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Promoted Hydrolysis of Nitriles using Hydrogen Peroxide: The Isolation and the Characterization of a Paramagnetic Nickel(II)-peroxoacetimido Derivative

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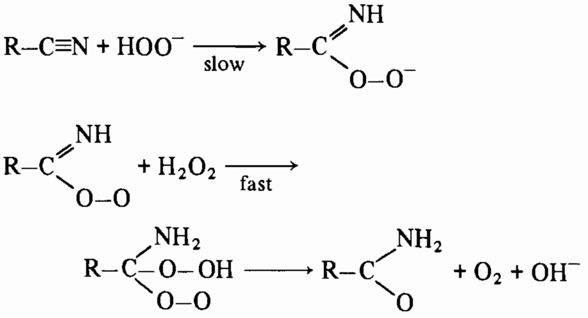
It is well known that nitriles can be advantageously hydrolyzed to amides using hydrogen peroxide in alkaline medium [1]. The reaction develops quickly (usually 1–3 h in the standard procedures) and can be carried out at room temperature in good yield [2]. Kinetic studies suggest that the first step of the reaction involves the nucleophilic attack of the hydroperoxide anion on the nitrile carbon [3]. The peroxoimido species so formed further reacts with an hydrogen peroxide molecule giving the amide and dioxygen. The reaction mechanism can be schematized as follows



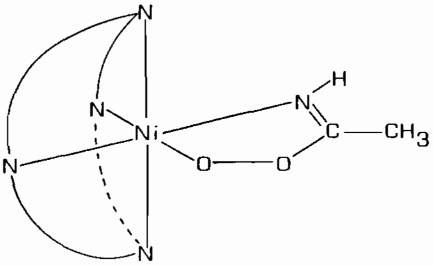
$$R{-}C{\equiv}N + HOO^- \xrightarrow[\text{slow}]{} R{-}C({=}NH){-}O{-}O^-$$

$$R{-}C({=}NH){-}O{-}O + H_2O_2 \xrightarrow[\text{fast}]{}$$

$$R{-}C(NH_2)(O{-}OH)(O{-}O) \longrightarrow R{-}C(NH_2){=}O + O_2 + OH^-$$

We have found that when a solution of Ni(DL-Me_6-14-aneN_4)$(ClO_4)_2$* (α-form) in acetonitrile is mixed at room temperature with an aqueous solution of hydrogen peroxide (0.5–1.0%) made alkaline with NaOH (pH = 12.5–13), an immediate reaction occurs and light violet crystals precipitate in few seconds. Working at 0 °C the reaction is somewhat slower, but a quantitative precipitation is practically obtained. On the other hand working at higher temperatures, e.g. 40–50 °C, oxidation processes involving the coordinated ligand occur. In this case the violet precipitate is not obtained, but it is possible to isolate some diamagnetic complexes of nickel(II) containing the ligand at various degrees of unsaturation. The same negative result is achieved when acetonitrile–water mixtures in a ratio greater than 1:2 are used.

The violet compound is stable for some hours at room temperature in the solid state, but decomposes immediately when dissolved in acetonitrile or dimethylformamide. The analytical data (Found: C, 40.2; H, 8.0; N, 13.0. Calc. for $C_{18}H_{42}N_5NiClO_7$: C, 40.43; H, 7.92; N, 13.10%.) and the physical and chemical properties of this compound are consistent with the formula Ni(DL-Me_6-14-aneN_4)CH_3CO_2NH-$ClO_4 \cdot H_2O$, in which the peroxoacetimido anion acts as ligand towards the metal ion, thus forming a five-membered dioxa-metallacyclic adduct (Scheme 1).



Scheme 1.

Similar dioxametallacyclic adducts are formed by many transition metal dioxygene complexes by reaction with olefins, chetones and other organic substrates [4–6].

This suggestion appears appropriate on the basis of the following experimental evidences.

(i) Iodometric titrations in acidic solutions of this complex indicate the presence of one peroxo group per nickel(II) ion.

(ii) The starting yellow α-diperchlorate complex is obtained when the compound is treated with diluted perchloric acid, thus indicating, on the basis of the configurational properties of donor atoms, that a *cis*-hexacoordinated adduct should be present in the reacting complex.

(iii) The intact macrocyclic ligand is recovered after metal stripping with potassium cyanide.

The infrared spectrum shows the existence of three N–H stretching vibrations (3360, 3280 and 3215 cm^{-1}) as well as a band at 1650 cm^{-1} overlapping with the HOH bending absorption) consistent with the presence of a C=N group. The electronic spectrum, which shows bands at 9.6, 17.6 and 27.4 kK with a shoulder at 11.4 kK, is characteristic of distorted *cis*-octahedral nickel(II) chromophores [7].

Similar compounds are apparently obtained when solutions of aromatic nitriles in dimethylformamide are used in the place of acetonitrile. In this case, however, all the compounds obtained, either as

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*DL-Me_6-14-aneN_4 = DL-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

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perchlorate or hexafluorophosphate derivatives, decompose in a few minutes, thus making difficult any attempt of characterization.

It is worth noting that the use of the nickel(II) analogue formed by the *meso*-Me_6-14-aneN_4 ligand does not allow the isolation of the peroxoimido derivative. This different behaviour can be explained taking into account the difficult formation of the *cis*-octahedral adduct of this acceptor, owing to the unfavourable conformational energy of the ligand in a folded arrangement.

The isolation of the peroxoimido derivative supports the postulated reaction mechanism. Furthermore it offers a perspective for the separation of the reaction products in the hydrolysis of nitriles. These data, however, do not provide information about the catalytic role of the complex in the reaction. A kinetic investigation of this system is necessary in order to elucidate the mechanism.

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