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Hydrogen Peroxide Bleaching of Amaranth Catalysed by Nickel(II) Nitrilotriacetic Acid†

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The complex of Ni^{II} with nitrilotriacetic acid (NTA) (but not other aminocarboxylate complexes) autocatalyses the hydrogen peroxide bleaching of amaranth, although the reaction is inhibited by the absence of light or presence of alcohol, suggesting a radical-based mechanism.

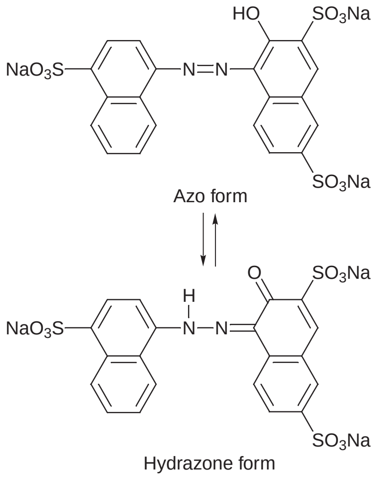
Oxidation of organic substrates with Fe^{II}–hydrogen peroxide (Fenton's reagent) have been widely studied and have potential applications in the 'clean' degradation of organic pollutants such as herbicides.[1] Fe^{II} reacts with hydrogen peroxide forming hydroxyl radicals, which are either scavenged by further Fe^{II} or react with organic substrates. Cu^{II} reacts vigorously with hydrogen peroxide, but reaction is generally inhibited by chelating ligands. However, some Cu^{II}–complexes, for example certain Cu^{II}–peptide complexes, are reactive towards hydrogen peroxide.[2]

Unlike iron and copper, few nickel complex-hydrogen peroxide reactions are known. Histyl peptide ligands, such as glycine glycine histidine (GlyGlyHis), accentuate Ni^{II}; reactivity towards molecular oxygen[3] and hydrogen peroxide.[4] Ni^{II}(GlyGlyHis) has been shown to catalyse the hydrogen peroxide oxidation of proteins and peptides.[5] ESR studies indicate that Ni^{II}(GlyGlyHis) reacts with hydrogen peroxide to produce superoxide, hydroxyl radicals and singlet oxygen, whereas other Ni^{II} peptide complexes such Ni^{II} oligoglycine complexes or Ni^{II}(GlyHis) are relatively inert towards hydrogen peroxide.[4] Nickel(II) tetraazamacrocycles reduce acyl peroxyl radicals to the corresponding peroxyacids, reaction is dependent on the ability of the chelating ligand to stabilise Ni^{III} relative to Ni^{II}.[6]

This investigation focuses on the influence of aminocarboxylate ligands on Ni^{II} reactivity towards hydrogen peroxide, using amaranth as an indicator for the reaction. Dye bleaching assays have previously been suggested as an effective method for studying Fenton reactions.[5,7] Low amaranth concentrations were used to avoid the possibility of dye aggregation. Similarly the use of buffers was also avoided. Amaranth was selected as a substrate as it reacts slowly with hydrogen peroxide in distilled water and extensive bleaching is only seen in the presence of hydrogen peroxide and a transition metal ion catalyst. Dyes, such as amaranth, containing hydroxy groups conjugated to azo groups exhibit azo–hydrazone tautomerism (Scheme 1). For dyes where the hydroxy group is *ortho* to the azo link, the hydrazone form is favoured in aqueous solution.[8]

Addition of Ni^{II} or the Ni^{II} complexes investigated to solutions of amaranth did not produce any changes to the absorption spectrum of amaranth, suggesting that there is no Ni^{II}; amaranth complex formation.

Ni^{II} chelated with iminodiacetic acid (IDA), (2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), ethylenediaminediacetic acid (EDDA) or diethylenetriaminepentaacetic acid (DETAPA) did not catalyse hydrogen peroxide bleaching of amaranth (Table 1). EDTA, EDDA and DETAPA, in addition to chelating Ni^{II}, appear to deactivate indigenous trace metal ions and hence inhibit the residual bleaching observed in the absence of these chelators.



Scheme 1 Amaranth tautomers

Ni^{II} chelated with NTA [$N(CH_2CO_2^-)_3$] catalyses hydrogen peroxide bleaching of amaranth. The reaction is apparently autocatalytic: bleaching is initially slow but increases with time until the reactants become diluted and the reaction again slows down (Fig. 1). The solution pH remains stable during the course of the reaction. Ni^{II}(NTA) does not catalyse hydrogen peroxide bleaching of amaranth in the absence of light. The usual mechanism given for photoactivated Fenton reactions involves hydroxyl radical generation from photolysis of metal ion hydroxides or photolysis of metal ion–ROH or RCO_2H complexes, releasing $R^\bullet$ and the reduced metal ion.[9]

Ethanol undergoes a rapid and well known reaction with hydroxyl radicals and has been employed as an effective hydroxyl radical scavenging agent. Low concentrations of ethanol have been found to inhibit oxidations initiated by Co^{II} driven Fenton reactions[10] and *tert*-butyl alcohol strongly

Table 1 Decrease in amaranth absorbance over 240 min in the presence of 2×10^3 mol dm^{-3} hydrogen peroxide and 6×10^5 mol dm^3 Ni^{II} complexes. Effect of hydrogen peroxide only and NTA without added Ni^{II} are also shown.

Reactant	% Decrease in Absorption after 240 min
1×10^{-3} mol dm^{-3} H_2O_2 only	9
2×10^{-3} mol dm^{-3} H_2O_2 only	8
8×10^{-5} mol dm^{-3} NTA only	9
Ni^{II}_{aq}	3
Ni^{II}(IDA)	4
Ni^{II}(HEDTA)	12.5
Ni^{II}(EDTA)	1
Ni^{II}(EDDA)	0
Ni^{II}(DETAPA)	0
1×10^{-3} mol dm^{-3} H_2O_2 + Ni^{II}(NTA)	70
Ni^{II}(NTA)	92
Ni^{II}(NTA) + 5×10^{-5} mol dm^{-3} EtOH	7
Ni^{II}(NTA) in the dark	0

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

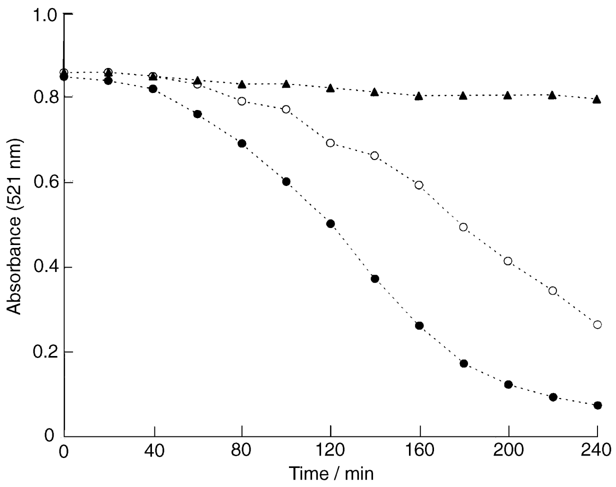

Fig. 1 Bleaching of 4×10^{-5} mol dm^{-3} amaranth by 1×10^{-3} mol dm^{-3} H_2O_2 (▲), 1×10^{-3} mol dm^{-3} H_2O_2 with 6×10^{-5} mol dm^{-3} Ni^{II}(NTA) (○) and 2×10^{-3} mol dm^{-3} H_2O_2 with 6×10^{-5} mol dm^{-3} Ni^{II}(NTA) (●).

retards Fe^{II}(NTA) catalysed hydrogen peroxide decomposition.[11] 5×10^{-5} mol dm^{-3} ethanol inhibits Ni^{II}(NTA) catalysed hydrogen peroxide bleaching of amaranth, which may indicate that hydroxyl radicals are involved in the bleaching mechanism.[7]

The simplest explanation for the results would be a Fenton reaction between Ni^{II}(NTA) and hydrogen peroxide.

$$Ni^{II}(NTA) + H_2O_2 \rightarrow Ni^{III}(NTA) + HO^{\bullet} + HO^{-}$$

Formation of Ni^{III} may be stabilised by the presence of three carboxylate anions in the NTA ligand, which effectively modulates Ni^{II} reactivity. It may also be significant that NTA is a small ligand that leaves two free coordination sites around the chelated Ni^{II} ion. Ni^{III}(NTA) is also likely to be highly oxidising and a further element in the mechanism may be a direct amaranth–Ni^{III}(NTA) reaction. Absence of a dark reaction may indicate that formation and photolysis of a Ni^{II}(NTA)–hydrogen peroxide complex might be a necessary precursor for reaction to occur. There is insufficient evidence to draw conclusions on the varying behaviour of the other five complexing agents.

Experimental

General Procedure.—Changes in amaranth absorbance ($\lambda_{max} = 521$ nm, $\epsilon = 2.2 \times 10^4$ mol^{-1} cm^{-1}) at room temperature were followed at 521 nm using a Perkin Elmer Lambda 2 spectrophotometer. Reactions were initiated by the addition of hydrogen peroxide to aqueous solutions containing 4×10^{-5} mol dm^{-3} amaranth, 6×10^{-5} mol dm^{-3} $Ni(NO_3)_2$ and 8×10^{-5} mol dm^{-3} aminocarboxylate ligand. All materials were purchased from Sigma-Aldrich and were of the highest available grade.

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