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THERMOANALYTICAL INVESTIGATIONS ON HETEROCYCLIC ORGANIC COMPOUNDS. PART III. THE EFFECT OF INTRODUCING A RING NITROGEN ATOM ON THE FUNCTION OF 1-NAPHTHOL AS ANTIOXIDANT. A DIFFERENTIAL SCANNING CALORIMETRIC STUDY

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ABSTRACT

The introduction of a ring nitrogen atom into the aromatic skeleton of 1-naphthol affects its function as an additive in inhibiting oxidation in a lubricating oil medium. 1-Naphthol with a nitrogen atom in the 2 and 8 positions (isocarbostyril and 8-hydroxyquinoline) exhibited weak antioxidant activity, whereas the derivatives with the nitrogen atom in the 5 and 6 positions (5-hydroxyquinoline and 5-hydroxyisoquinoline) were of comparable activity to that of 1-naphthol. The systems were also studied in the presence of soluble metal catalysts and results are given. Explanations on the basis of the stability of phenoxy radicals and the coordination ability of the species are discussed.

INTRODUCTION

Phenolic and aromatic amine compounds have been used extensively as antioxidants in organic materials by interaction with the free radicals formed yielding a non-radical substrate product and a phenoxy or phenimino radical. The resulting antioxidant radical is well stabilized through resonance with the aromatic systems, such as in naphthols or amines, or sterically prevented from reacting further such as in butylated hydroxytoluene compounds [1].

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Substituted phenols and hydroxynaphthalenes have been used extensively as additives in the prevention of oxidation of lubricating oils and greases, thus increasing the useful lifetime of these materials [2].

Differential scanning calorimetry (DSC) has been used to determine the oxidation stability of mineral oils and to study the effect of a range of oxidation inhibitors on lubricating oils [3,4]. On heating a sample of oil in air, using a DSC apparatus, an exothermic effect resulting from the oxidative degradation of the oil is recorded. The onset temperature of the exotherm can be taken as a measure of the thermal stability of the lubricating oil.

Several workers have used this technique to study the effect of a range of oxidation inhibitors on lubricating oils. The higher the onset temperature of the exothermic reaction, the more effective the inhibitor, and vice versa [5,6].

The aim of this paper is to study the changes in the behaviour of 1-naphthol upon the introduction of a ring nitrogen atom at different positions in its aromatic skeleton, and to evaluate their efficiency as antioxidants under different conditions using DSC techniques.

EXPERIMENTAL

Apparatus

The DSC measurements were carried out in a Heraeus TA 500 thermal analyser. Oil samples weighing 5–10 mg were heated at a rate of 10°C min^{-1} in an aluminium crucible under ambient conditions. The reference cell was left empty. Studies in an atmosphere of oxygen were performed under oxygen gas flowing at a rate of 100 cm^3 min^{-1}.

Materials

1-Naphthol, isocarbostyril, 5-hydroxyisoquinoline, 5-hydroxyquinoline and 8-hydroxyquinoline of more than 98% purity were purchased from Aldrich Chemical Co. Ltd. Di-tert-butyl *para*-cresol (DBPC) was purchased from ICI Chemical Co.

Procedure

Solutions of the above compounds in concentrations ranging from 0.1 to 0.4 by weight were prepared by dissolving them with heating in a standard lubricating oil. Studies in the presence of soluble metal catalysts were conducted by dissolving suitable amounts of solutions of copper and iron naphthenate in the oil mixture in order to obtain copper and iron concentrations of 20 ± 0.5 ppm.

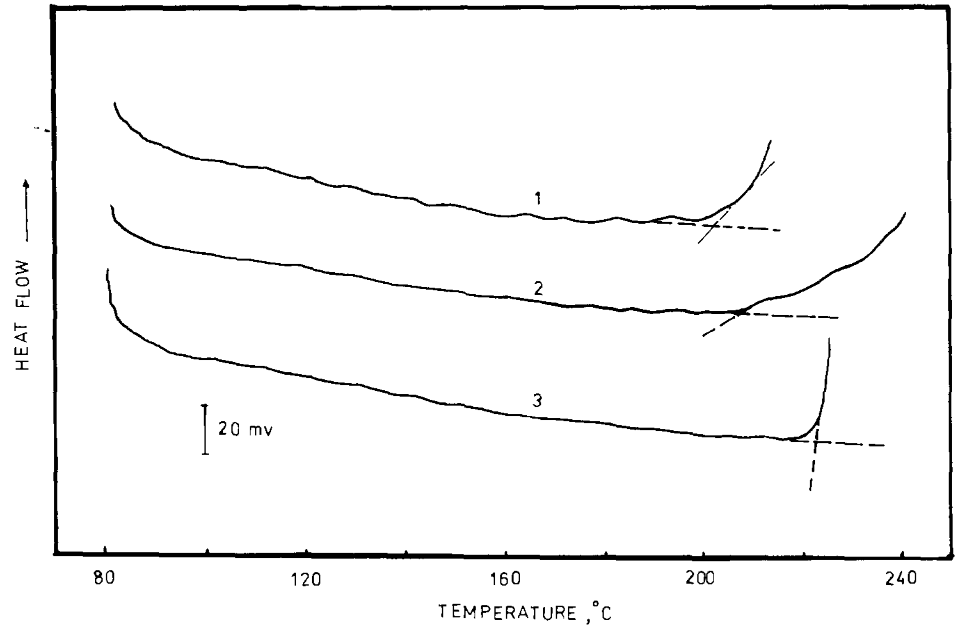


Fig. 1. Evaluation of the oxidation onset temperature.

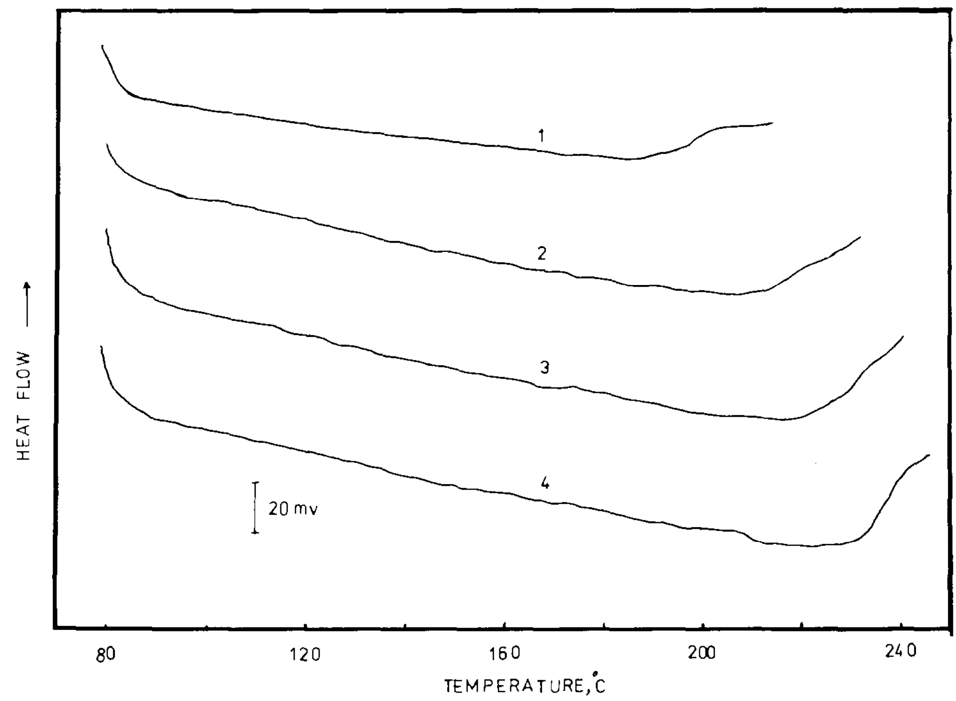


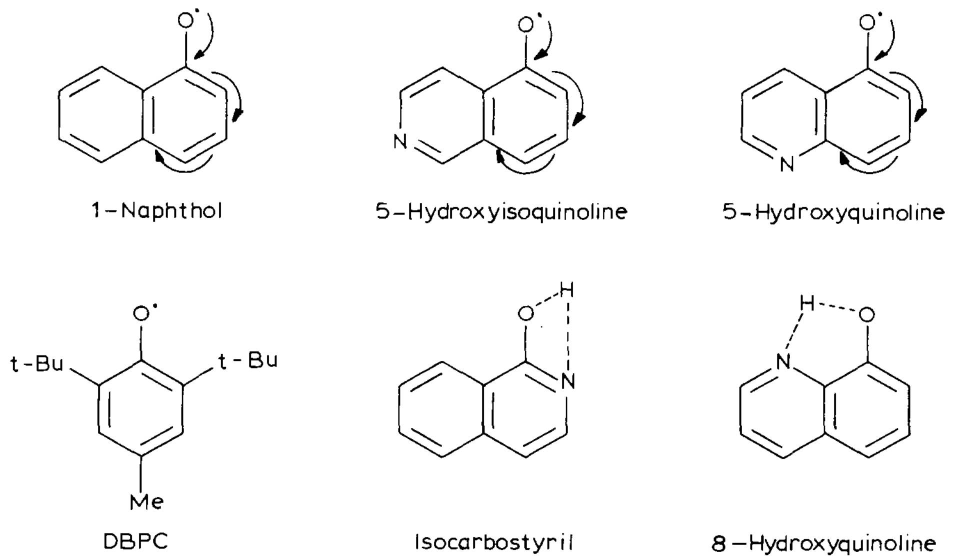
Fig. 2. DSC signals of the oxidation of the oil in the presence of DBPC additive: (1), 0%; (2), 0.1%; (3), 0.2%; (4), 0.4%.

RESULTS AND DISCUSSION

The onset temperature of the exothermic effect of oil oxidation was evaluated as in Fig. 1. The DSC signals of oil oxidation, with and without selected antioxidant, are shown in Fig. 2. The numerical evaluation of the DSC curves of the oxidation of oil in the presence of different concentrations of various antioxidants are given in Table 1. The onset temperature of oxidation of the oil on its own is 190°C.

The antioxidation effect of these compounds is closely related to the stability of their phenoxy radicals which are formed by the donation of a hydrogen atom from the antioxidant to the substrate radical [1]. With the exception of isocarbostyril and 8-hydroxyquinoline, the thermal stability of the oil increases with increasing concentration of antioxidant. The effect of 1-naphthol and 5-hydroxyquinoline is significant even at the lowest concentration.

The relative stability of the radicals formed by the proton donation from the antioxidant molecule can be deduced from Scheme 1.



Scheme 1

The DBPC radical is strongly stabilized by the steric hindrance character of the bulky tert- alkyl groups, while the radicals of 1-naphthol, 5-hydroxyisoquinoline and 5-hydroxyquinoline gain their stability from the conjugation with the aromatic system. The formation of radicals from isocarbostyril and 8-hydroxyquinoline is hindered due to intra-hydrogen bonding through the two adjacent electronegative sites, i.e., nitrogen and oxygen atoms. The hindrance is less significant with isocarbostyril than in 8-hydroxyquinoline

TABLE 1

The onset temperature of oxidation of the oil in the presence of different concentrations of various antioxidants (results are the average of three determinations)

Antioxidant	0.1%	0.2%	0.4%
DBPC	212	220	233
1-Naphthol	233	242	267 [a]
5-Hydroxyisoquinoline	209	228	250
5-Hydroxyquinoline	241	244	246
8-Hydroxyquinoline	200	208	212
Isocarbostyril	214	214	216

[a] Evaporation occurs prior to oxidation.

due to the instability of the strained four-membered ring formed. These effects are tailored with the results shown in Table 1.

Effect of copper and iron catalysts

Catalysts are often used to facilitate the oxidation of oils so that the laboratory measurements for the oxidation stability can be performed more rapidly. In the present work the catalyst is not a contact surface [7] but a soluble copper and iron naphthenate which ensures intimate contact with the oil. The effect of copper naphthenate is relatively greater than iron in decreasing the oxidation stability of the oil. Oil oxidizes at 174°C in the presence of copper and at 178°C in the presence of the iron catalyst.

An attempt was made to study the effect of the antioxidants in the presence of these catalysts. The results are summarized in Table 2 and Fig. 3. With the exception of 5-hydroxyquinoline, in iron catalyst is more effective in bringing about oxidation than copper.

TABLE 2

The onset temperature of oxidation of the oil in the presence of different concentrations of various antioxidants and soluble metal catalysts (results are the average of three determinations)

Type of catalyst	Iron			Copper		
% antioxidant =	0.1	0.2	0.4	0.1	0.2	0.4
DBPC	203	206	206	210	212	215
1-Naphthol	214	220	235	231	235	251
5-Hydroxyisoquinoline	206	221	223	202	220	227
5-Hydroxyquinoline	232	237	237	220	226	228
8-Hydroxyquinoline	177 [a]	185	195	196	197	200
Isocarbostyril	158	168	198	167	177	198

[a] Oxidation proceeded slowly.

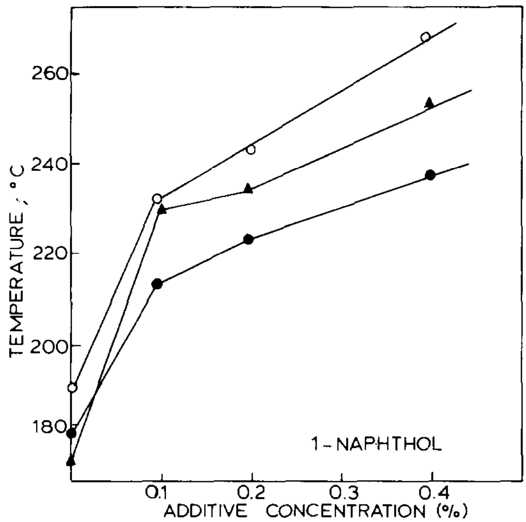


Fig. 3. The improvement in the oxidation stability of the oil upon addition of 1-naphthol and in the presence of metal catalysts. (○), oil; (●), oil + iron catalyst, and (▲), oil + copper catalyst.

It is clear that a concentration of 0.1% DBPC in the presence of both types of catalysts can be considered critical where higher concentrations do not improve the oxidation stability of the oil, while their effect is inferior when the concentration of 1-naphthol exceeds 0.2%.

The rate of increase in oxidation inhibition on increasing the concentration of 5-hydroxyisoquinoline is slower in the presence of these catalysts than that recorded in Table 1. It is also noticed that the catalysts are only slightly effective in lowering the antioxidation ability of 5-hydroxyquinoline, while the effect of isocarbostyril and 8-hydroxyquinoline in inhibiting oxidation is severely diminished in the presence of the soluble metal catalysts. This behaviour can be attributed to the complexing nature of the antioxidant with copper and iron. Thus, the bidentate isocarbostyril and 8-hydroxyquinoline are the most susceptible antioxidants among the others, since they possess a coordination site on one side of the molecule.

Studies under oxygen atmosphere

The results of the DSC study of the oil oxidation under oxygen atmosphere and in the presence of catalysts and 5-hydroxyisoquinoline are given in Fig. 4. 5-Hydroxyisoquinoline was chosen because its coordination characteristics are moderate and it possesses good antioxidation effect in the oil. The temperature of oxidation of the oil is similar to that recorded under normal atmosphere, i.e., 190°C. This may be attributed to the small sample size of the oil required in the DSC experiments and consequently a large

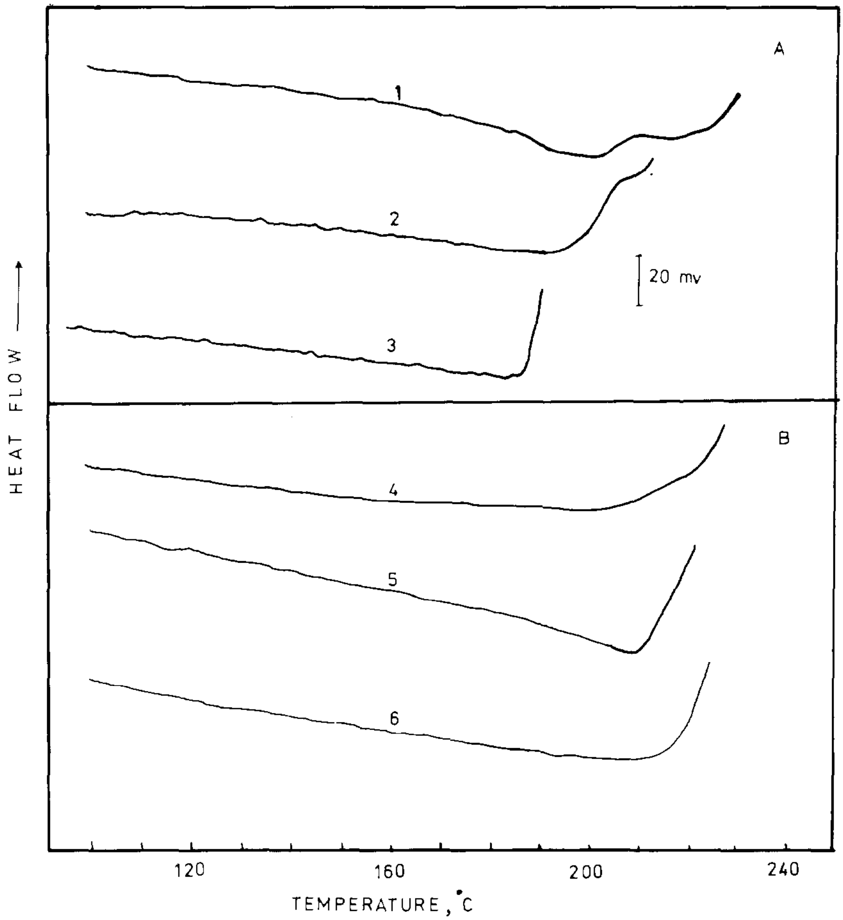


Fig. 4. DSC signals of oxidation of the oil under oxygen atmosphere and in presence of (A) 0.1% and (B) 0.4% of 5-hydroxyisoquinoline. Traces (1) and (4) are in the absence of catalysts, (2) and (5) in the presence of iron catalyst and (3) and (6) in the presence of copper catalyst.

surface area of contact. Thus, the oxygen content of air is sufficient to start oxidation of the oil at the temperature as when performed under oxygen atmosphere.

It is clear from Fig. 5 that 0.2% can be taken as a critical concentration beyond which 5-hydroxyisoquinoline in the absence of catalysts does not show any improvement in the oxidation stability of the oil.

The onset temperature of oxidation in the presence of the iron catalyst increases linearly as the concentration of the antioxidant in the oil increases. Such a behaviour can be attributed to the susceptibility of this metal to accommodate oxidation rather than the oil itself. However, the combined effect of the copper catalyst and oxygen atmosphere reduced the activity of the antioxidant at the 0, 0.1 and 0.2% concentrations and the significance of the antioxidation appeared at the 0.4% concentration.

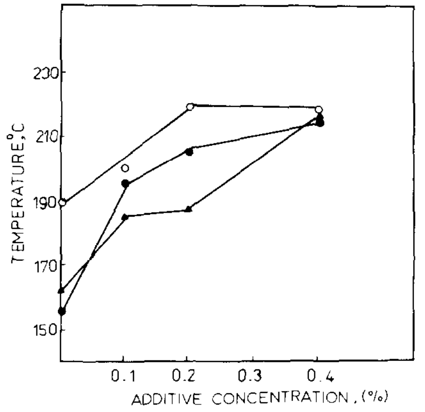


Fig. 5. The improvement in the oxidation stability of the oil upon addition of 5-hydroxyisoquinoline and under oxygen atmosphere. (○), oil; (●), oil + iron catalyst, and (▲), oil + copper catalyst.

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