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Stabilization Mechanisms of Hindered Amines*

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ABSTRACT

As a result of studying the interaction of hindered amine stabilizers (2,2,6,6-tetramethylpiperidines) with simple hydroperoxides, peroxy radicals, and acylperoxy radicals, the last two in AIBN-initiated oxidation experiments in chlorobenzene, the following conclusions have been reached:

1. Hindered amines have multiple mechanisms of functioning as photo-stabilizers of polymers.

2. Reactions between tetramethylpiperidines and simple hydroperoxides are too slow at moderate temperatures to make a significant contribution to polymer stabilization.

3. Reactions between tetramethylpiperidines and alkylperoxy radicals at moderate temperatures are very likely too slow and too inefficient for these to be important polymer photo-stabilizing reactions.

4. Hydrocarbon polymer photo-oxidation proceeds by two major paths—the usually accepted alkyl radical/alkylperoxy radical/hydroperoxide route and the usually neglected aldehyde/acyl radical/acylperoxy radical/peracid route.

5. Hindered amine stabilizers are able to participate in inhibiting both photo-oxidation reactions—they trap acylperoxy radicals, converting them to carboxylic acids and are converted to nitroxyl radicals in the process; the nitroxyl radicals trap alkyl radicals and the hindered amines trap alkylperoxy radicals to inhibit the other oxidation pathway.

6. Nitroxyls are regenerated from N-alkyloxy hindered amines in a fast, efficient reaction with acylperoxy radicals and in a slow, inefficient reaction

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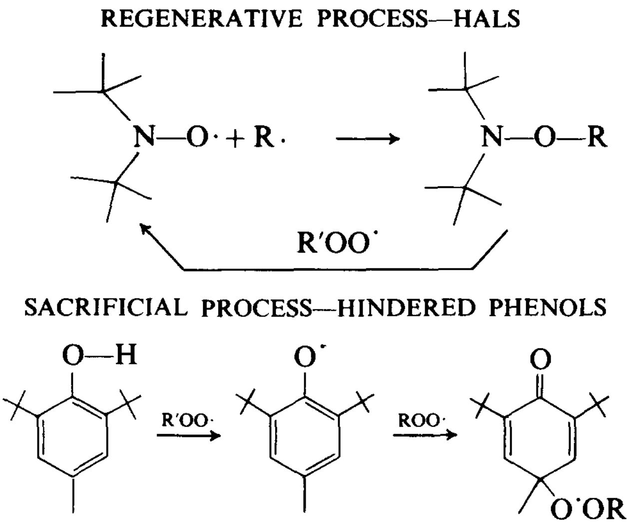
with alkylperoxy radicals. We postulate that neither reaction yields peroxides: carboxylic acids and oxidized alkyloxy substituents are obtained from the first reaction; alcohols and oxidized alkyloxy substituents are obtained from the second reaction.

INTRODUCTION

Since their introduction to the marketplace in the early 1970s in Japan by the Sankyo Corporation and elsewhere in the world by the Ciba-Geigy Corporation, hindered amine stabilizers based on 2,2,6,6-tetramethylpiperidine have become a highly important class of light stabilizers for polymers. They stabilize a wide range of commercial polymers and are particularly effective for the stabilization of polyolefins. Their effectiveness has permitted polyolefins to achieve markets which ordinarily would not be available to them, in particular those applications where resistance to deterioration by light and weathering are important.

Over the years, there have been many publications contributing to our understanding of the mechanisms by which hindered amines do and do not function. Thus we know that their activity is generally not due to the absorption of harmful UV radiation,[1] nor to the quenching of photo-excited carbonyl chromophores.[2] They have exhibited slight singlet oxygen quenching activity, and that primarily by nitroxyls and tertiary hindered amine stabilizers.[3] While they do not react with simple hydroperoxides at ambient conditions,[4] in prephoto-oxidized polypropylene, which has been proposed to contain 'activated' hydroperoxides, hindered amines have been shown to react with polymer hydroperoxides.[5] Their primary mode of functioning appears to be the trapping of carbon-centered radicals by nitroxyls and the regeneration of nitroxyls from the *N*-alkyloxy products of alkyl radical trapping.[6] Tetramethylpiperidines and their nitroxyls can form complexes with hydroperoxides and this is considered to improve their performance by increasing the effective concentrations of the stabilizers in the region of highest probability of photo-oxidation initiation.[7,8] Other potentially important mechanisms of functioning for hindered amines reported in the literature include alkylperoxy radical trapping by tetramethylpiperidine[9] and hydroxylamines,[10] the trapping of acylperoxy radicals,[11] and reactions with peracids.[12] Quite recently it has been suggested that some of the activity of the hindered amines may be due to their activity in complexing transition metals, such as iron, titanium and vanadium.[13,14]

Long considered a key to the high effectiveness of hindered amine stabilizers is the regenerative process which they appear to be capable of


REGENERATIVE PROCESS—HALS

SACRIFICIAL PROCESS—HINDERED PHENOLS

Scheme 1. Radical trapping.

undergoing. This process, largely attributed to Denisov,[6] is shown in Scheme 1. In it nitroxyl radicals react with polymer alkyl radicals to form alkyloxy hindered amine derivatives, which are postulated to react with alkylperoxy radicals to regenerate nitroxyls and form dialkylperoxides. That regenerative process can be contrasted with the sacrificial radical trapping exhibited by hindered phenols whereby, as a result of hydrogen abstraction and subsequent reaction with additional peroxy radicals, the phenols are converted to alkylperoxycyclohexadienones and other products.

In spite of all that is known about hindered amines and their mechanisms, there are still several mysteries associated with their functioning, some of which are:

1. How can the hindered amines be as effective as they are if the activity is dependent on nitroxyls—usually present in very low concentrations?
2. How are nitroxyls formed in oxidizing polymers from N–H or *N*-alkyl compounds?
3. Why have peracids been neglected as oxidation products of polyolefins, and concomitantly why have reactions of hindered amines with acyl radicals, acylperoxy radicals, and peracids been neglected?
4. What is (are) the primary mechanism(s) of stabilization by hindered amines?

The work reported in this paper was undertaken to study the radical trapping capabilities of hindered amines and hopefully shed some light on the mysteries which have been identified in the previous paragraph. For some time, we have utilized a radical trapping test method based on the controlled generation of free radicals from the thermal decomposition of azobisisobutyronitrile (AIBN). We adapted this method to study the radical trapping activity of hindered amines. As a result of this work, some additional light can be shed on the stabilizing mechanisms of hindered amines. Although almost all the work was done in solution, the results are so compelling that we feel they have relevance to, and significance for, polymer stabilization. As much as was learned in the course of this study, much more work is needed to elucidate the mechanisms of functioning of hindered amines in all their details.

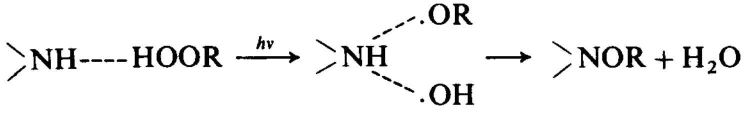
Some key published results of hindered amine mechanisms

The Denisov mechanism shown in eqn (1) and Scheme 1 was postulated on the basis of findings that nitroxyl radicals retarded the photo-oxidation of polypropylene powder containing dicumylperoxide as initiator.

$$>NO^{\cdot} + R'^{\cdot} \longrightarrow\ >NOR' \xrightarrow{ROO\cdot}\ >NO^{\cdot} + ROOR' \qquad (1)$$

When the photolysis of the polymer containing hindered amine nitroxyls was carried out in an argon atmosphere, the nitroxyl radical concentration was found to decrease to zero and subsequently, when air was introduced into the reaction vessel, nitroxyl radicals were again found to be formed during continued photolysis. These observations led to the proposal that the nitroxyls were being regenerated from the *N*-alkyloxy compounds by reaction with peroxy radicals, and dialkyl peroxides were also formed.

Sedlar and his co-workers[7] have proposed that complexation between hindered amine and hydroperoxides locates the hindered amine in the region where the radical products from photolysis of the polymer hydroperoxide can interact easily with the hindered amine and form products which do not have any oxidation propagating qualities:



$$>NH\text{----}HOOR \xrightarrow{h\nu}\ >NH\begin{smallmatrix}\cdot OR\\ \cdot OH\end{smallmatrix} \longrightarrow\ >NOR + H_2O \qquad (2)$$

Carlsson and his co-workers[8] at the National Research Council of Canada have also proposed complexation between hindered amines and polymer hydroperoxides. In addition, they found that when a prephoto-oxidized film of polypropylene was contacted with a solution of hindered amine, or when they had imbibed hindered amine into the polymer film from solution, dark reactions took place in which nitroxyls were generated probably through intermediate hydroxylamines.[8] The Canadian workers postulated that the prephoto-oxidized polypropylene film contained activated hydroperoxide functionalities on alternating carbon atoms based on the accepted back-biting mechanism of peroxy radicals in polyolefins. (The results of the work reported in the present paper suggest the prephoto-oxidized polypropylene films contained peracids which would explain the activated hydroperoxide behavior.)

They pointed out that activated hydroperoxides have been reported in the literature, most particularly in a paper by Ball and Bruice.[15] In their work, Ball and Bruice found that 4-α-hydroperoxyflavin reacted readily with amines. With secondary amines the activated hydroperoxide formed hydroxylamines; with tertiary amines, amine oxides; and hydroxylamines were found to be further oxidized to nitrones by this reagent. In that paper, Ball and Bruice reported the rate constant for the reaction of 4-α-hydroperoxyflavin with *N,N*-dimethylaniline to be about 400 000 times greater than the rate constant for the reaction of di-*t*-butyl hydroperoxide with that same tertiary amine.

In another paper,[10] Carlsson *et al.*, investigators at the National Research Council of Canada, reported that the reaction between triacetoneamine and cyclohexylperoxy radicals had a rate constant of 3 $\mathrm{mol^{-1}\,s^{-1}}$ and yielded cyclohexylperoxide and aminyl radicals. The aminyl radicals were subsequently oxidized to nitroxyls.

Toda and his co-workers of the Sankyo Corporation of Japan reported that hindered amines react rapidly with peracids as indicated in eqn (3).[12] The reaction is stoichiometric and results in the formation of nitroxyl radicals:

$$3\mathrm{RCOOOH} + {>}\mathrm{NH} \longrightarrow 3\mathrm{RCOOH} + 2{>}\mathrm{NO}\cdot + \mathrm{H_2O} \tag{3}$$

Felder and his co-workers[11] of the Ciba-Geigy Corporation in Switzerland reported that hindered amines are effective scavengers of acylperoxy radicals:

$$\mathrm{RCOOO}\cdot + {>}\mathrm{NH} \longrightarrow \mathrm{RCOOH} + {>}\mathrm{NO}\cdot \tag{4}$$

The Felder group also reported that the photo-oxidation of isooctane, a model for polypropylene, initiated by *t*-butoxy radicals from the photolysis of di-*t*-butyl peroxide, resulted in the formation of peracids, hydroperoxides, and peroxides. About 40% of the active oxygen in the products was in the form of peracids.[11] Furthermore, on analysis of the products formed, the Felder group established that the attack of isooctane by alkylperoxy radicals was nearly statistical and that primary hydrogens were as readily abstracted as secondary or tertiary hydrogens. This result is in contrast to the generally accepted concept of hydrogen atom abstraction in polymer molecules, with the tertiary carbon atoms in polypropylene, for instance, generally being accepted as the preferred site of attack.

Felder's results[16] of random attack by *t*-butoxy radicals in the photo-oxidation work contrast with results obtained by Niki and Kamiya in the thermal oxidation of hydrocarbons also with *t*-butoxy radicals, generated from the thermolysis of di-*t*-butyl peroxyoxalate.[17] In the latter work with a number of hydrocarbons the attack at the primary, secondary and tertiary positions was in the ratio 1:7:20, respectively.

Felder and his co-workers postulated further[16] that since primary attack occurred frequently in the photolysis of isooctane it was likely that significant amounts of aldehydes were being formed as a result of termination of primary peroxy radicals and that subsequently the oxidation of these aldehydes resulted in peracids. That was one of the first publications in which the suggestion was made that aldehyde oxidation may be a key, but neglected, pathway in the photo-oxidation of hydrocarbon polymers. In fact, a number of articles in the literature indicate that among the photo-oxidation products of polyolefins are acids, esters and even peracids. Papers by Adams[18] and Amin and co-workers[19] are among them.

More recently, Carlsson[20] has reported on work in which they used a variety of reagents, SF_4, NO, diazomethane, to convert oxidation products of polypropylene and polyethylene to functional groups more readily quantified by infrared spectroscopy. Their treatments derivatize many of the carbonyl components of oxidized polymers, making the remaining carbonyl region simpler and more easily interpreted. Carlsson studied the oxidation of polyethylene and polypropylene initiated by gamma radiation and by UV radiation. In the case of polyethylene, ketones were found to be major products and present in much greater amounts than secondary alcohols, but also high yields of carboxylic acids were observed. In the case of polypropylene, secondary and tertiary alcohols and hydroperoxides were found as well as pendant carboxylic acid groups which imply the intermediacy of primary hydroperoxides (Table 1). Carlsson has commented that because ketones are present in much greater amounts than secondary alcohols from polyethylene oxidation, this raises some question about the degree to which the Russell mechanism operates in the oxidation of solid polymer. As shown in eqn (5), the Russell mechanism would be expected to provide equal amounts of ketones and secondary alcohols from the termination of two secondary peroxy radicals. Carlsson has postulated that in polyethylene there may be reactions similar to those in polypropylene where chain cleavage of an alkyloxy radical takes place with the formation of terminal aldehydes. The terminal aldehydes would be subsequently

TABLE 1
Identification of Oxidation Products in Polyolefin Oxidation[a]

		Oxidation products (mole/kg) × 10^3				
		Total OOH	*Total OH*	*C=O*	*—C(O)OH*	*—C(O)OR*
HDPE	20 Mrad	61	19	74	29	0
	2·5 Mrad	8	3	12	4	0
	UV, 616 h	12	3	30	26	6
LLDPE	20 Mrad	55	14	78	29	0
	UV, 616 h	31	30	85	82	54
PP	20 Mrad	410	44	240	33	30
	2·5 Mrad	43	7	20	17	1·5
	UV, 102 h	74	5	30	7	15

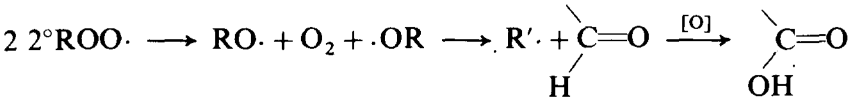
[a] From Ref. 20 with permission.

oxidized to carboxylic acids. These reactions are depicted in eqn (6). It is also conceivable that on photolysis of secondary hydroperoxides in polyethylene the resultant alkoxy radicals could undergo chain cleavage to yield terminal aldehydes, as shown in eqn (7). These also would be oxidized to carboxylic acids.

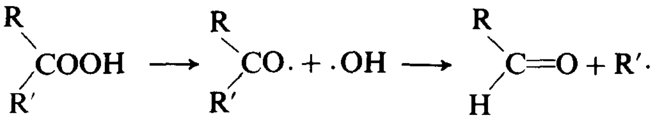
Russell mechanism:

$$2\ 2^\circ\mathrm{ROO}\cdot \longrightarrow [\mathrm{ROOOOR}] \longrightarrow \rangle\mathrm{C{=}O} + \rangle\mathrm{COH} + \mathrm{O_2} \qquad (5)$$

Alternate reaction pathways:



$$2\ 2^\circ\mathrm{ROO}\cdot \longrightarrow \mathrm{RO}\cdot + \mathrm{O_2} + \cdot\mathrm{OR} \longrightarrow \mathrm{R'}\cdot + \mathrm{H{-}C{=}O} \xrightarrow{[\mathrm{O}]} \mathrm{HO{-}C{=}O} \qquad (6)$$



$$\mathrm{RR'COOH} \longrightarrow \mathrm{RR'CO}\cdot + \cdot\mathrm{OH} \longrightarrow \mathrm{RHC{=}O} + \mathrm{R'}\cdot \qquad (7)$$

The literature thus discloses considerable activity of hindered amine stabilizers with hydroperoxides and peroxy radicals but also considerable potential for involvement with acyl and acylperoxy radicals, and peracids. The latter group of compounds would result from aldehyde oxidation. It is reasonable, in view of the many literature reports of carboxylic acid products being present in oxidized polyolefins, to propose that these result from the oxidation of aldehydes to peracids and subsequent conversion to carboxylic acids. Surprisingly, this group of chemical reactions which occur in photo-oxidizing polymers, most notably polyolefins, has been neglected in the literature for the most part. We suggest, based on data in the literature and results in this paper, that a significant part of the functioning of hindered amines as stabilizers against polymer photo-oxidation is likely to be due to their ability to intervene in both aldehyde and hydrocarbon oxidation reactions.

EXPERIMENTAL

General methods

Unless otherwise noted, all materials were used as received. Chlorobenzene and isooctane were Aldrich HPLC grade. AIBN was recrystallized from methanol and stored at 0°C. Tetralin was distilled and stored under nitrogen at 0°C.

General oxygen uptake procedure: AIBN-induced

Chlorobenzene solution (20 ml), 1·0M in oxidizing substrate and 2×10^{-3}N in additive, was charged into a 100 ml reaction flask equipped with a ball joint side arm. (In some instances tetralin was used as the oxidizing substrate at a concentration of 2·5M.) The assembly was then connected to a pressure transducer which allowed automatic monitoring of pressure changes within the sealed flask as oxygen was consumed. The system was partially evacuated and flushed with pure oxygen five times, sealed, placed in an oil bath at 60°C, and stirred with a magnetic stirring bar. After thermal equilibration (15 min), the system was vented to atmospheric pressure, 98·5 mg (0·60 mmol, $3{\cdot}0 \times 10^{-2}$M) AIBN was added, and the system resealed. The pressure in the sealed system was monitored continuously as oxygen was being consumed (total gas volume was approximately 95 ml).

General oxygen uptake procedure: photo-induced

An isooctane solution (4 ml), 1·0M in lauryl aldehyde and 2×10^{-3}N in additive, was charged into a Pyrex reaction tube. The assembly was then connected to a pressure transducer which allowed automatic monitoring of pressure changes within the sealed flask as oxygen was consumed. The system was partially evacuated and flushed with pure oxygen five times, sealed, placed in a Rayonet photoreactor equipped with 300 nm bulbs, and vigorously shaken with a Fisher Vortex-Genie Test Tube Mixer. The pressure in the sealed system was monitored continuously as oxygen was being consumed (total gas volume was approximately 67 ml).

Reactions with isobutyronitrile and isobutyronitrileperoxy radicals

The same procedure as described under 'General Oxygen Uptake Procedure: AIBN-Induced' was used except that no oxidizable substrate was added.

Treatment of oxygen pressure data

The oxygen consumption data were processed by an in-house program for an IBM-XT. The amount of oxygen consumed was calculated, from the pressure data, over the experimental time span. From the plots of oxygen consumption versus time the following parameters were determined: induction period; time to 1·0 mmole oxygen consumption; initial rate of oxygen uptake; and final (failure) rate of oxygen uptake. Oxidative chain lengths were calculated from the quantity of oxygen consumed and the initial rate of free radical generation by AIBN; for 0·03M AIBN $4{\cdot}1 \times 10^{-7}$ mol radicals s^{-1} were generated; for 0·2M AIBN the number was $2{\cdot}8 \times 10^{-6}$ mol s^{-1}.

Analyses

Gas chromatography

Gas chromatography was performed on a Perkin-Elmer model 8410 chromatograph equipped with a flame ionization detector. Helium was used as the carrier gas, and all columns used were 5 ft × 1/8 in. Quantitative analyses of 2,2,6,6-tetramethylpiperidin-4-yl benzoate derivatives were performed on a 5% SP2401 column using tetracosane as either internal or external standard. Relative retention times (RRT) were: tetracosane = 1·00; N–H, 0·51; *N*-oxyl, 1·24: *N*-cyclohexyloxy, 2·11. The *N*-lauryloxy derivative decomposed to give the N–H derivative during gas chromatography; both the *N*-isobutyronitrileoxy and *N*-hydroxy adducts gave the nitroxyl. Lauric acid was converted into the methyl ester (RRT = 0·62) using 'Methyl Prep II' (Alltech) and was analyzed on a 10% SP2340 column. A 20% 20M Carbowax column was used to quantify cyclohexanone (RRT = 3·50; toluene standard = 1·00), while a 10% SP2250 column was used for BHT (RRT = 0·88; octadecane standard = 1·00).

Active oxygen

Perlauric acid, cumyl, *t*-butyl hydroperoxide, and active oxygen, in general, were determined by iodometric titration. Di-*t*-butyl peroxide could be detected using a 5 ft × 2 mm glass GC column packed with 10% OV-17.

Syntheses

Syntheses of non-commercial compounds were performed in the Ciba-Geigy Research Laboratories. (We are indebted to Drs R. Ravichandran and J. Galbo for the compounds.) These compounds satisfied spectral and elemental analyses. 2,2,6,6-Tetramethylpiperidin-4-yl benzoate was prepared from the commercially available 2,2,6,6-tetramethylpiperidin-4-ol by esterification. Oxidation of secondary hindered amines with *m*-chloroperbenzoic acid gave the corresponding nitroxyl.[12] Catalytic hydrogenation of the nitroxyl yielded the hydroxyl amine. *N*-acyloxy compounds were obtained by reaction of the hydroxyl amine with the corresponding acid chloride. *N*-cyclohexyloxy-2,2,6,6-tetramethylpiperidinyl benzoate was obtained via photolysis of di-*t*-butyl peroxide with the nitroxyl derivative in cyclohexane.[9]

Reactions

Reaction of 2,2,6,6-tetramethylpiperidin-4-yl benzoate with t-*butylhydroperoxide*

In a 25 ml flask were mixed 10 ml of a $3{\cdot}8 \times 10^{-2}$M chlorobenzene solution of 2,2,6,6-tetramethylpiperidinyl benzoate, 1·5 ml of 4·7N *t*-butyl hydroperoxide (20 equivalents) in chlorobenzene, and 5·0 ml chlorobenzene. The resulting solution was heated in a 120°C oil bath under air. Periodically, an aliquot was removed and analyzed by VPC (external standard) for hindered amine derivatives, and by iodometric titration for remaining hydroperoxide.

Reaction of 2,2,6,6-tetramethylpiperidin-4-yl benzoate with cumyl hydroperoxide

In a 25 ml flask were mixed 10 ml of $3{\cdot}8 \times 10^{-2}$M 2,2,6,6-tetramethylpiperidinyl benzoate in chlorobenzene, 1·0 ml of 7·3N cumyl hydroperoxide (20 equivalents) in chlorobenzene, and 5·0 ml chlorobenzene. The resulting solution was heated in a 120°C oil bath under air. Periodically, an aliquot was removed and analyzed by VPC (external standard) for hindered amine derivatives, and by iodometric titration for remaining hydroperoxide.

RESULTS

Reaction between hindered amines and *t*-butylhydroperoxide

Based on literature reports of radical trapping by hindered amine stabilizers and on reactions between activated hydroperoxides and hindered amines, but not with simple hydroperoxides, we became interested in examining the influence of hindered amines on the rate of photolysis of *t*-butylhydroperoxide. As shown in Fig. 1, neither tetramethylpiperidinyl benzoate nor pentamethylpiperidinyl benzoate had a significant influence

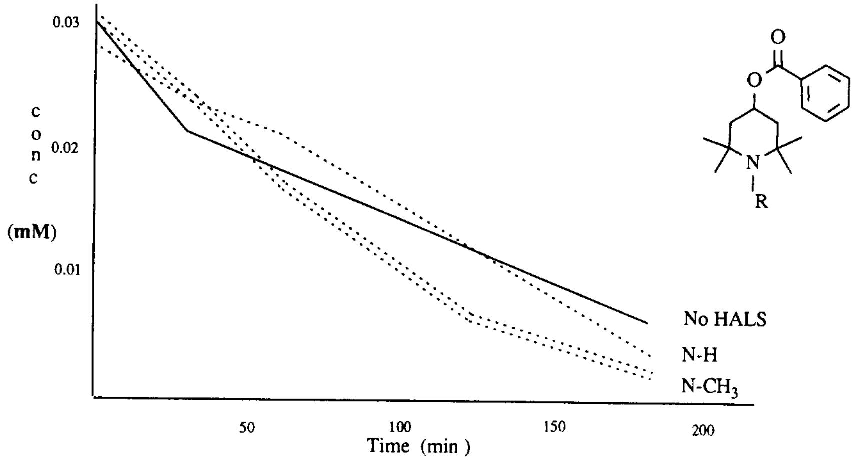


Fig. 1. Influence of tetramethylpiperidinyl benzoates on the rate of photolysis of ^{t}BuOOH under nitrogen. 300 nm Rayonet Merry-Go-Round®, 0·03 M ^{t}BuOOH, 0·03 M HALS, heptane solution.

on the rate of photolysis of the *t*-butylhydroperoxide under nitrogen. Moreover, the N–H compound survived the photolysis without undergoing any significant change in concentration, indicating virtually no interaction between the N–H compound and the hydroxy, alkyloxy, peroxy, and methyl radicals generated from the photolysis of the hydroperoxide (Table 2). The *N*-methyl compound underwent a small degree of oxidation during the 3 h photolysis, during which most of the di-*t*-butyl hydroperoxide was decomposed (Table 2). Slight conversion of the *N*-methyl compound to the N–H compound took place during photolysis. The nitroxyl did show some reduction in concentration during this time period.

When the photolysis was carried out in air, the influences of the N–H and

TABLE 2

Fate of Tetramethylpiperidinyl Benzoate Derivatives During the Photolysis of *t*-Butyl Hydroperoxide under Nitrogen

N-*Substituent*	*0·03*M t-*BuOOH*, n-*heptane* (*300 nm*), *concentration at time*		
	0	*1 h*	*3 h*
H	0·03M	0·03M	0·03M
CH$_3$	0·025M	0·03M	0·025M 0·004M R=H
O·	0·029M	0·025M 0·000 5M R=OH	0·018M 0·002M R=OH

TABLE 3
Fate of Tetramethylpiperidinyl Benzoate Derivatives During the Photolysis of *t*-Butyl Hydroperoxide in Air

N-*Substituent*	*0·03*M t-*BuOOH*, n-*heptane* (*300 nm*), *concentration at time*		
	0	*1 h*	*3 h*
H	0·031M	0·034M	0·034M
CH_3	0·033M	0·031M	0·022M
		0·004M R=H	0·008M R=H
O·	0·029M	0·029M	0·029M
		0·007M unknown	0·002M unknown

N-methyl compounds on the rate of photolysis were comparable to what they had been under nitrogen. There was virtually no change in concentration of the N–H compound during the photolysis and only a slight change in that of the *N*-methyl compound (Table 3), the main reaction being conversion to the N–H compound. Hardly any conversion of the nitroxyl compound took place during the photolysis.

These results clearly show very little interaction between hindered amines and free radicals generated from the photolysis of *t*-butyl hydroperoxide, suggesting that the various radicals generated in the photolysis were not sufficiently active to be involved in reactions with the hindered amines. Part of the explanation may be due to the existence of *t*-butyl hydroperoxide in clusters in non-polar solvents[21] and the reactions in the clusters involve mainly *t*-butylperoxy radicals from induced decomposition with limited opportunity for disruption by cluster-external polar compounds, such as hindered amines.

When reaction between 2,2,6,6-tetramethylpiperidinyl benzoate and cumyl hydroperoxide was attempted at 120°C in chlorobenzene the rate was again very slow (Table 4). Even at this elevated temperature the reaction of the hindered amine with cumyl hydroperoxide was too slow to be a reasonable mechanism for nitroxyl formation in oxidations at ambient conditions.

Radical trapping experiments

Tetralin

For some time we have been using AIBN-initiated oxidation of tetralin in chlorobenzene solution to study the radical trapping activity of a number of phenolic antioxidants. The advantages of using AIBN in this work are that, at a given temperature, the rate of decomposition of the AIBN is known with

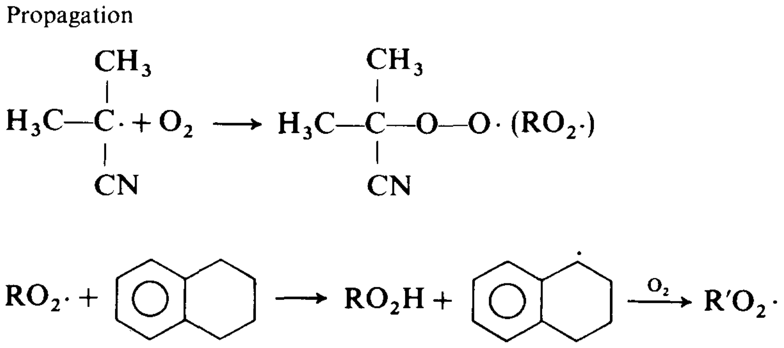
TABLE 4

Reaction of 2,2,6,6-Tetramethylpiperidinyl Benzoate with Cumyl Hydroperoxide in Chlorobenzene at 120°C
0·03M Additive, 0·7M Hydroperoxide, Air

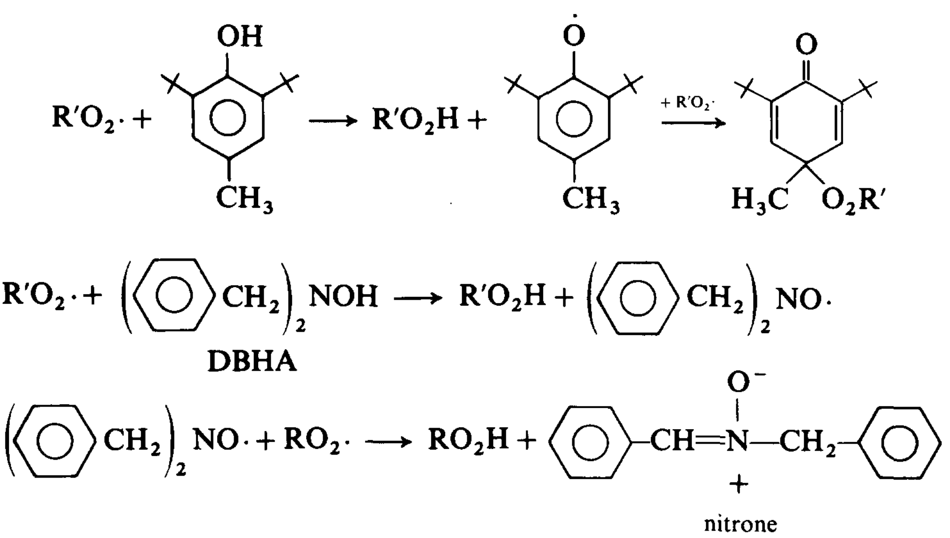
Time (h)	*Concentration (mM)*	
	$>$NH	*Active O*
0·0	26·8	724
1·0	27·1	728
2·0	27·2	530
3·5	23·9	470

reasonable certainty and the number of free radicals escaping the cage and becoming available to initiate oxidation is also known.[22] In chlorobenzene at 60°C, 1·2 isobutyronitrile free radicals are generated from each molecule of AIBN. By measuring oxygen consumption as a function of time in an AIBN-initiated oxidation, one can determine the rate of oxygen consumption, the length of the induction period, the number of radicals trapped per initiating radical, and the oxidative chain length, i.e. the number of molecules of oxidant (substrate) oxidized per initiating radical. Experiments conducted using this method provide an excellent means of assessing the effectiveness of compounds in trapping radicals and inhibiting oxidation.

As shown in Scheme 2 the isobutyronitrile radicals obtained from decomposition of the AIBN react readily with oxygen to form isobutyronitrileperoxy radicals. These subsequently abstract benzylic hydrogen atoms from tetralin forming hydroperoxides and tetralin free radicals, which react readily with oxygen to form tetralinperoxy radicals. Tetralinperoxy radicals abstract hydrogen from BHT to form tetralin



Scheme 2. AIBN-initiated tetralin oxidation.



Scheme 3. AIBN-initiated tetralin oxidation trapping peroxy radicals.

hydroperoxide and phenoxyl radicals which, in solution, often react with a second molecule of tetralinperoxy radical to form the peroxycyclohexadienones (Scheme 3). When dibenzyl hydroxylamine (DBHA) is used as the radical trapper, hydroperoxides and nitroxyl radicals are formed. Subsequent reaction between a nitroxyl radical and a second peroxy radical results in nitrone and an additional hydroperoxide molecule.

A plot of the oxygen uptake results for the AIBN-initiated oxidation of tetralin inhibited by BHT and by dibenzylhydroxylamine (Fig. 2) shows the hydroxylamine to provide a slower rate of oxygen consumption during the induction period. The data in Table 5 confirm the superior activity of

TABLE 5
Comparison of DBHA and BHT as Free Radical Trappers

Stabilizer (0·002M)	*Induction period (h)*	*Initial rate of uptake (mmoles O_2/h)*	*Initial oxidative chain length*[a]
None	≈0	1·1	20
BHT	3·3	0·058	0·79
DBHA	2·8	0·018	0·20

AIBN-initiated oxidation of tetralin (2·5M) in chlorobenzene solution at 60°C; 0·03M AIBN, 0·002M stabilizers, 1 atm. O_2.

[a] Number of tetralin molecules oxidized (= number of oxygen molecules consumed) per initiating radical.

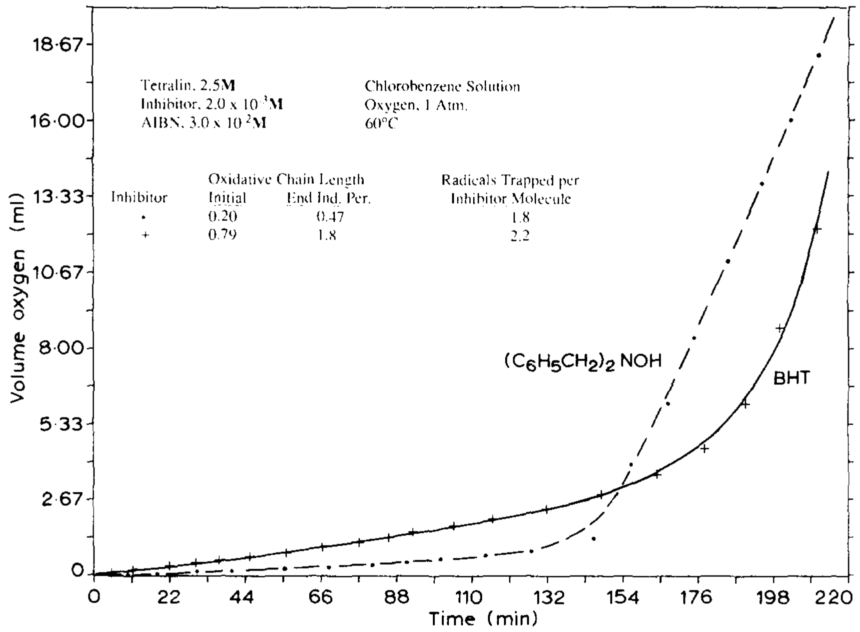


Fig. 2. Inhibition of AIBN-initiated tetralin oxidation by dibenzylhydroxylamine.

DBHA. Both inhibitors trapped approximately two radicals per molecule up to the induction period in accordance with the chemistry described in Scheme 3.

When similar experiments in tetralin oxidation were carried out with tetramethylpiperidinyl sebacate derivatives, neither the N–H nor the nitroxyl compound exhibited significant degrees of radical trapping, especially in comparison with that of BHT (Table 6). The hydroxylamine derivative, on the other hand, was an extremely effective radical trapper, reducing the rate of oxygen consumption to the lowest level we have seen with a large number of compounds. These results bring into question the effectiveness of N–H and even nitroxyl hindered amine derivatives in trapping alkyl and alkylperoxy radicals (isobutyronitrile and tetralin).

The effectiveness of the hydroxylamine suggests that, provided hydroxylamines could be formed in sufficient quantities from the hindered amine compounds originally added to the polymers, they would be highly efficient radical trappers and could make an important contribution to the stabilizing effectiveness of hindered amine stabilizers. At this time it is not possible to estimate the importance, if any, of hydroxylamine derivatives of tetramethylpiperidines to polymer stabilization by hindered amines.

Analyses for BHT and tetramethylpiperdinyl benzoate in reactions where no oxidizable substrate was present and only isobutyronitrile radicals and

TABLE 6

Free Radical Trapping by Tetramethylpiperidinyl Sebacate Derivatives in the AIBN-Initiated Oxidation of Tetralin[a]

Inhibitor	*Induction period (h)*	*Initial uptake rate (mmoles-O_2/h)*	*Oxidative chain length*[b]
None	0	1·1	20
BHT	3·3	0·06	1·0
>N—H	0·0	1·02	17
>NO·	0·0	0·92	15
>NOH	1·5	0·00	0

[a] 60°C, 2·5M tetralin, 0·03M AIBN, 0·002N inhibitor, 1 atm. O_2, chlorobenzene solution.

[b] Number of tetralin molecules oxidized per initiating radical.

isobutyronitrile peroxy radicals were being generated showed that BHT was consumed relatively rapidly as expected from its functioning as an effective peroxy radical trapper. Assuming two peroxy radicals to be trapped by each BHT molecule the rate of consumption of peroxy radicals by BHT is calculated to be $3{\cdot}7 \times 10^{-7}$ mol liter^{-1} s^{-1}, not much lower than the rate of radical generation, $4{\cdot}1 \times 10^{-7}$ mol liter^{-1} s^{-1}. But the rate of consumption of the hindered amine was much lower (Table 7) indicating much lower reactivity between the generated radicals and the tetramethylpiperidinyl benzoate molecules.

TABLE 7

Reactions of BHT and Tetramethylpiperidinyl Benzoate with Isobutyronitrile and Isobutyronitrileperoxy Radicals: Rate of Consumption of Inhibitors[a]

	Rate (moles/liter/s) ($\times 10^7$)	
	0·03M AIBN	*0·20M AIBN*
Radical generation	4·1	28
Consumption of BHT	1·85	9·9
Consumption of >NH	0·69	3·1[b]

[a] 60°C, no oxidant, 0·010M initial inhibitor concentration except where noted, 1 atm. O_2, chlorobenzene solution.

[b] Initial inhibitor concentration 0·020M.

TABLE 8

Concentration of Components in *N*-Substituted Tetramethylpiperidinyl Benzoate-inhibited Tetralin Oxidation[a,b]

Time (*h*)	$>NO^{\cdot}$		$>NH$	
	$>NO^{\cdot}$	$>NH$	$>NH$	$>NO^{\cdot}$
0·0	1·8	0·0	1·9	0·0
4·6	—	—	1·8	0·0
6·6	0·5	0·1	—	—
22·0	0·3	0·4	1·3	0·1

[a] 60°C, 1·0M tetralin, 0·02M inhibitor, 0·03M AIBN, 1 atm. O_2, chlorobenzene.

[b] All concentrations in mM.

Comparable results were obtained with tetramethylpiperidinyl benzoate from similar experiments when tetralin was being oxidized (Table 8)—the tetramethylpiperidinyl benzoate underwent little change in concentration even after 22 h. The corresponding nitroxyl, however, did show evidence of being consumed in the process even though there was not a marked reduction in the rate of oxidation of tetralin as had been the case with BHT. These results indicate that the nitroxyl radical is involved to some degree with radical trapping in these experiments.

These results with tetramethylpiperidinoxyl benzoate led us to explore further its ability to inhibit AIBN-initiated tetralin oxidation. When air was substituted for oxygen in our oxidation experiments the nitroxyl radical was able to compete more effectively with oxygen at the lower concentration and caused a reduction in the rate of oxygen consumption (Table 9). Moreover, a tenfold increase in the concentration of the nitroxyl radical resulted in further reduction in the rate of oxygen consumption indicating the nitroxyl

TABLE 9

Effect of Oxygen Concentration on Rate of Oxygen Uptake in Tetralin Oxidation Inhibited by Tetramethylpiperidinoxyl Benzoate[a]

$>NO^{\cdot}$	*Rate of oxygen uptake* (*mM/h*)	
	Air	*100% O_2*
None	0·27	0·29
0·002M	0·09	0·21
0·02M	0·02	—

[a] 60°C, 1·0M tetralin, 0·03M AIBN, chlorobenzene solution.

radical can participate in oxidation-inhibiting radical trapping when circumstances, low oxygen concentration and relatively high nitroxyl concentration, are favorable. Although, in these experiments, the nitroxyl radical was not as effective in competing with oxygen for the isobutyronitrile radicals as BHT was in trapping alkylperoxy radicals, it is conceivable that in polymers the effective oxygen concentration in regions undergoing oxidation may be limited by the rate of oxygen diffusion and thus the nitroxyl radicals may have a suitable opportunity to trap carbon free radicals before they have an opportunity to react with oxygen.

Lauryl aldehyde and other model substrates

In our radical trapping work we have examined several oxidizable substrates in addition to tetralin. In Table 10 are shown oxidative chain length and oxygen uptake results for eight organic substrates whose oxidation was initiated by AIBN, but was uninhibited. The two models for polyolefin polymers, isooctane and *n*-heptane, were among the least oxidizable of the substrates evaluated. Lauryl aldehyde, on the other hand, was the most oxidizable. Other substrates, some models for unsaturated substrates, another a model for polyols, were intermediate in their oxidizability. BHT was an effective inhibitor and produced induction periods with all the substrates except lauryl aldehyde (Table 11). BHT was virtually ineffective as an inhibitor of lauryl aldehyde oxidation. In contrast, tetramethylpiperidinyl benzoate inhibited the oxidation of lauryl aldehyde very effectively but had slight to no retarding effect on the oxidation of any of the other substrates

TABLE 10

AIBN-Initiated Oxidation of Organic Substrates[a] 60°C, Uninhibited

	Oxidative chain length[b]	*Time to 1·0 mmol oxygen uptake*
Lauryl ald.	105	0·3 h
Squalene	17	2·1
Tetralin	10	3·7
Liq. butad. (PBD)	7	5·6
Polyeth glycol (PEG-600)	3	15
Isooctane	0·5	7·7[c]
n-Heptane	0·5	7·6[c]
Cyclohexane	0·8	7·4[c]

[a] 60°C, 1·0M substrate, 0·03M AIBN, 1 atm. O_2, chlorobenzene solution.

[b] mmol substrate oxidized per mmol free radical generated.

[c] Time to 0·1 mmol O_2 uptake.

TABLE 11

AIBN-Initiated Oxidation of Organic Substrates[a] 60°C; BHT-Inhibited

Substrate	*Oxidative chain length*[b]	*Time to 1·0 mmol oxygen uptake* (*h*)	*Induction period* (*h*)
Lauryl ald.	60	0·7	None
Squalene	3·2	5·4	3·4
Tetralin	1·0	6·8	3·0
PBD	1·5	8·3	3·0
PEG-600	0·5	18	3·0
Isooctane	0·1	9·9[c]	3·1
n-Heptane	0·1	10[c]	3·2

[a] 60°C, 1·0M substrate, 0·03M AIBN, 0·002M inhibitor, 1 atm. O_2, chlorobenzene solution.

[b] mmol substrate oxidized per mmol free radical generated.

[c] Time to 0·1 mmol O_2 uptake.

(Table 12). The corresponding nitroxyl was also highly effective in inhibiting lauryl aldehyde oxidation and also exhibited some oxidation inhibiting activity with the other substrates (Table 13). The nitroxyl exhibited induction periods with isooctane and *n*-heptane as well as polyethylene glycol. Data for the three inhibitors in Table 14 compare how long it took to absorb 1·0 mmole of oxygen. The oxidation of saturated hydrocarbons was so slow that only the times to 0·1 mmole oxygen consumption could be obtained within reasonable time.

In Scheme 4 are summarized reactions and side reactions involved in the

TABLE 12

AIBN-Initiated Oxidation of Organic Substrates[a] 60°C; Tetramethylpiperidinyl Benzoate-Inhibited

Substrate	*Oxidative chain length*[b]	*Time to 1·0 mmol oxygen uptake* (*h*)	*Induction period* (*h*)
Lauryl ald.	2·0	8·0	9·0
Squalene	9·8	4·0	none
Tetralin	9·4	4·0	none
PBD	5·0	11	none
PEG-600	1·7	2·4[c]	none
Isooctane	0·4	13[c]	none
n-Heptane	0·6	9·1[c]	none
Cyclohexane	0·6	13·7[c]	none

[a] 60°C, 1·0M substrate, 0·03M AIBN, 0·002M inhibitor, 1 atm. O_2, chlorobenzene solution.

[b] mmol substrate oxidized per mmol free radical generated.

[c] Time to 0·1 mmol O_2 uptake.

TABLE 13

AIBN-Initiated Oxidation of Organic Substrates[a] 60°C; Tetramethylpiperidinoxyl Benzoate-Inhibited

Substrate	*Oxidative chain length*[b]	*Time to 1·0 mmol oxygen uptake (h)*	*Induction period (h)*
Lauryl ald.	2·5	8·3	9·8
Squalene	6·8	5·3	none
Tetralin	7·2	5·2	none
PBD	3·8	13	none
PEG-600	0·1	6·7[a]	1·6
Isooctane	0·0	15[a]	3·1
n-Heptane	0·0	12[a]	3·2

[a] 60°C, 1·0M substrate, 0·03M AIBN, 0·002M inhibitor, 1 atm. O_2, chlorobenzene solution.

[b] mmol substrate oxidized per mmol free radical generated.

[c] Time to 0·1 mmol O_2 uptake.

AIBN-initiated lauryl aldehyde oxidation. Acyl and acylperoxy radicals are propagating radicals in aldehyde oxidation. Perlauric acid is a product of uninhibited oxidation.

The high order of effectiveness of several tetramethylpiperidinyl benzoate derivatives in inhibiting the thermal and photo-oxidation of lauryl aldehyde, as summarized in Tables 15, 16 and 17 and as shown in Fig. 3, suggests they have a strong ability to react with acyl and acylperoxy radicals and with the peracid products of aldehyde oxidation but are less effective in retarding tetralin oxidation (Table 15). As can be seen (Table 17) the *N*-lauryloxy

TABLE 14

AIBN-Initiated Oxidation of Organic Substrates[a] 60°C, Comparison of Inhibitors

Substrate	*Time to 1·0 mmol oxygen uptake (h)*			
	No inhibitor	*BHT*	*>N—H*	*>N—O·*
Lauryl aldehyde	0·3	0·7	8·0	8·3
Squalene	2·1	5·4	4·0	5·3
Tetralin	3·7	6·8	4·0	5·2
PBD	5·6	8·3	11	13
PEG-600	15	18	2·4[b]	6·7[b]
Isooctane	7·7[b]	9·9[b]	13[b]	15[b]
n-Heptane	7·7[b]	10[b]	9·1[b]	12[b]
Cyclohexane	7·4[b]	—	13·7[b]	13·3[b]

[a] 60°C, 1·0M oxidant, 0·03M AIBN, 0·002M inhibitor, 1 atm. O_2, chlorobenzene solution.

[b] Time to 0·1 mmol O_2 uptake.

$$(CH_3)_2C(CN)OO\cdot + C_{11}H_{23}CHO \longrightarrow (CH_3)_2C(CN)OOH + C_{11}H_{23}(CO)\cdot$$

$$C_{11}H_{23}(CO)\cdot + O_2 \longrightarrow C_{11}H_{23}(CO)OO\cdot$$

$$C_{11}H_{23}(CO)OO\cdot + C_{11}H_{23}CHO \longrightarrow C_{11}H_{23}(CO)OOH + C_{11}H_{23}(CO)\cdot$$

Side reactions:

1.

$$C_{11}H_{23}(CO)\cdot \longrightarrow C_{11}H_{23}\cdot + CO$$

$$C_{11}H_{23}\cdot + O_2 \longrightarrow C_{11}H_{23}O_2\cdot$$

$$C_{11}H_{23}O_2\cdot + C_{11}H_{23}CHO \longrightarrow C_{11}H_{23}O_2H + C_{11}H_{23}(CO)\cdot$$

2.

$$C_{11}H_{23}(CO)O_2H + C_{11}H_{23}CHO \longrightarrow 2\, C_{11}H_{23}CO_2H$$

Scheme 4. AIBN-initiated lauryl aldehyde oxidation.

hindered amine derivative showed only slight activity in radical trapping, indicating that this compound may be, except possibly for hydrolysis, a terminal product of aldehyde oxidation inhibition.

The analysis of the various components present in the tetramethylpiperidinyl benzoate-inhibited lauryl aldehyde oxidation yielded the data shown in Table 18. Unfortunately, the *N*-lauryloxy derivative was converted to the N–H compound on our gas chromatography column and so it was not possible to distinguish between the concentrations of starting material and product. From the data in Table 18, it can be seen that the nitroxyl concentration gradually built up during the reaction and ultimately dropped off. The lauric acid content was nominal until the nitroxyl was virtually gone. Similar data are presented in Table 19 for the tetramethylpiperidinoxyl benzoate-inhibited lauryl aldehyde oxidation.

TABLE 15

Amounts of Oxygen Consumed in the AIBN-Initiated Oxidation of Tetralin and Lauryl Aldehyde at the End of the Calculated Induction Period, 3·04 h[a]

Compound	*Tetralin oxid.*[b]		*Lauryl ald. oxid.*[b]	
	mmoles O_2	*% of blank*	*mmoles O_2*	*% of blank*
None	0·80	100	10·9[c]	100
BHT	0·08	10	5·8[c]	94
>NH	0·77	96	0·20	1·8
>NO˙	0·61	76	0·18	1·7
$(C_6H_5CH_2)_2NOH$	0·15	19	—	—
>NOH	—	—	0·18	1·7

[a] Time at which two radicals have been liberated from AIBN per molecule of inhibitor.
[b] 60°C, 1·0M oxidant, 0·03M AIBN, 0·002M inhibitor, 1 atm. O_2, chlorobenzene solution.
[c] Extrapolated from initial rate of oxidation.

TABLE 16

Inhibition of Lauryl Aldehyde Oxidation by Tetramethylpiperidinyl Benzoate Derivatives

Inhibitor	*Thermal*[a]		*Photo-chemical*[b]	
	Induction period (h)	*Rate of oxygen uptake (mmol/h)*	*Induction period (h)*	*Rate of oxygen uptake (mmol/l)*
None	none	3·6	none	2·2
BHT	none	1·9	none	2·1
TEMPO[c]	9·8	0·08	1·8	0·05
$>N-CH_3$	2·5	0·15	—	—
$>N-H$	9·0	0·06	2·8	0·04
$>N-OH$	8·3	0·05	—	—
$>N-O^{\cdot}$	9·8	0·07	2·8	0·03

[a] Conditions: 60°C, 1M lauryl aldehyde, 0·03M AIBN, 0·002N additive, 1 atm. O_2, chlorobenzene solution.

[b] Conditions: 300 nm, 1M lauryl aldehyde, 0·002M additive, 1 atm. O_2, isooctane solution, Rayonet Merry-Go-Round®.

[c] Tetramethylpiperidin-1-oxyl.

Similar data were obtained with *N*-cyclohexyloxytetramethylpiperidinyl benzoate-inhibited lauryl aldehyde oxidation (Table 20). In this experiment, cyclohexanone was isolated as the major product from the *N*-cyclohexyloxy substituent. The analytical data for the *N*-cyclohexyloxy compound contained in Table 20 are plotted in Fig. 4.

TABLE 17

Inhibition of AIBN-Initiated Lauryl Aldehyde Oxidation by Tetramethylpiperidinyl Benzoate Derivatives[a]

Inhibitor	*Oxidative chain length*	*Rate of O_2 uptake (mmol/h)*	*Induction period (h)*	*Time to 1·0 mmole O_2 uptake (h)*
None	105	3·6	none	0·3
$>N-H$	2·0	0·06	9·0	8·0
$>N-O^{\cdot}$	2·5	0·07	9·8	8·3
$>N-OH$	1·9	0·05	8·3	8·2
$>NOC(CH_3)_2CN$	25	0·74	none	3·7
$>NOC(O)C_{11}H_{23}$	36	1·03	none	0·8
$>NOC_6H_{11}$	2·1	0·06	7·9	8·2

[a] 60°C, 1·0M lauryl aldehyde, 0·03M AIBN, 0·002M inhibitor, 1 atm. O_2, chlorobenzene solution.

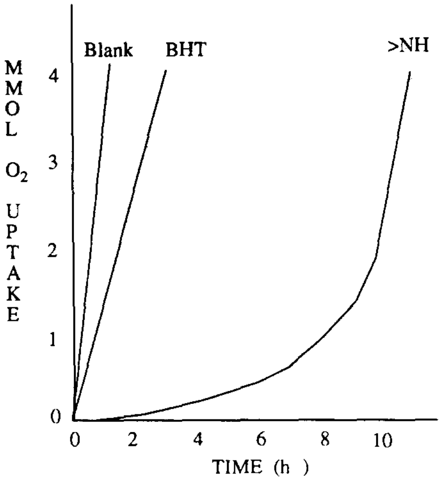


Fig. 3. Oxygen uptake during AIBN induced lauryl aldehyde oxidation.

Cyclohexane

The data in Table 10 for isooctane, *n*-heptane and cyclohexane show that these three saturated hydrocarbon models for saturated hydrocarbon polymers did not exhibit chain reactions under the conditions of oxygen uptake experiments. The oxidative chain lengths for all three were less than one, indicating that termination reactions of radicals dominated propagation. These experiments would not be good models for the chain-reaction

TABLE 18

Concentration of Components in Tetramethylpiperidinyl Benzoate-Inhibited Lauryl Aldehyde Oxidation[a,b]

Time (*h*)	$>NO^{\cdot}$	$>NH$[c]	*Lauric acid*	*Active O*
0·00	0·0	9·3	13	—
0·25	0·6	7·4	59	5
0·75	1·4	5·9	66	11
1·25	2·0	4·0	44	16
2·00	2·3	2·3	86	21
3·00	0·8	3·2	76	27
4·00	0·3	4·1	160	31
5·00	0·2	4·7	290	31
6·00	0·2	4·8	430	83

[a] 60°C, 1·0M lauryl aldehyde, 0·20M AIBN, 0·010M inhibitor, 1 atm. O_2, chlorobenzene solution.

[b] All concentrations in mM.

[c] $>NOC(O)C_{11}H_{23}$ appears as $>NH$ in GC analysis.

TABLE 19

Concentration of Components in Tetramethylpiperidinoxyl Benzoate-Inhibited Lauryl Aldehyde Oxidation[a,b]

Time (h)	$>NO^{\cdot}$	$>NOC(O)R$[c]	*Lauric acid*	*Active O*
0·00	8·4	1·4	25	11
0·25	5·4	2·4	25	13
0·75	4·8	2·5	23	19
1·25	4·2	2·9	28	—
2·00	3·1	3·5	29	31
2·75	1·9	4·1	53	32
3·50	0·8	5·5	110	45
4·50	0·1	5·2	550	62
6·25	0·0	4·9	650	84

[a] 60°C, 1·0M lauryl aldehyde, 0·20M AIBN, 0·010M inhibitor, 1 atm. O_2, chlorobenzene solution.

[b] All concentrations in mM.

[c] $>NOC(O)C_{11}H_{23}$ appears as $>NH$ in GC analysis.

oxidation of saturated hydrocarbon polymers. Changes in reaction conditions—lower AIBN concentration, higher temperature, for example—would need to be made in future studies to permit the solution experiments with the three saturated hydrocarbons to be better models for saturated hydrocarbon polymer oxidation.

TABLE 20

Concentration of Components in *N*-Cyclohexyloxytetramethylpiperidinyl Benzoate-Inhibited Oxidation of Lauryl Aldehyde[a,b]

Time (h)	$>NOC_6H_{11}$	$>NO^{\cdot}$	$>NOC(O)R$[c]	*Lauric acid*	$C_6H_{10}O$	*Active O*
0·00	10·8	0·2	0·0	25	0·0	3
0·30	7·9	0·7	0·4	33	3·8	—
0·75	6·7	1·5	0·7	27	5·0	—
1·25	3·8	2·2	1·7	35	5·6	23
2·00	1·8	2·5	2·3	49	7·8	30
3·00	0·0	2·7	3·0	55	9·2	—
4·00	0·0	1·0	3·8	110	7·2	—
4·50	0·0	0·2	4·6	610	7·0	56
5·70	0·0	0·0	4·9	560	5·3	95
7·50	0·0	0·0	5·4	560	6·7	135

[a] 60°C, 1·0M lauryl aldehyde, 0·20M AIBN, 0·010M inhibitor, 1 atm. O_2, chlorobenzene solution.

[b] All concentrations in mM.

[c] $>NOC(O)C_{11}H_{23}$ appears as $>NH$ in GC analysis.

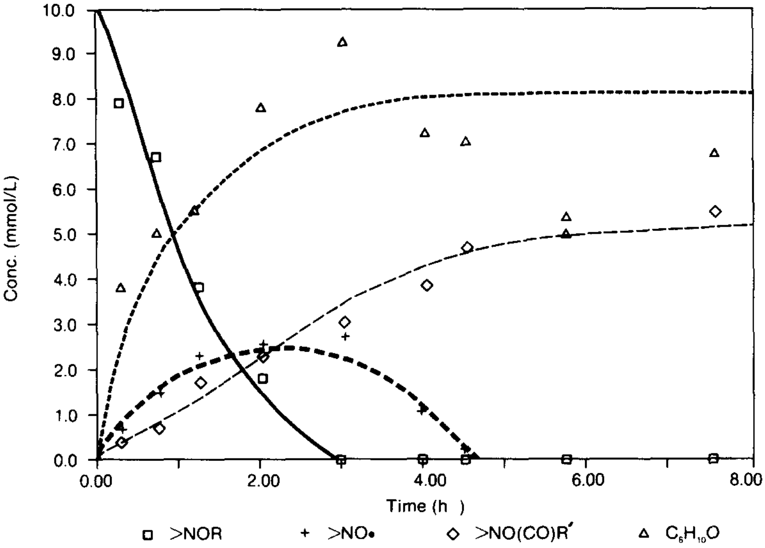


Fig. 4. Concentration of components in *N*-cyclohexyloxytetramethylpiperidin-4-yl benzoate-inhibited oxidation of 1·0M lauryl aldehyde.

The findings with the saturated alicyclic hydrocarbons led us to explore further AIBN-initiated oxidations of cyclohexane. The oxidation initiated with 0·03M AIBN and inhibited with 0·002M tetramethylpiperidinyl benzoate provided the data in Table 21 for the analysis of the hindered amine and the corresponding nitroxyl.

Analyses carried out for the *N*-cyclohexyloxy intermediate showed trace

TABLE 21

Concentration of Tetramethylpiperidinyl Benzoate and Derivatives in the AIBN-Initiated Cyclohexane Oxidation[a,b]

Time (h)	$>NH$	$>NO^{\cdot}$	$>NOC_6H_{11}$
0·0	2·0	0·0	0·0
0·5	1·8	0·1	0·0
1·0	1·8	0·2	0·0
2·0	1·6	0·3	0·0
3·0	1·6	0·6	trace[c]
4·0	1·3	0·7	trace[c]
6·0	0·9	0·8	trace[c]
7·0	0·8	0·9	trace[c]

[a] 60°C, 1·0M cyclohexane, 0·03M AIBN, 0·002M inhibitor, 1 atm. O_2, chlorobenzene solution.

[b] All concentrations in mM.

[c] Less than 0·05 mM.

TABLE 22

Rates of Consumption of Tetramethylpiperidinyl Benzoate During AIBN-Initiated Oxidations[a]

Oxidant	*Rate of loss of* $>NH$[b]
None	2×10^{-8} mol s^{-1}
Tetralin	1×10^{-8} mol s^{-1}
Cyclohexane	$4{\cdot}7 \times 10^{-8}$ mol s^{-1}

[a] 60°C, 1·0M oxidant, 0·03M AIBN, 0·002M inhibitor, 1 atm. O_2, chlorobenzene solution.

[b] Rate of radical generation from AIBN: 41×10^{-8} mol s^{-1}.

amounts present, less than 0·05 mM after 3 h reaction. The rate of consumption of the hindered amine was higher than the rate found for the rate of consumption when no oxidant was present (Table 22). It was also significantly higher than when tetralin was being oxidized. Nearly all the consumed hindered amine could be accounted for as the nitroxyl (Table 21).

Additional experiments with tetramethylpiperidinyl benzoate, the corresponding nitroxyl, and the corresponding *N*-cyclohexyloxy derivative gave the data summarized in Table 23. All these results (Tables 21, 22 and 23) show definite reactions involving the hindered amine derivatives at low rates, with the nitroxyl being the preferred species formed from both the hindered amine and the *N*-cyclohexyloxy compound. Interestingly, the *N*-cyclohexyloxy compound, which is considered an intermediate arising from

TABLE 23

Concentration of Tetramethylpiperidinyl Benzoate Derivatives after ~20 h in AIBN-Initiated Oxidation of Cyclohexane[a]

Starting conc.	*Concentration (mM) after ~20 h*		
	$>NH$	$>NO^{\cdot}$	$>NOC_6H_{11}$
2 mM $>NH$	0·2	1·1	0·0
2 mM $>NO^{\cdot}$	0·3	0·8	0·0
2mM $>NOC_6H_{11}$	0·2	1·5	0·0
10 mM $>NH$	6·9	2·3	0·1
10 mM $>NO^{\cdot}$	1·0	6·0	0·1
10 mM $>NOC_6H_{11}$	0·3	2·3	7·0
20 mM $>NH$	16·7	3·2	0·1
20 mM $>NO^{\cdot}$	1·5	12·5	0·3
20 mM $>NOC_6H_{11}$	0·3	2·4	16·7

[a] 60°C, 1·0M cyclohexane, 0·03M AIBN, 1 atm. O_2, chlorobenzene solution.

the reaction of the nitroxyl with cyclohexyl radicals, yields the nitroxyl on subsequent reaction. Also interesting is the conversion of small amounts of nitroxyl in these oxidation experiments to the hindered amine.

These results with cyclohexane clearly show reactions taking place between the hindered amines and peroxy radicals and also between the *N*-cyclohexyloxy compound and peroxy radicals. That the rates of those two reactions may be nearly the same as evidenced by the additive concentration after 20 h, is noteworthy. Whether these results are fortuitous and specific to cyclohexane or whether they are generally applicable to hydrocarbon and hydrocarbon polymer oxidation and photo-oxidation cannot be answered without more experimentation.

Investigations of the regenerative mechanism of nitroxyls

As mentioned earlier, the regeneration of nitroxyl radicals from the reaction of peroxy radicals with *N*-alkyloxy hindered amine derivatives, commonly referred to as the Denisov Mechanism, is generally accepted as an important mechanism in the functioning of hindered amine stabilizers.[6] The results reported in Table 20 wherein cyclohexane was the major product from the cyclohexyloxy substituent caused us to look further into this mechanism.

The *N*-cyclohexyloxytetramethylpiperidinyl benzoate underwent virtually no consumption in the reaction with isobutyronitrile radicals and isobutyronitrileperoxy radicals (Table 24). That behavior is in strong contrast to the results with BHT which was consumed relatively rapidly in reaction with the isobutyronitrileperoxy radicals. Similar results were found in the AIBN-initiated oxidation of tetralin (Table 25). If the regenerative mechanism were operating in these instances, we would have expected significant reductions in the concentration of the *N*-cyclohexyloxy hindered amine. Since that did not happen, we conclude that at least in the case of the *N*-cyclohexyloxy compound in chlorobenzene solution, reactions with isobutyronitrile peroxy and tetralinperoxy radicals do not take place and do not regenerate nitroxyl.

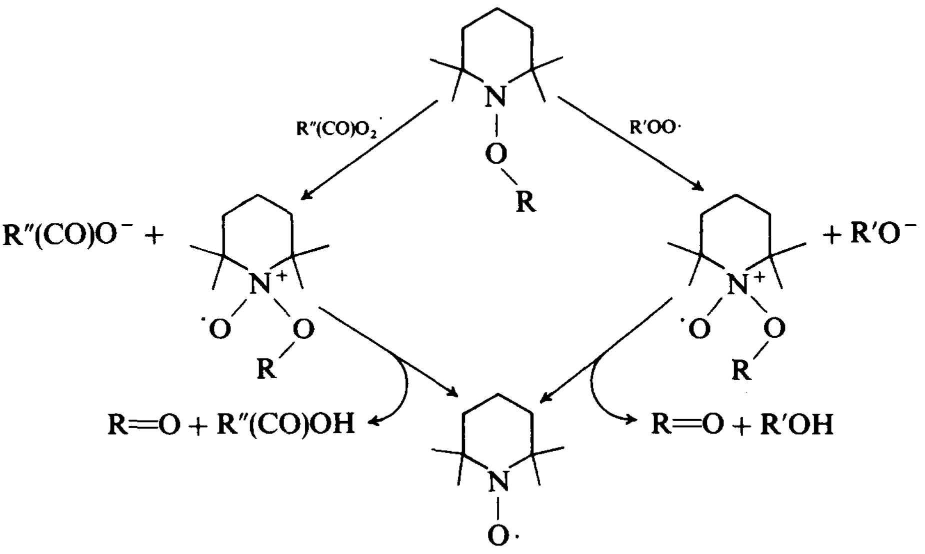
On the other hand, data in Tables 21 and 23 show that reaction took place between cyclohexylperoxy radicals and the *N*-cyclohexyloxy compound. Although at this time we do not have confirming evidence, we would like to propose that reactions between *N*-alkyloxy hindered amines and both alkylperoxy radicals and acylperoxy radicals, although taking place at different rates, result in the formation of the nitroxyl and oxidation of the *N*-alkyloxy substituents to aldehydes or ketones for primary or secondary alkyl substituents, respectively. In this same reaction, reduction of the alkylperoxy radicals to alcohols and acylperoxy radicals to carboxylic acids takes place (Scheme 5). As a consequence, all the products of the reactions

TABLE 24

Consumption of Inhibitors in Reaction with Isobutyronitrile and Isobutyronitrileperoxy Radicals[a]

Time (h)	*Inhibitor conc. (mM)*				
	0·03M AIBN			*0·2M AIBN*	
	BHT	*>NH*	*>NOC$_6$H$_{11}$*	*BHT*	*>NH*
0·0	10·1	21·9	15·9	9·9	10·1
0·5	10·0	—	—	7·8	—
1·0	9·7	22·3	16·0	5·8	8·1
2·0	—	17·7	—	2·9	7·6
2·5	—	—	18·9	0·2	—
3·0	8·2	—	—	0·0	6·6
3·5	—	—	16·3	0·0	—
4·0	7·6	18·8	—	0·0	5·7
4·5	—	—	16·5	—	—
5·0	6·4	—	—	—	—
6·0	6·0	18·8	—	—	4·8

[a] 60°C, 1 atm. O_2, chlorobenzene solution.



Scheme 5. Radical reactions of *N*-alkoxy hindered amines—nitroxyl regeneration mechanisms.

TABLE 25

Concentration of Components in *N*-Substituted Tetramethylpiperidinyl Benzoate-Inhibited Tetralin Oxidation[a,b]

Time (*h*)	$>NOC_6H_{11}$		$>NO^{\cdot}$		$>NH$	
	$>NOR$	$>NO^{\cdot}$	$>NO^{\cdot}$	$>NH$	$>NH$	$>NO^{\cdot}$
0·0	1·9	0·0	1·8	0·0	1·9	0·0
4·6	—	—	—	—	1·8	0·0
6·6	—	—	0·5	0·1	—	—
6·8	1·8	0·0	—	—	—	—
22·0	—	—	0·3	0·4	1·3	0·1
29·0	1·8	0·1	—	—	—	—

[a] 60°C, 1·0M tetralin, 0·03M AIBN, 0·002M inhibitor, 1 atm. O_2, chlorobenzene solution.
[b] All concentrations in mM.

are relatively innocuous especially in comparison to the usually proposed dialkyl peroxide oxidation products.

DISCUSSION

Literature results and the results reported in this paper confirm that there are multiple mechanisms of stabilization by hindered amines. However, literature reports and our work show that the reactivity of hindered amine stabilizers with simple hydroperoxides is low at ambient conditions. Furthermore, our work has shown the reactivity of hindered amine stabilizers with peroxy radicals also to be low at ambient conditions. These results suggest that interactions between hindered amines and simple hydroperoxides or peroxy radicals are not the sole, and probably not the major, stabilizing mechanisms for hindered amines.

The reaction of hindered amine nitroxyls with alkyl radicals is an effective oxidation inhibition mechanism where the oxygen concentration is sufficiently low to allow the nitroxyls to compete with oxygen for alkyl radicals (Table 9). While nitroxyls do not seem to be generated at fast enough rates and in useful quantities from the reaction of hindered amines with simple hydroperoxides, at least in solution, they can be generated readily by reaction of the hindered amines with peracids, acylperoxy radicals and/or other activated hydroperoxides as evidenced by the inhibition of lauryl aldehyde oxidation (Tables 12, 15, 16, 17 and 18). These rapid reactions of hindered amines with active oxygen-containing compounds may be a major route to nitroxyls in polymers and very likely is a major stabilizing mechanism of hindered amines.

Literature results which show significant amounts of carboxylic acids, peracids, and peresters among the oxidation products of polyolefins[18,19] support this hypothesis. The most likely route for formation of these products is aldehydes → peracids → carboxylic acids. Aldehydes are much more prone to oxidation than hydrocarbons so they should preferentially be oxidized.

The presence of hydroperoxides and carboxylic acids in oxidizing polyolefins suggests that two major mechanisms are operating—hydrocarbon oxidation to yield hydroperoxides and aldehyde oxidation to yield peracids, acids, and esters. Until now, more emphasis has been on hydrocarbon oxidation to hydroperoxides and related chemistry. The results of this work suggest aldehyde oxidation needs also to be considered among the main reactions taking place in polyolefin oxidation. The special effectiveness of hindered amines in retarding the thermal and photo-oxidation of aldehydes suggests inhibition of aldehyde oxidation to be an important mechanism in stabilization by hindered amines.

Hindered amine stabilizers can play a dual role in retarding polymer photo-oxidation by inhibiting both aldehyde and hydrocarbon oxidations. In one role they trap acylperoxy radicals in aldehyde oxidation, forming nitroxyls, which trap alkyl radical intermediates in hydrocarbon oxidation. In a second role, hindered amine stabilizers react at low rates with alkylperoxy radicals to yield nitroxyls, thereby retarding hydrocarbon oxidation. Within the polymer matrix the nitroxyls can apparently effectively compete with oxygen for alkyl radicals.

The low reactivity of *N*-cyclohexyloxytetramethylpiperidinyl benzoate, an expected intermediate in cyclohexane oxidation inhibited by tetramethylpiperidinyl benzoate, with tetralinperoxy radicals suggests that the usually accepted regenerative mechanism may be too slow to be a major factor in some oxidations:

$$\mathrm{ROO_2\cdot} + \rangle\mathrm{NOR'} \longrightarrow \mathrm{ROOR'} + \rangle\mathrm{NO\cdot} \tag{8}$$

However, the reaction of the *N*-cyclohexyloxytetramethylpiperidinyl benzoate with cyclohexylperoxy radicals (Table 23), although slow, suggests that the following reaction may be taking place:

$$\rangle\mathrm{NOC_6H_{11}} + \mathrm{C_6H_{11}OO\cdot} \longrightarrow \rangle\mathrm{NO\cdot} + \mathrm{C_6H_{10}O} + \mathrm{C_6H_{11}OH} \tag{9}$$

Moreover, the fast reaction of *N*-cyclohexyloxytetramethylpiperidinyl benzoate with lauroylperoxy radicals suggests that the reaction may play the most important role in the regeneration of nitroxyls from *N*-alkyloxy compounds:

$$\mathrm{RC(O)OO\cdot} + \rangle\mathrm{NOR'} \longrightarrow \mathrm{RC(O)OH} + \rangle\mathrm{NO\cdot} + \mathrm{R'{=}O} \tag{10}$$

Equations (9) and (10) are preferable to eqn (8) from a stabilization point of view since the peroxide products of eqn (8) are more likely, via homolysis, to initiate photo-oxidation than the ketone and alcohol products of eqn (9) and the ketone and carboxylic acid products of eqn (10).

Photo-oxidation probably involves different reactivities for primary, secondary, and tertiary hydrogens than thermal oxidation. The results of Felder[11] and Niki and Kamiya[17] suggest this. Hydrocarbon polymer photo-oxidation may be less selective than thermal oxidation in a preference for abstraction of tertiary hydrogens. The resulting higher yields of primary radicals in photo-oxidation may, in part, explain the high activity of hindered amines in retarding hydrocarbon polymer photo-oxidation since, in branched polymers, and especially polypropylene, this will give rise to primary peroxy radicals whose termination will yield aldehydes, acyl radicals, acylperoxy radicals, and peracids.

Saturated aliphatic hydrocarbons, cyclohexane, isooctane, and *n*-heptane behaved differently from tetralin in our oxygen uptake tests in chlorobenzene with 0·03M AIBN as initiator. For one thing, the oxidative chain lengths with the saturated aliphatic hydrocarbons have been less than one, indicating they have not been undergoing chain reaction oxidations under the conditions of our test. For another, they have been showing some response to oxidation inhibition by hindered amines as can be seen by the times to 0·1 mmole oxygen absorption in Table 14. In common with other substrates, but least of all tetralin, the nitroxyl has also inhibited the oxidation of these alkanes (Table 14).

A comparison of the rate of consumption of tetramethylpiperidinyl benzoate during oxygen uptake experiments initiated by 0·03M AIBN with no oxidant, with tetralin, and with cyclohexane showed that the rate of consumption during tetralin oxidation was not much different, even a little lower, than when no oxidant was present (Table 22). The consumption during oxidation of cyclohexane was significantly greater (Table 22). These results show that although there is little to no reaction between tetralinperoxy radicals and tetramethylpiperidinyl benzoate there is measurable reaction between cyclohexylperoxy radicals and the hindered amine. Since cyclohexane, isooctane, and hexane are better models for hydrocarbon polymers, especially polyolefins, than tetralin, the reactivity of their peroxy radicals with tetramethylpiperidinyl benzoate, albeit at low rates, indicates that these reactions may also play a role in inhibiting polymer oxidation.

The differences in reactivity between tetralinperoxy radicals and cyclohexylperoxy radicals with tetramethylpiperidinyl benzoate may possibly be related to differences in propagation and termination rates for oxidation of the hydrocarbons. At 30°C, the propagation rate constant for cyclohexane oxidation was reported to be 0·048 and that for tetralin, 6·4.[23] The propagation rate constants for oxidation initiation of hydrocarbons with *t*-butyl peroxy radicals at 30°C were 0·0031 for cyclohexane and 2 for tetralin.[23] Thus tetralin has a much greater affinity for reaction with tetralin peroxy radicals than does cyclohexane for reaction with cyclohexylperoxy radicals. These reactivity differences could explain the differences we observed in reactions with tetramethylpiperidinyl benzoate.

CONCLUSIONS

Although more work is needed before we can be confident that the mechanisms of stabilization by hindered amines are known in all their details, the work reported here brings us closer to understanding how hindered amines function in the photo-stabilization of polymers. Moreover, the results are revealing about the processes taking place in the photo-oxidation of polymers.

The equations summarized in Scheme 6 indicate that the reactions involved in stabilization by hindered amines are many. Differences among them are due primarily to different rates of reaction. The hindered amines

1. **Probably** too slow to play a major role in polymer photostabilization

$$>\mathrm{NH} + \mathrm{ROOH} \longrightarrow\ >\mathrm{NOH} + \mathrm{ROH}$$

$$>\mathrm{NOR'} + \mathrm{ROO\cdot} \longrightarrow\ >\mathrm{NO\cdot} + \mathrm{ROOR'}$$

2. Reactions significant in polymer photostabilization

$$>\mathrm{NH} + \mathrm{ROOH} \xrightarrow[\text{[proc.]}]{>200^\circ\mathrm{C}}\ >\mathrm{NOH} + \mathrm{ROH}$$

$$>\mathrm{NH} + \mathrm{ROOH\ (act.)} \longrightarrow\ >\mathrm{NO\cdot} + \mathrm{ROH}$$

$$>\mathrm{NH} + \mathrm{ROO\cdot} \xrightarrow{[\mathrm{O}]}\ >\mathrm{NO\cdot} + \mathrm{ROOH}$$

$$>\mathrm{NOR'} + \mathrm{ROO\cdot} \longrightarrow\ >\mathrm{NO\cdot} + \mathrm{R'{=}O} + \mathrm{ROH}$$

$$>\mathrm{NH} + \mathrm{RC(O)O_2\cdot} \longrightarrow\ >\mathrm{NO\cdot} + \mathrm{RCO_2H} \qquad *$$

$$2>\mathrm{NH} + 3\ \mathrm{RC(O)O_2H} \longrightarrow 2>\mathrm{NO\cdot} + 3\ \mathrm{RCO_2H} + \mathrm{H_2O} \qquad *$$

$$>\mathrm{NO\cdot} + \mathrm{R\cdot} \longrightarrow\ >\mathrm{NOR} \qquad *$$

$$>\mathrm{NO\cdot} + \mathrm{RC(O)\cdot} \longrightarrow\ >\mathrm{NOC(O)R} \qquad *$$

$$>\mathrm{NOR} + \mathrm{R'C(O)O_2\cdot} \longrightarrow\ >\mathrm{NO\cdot} + \mathrm{R'CO_2H} + \mathrm{R{=}O} \qquad *$$

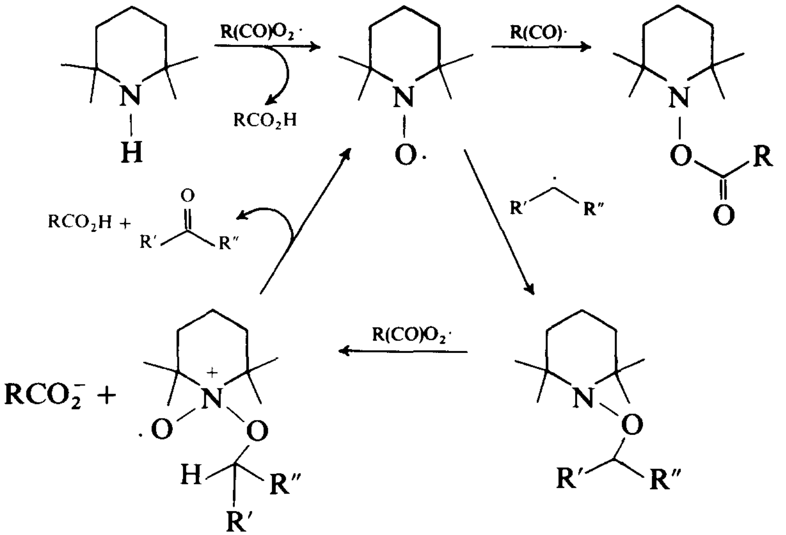
* Fast stabilizing reactions of hindered amines

Scheme 6. Reactions relevant to photostabilization of hydrocarbon polymers by hindered amines.

were found not to react fast enough nor efficiently enough with peroxy radicals and simple hydroperoxides at ambient conditions for these to be major stabilizing mechanisms. On the other hand, they were found to react rapidly with acylperoxy radicals which is an important stabilizing mechanism. In addition, *N*-alkyloxy hindered amines were found to react readily with acylperoxy radicals providing stabilization and nitroxyl regeneration (Scheme 7). *N*-alkyloxy hindered amines are postulated to react also, but more slowly, with alkylperoxy radicals to yield nitroxyls and, from secondary hydrocarbon oxidations, alcohols and ketones (Scheme 5).

The main points are that both hydrocarbon and aldehyde oxidation processes very likely take place in hydrocarbon polymer photo-oxidation and hindered amine stabilizers are able to inhibit both processes. Hindered amines inhibit aldehyde oxidations by trapping acylperoxy radicals to yield nitroxyls and carboxylic acids. They inhibit hydrocarbon oxidation through the trapping of alkyl radicals (by nitroxyls) to yield *N*-alkyloxy hindered amines and through slow reactions with alkylperoxy radicals which generate nitroxyl. The *N*-alkyloxy hindered amines efficiently trap acylperoxy radicals and, less efficiently, alkylperoxy radicals. Nitroxyls are regenerated from both reactions for additional alkyl radical trapping.

If our postulates prove correct, the hindered amines are effective because they inhibit both major polymer photo-oxidation reactions and because the products of the reactions, carboxylic acids, alcohols, and ketones, are more innocuous than hydroperoxides, obtained even in hindered phenol-inhibited oxidations, and peroxides, postulated previously as products in the



Scheme 7. Facile reactions in hindered amine stabilization mechanisms.

regenerative mechanism of nitroxyls from *N*-alkyloxy-hindered amines. The light stability of hindered amines and the light stability of the products from their functioning as stabilizers also contribute to their high effectiveness as photo-stabilizers. The fact that they usually do not generate chromophores which absorb visible light, unlike hindered phenols, is an additional feature in favor of hindered amine stabilizers.

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