* ionic strength according to equation (7) gave a straight line with a slope (Z_aZ_b) of ≈2.84 from which the charge of the transient species **II** was determined to be -1 {note the charge of $[\mathrm{Ni^{I}(edta)}]^{3-}$}. (*c*) Under argon-saturated conditions, in which $[\mathrm{Ni^{I}(edta)}]^{3-}$ is produced, no stable organic product such as formaldehyde or glyoxylic acid was formed. This suggests that the $\mathrm{Ni^{III}}$–edta species formed by reaction with $\mathrm{CO_3^{\bullet -}}$ is reduced readily by $[\mathrm{Ni^{I}(edta)}]^{3-}$ {formed by the reaction of e_{aq}^- with $[\mathrm{Ni^{II}(edta)}]^{2-}$} so regenerating the parent $\mathrm{Ni^{II}}$ complex [equation (9)] and leading to no, or much reduced, degradation products.

It is noteworthy that Lati and Meyerstein[7a] observed the formation of an unstable form of a $\mathrm{Ni^{III}}$–edta complex by treating $\mathrm{OH^{\bullet}}$ with $[\mathrm{Ni^{II}(edta)}]^{2-}$ using pulse radiolysis. This unstable form was then converted to a stable one with a rate constant of 2×10^3 s^{-1}. They suggested that the two forms differ in the number of co-ordination sites occupied by the edta ligand or by the addition of H_2O or OH^- to the co-ordination sphere. The UV absorption spectra (Fig. 4) of species **I** and **II** observed in this investigation are very similar to those of the 'unstable' and 'stable' forms observed by Lati and Meyerstein.[7a] The rate of conversion of **I** to **II** observed by us [$(1.1 \pm 0.3) \times 10^3$ s^{-1}] is also comparable. Further, the stable form observed by Lati and Meyerstein (intermediate **II** in this investigation) was fairly stable in the pH range 4–9. However, under our experimental conditions at pH ≈ 11.4, this species, **II**, assigned to $[\mathrm{Ni^{III}(edta)(H_2O)}]^-$ was found to undergo transformation to a further species **III** [Fig. 4(*d*)] whose absorption spectrum shows that unlike $[\mathrm{Ni^{III}(edta)}]^-$ its absorption maximum in the UV region is shifted to a slightly higher wavelength. The first-order rate constant for this transformation was found to be independent of the initial concentration of the $\mathrm{Ni^{II}}$ complex. Similarly the rate constant remained unaltered upon increase of pH from 11.4 to 13.0. The results are shown in Table 1.

It has been reported[27] that nickel(III) complexes of macrocyclic ligands produced in acetonitrile undergo deprotonation in water to give radical intermediates which remain in equilibrium with the $\mathrm{Ni^{III}}$ complex. In a similar manner, it could be argued that $[\mathrm{Ni^{III}(edta)(H_2O)}]^-$ undergoes deprotonation at the ligand to give a radical intermediate **III** as shown in equation (10) [$\mathrm{R = -(CH_2)_2N(CH_2CO_2^-)_2}$, $\mathrm{R' = -CH_2CO_2^-}$].

$$\underset{\textbf{II}}{[\mathrm{Ni^{III}(RR'NCH_2CO_2)(H_2O)}]^-} + \mathrm{OH^-} \rightleftharpoons [\mathrm{Ni^{III}(RR'NCH_2CO_2)(OH)}]^{2-} \longrightarrow \underset{\textbf{III}}{[\mathrm{Ni^{II}(RR'N\dot{C}HCO_2)}]^{2-}} + \mathrm{H_2O} \quad (10)$$

As a result of the electron deficient nature of the metal centre, the acidic character of the hydrogen atom in the $\mathrm{CH_2CO_2^-}$ group of **II** is increased and base-catalysed deprotonation takes place. The equilibrium constant for reaction (10) was, however, found to decrease with increase in pH of the solution. That the transient **III** [Fig. 4(*d*)] is a radical species is also supported from the following studies.

The radical species **III** is fairly long-lived and undergoes first-order decay the rate of which was found to be dependent on the initial concentration of the complex. From this dependence, the second-order rate constant was determined to be $(9.3 \pm 0.3) \times 10^4$ dm^3 mol^{-1} s^{-1}. This value was found to vary with the ionic strength of the solution, and by application of equation (7) the charge of the transient **III** was evaluated to be -2.

The relevant decay reactions for intermediate **III** can be represented by equations (11)–(13) [$\mathrm{R = -(CH_2)_2N(CH_2CO_2^-)_2}$, $\mathrm{R' = -CH_2CO_2^-}$].

$$\underset{\textbf{III}}{[\mathrm{Ni^{II}(RR'N\dot{C}HCO_2)}]^{2-}} + [\mathrm{Ni^{II}(RR'NCH_2CO_2)(H_2O)}]^{2-} \longrightarrow [\mathrm{Ni^{II}(RR'N\overset{+}{C}HCO_2)}]^- + [\mathrm{Ni^{I}(RR'NCH_2CO_2)(H_2O)}]^{3-} \quad (11)$$

$$[\mathrm{Ni^{II}(RR'N\overset{+}{C}HCO_2)}]^- \xrightarrow{\mathrm{H_2O}} [\mathrm{Ni^{II}(RR'NCH_2OH)}]^- + \mathrm{CO_2} \quad (12)$$

$$[\mathrm{Ni^{II}(RR'N\overset{+}{C}HCO_2)}]^- \xrightarrow{\mathrm{H_2O}} [\mathrm{Ni^{II}\{RR'NCH(OH)CO_2\}}]^{2-} \longrightarrow [\mathrm{Ni^{II}(RR'NH)}]^- + \mathrm{CHOCO_2^-} \quad (13)$$

As observed with other nickel aminopolycarboxylates[28] the nickel(I) species formed in reaction (11) decays very rapidly and does not give rise to any ligand degradation products. The sequence of reactions suggested for the decay of the radical intermediate **III** has also been supported from the analysis of the reaction products of the steady-state γ-radiolysis experiments. According to reaction (13), the ligand degradation product should be glyoxylic acid, as observed experimentally. A similar mechanism for the product formation has been proposed previously in the oxidation of cobalt(II) iminodiacetate by $\mathrm{OH^{\bullet}}$ radicals.[6] The nickel(II) product of reaction (12) could lead to the partial formation of formaldehyde under the drastic conditions required in the chromotropic acid method for the determination of formaldehyde. In fact, a small amount of formaldehyde ($G \approx 0.5$) has been obtained upon radiolysis of a $\mathrm{N_2O}$-saturated solution of $[\mathrm{Ni^{II}(edta)}]^{2-}$ in the presence of $\mathrm{Na_2CO_3}$. The difference spectrum shown in Fig. 2 probably results from the hydroxy compound formed in reaction (12).

One-electron Reduction Potential of the Ni^{III}–Ni^{II} *Couple in the* Ni–edta *System*.—The reaction of $CO_3^{•-}$ with $[Ni^{II}(edta)]^{2-}$ has been studied using a high concentration of Na_2CO_3. Under this condition, the absorption due to $CO_3^{•-}$ species formed by reactions (2)–(4) does not decay completely to pre-flash levels on reaction with $[Ni^{II}(edta)]^{2-}$, but a residual absorption due to $CO_3^{•-}$ persists over a longer time scale which decays by a slow second-order process. However, it could be assumed that within this time scale, prior to decay of the Ni^{III}-edta species, **I**, that an approximate equilibrium exists between $CO_3^{•-}$ and **I**. This is also evident from the pseudo-first-order dependence of the observed rate constant for the decay of $CO_3^{•-}$ with concentration of $[Ni^{II}(edta)]^{2-}$. The relatively large intercept suggests that the process (14) is an equilibrium reaction. The

$$[Ni^{II}(edta)]^{2-} + CO_3^{•-} \underset{k_{-1}}{\overset{k}{\rightleftharpoons}} [Ni^{III}(edta)]^{-} + CO_3^{2-} \qquad (14)$$

slope of the linear plot corresponds to the second-order rate constant, k, for the forward reaction whereas the intercept corresponds to the pseudo-first-order rate constant k_{-1} for the back reaction (a second-order rate constant, k_b, multiplied by $[CO_3^{2-}]$). The second-order rate constants for the forward and back reactions were determined as $k = (4.5 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1} and $k_b = (8.8 \pm 0.8) \times 10^4$ dm^3 mol^{-1} s^{-1}. From these data the effective equilibrium constant, $K = 511 \pm 92$, was derived.

If $[Ni^{III}(edta)]^-$ **I** is indeed formed in the equilibrium reaction (14), then its absorbance (A) (at 300 nm) should obey the relation (15) where A_∞ is the absorbance of the transient at

$$\frac{1}{A} = \frac{1}{A_\infty} + \frac{[CO_3^{2-}]}{KA_\infty[Ni^{II}(edta)^{2-}]} \qquad (15)$$

saturation, *i.e.*, $[Ni^{II}(edta)^{2-}] = \infty$. A linear plot of $1/A$ *vs.* $[CO_3^{2-}]/[Ni^{II}(edta)^{2-}]$ indicated the validity of relation (15) (plot not shown). From the intercept the absorption coefficient, ε, of the transient $[Ni^{III}(edta)]^-$ **I** at 300 nm was calculated to be 2437 ± 800 dm^3 mol^{-1} cm^{-1}, in good agreement with the value (2600 ± 700 dm^3 mol^{-1} cm^{-1}) obtained from direct measurements. The value of $K = 556 \pm 150$ is also in good agreement with the value of 511 ± 92 obtained from the kinetic data.

From the equilibrium constant data obtained above the one-electron reduction potential of the Ni^{III}–Ni^{II} couple for the $[Ni^{III}(edta)]^-$–$[Ni^{II}(edta)]^{2-}$ system can be determined.[29]

Providing that redox equilibrium (14) is achieved in the rate-determining step, the one-electron reduction potential of either of the half-cell reactions (16a) or (16b) can be determined from

$$CO_3^{•-} + e^- \longrightarrow CO_3^{2-} \qquad (16a)$$

$$[Ni^{III}(edta)]^- + e^- \longrightarrow [Ni^{II}(edta)]^{2-} \qquad (16b)$$

the relation (17), where $\Delta E^1_{11.4}$ denotes the one-electron redox

$$\Delta E^1_{11.4} = 0.059 \log K \qquad (17)$$

potential difference between half-cells (16a) and (16b) at pH 11.4. From the measured value of K, assuming[12] $E^\circ = 2.1$ V for the CO_3^{2-}–$CO_3^{•-}$ couple, the one-electron redox potential for the half-cell (16b) was determined to be 1.94 ± 0.08 V at pH 11.4.

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