# **REACTION OF BIS-(1,2-DIPHENYLETHYLENE-1,2-DITHIOLATO)NICKEL WITH CUMENE HYDROPEROXIDE**

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#### Summary

Cumene hydroperoxide has been shown to react with bis-(1,2-diphenylethylene-1,2-dithiolato)nickel in cumene solution at 40 - 60 °C via a twostage process. Cumylperoxy radicals generated in the first radical step oxidize the sulphur atoms of the dithiolate ligands leading to destruction of the nickel complex and formation of 1,2-diphenylacetylene, benzoic acid and sulphur oxides, probably sulphur dioxide and  $H_2SO_4$ . In the second stage, these acidic compounds decompose the main part of the hydroperoxide to phenol via an ionic process.

### Introduction

Many metal complexes or their decomposition products have been known for a long time as possessing antioxidant properties and the ability to catalyze the decomposition of hydroperoxides; for this reason they have been used as additives for hydrocarbons and polymers [1]. The most important complexes are sulphur-containing chelates of heavy metals, such as dithiophosphates  $M[S_2P(OR)_2]_2$ , dithiocarbamates  $M[S_2CNR_2]_2$  and xanthates  $M[S_2COR]_2$ . Previous studies of the mechanism of antioxidant action have established that the above-mentioned types of metal complexes primarily promote the decomposition of hydroperoxides, and depending on the ratio of hydroperoxide to the metal complex ionic and free-radical mechanisms have been proposed for this reaction [2 - 8]. More recently, Al-Malaika and Scott [9] have shown that the mechanism of the antioxidant action of the nickel O,O-dialkyl dithiophosphates involves two distinct catalytic processes. The first involves the homolytic breakdown of the peroxide and the second is an ionic process. It has been proposed that the initial stage of the reaction leads to the formation of the corresponding disulphides which then undergo further oxidation to sulphur acids; these, in turn, are responsible for the ionic catalytic decomposition of hydroperoxides.

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The 1,2-dithiolate metal chelates are similar to these types of complexes, and are characterized by unusual redox properties [10]. In these complexes, the formal valency state of the metal is difficult to determine; for example, in bis-(1,2-diphenylethylene-1,2-dithiolato)nickel,  $NiS_4C_4Ph_4$ , it may be +4 or 0, depending upon whether the ligand is regarded as a dinegative ion (I) or a neutral species (II).



1,2-Dithiolate metal complexes are very efficient inhibitors of hydrocarbon autoxidation [11 - 13] and peroxide decomposers [14]. Copping and Uri [12] have reported that 1 mol of  $NiS_4C_4Ph_4$  or  $PdS_4C_4Ph_4$  decomposes more than 1000 mol of tetralin hydroperoxide. Investigation of the mechanism of their interaction with hydroperoxides has shown differences in the nature of the products generated by dithiolene and dithiocarbamate complexes; the following scheme which includes regeneration of the nickel complex has been suggested [15, 16]

 $ML_2 + ROOH \rightleftharpoons [RO_2 \cdot ML_2]^- [H]^+$ 

 $[RO_2 \cdot ML_2]^- [H]^+ + ROOH \rightleftharpoons [ML_2]^{2-} 2[H]^+ + ROOR + O_2$ 

 $[ML_2]^{2-} 2[H]^+ + ROOH \rightleftharpoons [RO \cdot ML_2]^- [H]^+ + H_2O$ 

 $[RO \cdot ML_2]^- [H]^+ + ROOH \longrightarrow ML_2 + H_2O + ROOR$ 

 $[ML_2]^{2-} 2[H]^+ + 2 RO_2 \cdot \longrightarrow ML_2 + ROOR + H_2O_2$ 

In the present paper, the decomposition of highly concentrated solutions of cumene hydroperoxide by the nickel 1,2-dithiolate complex is explained in terms of a two-stage process. The first step of the reaction involves a free-radical decomposition of hydroperoxide induced by the metal complex leading to its oxidative destruction by peroxy radicals. The acidic species of sulphur thus formed subsequently catalyze almost quantitatively a rapid ionic decomposition of the hydroperoxides to yield phenol as the final product.

## Experimental

### Materials

Cumene hydroperoxide (CHP) of 92.7% purity, containing 7.1 wt.% of cumyl alcohol (CA) and 0.2 wt.% of acetophenone (AP), was used for the

preparation of solutions in toluene or other solvents. Cumene, CA, AP, phenol, pyridine, 2,6-di-t-butyl-4-methylphenol and all the solvents were purified using standard procedures. The  $NiS_4C_4Ph_4$  complex was synthesized according to the method of Schrauzer and Mayweg [17] while pyridine N-oxide was synthesized by a published method [18].

### Methods

The reaction of ca. 25 - 75 wt.% cumene hydroperoxide solutions (3 - 5 ml) was carried out in a 30 ml thermostatted glass vessel placed behind a thick glass screen. The reaction vessel was equipped with a Teflon magnetic stirrer, reflux condenser, an inlet tube for inert gas (carbon dioxide) and an outlet for the products. After the solution had reached the reaction temperature, the nickel complex was added. Samples were taken with a syringe and analyzed iodometrically for cumene hydroperoxide, and in some cases for acetophenone, cumyl alcohol and dicumyl peroxide using <sup>1</sup>H NMR spectroscopy (JEOL FX-100) [19] in benzene as a solvent. Phenol, acetone and  $\alpha$ -methylstyrene were analyzed using a Hewlett-Packard 5830 A gas chromatograph equipped with flame ionization detectors. Glass columns (0.3 × 120 cm) packed with 10% Apiezon L + 2% H<sub>3</sub>PO<sub>4</sub> on Chromosorb W (80 - 120 mesh) were employed. Before analysis, cumene hydroperoxide was decomposed by reaction with triphenylphosphine [20].

Visible spectra of the reaction mixture were measured at 20 °C on a Specord spectrometer (Zeiss, Jena, GDR). Electron spin resonance studies of radicals produced by the reaction of the nickel complex with cumene hydroperoxide (*ca.* 30 wt.% in cumene) were performed *in situ* in the cavity of a Varian E-3 spectrometer at  $55 \pm 2$  °C bubbling an inert gas through the sample.

NMR spectroscopic analysis of the products formed through destruction of the nickel complex was carried out using the following procedure. The NiS<sub>4</sub>C<sub>4</sub>Ph<sub>4</sub> complex and a 50 - 100 fold excess of t-butyl hydroperoxide (ca. 80% solution in t-butanol) were heated at 80 °C in a glass tube until the dark colour of the complex had disappeared. The resulting mixture consisted of two phases. The upper colourless phase was analyzed for hydroperoxide and the decomposition products of the metal complex, while the lower light green phase contained nickel sulphate dissolved in the water generated by the reaction.

### **Results and discussion**

Highly concentrated solutions of cumene hydroperoxide in cumene react with the  $NiS_4C_4Ph_4$  complex via a two-stage process. An initial induction period is followed by a rapid autocatalytic decomposition of the hydroperoxide. Over the concentration range 25 - 75 wt.% CHP at a fixed temperature and catalyst concentration, the induction period is only slightly dependent on the initial CHP concentration (Fig. 1), but the second stage of the



Fig. 1. The dependence of the extent of CHP decomposition on time for various concentrations. Conditions: 55 °C; complex,  $NiS_4C_4Ph_4$  at a concentration of  $1.84 \times 10^{-3}$  mol dm<sup>-3</sup>.

decomposition is very much influenced by this concentration. At higher concentrations (ca. 50% CHP) decomposition over this second stage is almost instantaneous (shown by dashed lines in the figure) but proceeds more slowly at lower concentrations, e.g. 28% CHP. The induction period decreases with increasing reaction temperature (Fig. 2) and is strongly dependent on the solvent employed (Fig. 3). Increasing the concentration of the nickel complex from  $9.2 \times 10^{-4}$  to  $4.6 \times 10^{-3}$  M almost halves the length of the induction period.



Fig. 2. The effect of temperature on the decomposition rate of CHP. Conditions: complex, NiS<sub>4</sub>C<sub>4</sub>Ph<sub>4</sub> at a concentration of  $1.84 \times 10^{-3}$  mol dm<sup>-3</sup>; curve 1, 30 °C; curve 2, 40 °C; curve 3, 45 °C; curve 4, 50 °C; curve 5, 55 °C.

Fig. 3. The influence of various solvents on the decomposition of CHP at 55 °C. Conditions: complex, NiS<sub>4</sub>C<sub>4</sub>Ph<sub>4</sub> at a concentration of  $2.3 \times 10^{-3}$  mol dm<sup>-3</sup>; solvent, toluene in a 1:1 vol/vol ratio with (1) acetic acid; (2) chlorobenzene; (3) t-butanol; and (4) dioxan. The main products from the dcomposition of cumene hydroperoxide in the series of reactions catalyzed by the NiS<sub>4</sub>C<sub>4</sub>Ph<sub>4</sub> complex are phenol and acetone, with  $\alpha$ -methylstyrene, acetophenone and cumul alcohol being produced in small amounts. Analysis of the product distribution over the whole reaction shows that during the first stage of the reaction cumene hydroperoxide decomposes to acetophenone and cumyl alcohol (by *ca*. 85 - 90% of the theoretical yield). During this stage only trace amounts of phenol were detected. However, the amount of phenol increased sharply during the second stage of the reaction where acetone was also formed as the main product. The rate of decomposition of cumene hydroperoxide is very high with phenol and acetone being produced in yields greater than 80 mol%.

The experimental evidence presented in this study indicates that the decomposition of cumene hydroperoxide by the NiS<sub>4</sub>C<sub>4</sub>Ph<sub>4</sub> complex involves two catalytic processes. In the first stage, the homolytic decomposition of the hydroperoxide predominates and free-radical intermediates are formed. Thus, during the reaction of the hydroperoxide with the nickel complex, peroxy radicals were established by ESR spectroscopy being characterized by a singlet with a g-value of 2.014 and a peak to peak width of 1.1 mT. The concentration of these radicals decreases sharply over the first 20 min of reaction (Fig. 4); a time length which corresponds to the induction period in the decomposition of the hydroperoxide (Fig. 1). Thereafter, heterolytic decomposition predominates and the concentration of peroxy radicals levels off at a low stationary value. As a result of the metal complex induced decomposition of the hydroperoxide (in the absence of the complex the reaction does not proceed), the radical generating process leads to the oxidative destruction of the nickel complex. This phenomenon may be followed by means of the visible spectrum; the absorption band at 16 600 cm<sup>-1</sup>, corresponding to the NiS<sub>4</sub>C<sub>4</sub>Ph<sub>4</sub> complex [21] as a ca. 50%



Fig. 4. Concentration of peroxy radicals (g = 2.014) as a function of time in the reaction of the NiS<sub>4</sub>C<sub>4</sub>Ph<sub>4</sub> complex (concentration,  $2 \times 10^{-3}$  mol dm<sup>-3</sup>) with cumene hydroperoxide (30 wt.% in cumene) at 55 °C.



Fig. 5. The dependence of the induction period on the concentration of 2,6-di-t-butyl-4-methylphenol at (1) 0 mol dm<sup>-3</sup>; (2)  $6.82 \times 10^{-3}$  mol dm<sup>-3</sup>; (3)  $1.13 \times 10^{-3}$  mol dm<sup>-3</sup>; and (4)  $2.27 \times 10^{-2}$  mol dm<sup>-3</sup>. Conditions: 55 °C; complex, NiS<sub>4</sub>C<sub>4</sub>Ph<sub>4</sub> at a concentration of  $1.84 \times 10^{-3}$  mol dm<sup>-3</sup>.

solution of cumene hydroperoxide, completely disappeared during the induction period. The termination of complex oxidation is accompanied by the partial precipitation of nickel sulphate and an increase in the acidity of the reaction medium (pH  $\sim$ 5).

Experiments with the peroxy radical trapping agent 2,6-di-t-butyl-4methylphenol have also revealed the important role of peroxy radicals in the mechanism of complex destruction. Figure 5 shows that in the presence of the trapping agent there is an increase in the length of the induction period which corresponds to destruction of the complex by peroxy radicals.

The decomposition of the NiS<sub>4</sub>C<sub>4</sub>Ph<sub>4</sub> complex during the reaction with hydroperoxide may be confirmed by changes in the electronic spectra and also data from <sup>13</sup>C NMR spectroscopic studies of the reaction products. In order to simplify the NMR analysis of the reaction mixture containing decomposition products of both the hydroperoxide and the nickel complex, t-butyl hydroperoxide was used. The main products of the decomposition of t-butyl hydroperoxide by  $NiS_4C_4Ph_4$  are di-t-butyl peroxide and t-butanol; the products of the decomposition of the  $NiS_4C_4Ph_4$  complex are 1,2diphenylacetylene and benzoic acid. The <sup>13</sup>C NMR spectrum of 1,2-diphenylacetylene in  $CDCl_3$  ( $\delta$  77.0 ppm) is characterized by signals at 89.3 ppm (C=C), 123.2 ppm (C-C=C), 128.2 and 131.5 ppm (C-H ring) which are very close to the literature values [22]. Oxidation of the sulphur atoms in the ligands of the nickel complex does not stop at the sulphoxide or sulphone stage but leads predominantly to the breakdown of the carbonsulphur bond with the formation of sulphur oxides, probably sulphur dioxide. Other unidentified unstable products are also present in low concentration. Benzoic acid could be formed by the oxidation of intermediate sulphur compounds of the stilbene type by sulphur oxides.

The destruction of the nickel complex with cumylperoxy radicals as the oxidizing species probably proceeds via a subsequent oxidation of the sulphur atoms of the dithiolate ligands to sulphoxides and sulphones, as proposed by Howard and Chenier [23] for metal dithiocarbamates.



Further oxidation of the sulphur atoms of the nickel complex with peroxy radicals leads to the decomposition of the complex and the formation of the following products:



Sulphur dioxide,  $SO_3$  or  $H_2SO_4$ , *i.e.* the final acidic products, decompose cumene hydroperoxide during the second stage of the reaction via an ionic process forming phenol as the main product from cumene hydroperoxide.

$$SO_2 (SO_3) + H_2O \longrightarrow H_2SO_3 (H_2SO_4)$$
  
PhMe<sub>2</sub>COOH  $\xrightarrow{H^+}$  PhOH + Me<sub>2</sub>CO

The first step in the formation of peroxy radicals by metal complex induced decomposition of hydroperoxides probably involves the prior formation of the metal complex-hydroperoxide adduct [23]. Copping and Uri [12] have proposed this step to explain the second-order kinetics for the decomposition of tetralin hydroperoxide by the NiS<sub>4</sub> $C_4Ph_4$  complex. Evidence for adduct formation has been provided by experiments performed in the presence of pyridine or its N-oxide. Such bases can exchange with the hydroperoxide in the metal-hydroperoxide adduct and occupy the axial positions in the nickel complex. Thus, in the presence of a twice molar concentration of pyridine relative to the  $NiS_4C_4Ph_4$  complex, the induction period exceeds 5 h (whereas in the absence of pyridine it is only 20 min). With the less efficient ligand, pyridine N-oxide, under the same conditions and at a 4:1 molar ratio relative to the nickel complex, rapid decomposition of cumene hydroperoxide begins after 185 min. When the reaction is carried out in different solvents (Fig. 3), the induction period is also changed, probably as a result of the influence of the metal complex-hydroperoxide adduct.

The results of our investigations show that, contrary to the conclusions from previous studies [15, 16], the reaction of the  $NiS_4C_4Ph_4$  complex with cumene hydroperoxide occurs via a two-stage process with a mechanistic pathway similar to that for other classes of metal dithiolate complexes [9].

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