Decomposition of Chemically and Electrochemically Generated Nickel(III) Complexes with N_2O_2 Schiff-base Ligands

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Electrochemical oxidation and oxidation by iodine of nickel(II) complexes of tetradentate Schiff bases, derived from salicylaldehyde and 2-hydroxynaphthaldehyde, in dimethyl sulfoxide solutions yielded nickel(III) complexes, which underwent slow chemical decomposition. The kinetics of decomposition of these nickel(III) species has been studied, and the results compared with those previously reported for decomposition reactions of macrocyclic nickel(III) complexes with tetraaza macrocyclic and porphyrin ligands. It is suggested that decomposition proceeds through an initial intramolecular electron transfer, followed by reaction of the nickel(II) radical complex thus formed with other nickel species or substrates present in solution.

The chemistry of metal complexes in less-common oxidation states has been the subject of increasing interest in inorganic chemistry and related fields, due to the important role these compounds play in catalytic and biological processes. Specifically, that of nickel(III) complexes has received considerable attention since it was recognized that nickel in this oxidation state participates in the catalytic action of hydrogenases.[1] Although electronic and steric contributions from the ligands that are able to stabilize this often highly reactive nickel oxidation state have been extensively investigated,[2] there is relatively little information on the decomposition paths of the nickel(III) complexes. Most published data on this latter subject have been obtained in aqueous solutions and for nickel(II) complexes with tetraaza macrocyclic ligands oxidized *in situ* by radicals generated by pulse radiolysis.[3-5] In aqueous solutions, complex mechanisms were postulated to account for acid–base equilibria and for axial co-ordination.[3-5] In these systems, decomposition is believed to occur by electron transfer to the equatorial ligand, followed by ring fragmentation or subsequent reaction with other substrates.

Oxidation of nickel(II) compounds with porphyrin ligands has also been reported, and the oxidation site was found to be strongly dependent on the substituents of the equatorial ligand, on temperature, on the solvent and on good donors in solution.[6-8] In these systems the ligand and metal orbitals lie close in energy[6-8] and oxidation takes place at the metal centre only in the presence of axially co-ordinated ligands, as this interaction is expected to raise the energy of metal orbitals directed to these co-ordination positions. Facile conversion between $[\mathrm{Ni^{III}(por)}]$ and $[\mathrm{Ni^{II}(por^{\bullet})}]^+$, where por = a porphyrin ligand, is observed and the apparent equilibrium between these forms can be controlled by minor changes in experimental conditions. Characterization of the final products resulting from decomposition of these oxidized nickel complexes has shown that both oxidized forms disproportionate to give ultimately two electron ring-oxidized products.[7]

Previous work from our laboratory has focused on factors controlling the availability of this oxidation state for nickel complexes with pseudo-macrocyclic ligands obtained by Schiff condensation of salicylaldehyde and 2-hydroxynaphthaldehyde with aliphatic and aromatic diamines.[9,10] Cyclic voltammetry data[9,10] obtained in Me_2SO have shown that oxidation of nickel(II) complexes with these ligands takes place by a reversible one-electron transfer process at scan rates in the range from 20–100 mV s^{-1}. At lower scan rates the process is no longer reversible, and slower scan rates imply $i_{pc}:i_{pa}$ ratios less than unity. This behaviour has been interpreted to imply that a slow chemical reaction must take place after the oxidation step.[9,11] At more positive potentials a second anodic wave is also observed, but the oxidation process associated with this wave is totally irreversible.

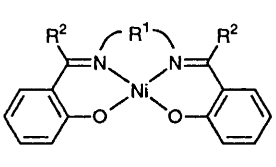
The ESR spectra of electrolysed solutions of these compounds in Me_2SO usually exhibit signals associated with nickel(III) centres, although some of these superimpose on that of radical species. At ambient temperature, a decay of these signals is observed thus supporting a slow decomposition reaction of the generated nickel(III) species.

A major difference in chemical behaviour between tetraaza macrocyclic and Schiff-base complexes relates to the solvents that are able to stabilize the +3 oxidation state for nickel in these complexes. Tetraaza macrocyclic nickel(III) complexes usually show a remarkable stability in acetonitrile and strongly acidic aqueous solutions, but decompose rapidly in the presence of basic solvents.[12] Contrastingly, nickel(III) complexes of Schiff-base tetradentate ligands are only obtained in good donating solvents, and oxidation in solvents that are weaker donors than dimethylformamide (*e.g.* acetonitrile) is believed to yield ligand-oxidized species.[11] This behaviour is reminiscent of that found for porphyrin nickel complexes, where the oxidation site was found to be strongly dependent on the co-ordination ability of the solvent or of other good donors in solution.[6-8]

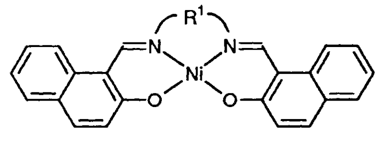
In the present study the decomposition of nickel(III) complexes obtained by chemical and electrochemical oxidation of nickel(II) compounds shown was examined to provide insight into the paths by which these unstable species decompose in Me_2SO solutions. The results obtained are compared with those for tetraaza macrocyclic and porphyrin complexes and suggest that the decomposition involves initially an intramolecular electron transfer from the ligand to the metal, followed by further reactions of the radical compounds formed.

Experimental

Reagents and Solvents.—The following nickel(II) complexes were prepared by methods described in the literature: [Ni(salen)] [H_2salen = *N,N'*-bis(salicylidene)ethane-1,2-diamine],[13] [Ni(salpd)] [H_2salpd = *N,N'*-bis(salicylidene)propane-1,3-diamine],[13] [Ni(dmsalpd)] [H_2dmsalpd = *N,N'*-bis(α-methylsalicylidene)propane-1,3-diamine],[14] [Ni(saldmbn)] [H_2saldmbn = 2,3-dimethyl-*N,N'*-bis(salicylidene)butane-



	R^1	R^2
[Ni(salen)]	$(CH_2)_2$	H
[Ni(salpd)]	$(CH_2)_3$	H
[Ni(dmsalpd)]	$(CH_2)_3$	Me
[Ni(saldmbn)]	CMe_2CMe_2	H
[Ni(salphen)]	o-C_6H_4	H



	R^1
[Ni(napen)]	$(CH_2)_2$
[Ni(nappd)]	$(CH_2)_3$
[Ni(napdmbn)]	CMe_2CMe_2
[Ni(napphen)]	o-C_6H_4

2,3-diamine],[11] [Ni(salphen)] [H_2salphen = *N,N'*-bis(salicylidene)benzene-1,2-diamine],[13] [Ni(napen)] [H_2napen = *N,N'*-bis(2-hydroxynaphthylmethylene)ethane-1,2-diamine],[10] [Ni(nappd)] [H_2nappd = *N,N'*-bis(2-hydroxynaphthylmethylene)propane-1,3-diamine],[10] [Ni(napdmbn)] [H_2napdmbn = *N,N'*-bis(2-hydroxynaphthylmethylene)-2,3-dimethylbutane-2,3-diamine][10] and [Ni(napphen)][H_2napphen = *N,N'*-bis(2-hydroxynaphthylmethylene)benzene-1,2-diamine].[11] Tetraethylammonium perchlorate was prepared by published procedures[15] from tetraethylammonium bromide (Aldrich) and perchloric acid (Merck, *p.a.*). **CAUTION**: perchlorates are hazardous and may explode. Dimethyl sulfoxide and iodine were from Merck (*pro analysis*), [$^2H_6$]-dimethyl sulfoxide and tetramethylsilane from Aldrich (99.9%) and copper nitrate (Spectrasol) from BDH.

Generation of Nickel(III) *Complexes*.—Nickel(III) complexes were generated *in situ* by chemical and electrochemical oxidation of the corresponding nickel(II) complexes, using Me_2SO as solvent. Chemical oxidation was performed by addition of different amounts of iodine to solutions of the nickel(II) complexes, with molar ratios ranging from 0.5:1 to 100:1. Electrochemical oxidation was performed by constant-potential electrolysis of solutions of nickel(II) complexes (10^{-3}–10^{-4} mol dm^{-3}, 0.1 mol dm^{-3} NEt_4ClO_4), using a Metrohm E-254 coulometer and a three-electrode cell; the electrodes were a platinum-gauze electrode, a platinum foil used as counter electrode, and a Ag–AgCl (1 mol dm^{-3} NaCl) reference electrode (all from Metrohm). All electrolyses were performed at a potential 50 mV more positive than the anodic peak potential of the corresponding complex, previously determined by cyclic voltammetry,[9–11,14] except for [Ni(saldmbn)] and [Ni(napdmbn)] for which the anodic peak potentials were used.

Physical Measurements.—The ESR spectra were obtained with a X-band Varian E 109 spectrometer (9 GHz) equipped with a variable-temperature accessory, and calibrated with diphenylpicrylhydrazyl (g = 2.0037); the magnetic field was calibrated by use of Mn^{2+} in MgO. Samples were contained in sealed quartz tubes, and spectra recorded at both room temperature (20 °C) and at −140 °C. Electronic spectra were recorded at room temperature with a Cary 17DX spectrophotometer, NMR spectra at 25 °C on a Bruker AC200 spectrometer using tetramethylsilane as reference.

Kinetic Measurements.—Decomposition reactions of chemically and electrochemically generated nickel(III) complexes were monitored by quantitative ESR spectroscopy. Reaction vessels were kept at 25 °C, and samples were taken at intervals of about 4 min into quartz tubes which were immediately sealed and quenched in liquid nitrogen. The spectra of the frozen solutions were recorded at −140 °C and the nickel(III) concentration was evaluated by double integration, including baseline and Aasa and Vänngard corrections,[16] using Me_2SO solutions of copper(II) nitrate (2.72×10^{-3} or 9.05×10^{-4} mol dm^{-3}) as concentration standards.

Results

Electrochemical Oxidation of Nickel(II) *Complexes*.—Cyclic voltammetry data for oxidation of the nickel(II) complexes obtained in this study are presented in Table 1. The voltammograms for all complexes, except [Ni(salpd)] and [Ni(napphen)], show an anodic and the corresponding cathodic wave, insensitive to the number of cycles, and an anodic–cathodic peak separation in the range 100–170 mV. This separation is larger than that expected theoretically for a one-electron reversible process, but under similar conditions the peak separation for the couple ferrocenium–ferrocene is 90 mV. Additional support for an electrochemically reversible process can be gained by noting that at scan rates higher than 10 mV s^{-1} a linear dependence is observed between E_p and i_p, and between i_p and $v^{\frac{1}{2}}$, and the ratio $i_{pc}:i_{pa}$ is 1:1. It must be pointed out that for scan rates lower than 10 mV s^{-1} this ratio becomes smaller than unity, indicative of the occurrence of a slow chemical reaction following the electron-transfer process.[15] In all these voltammograms another anodic wave appears near the higher limit potential which is partially masked by the solvent discharge. Cyclic voltammograms for [Ni(salpd)] and [Ni(napphen)] show only the anodic waves, even at scan rates higher than 200 mV s^{-1}, suggesting an irreversible process for their electrochemical oxidation.[11]

Electrolysis in Me_2SO of the [NiL] complexes (L = salen, napen, dmsalpd, nappd, saldmbn, napdmbn or salphen), and using potentials 50 mV higher than the corresponding anodic peak potential, yields solutions which exhibit room-temperature ESR spectra with $g_{iso} \approx 2.18$; all frozen-matrix spectra are rhombic, showing three well separated g features ($g_1 \approx 2.25$, $g_2 \approx 2.22$, $g_3 \approx 2.02$) and large g tensor anisotropy, which are typical of $S = \frac{1}{2}$ systems, which for nickel must be associated with the d^7 low-spin electron configuration expected for the +3 formal oxidation state. A typical spectrum is depicted in Fig. 1(*a*), and the paramagnetic centres are formulated as axially elongated six-co-ordinate nickel(III) complexes, $[NiL(Me_2SO)_2]^+$,[10,11,14] as supported by the pattern of g values.[10,11]

Frozen-matrix ESR spectra of electrolysed solutions of [Ni(napdmbn)] and [Ni(saldmbn)], even when the electrolysis was performed at the anodic peak potentials, show superimposed on the signal ascribed to Ni^{III} another band at $g \approx 2.0$, characteristic of a radical species [Fig. 1(*b*)]; similar spectra were obtained for the other complexes referred to above when the electrolysis was performed at potential substantially higher (> 100 mV) than the corresponding anodic peak potential. In all cases, the ratio [radical]/[Ni^{III}] was found to increase as the electrolysis potential was raised. Finally, oxidation of [Ni(salpd)] and [Ni(napphen)] was also attempted, but the electrolysed solutions were ESR silent, as expected from cyclic voltammetry data.

Solutions of the nickel(III) species thus obtained are unstable at room temperature and decay to ESR-silent solutions in a few

Table 1 Electrochemical data for nickel(II) complexes, type of EPR spectra observed for electrochemically oxidized solutions of these complexes, and kinetic results for decomposition of corresponding nickel(III) complexes[a]

Complex	E_{pa}/V	E_{pc}/V	$E_{\frac{1}{2}}$/V	E_{app}/V	EPR spectra	k_{obs}/dm^3 mol^{-1} s^{-1}
[Ni(salen)]	0.84	0.72	0.78	0.89	[Ni^{III}]	—
[Ni(salpd)]	0.73	—	—	0.73	*b*	—
[Ni(dmsalpd)]	0.69	0.55	0.62	0.67	[Ni^{III}]	0.6
[Ni(saldmbn)]	0.93	0.82	0.87	0.93	[Ni^{III}] + radical	—
[Ni(salphen)]	0.91	0.75	0.83	0.97	[Ni^{III}]	5
[Ni(napen)]	0.84	0.72	0.78	0.89	[Ni^{III}]	3
[Ni(nappd)]	0.69	0.56	0.63	0.75	[Ni^{III}]	10
[Ni(napdmbn)]	0.95	0.85	0.90	0.95	[Ni^{III}] + radical	0.8
[Ni(napphen)]	1.07	—	—	1.07	*b*	—

[a] All potentials reported *versus* Ag–AgCl (1 mol dm^{-3} NaCl): E_{pa} and E_{pc} are the anodic and the cathodic peak potentials, respectively, $E_{\frac{1}{2}} = \frac{1}{2}(E_{pa} + E_{pc})$, and E_{app} is the potential used in the electrolyses. Under the conditions used $E_{\frac{1}{2}}$ (ferrocenium–ferrocene) is 0.48 V. Cyclic voltammetry data for the complexes with napen, nappd and napdmbn were taken from ref. 10, for all other complexes from ref. 11. Values of k_{obs} were calculated from experimental data spanning at least three half-lives. [b] No EPR spectra could be observed.

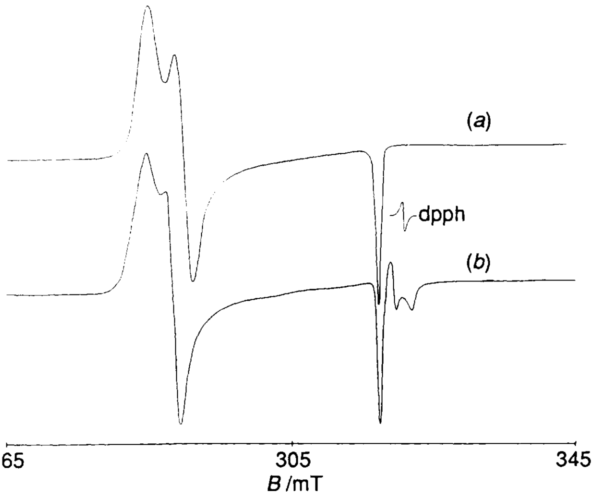


Fig. 1 Frozen-matrix (−140 °C) X-band (9 GHz) EPR spectra of electrolysed solutions of (*a*) [Ni(salphen)] and (*b*) [Ni(napdmbn)]

hours, except for [Ni(salen)(Me$_2$SO)$_2$]$^+$ solutions of which are stable for several days.

Chemical Oxidation of Nickel(II) *Complexes*.—Chemical oxidation was also performed in Me$_2$SO using iodine as oxidant, and the resulting solutions exhibit ESR spectra which are markedly dependent on the iodine concentration. For all complexes, except for that with nappd which will be considered separately, up to a molar ratio iodine:complex of about 40:1 only a weak isotropic signal at $g \approx 2.00$ could be observed; at higher ratios the ESR spectra start to show superimposed on this latter signal bands characteristic of nickel(III) centres the intensity of which increases with the iodine concentration. At very high iodine:complex ratios ($\approx$80:1) only bands ascribed to nickel(III) complexes are observed, except in the cases of [Ni(napdmbn)] and [Ni(saldmbn)] for which the signal at $g \approx 2.00$ is always observed, a behaviour reminiscent of that found upon electrochemical oxidation of these complexes. The ESR spectra due to the nickel(III) complexes are identical with those of the corresponding electrolysed solutions: co-ordination of iodine could not be inferred, as no hyperfine splitting, nor line broadening due to coupling to iodine ($I = \frac{7}{2}$), was detected. These observations suggest that the primary products of oxidation of the nickel(II) complexes are the same in both processes, namely [NiL(Me$_2$SO)$_2$]$^+$. For [Ni(nappd)], spectra of nickel(III) species could only be detected when the ratio iodine:complex was in the range 0.5:1–30:1; furthermore the intensity of the nickel(III) ESR signal was found to decrease with increasing iodine concentration, but in all cases the ESR spectra of the nickel(III) complex are identical with that observed for electrolysed solutions of [Ni(nappd)], thus implying the same co-ordination environment for the oxidized nickel complexes.

Decomposition of Nickel(III) *Complexes obtained by Electrochemical Oxidation*.—The extent of electrolysis was followed by ESR spectroscopy: samples were removed at fixed time intervals and the concentration of nickel(III) species generated estimated by double integration. A plot of concentration *versus* time shows that the concentration does not increase exponentially with time, as expected if the nickel(III) species were not involved in further reactions on the electrolysis time-scale. Instead, it reaches a maximum and then starts to decrease. Electrolysis times for maximum conversion of the nickel(II) complexes, *i.e. ca.* 40–50%, were determined under the conditions used and are reported in Table 1.

The kinetic experiments were performed with solutions of nickel(II) complexes that had been previously oxidized for the length of time corresponding to the maximum nickel(III) concentration in solution. Decomposition of electrochemically generated nickel(III) complexes follows a second-order dependence on [Ni^{III}] and the calculated rate constants are presented in Table 1. No reliable estimate of the nickel(III) concentration was possible for [Ni(saldmbn)(Me$_2$SO)$_2$]$^+$ due to a significant overlap of the two ESR signals (radical and Ni^{III}); this problem did not arise for [Ni(napdmbn)], as overlapping of the two ESR signals was negligible.

Electronic spectra of freshly electrolysed solutions exhibit new bands besides those attributable to the starting nickel(II) complexes; one broad band in near-infrared region (λ = 880–1040 nm, ε = 600–900 dm^3 mol^{-1} cm^{-1}), and two superimposed bands at higher energies (λ = 640–680 nm, ε = 490–820 dm^3 mol^{-1} cm^{-1}). The intensity of these new bands decreases with time, and for solutions that become ESR silent they disappear completely. The final electronic spectrum is very similar to that of the starting solutions and only those bands characteristic of square-planar nickel(II) complexes could be observed.

Decomposition of Nickel(III) *Complexes obtained by Chemical Oxidation*.—The maximum concentration of nickel(III) achieved by chemical oxidation is normally less than 5% of the starting nickel(II) complex {30% for [Ni(nappd)]}, and this fact associated with the low solubility of the starting nickel(II) complexes and with the detection limit of the method used precluded any decomposition studies except for [Ni(napen)(Me$_2$SO)$_2$]$^+$, [Ni(napdmbn)(Me$_2$SO)$_2$]$^+$ and [Ni(nappd)(Me$_2$SO)$_2$]$^+$.

For both [Ni(napdmbn)] and [Ni(napen)] the overall reaction follows a second-order dependence on [Ni^{III}] (Table 2). For all other complexes studied {for [Ni(nappd)] see below} the disappearance of nickel(III) species seems to follow the same

Table 2 Kinetic results for decomposition of nickel(III) complexes obtained by chemical oxidation with iodine in Me_2SO

Complex	$10^2[I_2]$/mol dm^{-3}	k_{obs}*
[Ni(nappd)]	1.92	3.0×10^{-4}
(4.5×10^{-2} mol dm^{-3})	3.96	4.6×10^{-4}
	6.23	6.6×10^{-4}
	8.37	7.8×10^{-4}
[Ni(napdmbn)]	80.5	0.21
(4.4×10^{-3} mol dm^{-3})		
[Ni(napen)]	48.8	21
(2.2×10^{-3} mol dm^{-3})		

* The units of k_{obs} are s^{-1} for nappd and dm^3 mol^{-1} s^{-1} for napdmbn and for napen. The values were calculated from experimental data spanning at least three half-lives, except for napdmbn for which only two half-lives could be followed.

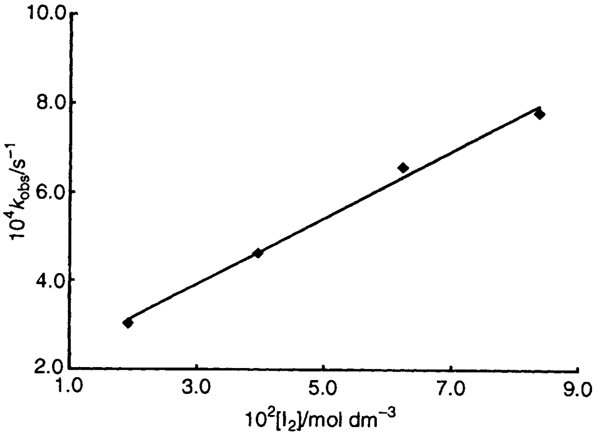


Fig. 2 Dependence of the rate of disappearance of $[Ni(nappd)(Me_2SO)_2]^+$ on the initial iodine concentration: $k_{obs} = 1.48 \times 10^{-4}$ s^{-1} + 7.57×10^{-3} dm^3 mol^{-1} s^{-1} × $[I_2]$

dependence on [Ni^{III}] but, as previously mentioned, the low concentrations that could be obtained precluded the determination of meaningful rate constants for these reactions, as the ESR signals were too weak to allow their integration for significant periods of reaction time. Electronic spectra of chemically oxidized solutions in the near-infrared region are identical with those observed for electrochemically oxidized solutions, but the expected similarities in the visible region could not be confirmed as the high-intensity bands of iodine masked completely any absorption bands due to other species in solution.

As the concentration of paramagnetic centres in solution is low, we also followed the oxidation reaction by ^1H NMR spectroscopy, in an attempt to obtain information about the diamagnetic products of the decomposition reaction. The NMR spectra of solutions of [Ni(napdmbn)] in $(CD_3)_2SO$ after iodine addition are almost identical with those of the pure nickel(II) complex, with no detectable shifts in the bands but with a slight increase in their width. After 48 h the solutions become ESR silent, and new bands appear superimposed on those of the original complex. These latter bands are slightly shifted with regard to the original ones (0.1–0.2 ppm) and their area is about 5% of the total band area. All other nickel(II) complexes, with the exception of [Ni(nappd)], present a similar behaviour, but the relative intensities of the new bands are much smaller than those observed for [Ni(napdmbn)].

The chemical behaviour of [Ni(nappd)] towards iodine oxidation is very different from that observed for the other complexes studied. For this compound, oxidation by iodine occurs to a larger extent, even when using less than the stoichiometric amount of oxidant, and our data clearly shows that an increase in the initial iodine concentration decreases the concentration of nickel(III) complexes formed immediately after iodine addition. The overall reaction follows a pseudo-first-order dependence on [Ni^{III}], and the rate constants were found to be linearly dependent on the initial iodine concentration (Fig. 2 and Table 2). The NMR spectra in $(CD_3)_2SO$ recorded immediately after addition of iodine show only minor changes compared to that of the starting solutions, although room-temperature ESR spectra of the same solutions also afford evidence for the existence of nickel(III) species, at concentrations ranging from 10 to 30% of that of the initial concentration of nickel(II) species. After a few minutes new NMR bands appear which are partially superimposed on those of the original complex (chemical shifts of *ca.* 0.3 ppm), and a simultaneous decrease in the intensities of the [Ni(nappd)] bands is observed. In 2 h the NMR spectra show several new bands, which cannot be assigned to the initial species or to free Schiff base, and after 24 h the spectra become very complex, exhibiting bands over the chemical shift range from 1 to 16 ppm, relative to $SiMe_4$.

Solutions of H_2nappd and iodine, in the same molar ratio used to oxidize the corresponding nickel complex, exhibit after 24 h NMR spectra containing bands due to the original Schiff base but superimposed on several other new bands and with the same pattern as that observed for [Ni(nappd)] in the presence of iodine. However, the extent of oxidation of the Schiff base by iodine, in the absence of nickel(II), is much smaller, and even after a few days the predominant bands in the spectra correspond to non-oxidized H_2nappd.

Discussion

Electrochemical Oxidation.—Electrolyses of the nickel(II) complexes were performed at potentials equal to, or higher than, the corresponding anodic peak potential. Electrolysed solutions of the nickel(II) complexes for which reversible electrochemical oxidation processes in Me_2SO have been observed show ESR spectra containing bands due to six-co-ordinate nickel(III) complexes, formulated as $[NiL(Me_2SO)_2]^+$, although in some cases superimposed on that of radical species.

Cyclic voltammetry data reveal that close to the first anodic wave of these nickel(II) complexes, but at more positive potentials, a second oxidation process takes place.[10,11] For [Ni(saldmbn)] and [Ni(napdmbn)], the complexes with the highest values of $E_{\frac{1}{2}}$ (870 and 900 mV), the two anodic waves are not sufficiently separated to allow for segregation of the two oxidation processes, and ESR spectra of their oxidized solutions always exhibit signals due to nickel(III) and radical species. Electrolysis at potentials more negative than the anodic peak potential were performed, but the rate of formation of nickel(III) centres is slower than that of their decomposition, as can be judged by the absence of any ESR signal.

For the other complexes, for which $E_{\frac{1}{2}}$ is lower than ≈830 mV and where there is a larger separation between the two anodic waves, electrolyses at the anodic peak potential or at potentials lower than the value of ($E_{\frac{1}{2}}$ + 50 mV) yields solutions with ESR spectra containing only bands assignable to nickel(III) complexes; however, solutions of the same complexes when electrolysed at potentials higher than the corresponding value of ($E_{\frac{1}{2}}$ + 50 mV) have ESR spectra containing bands due to nickel(III) complexes and to radical species. These observations suggest that the radical species must arise from further oxidation of nickel(III) complexes, a supposition that gains further support by noting that the ratio [radical] : [nickel(III) complex] increases with the applied potential.

Chemical Oxidation.—All nickel(II) complexes reported in this work can be oxidized to nickel(III) by iodine, but the yield is much lower than that obtained by electrolysis, except for [Ni(nappd)], thus not always allowing for a full kinetic analysis of their decomposition by the ESR method used. Only three compounds were amenable to this type of study: [Ni(nappd)], [Ni(napen)] and [Ni(napdmbn)]; for the others the initial concentration of paramagnetic centres was too low to allow its change with time to be monitored by quantitative ESR spectroscopy. That large amounts of iodine are necessary to oxidize the nickel(II) complexes is probably due to the mild oxidative power of iodine: $E_{\frac{1}{2}}$ (I_2–I^-) in Me_2SO is 690 mV determined under the conditions used in this work; a high concentration of iodine can thus overcome the weak thermodynamic driving force for these reactions. Bromine, a stronger oxidizing agent, cannot be used to obtain nickel(III) complexes of these systems, as even in low concentrations it must oxidize the parent nickel(II) complexes beyond $[NiL(Me_2SO)_2]^+$.

The key aspect in the chemical oxidation process lies with the iodine concentration: low iodine concentrations, nappd excluded, do not allow detection of the ESR signals due to the nickel(III) centres, and only those assignable to radical species can be observed; at very high iodine concentrations the reverse is true; and for molar ratios [iodine]:[complex] $\approx 20:1$–$40:1$ both types of signals are observed. The rate of oxidation is thus highly dependent on the iodine concentration: at low concentrations the rate of formation of nickel(III) centres must be smaller than that of the disappearance/formation of radical species; at high concentrations the reverse must be true. The observation of ESR signals due to nickel(III) centres for complexes with napphen and salpd in the presence of large amounts of iodine, a result that must contrast with that for electrolysed solutions of these complexes which are ESR silent, can be interpreted in terms of a greater rate of decomposition of the oxidized forms than that of their electrochemical generation under the conditions used.

The different behaviour for [Ni(nappd)] cannot be justified solely by its low oxidation potential, compared to those of the other complexes studied, as it is very similar to that of [Ni(dmsalpd)]. A possible insight into its unique behaviour can tentatively be ascribed to the known ability of [Ni(nappd)] to co-ordinate, albeit incipiently, other donor molecules at axial positions,[10,11] whereas the other nickel(II) complexes remain four-co-ordinate even in strong co-ordinating solvents: iodine could then act as an inner-sphere oxidant for [Ni(nappd)], providing an alternate path for oxidation that could explain the high yields obtained.

Decomposition of Nickel(III) *Species*.—Several decomposition studies of nickel(III) complexes with tetraaza[3–5] and porphyrinic[6–8] macrocyclic ligands have appeared in the literature, and provide evidence that for oxidation at the metal centre an intramolecular electron-transfer mechanism must be operative, followed by reaction of the radical species. Disappearance of the latter is believed to occur by a combination of several possible paths (Scheme 1), namely (*a*) ring fragmentation, (*b*) reaction with hydrogen-atom donors or abstractors, (*c*) reaction with similar radical species and (*d*) reaction with nickel(III) species. In the first two cases a first-order dependence on $[Ni^{III}]$ is expected;[3–5] the other two paths presuppose no fragmentation of the equatorial ligand and second-order kinetics on $[Ni^{III}]$ is anticipated, with the final reaction products being the original nickel(II) complexes and nickel(II) complexes where the original ligands have undergone a two-electron oxidation.[3c,17]

For tetraaza macrocyclic complexes in aqueous solution reactions (*a*) and (*b*) seem to be predominant, leading to first-order decay of the nickel(III) complex, while in acetonitrile mixed-order rate laws were found, implying that path (*c*) and/or (*d*) must have a significant contribution to the kinetic behaviour. Decomposition was also found to be base induced, and this has been attributed to deprotonation of the macrocyclic ligand, which is expected to promote initial intramolecular electron transfer, due to stabilization of radical species. Nickel(III) complexes with tetraaza macrocyclic ligands are kinetically stable in strongly acidic solutions, supporting the assumption that intramolecular electron transfer can only occur upon deprotonation of the equatorial ligand.[3–5]

$$[Ni^{III}L] \longrightarrow [Ni^{II}L^{\bullet}]$$

$$[Ni^{II}L^{\bullet}] \longrightarrow \text{products of ligand fragmentation}$$

$$[Ni^{II}L^{\bullet}] + [Ni^{II}L^{\bullet}] \longrightarrow [Ni^{II}L] + [Ni^{II}L^{ox}]$$

$$[Ni^{II}L^{\bullet}] + [Ni^{III}L] \longrightarrow [Ni^{II}L] + [Ni^{II}L^{ox}]$$

Scheme 1 L^{ox} = Two-electron oxidized ligand

For porphyrin complexes the ligand and metal orbitals lie close in energy[6–8] and a facile interconversion between the metal- and the ligand-oxidized forms is observed, which is markedly dependent on the equatorial ligand, on the co-ordinating ability of the solvent, and on temperature. The final products resulting from decomposition of these oxidized nickel complexes are the original porphyrin complex and a two-electron-oxidized porphyrinnickel(II) complex, thus supporting a mechanism with path (*c*) and/or (*d*) as the preferred ones.[7]

Our results for the decomposition of nickel(III) Schiff-base complexes (Tables 1 and 2) support a mechanism similar to that postulated for porphyrins, with reactions (*c*) and (*d*) preferred. Second-order rate laws were found, with one exception: decomposition of $[Ni(nappd)]^+$ generated by iodine oxidation shows a complex rate law, and in the foregoing discussion chemically oxidized [Ni(nappd)] is excluded and will be treated separately.

Although extensive characterization of the decomposition products was not pursued in our work, the similarity of the electronic and of the NMR spectra of the initial solutions of nickel(II) complexes and those of the final ESR-silent solutions seems to suggest that the final products are square-planar nickel(II) complexes with co-ordination environments similar to those of the starting complexes. This observation implies that the final decomposition products must retain most of the original ligand structure, thus precluding any significant fragmentation of the equatorial ligand.

Disproportionation of nickel(III) complexes also could be used to interpret our kinetic data. It must be remembered that disproportionation would yield the original nickel(II) complex and nickel(II) complexes where the ligand has undergone a two-electron oxidation. Nevertheless, the observation of ESR spectra of radical species when these systems are oxidized using low concentrations of iodine seems to give support to the mechanism described previously which proceeds *via* formation of intermediate radical species.

However, for chemically oxidized [Ni(nappd)] a different behaviour is observed: NMR data suggest that ligand fragmentation takes place; kinetic data show first-order behaviour on $[Ni^{III}]$ with k_{obs} being linearly dependent on the initial iodine concentration. This study was possible since the concentration of $[Ni(nappd)]^+$ was sufficiently high to allow for large variation in initial iodine concentration. The linear dependence of k_{obs} on the initial iodine concentration must imply that both iodine or the products of its reduction will react with paramagnetic nickel complexes. The component of k_{obs} that is independent of iodine concentration must be associated with reactions of paramagnetic nickel complexes with ligand fragments that may act as hydrogen donors or abstractors towards nickel(II) radical complexes, as has been proposed for tetraaza macrocyclic complexes.[3]

For the chemical oxidation of [Ni(napdmbn)] and [Ni(napen)] a second-order rate law was deduced, although for the latter compound only the first two half-lives of the decomposition reaction could be followed. For both compounds no drastic change is observed in k_{obs} for decomposition of chemically and electrochemically generated nickel(III) centres, although a slight decrease is observed for $[Ni(napdmbn)(Me_2SO)_2]^+$ generated chemically, whereas the reverse is found for $[Ni(napen)(Me_2SO)_2]^+$. No systematic study on the dependence of k_{obs} on iodine concentration could be performed as the solutions were practically saturated in iodine, and iodine concentrations lower than those used yielded amounts of nickel(III) centres unsuitable for kinetic studies. However, as a large excess of iodine is present in solution it is to be expected that the concentration of nickel(III) complexes will depend on their decomposition rate and on their replenishment by further oxidation of nickel(II) complexes: the resulting values of k_{obs} would then be smaller than those observed for electrochemically generated nickel(III) complexes. This behaviour is observed for [Ni(napdmbn)], but the value for [Ni(napen)] does not fit this model. An alternative pathway similar to that observed for [Ni(nappd)] must also be present, thus accounting for the higher value of k_{obs} found for decomposition of chemically oxidized species. We believe that both pathways must always be present for chemically generated nickel(III) complexes, and that their relative importance depends on the equatorial ligand.

Effect of the Equatorial Ligand on Decomposition Rates.—For nickel(III) complexes obtained electrochemically the observed decomposition rate constants decrease in the order [Ni(nappd)] > [Ni(salphen)] > [Ni(napen)] > [Ni(napdmbn)] > [Ni(dmsalpd)] > [Ni(salen)]. The main trend in this reactivity order is that the experimental rate constants increase with the extent of unsaturation of the equatorial ligand: ligands derived from naphthaldehyde decompose faster than those derived from salicylaldehyde, except for salphen which contains an aromatic bridge. This behaviour is expected as an increase in aromaticity will facilitate electron transfer.[18]

Conclusion

The key difference regarding the decomposition of nickel(III) species between tetraaza macrocyclic complexes and those generated in this study lies in the second-order rate law observed for the Schiff-base complexes, which can be ascribed to greater stabilization of radical complexes towards ring fragmentation. In tetraaza macrocyclic complexes the unpaired electron will lie in orbitals with a large nitrogen contribution,[3–5] whereas in our complexes it resides in delocalized orbitals with large aromatic character,[14] thus decreasing the tendency to bond breaking. Furthermore, for electrochemically generated species, the absence of extraneous substrates to react with the radical complexes will render other radical or nickel(III) complexes as the only possible targets for reaction, thus preventing first-order contributions in the rate law. Another difference between Schiff-base and tetraaza macrocyclic complexes is that the former are not expected to experience base-induced decomposition as they have no acidic hydrogen atoms. Electron transfer to the metal does not require proton abstraction as the aromatic rings will accommodate the electron deficiency, and the radical species can then be formed easily and will undergo further reactions. In contrast, the tetraaza macrocyclic complexes in solvents that are not able to abstract amine protons show much less tendency to decompose, which can be ascribed to non-formation of radical species, and their ESR spectra exhibit only signals due to nickel(III) complexes.

Our results should also be compared to those obtained for porphyrinnickel complexes where, as already pointed out, the ligand and metal orbitals lie close in energy and the oxidation site is largely dependent on the equatorial ligand and on the co-ordinating ability of the solvent. In these complexes oxidation at the metal centres requires axial co-ordination to raise the energy of the metal orbitals above those of the equatorial ligand. For our complexes a similar behaviour is observed and metal oxidation occurs only in strong donating solvents. In acetonitrile the oxidation process is complex and the final products are of radical type.[11] These results suggest that using very strong bases would further stabilize the high oxidation state for nickel, but preliminary results have shown that addition of pyridine or phosphine to freshly electrolysed solutions of nickel(II) complexes with Schiff-base ligands increases the decomposition rate of the oxidized species. Further studies with a broader range of donor solvents is necessary to elucidate this aspect of the chemistry of nickel(III) complexes with Schiff-base ligands.

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