

Mechanisms of antioxidant action: Intermediates involved in the formation of sulphur acids from nickel dialkyl dithiophosphates

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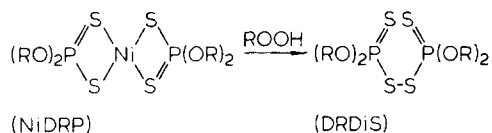
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The oxidation of nickel dibutyl dithiophosphate by cumene hydroperoxide is shown to involve the formation of unstable sulphur acids which break down to give ionic catalysts for the decomposition of hydroperoxides.

Keywords Antioxidants; nickel dialkyl dithiophosphates; oxidation; hydroperoxides; catalysts; stabilizers

It was shown in a recent publication¹ that two quite different processes are involved in the mechanism of antioxidant action of the nickel dialkyl dithiophosphates. The first involves homolysis of hydroperoxides¹⁻³ and the second results in ionic decomposition of hydroperoxides^{1,3}. It was proposed that the ionic catalyst for peroxide decomposition was derived from the intermediate disulphides (DRDiS) which are primary products of the oxidation of the nickel complexes (NiDRP).



The distribution of products in the reaction of cumene hydroperoxide (CHP) with nickel dibutyl dithiophosphates, NiDRP, R = *n*Bu, at different molar ratios was found¹ to be strikingly similar to that observed for the reaction of CHP with sulphur dioxide⁴. It was proposed¹ that sulphur acids might be formed which would therefore contribute to the second catalytic ionic process in the case of NiDBP.

Here we report further results which confirm the formation of a disulphide (DRDiS) as an intermediate during the reaction of NiDBP with cumene hydroperoxide at elevated temperatures. This compound is further oxidized to unstable intermediates which break down to give the catalysts responsible for the effective hydroperoxide-decomposing activity of NiDBP. T.l.c. analysis of the products formed during the early stages (0–3 mins) of the stoichiometric reaction between CHP (1×10^{-2} M) and NiDBP (1×10^{-2} M) in chlorobenzene at 110°C in an inert atmosphere showed the presence of NiDBP ($R_f \approx 0.003$), acetophenone ($R_f \approx 0.53$), and DBDiS ($R_f \approx 0.8$). Furthermore, it was found that the oxidation product, DBDiS, disappeared at longer re-

action times. Although the conditions used for t.l.c. analysis (Kiesel gel plates F524, developed in benzene, u.v. detection) did not provide an unequivocal separation of α -methyl styrene and DBDiS, the formation of the former is excluded on the following grounds.

(1) Since α -methyl styrene is a stable product it should persist throughout the course of the reaction, as indeed was found to be the case in related reactions. The present t.l.c. results however reveal only a transitory existence of the product with $R_f = 0.8$.

(2) At the same molar ratio of CHP:NiDBP, product analysis by g.l.c. did not reveal the formation of α -methyl styrene.

Figure 1 shows the kinetics of the formation of intermediates during the course of CHP decomposition by

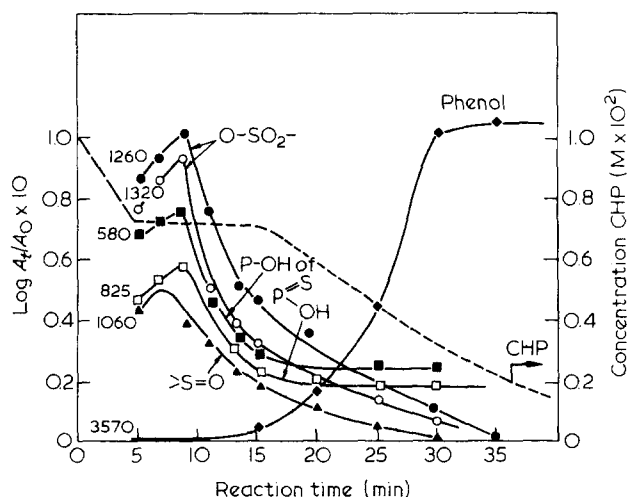
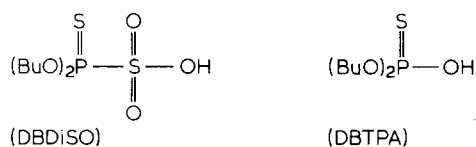


Figure 1 Kinetics of the formation of transformation products (by infra-red spectroscopy) in the reaction of CHP (1×10^{-2} M) with NiDBP (1×10^{-4} M) in chlorobenzene at 110°C (numbers on curves are i.r. absorption frequencies)

NiDBP in chlorobenzene at 110°C and at a molar ratio of 100:1 ($\text{CHP} = 1 \times 10^{-2} \text{ M}$). It can be seen that both sulphonic (DBDiSO) and thionophosphoric (DBTPA) acids are formed slowly during the induction period whereas no phenol is formed initially, i.e. during the build-up period of DBDiSO and DBTPA. Thus the concentration of DBTPA, which is formed by elimination of



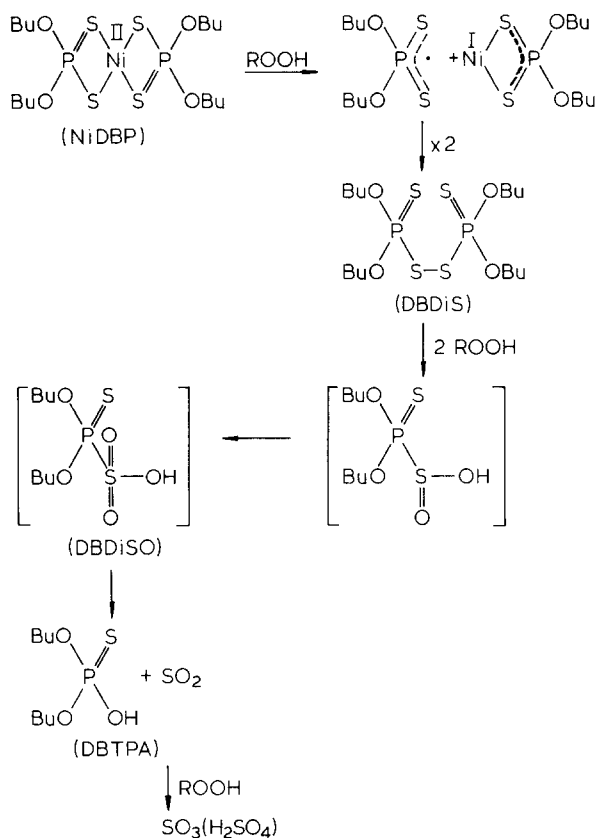
DBDiSO, appears to remain steady after an initial decomposition. The resulting SO_3 or H_2SO_4 would certainly account for the formation of phenol and acetone during CHP decomposition⁴.

Scheme 1 outlines the reactions involved in the conversion of NiDBP (in the presence of CHP at 100 fold excess) to SO_2 and H_2SO_4 which catalyse the ionic decomposition of CHP and which inhibit the hydroperoxide-initiated oxidation.

This process is analogous to the formation of an ionic catalyst for hydroperoxide decomposition from mercaptobenzthiazole and its metal complexes through the intermediate disulphide⁵ and it is also consistent with the mechanism proposed earlier^{6,7} for the antioxidant function of metal dithiocarbamates in hydroperoxide initiated systems. Further work is in progress to elucidate the detailed mechanism of the SO_2 elimination.

References

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Scheme 1 Antioxidant mechanism of nickel dibutyldithiophosphate

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