Some Aspects of the Radiolysis of Cobalt(II) Iminodiacetate in Aqueous Solution †

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The radiolysis of cobalt(II) iminodiacetate has been studied. Both pulse radiolysis and product analysis after γ-irradiation indicate that OH attack proceeds 55% at the metal ion in the complex and 45% at the ligand. The rate constant for the overall reaction is 5.8×10^8 dm^3 mol^{-1} s^{-1}; that for metal-ion oxidation is 3.2×10^8 dm^3 mol^{-1} s^{-1} and for hydrogen abstraction from the ligand is 2.6×10^8 dm^3 mol^{-1} s^{-1}. The ions Br_2^- and O_2^- react with the complex wholly *via* oxidation of the metal ion, with rate constants of 8.9×10^7 and 3.0×10^7 dm^3 mol^{-1} s^{-1} respectively.

The mechanism of the radiolytic reactions of aminocarboxylate complexes of the transition metals is fairly well understood. In the case of the substitution-labile complexes there are often two kinds of reaction with OH radicals, either oxidation of the central metal ion or hydrogen abstraction from the ligand. It was reported earlier [1-3] that OH does not oxidize the metal ion in $Co^{II}L$ or $Ni^{II}L$ complexes [L = ethylenediaminetetraacetate (edta) or nitrilotriacetate (nta)] to the trivalent state. This was traced to the tendency of these metal ions to react *via* inner-sphere processes, in which the water-exchange rate plays a dominant role. Only when this rate is greater than that for hydrogen abstraction from the ligand by OH is the metal ion oxidized. When the oxidizing radical has low hydrogen-abstraction rates, *e.g.* Br_2^- or O_2^-, it specifically attacks the central metal ion. For the same type of complexes, if the reactivity of the ligand with OH is reduced while retaining similar water-exchange rates, then the reaction of the central metal ion with OH should be preferred over hydrogen abstraction.

In the present study, cobalt(II) iminodiacetate, [Co(ida)], was selected to study this aspect since the ligand ida has almost a ten-fold reduced reactivity [4] with OH compared to edta [5] and nta.[6]

Experimental

All chemicals were of analytical reagent grade and used without further purification. Solutions were made up in triply distilled water for γ-radiolysis and in water from a Milli-RO15 system for pulse radiolysis. The gases N_2O, Ar, or N_2 used for degassing were of high purity.

Cobalt(II) iminodiacetate was prepared by adding iminodiacetic acid to freshly prepared alkali-free cobalt hydroxide such that a slight excess of $Co(OH)_2$ remained. The solution was filtered, the complex crystallized, and then recrystallized from triply distilled water. It was finally dried at 100 °C and verified as the dihydrate by microanalysis.

Analyses.—Glyoxylic acid, the only carbonyl product, was determined [7] with 2,4-dinitrophenylhydrazine, extracting the hydrazone into aqueous Na_2CO_3. Its formation was linearly related to the dose up to a dose of 2.5×10^{18} eV g^{-1} in N_2O-saturated solutions; in argon-saturated and aerated solutions the linearity was lost at lower doses. Hydrogen peroxide was determined by use of tri-iodide [8] and titanium(III) sulphate.[9] Initial yields were calculated from plots of product concentration *versus* dose absorbed.

Spectrophotometric measurements were made on a Hilger Uvispeck or a Perkin-Elmer 554 recording spectrophotometer.

Irradiation.—A ^{60}Co source was used for γ-irradiation and the absorbed dose measured by a Fricke dosimeter taking $G(Fe^{3+}) = 15.6$. Solutions for recording difference spectra were irradiated in stoppered spectrophotometer cells. For pulse radiolysis, the 10-MeV LINAC and set-up were as described previously.[10,11] Solutions were buffered to pH 7 with 10^{-3} mol dm^{-3} phosphate.

Kinetics.—The pulse-radiolysis experiments invariably involved two or more first- or pseudo-first-order overlapping reactions and accordingly no direct estimation of the rate constants could be made. Also, in the majority of cases the spectra of transients overlapped. The absorption–time data were fed into a PDP 11 computer and analysed with the help of an iterative curve-fitting routine. Fitted data were subsequently averaged for different doses and concentrations.

Results and Discussion

Under all conditions, γ-irradiated solutions of [Co(ida)] showed a difference spectrum involving strong absorption around 220—250 nm. Such spectra were unstable and susceptible to oxygen when the irradiations were performed under deaerated conditions. All cobalt(II) species have some absorption in this spectral region, but the corresponding cobalt(III) species have absorptions of at least an order of magnitude higher intensity. The difference spectra under aerated, deaerated, and N_2O-saturated conditions are shown in Figures 1—3. The spectra of deaerated and N_2O-saturated solutions gradually increased in intensity with time after irradiation and reached maximum intensity within about 0.5 h. Introduction of O_2 rapidly resulted in identical results, suggesting that slow diffusion of O_2 into the Teflon-stoppered spectrophotometric cells may be responsible for the slow increase in absorbance.

The product of degradation of the ligand was found to be glyoxylic acid, while the N-containing fraction, glycine, could not be analysed in the presence of the large excess of [Co(ida)]. Table 1 summarizes the *G* values of glyoxylic acid and H_2O_2 under different conditions.

Figure 4 shows the spectra of transients in the reaction of Br_2^- with [Co(ida)] upon pulse radiolysis, Figure 5 those for

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† *Non-S.I. unit employed*: eV ≈ 1.60×10^{-19} J.

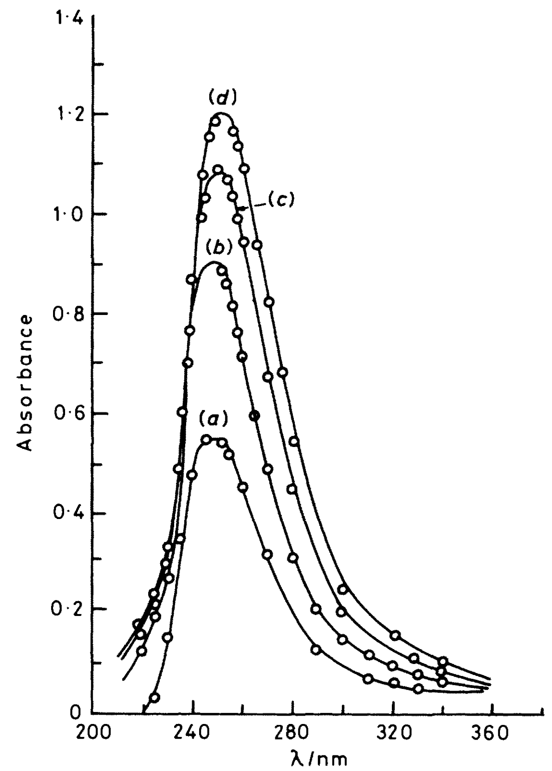

Figure 1. Difference spectra of neutral oxygenated [Co(ida)] solutions (5×10^{-3} mol dm^{-3}) irradiated with doses of (*a*) 0.68×10^{18}, (*b*) 1.37×10^{18}, (*c*) 2.05×10^{18}, and (*d*) 2.74×10^{18} eV g^{-1}. The presence of 0.1 mol dm^{-3} formate ensured complete conversion of OH into O_2^-

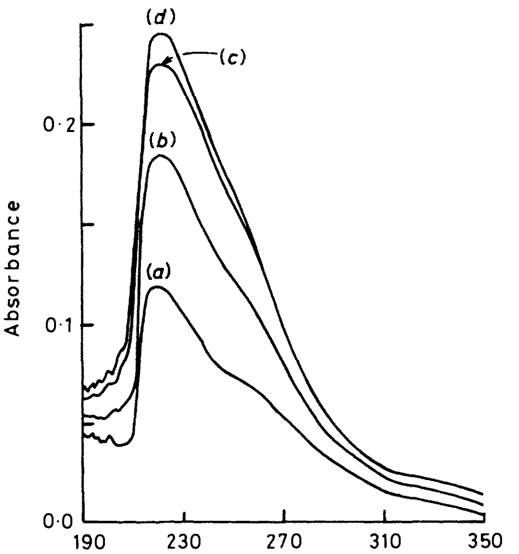

Figure 2. Difference spectra of neutral deaerated solutions of [Co(ida)] (5×10^{-3} mol dm^{-3}) irradiated with a dose of 1.6×10^{18} eV g^{-1}, measured (*a*) 5, (*b*) 15, (*c*) 35 min after irradiation, and (*d*) after introduction of oxygen

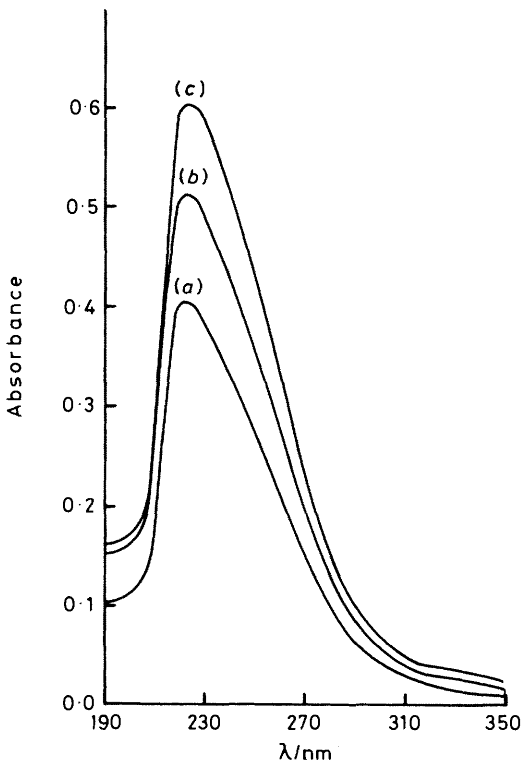

Figure 3. Difference spectra of neutral N_2O-saturated solutions of [Co(ida)] (5×10^{-3} mol dm^{-3}) irradiated with a dose of 1.6×10^{18} eV g^{-1}, measured (*a*) 5, (*b*) 10, and (*c*) 28 min after irradiation. On exposure to air at any time after irradiation the spectra were identical to (*c*)

Table 1. Observed initial *G* values in the radiolysis of [Co(ida)] (5×10^{-3} mol dm^{-3}) in neutral aqueous solution

Scavenger, S	[S]/mol dm^{-3}	G(CHOCO$_2$H)	G(H$_2$O$_2$)
None	—	1.9 ± 0.2	0 [a] 1.6 ± 0.2 [b]
N_2O	1.6×10^{-2}	3.2 ± 0.3	0 [a] 2.5 ± 0.3 [b]
N_2O + NaBr	1.6×10^{-2} 0.1	0.4	—
O_2	2.6×10^{-4}	1.4 ± 0.1	2.0 ± 0.2 [a] 3.9 ± 0.2 [b]

[a] Titanium sulphate method. [b] Tri-iodide method.

the corresponding reactions with OH, and Figure 6 those for the reaction with O_2^-. All the spectra were recorded in neutral phosphate-buffered solutions containing appropriate scavengers to ensure predominant conversion into Br_2^-, OH, or O_2^- respectively. Table 2 lists the kinetic and spectral characteristics of the above transients.

Reaction with Br_2^-.—Figure 4(*a*) shows the spectrum of Br_2^- at 6 μs after the pulse as identified [12] by its $\lambda_{max.}$ and ε values. From a consideration of Figure 4 along with the rate constants in Table 2 it appears that the reaction with Br_2^- proceeds in two stages, the first being very fast with a half-life of about 4 μs and the second with a half-life of about 70 μs, both kinetically first order. The kinetic sequence is accordingly suggestive of an initial attack by the Br_2^- on the co-ordination sphere of [Co(ida)] which obeys pseudo-first-order kinetics; subsequently the Br_2^- removes an electron from the metal ion and departs from the inner sphere according to first-order kinetics. The spectrum of the short-lived transient in Figure 4(*b*) shows remarkable similarity to that of Br_2^- itself, except that the intensity at 360 nm is much reduced in

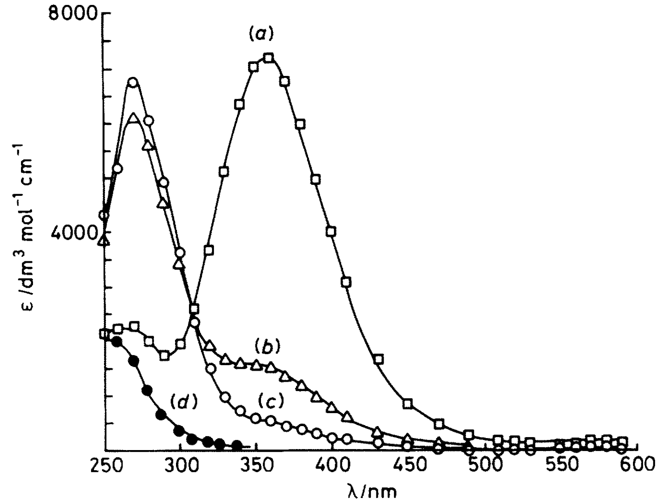

Figure 4. Difference spectra observed in the pulse radiolysis of 2×10^{-3} mol dm^{-3} [Co(ida)] saturated with N_2O and containing 0.1 mol dm^{-3} NaBr buffered with phosphate to pH 7: (*a*) 6, (*b*) 92, (*c*) 290 μs, and (*d*) 5 ms after the pulse

comparison to the latter; this leads to the conclusion that the Br_2^- attack results initially in the formation of an inner-sphere adduct [equation (1)].

$$[Co(ida)] + Br_2^- \longrightarrow Co(ida)Br_2^- \quad (1)$$

Earlier references [6,13] to the mode of attack of Br_2^- on metal complexes have generally assumed a reaction of the type (2). The Br_2^- adduct in reaction (1), however, subsequently loses a Br^- [equation (3)]. This brominated complex

$$CoL + Br_2^- \longrightarrow CoLBr + Br^- \quad (2)$$

$$Co(ida)Br_2^- \longrightarrow Co(ida)Br + Br^- \quad (3)$$

is probably the longer-lived intermediate which has significant absorption only in the u.v. region [Figure 4(*c*)]. The anion Br^- is ultimately exchanged for an H_2O group resulting in the final decrease in absorbance at 270 nm [equation (4)].

$$Co(ida)Br \xrightarrow{H_2O} [Co^{III}(ida)]^+ + Br^- \quad (4)$$

If the reaction with Br_2^- proceeded according to equation (2), as proposed earlier, two of the observed facts in the present system would be difficult to explain. (*a*) The close similarity of the peak at 360 nm in Figure 4(*b*) to that of Br_2^- itself; also this peak has too high an absorption to be accounted for by Co(ida)Br. (*b*) The initial decay of the absorption at 360 nm, the simultaneous increase at 270 nm, followed by the subsequent decay at 270 nm indicate the occurrence of two reactions, both first order. However, the only reaction possible with Co(ida)Br is an exchange reaction with water and the second reaction cannot be accounted for.

Under these conditions the only primary radical responsible for ligand degradation is H which can react through hydrogen abstraction [equation (5)] followed by rearrangement of the radical species, discussed subsequently. The yield of glyoxylic acid observed, *G ca.* 0.4, is in agreement with this scheme.

$$Co^{II}(RNHCH_2CO_2^-) + H \longrightarrow Co^{II}(RNH\dot{C}HCO_2^-) \quad (5)$$

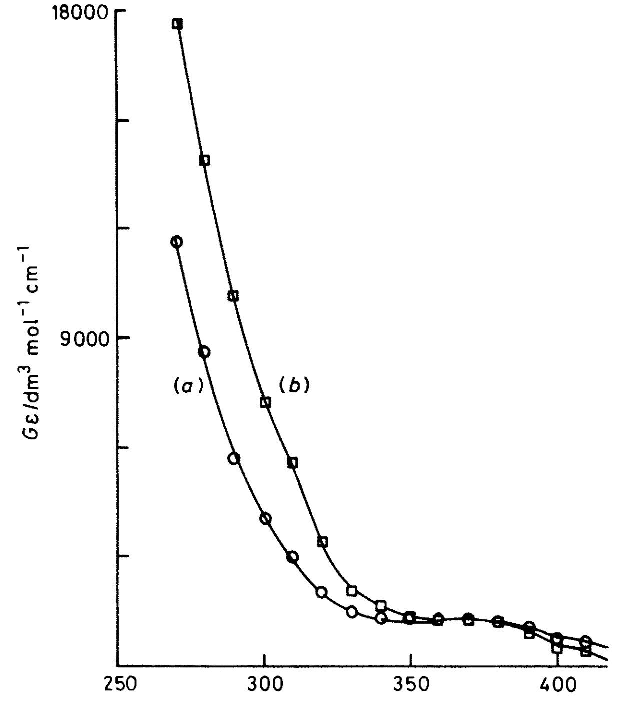

Figure 5. Difference spectra observed in the pulse radiolysis of N_2O-saturated 5.1×10^{-4} mol dm^{-3} [Co(ida)] buffered to pH 7: (*a*) 90—95 and (*b*) 200—250 μs after the pulse

Reaction with OH.—Reaction of the complex with OH appears to be more complicated than that with Br_2^-. It is therefore convenient to consider the results from gamma and pulse radiolysis separately.

Gamma radiolysis. The formation of a cobalt(III) or related species under all conditions of radiolysis is clearly indicated by the difference spectra in Figures 1—3. Since such spectra represent the differences between irradiated and unirradiated solutions they show only the increase or decrease respectively due to the formation of products with higher or lower absorption coefficients than the reactants. While all the cobalt(II) aminopolycarboxylates have nearly equal absorption coefficients in the u.v. region, the corresponding cobalt(III) complexes have a ten-fold higher absorption in this region. Accordingly the spectra shown suggest that at least a part of the [Co(ida)] is oxidized to a trivalent state [equation (6)].

$$[Co^{II}(ida)] + OH \longrightarrow [Co^{III}(ida)]^+ + OH^- \quad (6)$$

The low redox potential for the Co^{III}-Co^{II} system precludes any ligand oxidation by the $[Co^{III}(ida)]^+$; nor has this been observed with the product of reaction (4). But a further rearrangement of the product in reaction (6) may occur at longer times so that the (1 : 1) complex is converted into a (1 : 2) complex or reduced again to [Co(ida)]. However, apart from reaction (6), there must exist an alternative path for the reaction of OH to account for the considerable amounts of glyoxylic acid formed. Since this compound can only arise as a result of oxidation of the ligand, reaction (6) and subsequent rearrangement reactions will clearly not be responsible for ligand oxidation. A comparison of the rate constants for hydrogen abstraction from the free ligand ida [4] by OH and that for reaction of OH with the complex (Table 2) reveals that they are sufficiently similar for a hydrogen abstraction [equation (7)] to occur, at least in part.

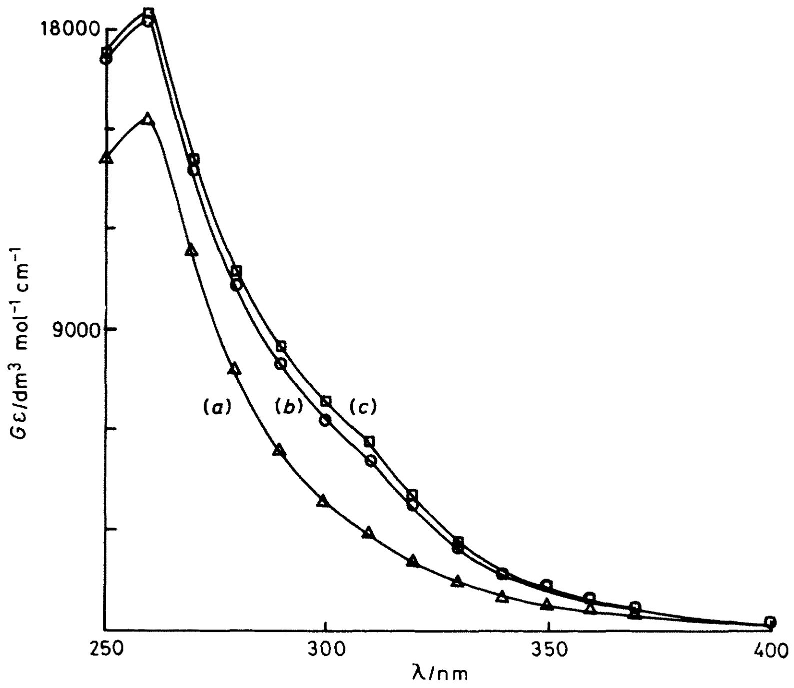

Figure 6. Difference spectra observed in the pulse radiolysis of oxygen-saturated 10^{-3} mol dm^{-3} [Co(ida)] buffered to pH 7 and containing 5×10^{-2} mol dm^{-3} HCO_2Na: (*a*) 40—80, (*b*) 600 μs, and (*c*) 2.6 ms after the pulse

Table 2. Kinetic and spectral characteristics of the reactions and transients observed in the pulse radiolysis of [Co(ida)]

Reactants	Products	Rate constant	$\lambda_{max.}$/nm of product
$[Co(ida)] + Br_2^-$	$Co(ida)Br_2^-$	$k_1 = 8.9 \times 10^7$ dm^3 mol^{-1} s^{-1}	270, 360
$Co(ida)Br_2^-$	$Co(ida)Br + Br^-$	$k_3 = 9.5 \times 10^3$ s^{-1}	270
$Co(ida)Br + H_2O$	$[Co(ida)] + Br^-$	$k_4 = 5.4 \times 10^2$ s^{-1}	—
$[Co(ida)] + OH$	$Co(ida)(OH)$	$k_{10} = 5.8 \times 10^8$ dm^3 mol^{-1} s^{-1}	260(?), 360
$Co(ida)(OH) + H_2O$	$[Co^{III}(ida)]^+ + OH^-$	$k_{11} = 1.2 \times 10^4$ s^{-1}	360
$Co(RNHCHCO_2^-) + [Co(ida)]$	$Co(RNH_2) + CHOCO_2^-$	$k_{8,9} = 3.5 \times 10^6$ dm^3 mol^{-1} s^{-1}	—
$[Co(ida)] + O_2^-$	$Co(O_2)(ida)^-$	$k_{13} = 3.0 \times 10^7$ dm^3 mol^{-1} s^{-1}	260
$Co(O_2)(ida)^- + [Co(ida)]$	$(ida)Co(O_2)Co(ida)$	$k_{14} = 2.4 \times 10^6$ dm^3 mol^{-1} s^{-1}	—

$$Co(RNHCH_2CO_2^-) + OH \longrightarrow Co(RNH\dot{C}HCO_2^-) + H_2O \quad (7)$$

The radical formed in reaction (7), in contrast to the $[Co(nta)]^-$ system,[3] does not appear to disproportionate, as revealed by the yields observed. The value of *G*(gly) (throughout, gly = glyoxylic acid) in the deaerated system is too high for a disproportionation mechanism to be operative. Thus it is likely that the glyoxylic acid is formed through reactions (8) and (9).

$$Co(RNH\dot{C}HCO_2^-) + [Co(ida)] \longrightarrow Co(RNH\overset{+}{C}HCO_2^-) + Co^I(ida)^- \quad (8)$$

$$Co(RNH\overset{+}{C}HCO_2^-) \xrightarrow{H_2O} Co(RNH_2) + CHOCO_2^- \quad (9)$$

On the basis of the above scheme [reactions (5)—(9)] the fraction of OH which attacks the metal ion can be calculated from the ratio of the yields obtained in deaerated and N_2O-saturated solutions after subtraction of the contribution from the H atoms. Taking the *G* values for OH and H as 6.0 and 0.6 in N_2O and 2.7 and 0.6 in N_2 respectively, 55% of OH attacks the metal ion while the remaining 45% attacks the ligand.

Measurements of the yields of H_2O_2 in γ-irradiated solutions were found to be potentially useful in obtaining evidence for the formation of cobalt(III) species in the reaction of OH with the [Co(ida)] complex. Hydrogen peroxide was determined both by use of the titanium sulphate reagent and by means of oxidation of KI. The observed yields (Table 1) in the latter method were consistently higher than those in the former. This indicates that the amount of iodide oxidized cannot be wholly attributed to H_2O_2 because iodide also reacts with Co^{III} while titanium sulphate does not. In aerated solutions the H atoms are likely to be scavenged by O_2 leading to the formation of H_2O_2 and accordingly its contribution to *G*(gly) will be nil. The observed yields are in good agreement with the above: * in N_2O, $G(gly) = 0.45\ G(OH) + G_H = 0.45 \times 6.0 + 0.6 = 3.3$; in N_2, $G(gly) = 0.45\ G_{OH} + G_H = 0.45 \times 2.7 + 0.6 = 1.8$; in O_2, $G(gly) = 0.45\ G_{OH} = 0.45 \times 2.7 = 1.2$; $G(H_2O_2)$ (from Ti^{III}) $= G_{H_2O_2} + \frac{1}{2} G_{e_{aq}^-} + \frac{1}{2} G_H = 0.7 + 1.3 + 0.3 = 2.3$; $G(H_2O_2)$ (from KI) $= G(H_2O_2)$ (from Ti^{III}) $+ G(Co^{III}) = 2.3 + (2.7 - 1.2) = 2.3 + 1.5 = 3.8$.

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* The OH radical yield in N_2O-saturated solution is denoted by *G*(OH), and that from the primary step in the absence of N_2O by G_{OH}.

Pulse radiolysis. The transient spectra obtained in the pulse radiolysis of N_2O-saturated solutions of [Co(ida)] show interesting features in conformity with the gamma irradiations. The spectrum in Figure 5(*a*) is that of the immediate product of the reaction, between OH and the complex, the rate constant of which was evaluated at various initial complex concentrations. In view of the fact that both reactions (6) and (7) are pseudo-first order involving the same reactants and overlapping spectra, it is not possible to discern the individual reactions. The rate constant observed is that of the overall reaction with OH, $k = (k_6 + k_7)$.

The spectrum displays a broad band between 350 and 400 nm with a nominal peak at 370 nm, while an intense band in the u.v. region has a probable maximum at 260 nm. All subsequent changes in the spectrum involve only the u.v. part and with increasing absorption in the u.v. the band at 370 nm tends to a shoulder. However, a gradual decrease in the u.v. absorption was observed over longer periods and in view of the low ε values the changes could not be determined clearly. This part is not shown in Figure 5.

The following considerations enable the assignment of the broad absorption band in the visible region to Co^{III}. (1) The unco-ordinated ligand radical has no absorption[14] at all in this wavelength range. (2) The absorption remains unaffected by subsequent changes, which would be unlikely if it were due to the radical in reaction (7). (3) Many cobalt(III) aminopolycarboxylates have weak absorptions[2,6] in this wavelength region. (4) Although Co^{I} has very intense absorption at this wavelength, its direct formation from the reaction of OH with the complex is unlikely, nor is it likely to remain unaffected at longer times.

The u.v. part of the spectrum has contributions from Co^{III} as well as the radical in reaction (7). Identification of the reactions responsible for the increase in absorbance in this region after the initial reaction with OH and its final decay is rendered difficult by the fact that two species are present, *viz.* a reactive Co(ida)(OH) adduct and a radical species. The initial reaction of OH with the metal ion is likely to proceed through an inner-sphere mechanism resulting in the formation of an OH adduct [equation (10)], similar to Br_2^- attack [reaction (1)]. The OH adduct may subsequently undergo water exchange with the solvent and substitution of an H_2O for OH^- [equation (11)]. The rate constant measured for the reaction has a value similar to that expected for such a reaction. Since this exchange is a self-exchange reaction for OH^- with water it is likely to be considerably faster than that for Br^- exchange with H_2O.

$$[\mathrm{Co(ida)}] + \mathrm{OH} \longrightarrow \mathrm{Co(ida)(OH)} \qquad (10)$$

$$\mathrm{Co(ida)(OH)} \xrightarrow{H_2O} [\mathrm{Co^{III}(ida)}]^+ + \mathrm{OH}^- \qquad (11)$$

Such a reaction involving the substitution of H_2O for an OH^- in the co-ordination sphere may easily give rise to absorption changes in the u.v. region since the charge-transfer bands will be significantly affected by the nature of the ligand. However, any reaction of the radical formed in reaction (7) is only expected to result in loss of the radical site [reaction (8)] and consequently lead only to a decrease in absorption. From the above considerations one may conclude that the increase in absorption in the u.v. region is brought about by substitution of H_2O for OH^- in the Co(ida)(OH) adduct, while the final decrease in absorption is brought about by loss of the radical site through reaction (8).

Thus, both gamma and pulse radiolysis results seem to indicate a mechanism in which OH attacks the metal complex at both sites, metal ion and ligand. The $[Co^{III}(ida)]^+$ so formed is likely to be unstable and highly reactive towards O_2, H_2O_2, *etc.* or it may be reconverted into the more stable [Co(ida)]. The slow spectral change observed after gamma radiolysis is probably due to reaction with O_2 [equation (12)].

$$[\mathrm{Co^{III}(ida)}]^+ + \mathrm{O_2} \longrightarrow \mathrm{Co(O_2)(ida)} \longrightarrow \text{Products} \qquad (12)$$

The formation of such oxygenated species has also been observed in the reaction of the complex with O_2^-.

Reaction with O_2^-.—The reaction of O_2^- with the complex proceeds along the expected course, the initial attack being pseudo-first order with a rate constant of 3.0×10^7 dm^3 mol^{-1} s^{-1}. The rate is somewhat slower than that for $[Co(nta)]^-$,[3] suggesting a similar reaction (13). This is followed by another pseudo-first-order reaction in which the oxygenated complex reacts with another molecule of the starting complex to form a binuclear species [equation (14)].

$$[\mathrm{Co(ida)}] + \mathrm{O_2}^- \longrightarrow \mathrm{Co(O_2)(ida)}^- \qquad (13)$$

$$\mathrm{Co(O_2)(ida)}^- + [\mathrm{Co(ida)}] \longrightarrow \mathrm{(ida)Co(O_2)Co(ida)} \qquad (14)$$

The difference spectrum shown in Figure 1 is likely to be that of the product in reaction (14) or alternatively some product of further reaction.

Conclusions

The results obtained in the present study are consistent with the conclusions reached earlier from the $[Co(nta)]^-$, $[Ni(nta)]^-$, and $[Co(edta)]^{2-}$ systems that these complexes essentially react through inner-sphere processes, reasons for which have already been elaborated.[2,3] Thus the trend of decreasing reactivity is maintained with all three radicals studied OH, Br_2^-, and O_2^- from $[Co(nta)]^-$ to [Co(ida)]. Nitrilotriacetate as a ligand seems to accelerate water-exchange rates more than does edta or ida.

At least in these substitution-labile complexes, the reactivity of the ligand with OH *via* hydrogen abstraction is little affected, as revealed by earlier observations on the reaction of the edta and nta complexes of Co^{II} and Ni^{II}. For [Co(ida)] where the hydrogen abstraction rate from the ligand ida is comparable to the rate of inner-sphere oxidation (water-exchange rate) by OH, both reactions have indeed been observed. Accordingly, any mechanism in which the metal ion is wholly oxidized by OH without taking into consideration the reaction with the ligand must be suspect.

As a corollary to this work it may be suggested that a cobalt(II) complex with another less reactive ligand would probably be completely oxidized by OH at the metal with little ligand reaction. However, some of the difficulties observed in the present system such as overlapping spectra and kinetics and the instability of the oxidized metal ion may remain or render such a study more complicated.

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