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Polypropylene Photostabilization by a Tertiary Hindered Amine*

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Summary

The products from a 1,2,2,6,6-pentamethyl-piperidine have been identified both in photo-oxidizing polypropylene film and in model liquid phase photo-oxidations. In both cases, the tertiary amine is found to undergo attack by oxygen centered radicals at the N-methyl group and to generate the corresponding 2,2,6,6-tetramethylpiperidine in high yields. The latter can then take part in the cascade of protective reactions previously identified for secondary hindered amines.

Introduction

Hindered amine light stabilizers (HALS) have proven to be outstandingly effective in the protection of polyolefins and other polymers against solar radiation (SEDLAR et al, 1982, FELDER et al 1981, DURMIS et al 1981, GUGUMUS 1982). A polymer (RH) undergoes photo-oxidation by reaction scheme 1. In broad outline, the mechanism by which secondary hindered amines based upon 2,2,6,6-tetramethylpiperidine stabilize has been established (reaction scheme 2). It includes the scavenging of macro-radicals ($R^\bullet$, $RO_2^\bullet$) involved in the oxidative chain process, with cyclical regeneration of a nitroxide ($>NO^\bullet$, reaction sequence 2) although some precise details are still in question (SEDLAR et al 1982, CARLSSON and WILES in press). Tertiary hindered amines are known to be comparable in effectiveness to the secondary amines (FELDER et al 1981, GUGUMUS 1982). It is obviously of relevance to establish how tertiary amines photoprotect, and whether they fit within or integrate with the general scheme established for the secondary amines ($>NH$).

Scheme 1

$$\begin{aligned} RH &\xrightarrow{\text{Radicals}} R^\bullet \\ O_2 + R^\bullet &\longrightarrow RO_2^\bullet \\ RH + RO_2^\bullet &\longrightarrow R^\bullet + ROOH \end{aligned}$$

Scheme 2

$$\begin{aligned} >NH &\xrightarrow[O_2]{\text{Radical}} >NO^\bullet \\ >NO^\bullet + R^\bullet &\longrightarrow >NOR \\ >NOR + RO_2^\bullet &\longrightarrow >NO^\bullet + ROOR \end{aligned}$$

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Experimental

Rather than using the multifunctional N-alkylpiperidines available commercially, we have synthesized and studied a long chain, mono-amine, 1,2,2,6,6-pentamethyl-4-piperidyl octadecanoate (St--NCH_3) by esterifying 4-hydroxy-1,2,2,6,6-pentamethylpiperidine. The latter was prepared by formaldehyde condensation with 4-hydroxy-2,2,6,6-tetramethylpiperidine (Aldrich). For convenience all 4-piperidyl octadecanoate compounds in this study are written as St--NX where X represents the appropriate N-substituent. After diffusion of St--NCH_3 (hexane solution) into additive-free polypropylene (PPH) film or pre-oxidized PPH film (PPOOH), dried films were irradiated in a xenon arc WeatherOmeter (Atlas 6000W) and periodically analyzed by infrared (IR) spectroscopy and by extraction with hexane or hexane/2-propanol (95/5 vol %) followed by liquid chromatography (HPLC) and electron spin resonance (e.s.r.) spectroscopy. Two HPLC methods were employed for the highly basic amines and polar products: normal phase on 10 μm silica using hexane saturated with anhydrous ammonia as eluent and reverse phase (for very high polarity compounds such as amine oxides) using a C_8 capped column with methanol/water (96/4 vol %) containing a paired ion reagent (heptane sulfonic acid) as eluent. Product fractions from HPLC were collected and analyzed off-line by IR and chemical-ionization mass spectrometry (CI-MS). Polymer-grafted, substituted hydroxylamines (St--NOPP) were estimated by m-chloroperoxybenzoic acid treatment of extracted film as described previously (DURMIS et al 1981).

Model, liquid phase, oxidations were also performed by irradiating (Xe arc) air or O_2 saturated solutions of St--NCH_3 in a variety of solvents containing either tert-butyl hydroperoxide or di-tert-butyl peroxide as photoinitiator. Products were analyzed as for film extracts with the addition of gas chromatographic estimation of formic acid (as methyl formate formed by treatment with BF_3/methanol) and formaldehyde quantification with pararosaniline.

For comparison with reaction products from St--NCH_3 the following piperidyl compounds were prepared: the N-oxyl, St--NO• (from octadecanoyl chloride with 4-hydroxy-2,2,6,6-tetramethyl-piperidyl-N-oxyl), the secondary amine, St--NH (photo-reduction at 80°C of St--NO• with sodium sulfide in O_2-free dimethyl sulfoxide/ethyl acetate), the amine oxide, St--N($\rightarrow$O)CH_3 (by per-acid oxidation of St--NCH_3, CASTAGNOLI et al 1970) and the substituted hydroxylamine, St--NOhexyl (St--NO• in O_2-free hexane with di-tert-butyl peroxide, Xe irradiated). Structures were confirmed by IR, CI-MS and nuclear magnetic resonance (NMR).

Results and Discussion

The concentrations of piperidyl species and absorbances of photo-oxidation products from PPH(-OH species at ~ 3400 cm^{-1} and $>C=O$ species at ~ 1720 cm^{-1}) are collected in Figure 1 for a PPH film initially containing

St--NCH_3. (Without stabilizer, photo-oxidation products accumulate very rapidly at ~ 100 h Xe irradiation.) At higher concentrations (not shown), the tertiary amine is a good UV stabilizer with photo-oxidation delayed to ~ 1200 h at 0.3 wt% level, although St--NCH_3 is not quite as effective as the commercial secondary amine bis(2,2,6,6-tetramethyl-4-piperidyl) decanedioate on a weight percent basis (CARLSSON and WILES, in press).

From Figure 1 (and results at higher amine levels in PPH and PPOOH), St--NCH_3 is rapidly destroyed, with the sequential formation of St--NH, St--NO• and St--NOPP. The progressive decrease in the level of total measured piperidyl species is consistent with the formation of unreactive (ie. non-stabilizing) species which accumulate as photo-oxidation proceeds (CARLSSON and WILES, in press). However, loss of piperidyl species by migration and blooming is also a possibility.

Liquid phase oxidations are much more amenable to detailed chemical analyses than solid polymers. Irradiation

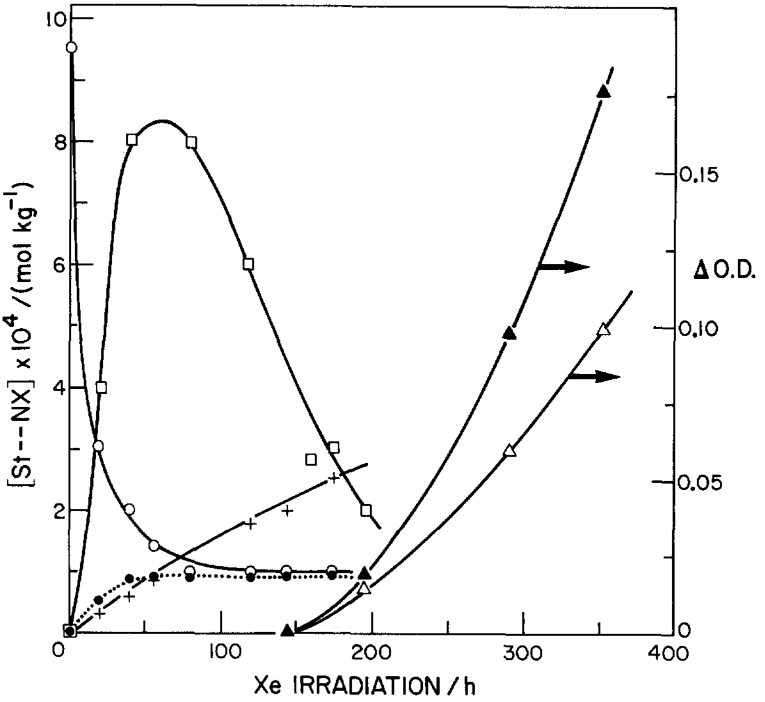


Figure 1 Piperidyl and PPH oxidation products
PPH film (25 μm) irradiation. Optical density changes measured by transmission IR at ~ 3400 cm^{-1} (Δ) and ~ 1720 cm^{-1} (▲).

○ St--NCH_3 □ St--NH
● St--NO• + St--NOPP

of solutions of St--NCH$_3$ (0.5 - 5 x 10^{-3}mol dm^{-3}) in air or O$_2$ saturated n-hexane, iso-octane or cyclohexane containing di-tert-butyl peroxide or tert-butyl hydroperoxide (1-5 x 10^{-3}mol dm^{-3}) all gave very similar changes. Representative data are shown in Figure 2. In the early stages ($<$ 20 h irradiation), based on St--NCH$_3$ loss, a quantitative yield of St--NH was found and also an approximately quantitative yield of formic acid [which precipitated at above 3 x 10^{-3}mol dm^{-3} as the formate salt St--NH$_2^{+-}$O(C=O)H which was identified by ^{13}C NMR]. Under both HPLC conditions the amine salt dissociated and chromatographed as the free St--NH. Prolonged photo-oxidation caused the progressive loss of St--NH and formation of St--NO• and St--NOS (where S represents a radical formed by hydrogen abstraction from the solvent). The overall concentration of detected piperidyl species dropped steadily during irradiation (especially at the lower initial amine concentration) clearly indicating that other piperidyl or fragmented species were formed. At high initial St--NCH$_3$ concentrations, the progressive formation of a N-formyl derivative [St--NC(=O)H] was indicated by IR (1660 cm^{-1} absorption) and CI-MS of

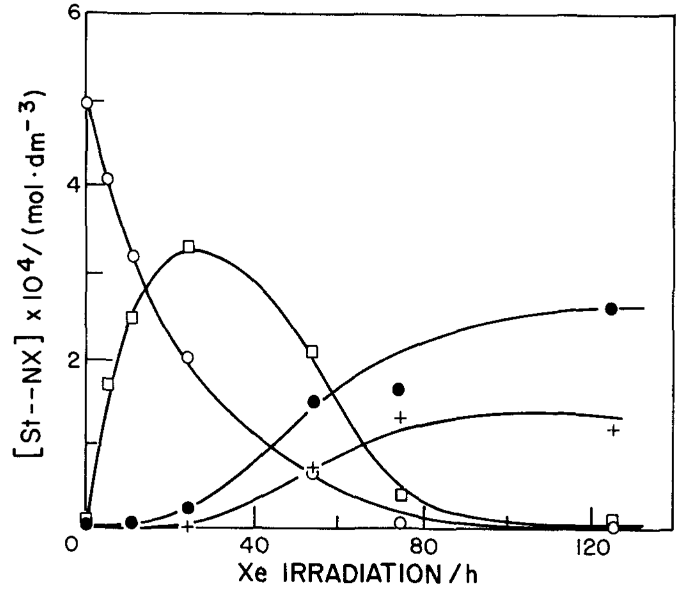


Figure 2 Piperidyl products from liquid phase oxidations

Tert-butyl hydroperoxide initiator (2.5 x 10^{-3} mol dm^{-3} in air saturated hexane).
Irradiation of 1 mm path quartz cells.
○ St--NCH$_3$ ☐ St--NH
● St--NO• + St--NO-Hexyl

collected HPLC fractions but not quantified. At low initial St--NCH_3 concentrations, formation of a nitro product was indicated by IR (1540 cm^{-1} absorption) of a collected HPLC fraction.

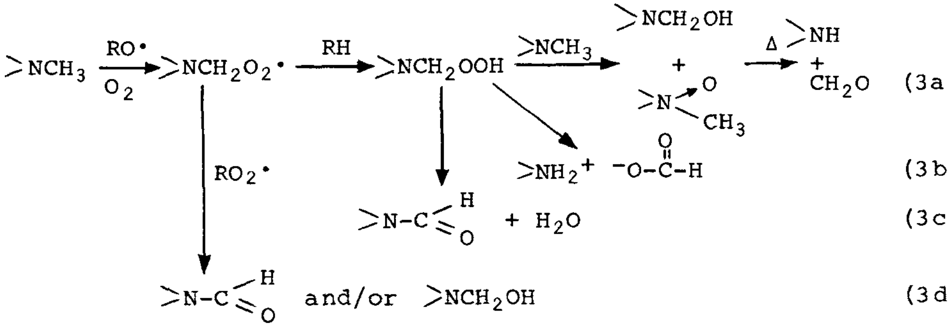
Irradiation of a methanol solution of St--NCH_3 containing tert. butyl hydroperoxide showed a four fold slower rate of St--NCH_3 loss than in alkanes, although St--NH was again quantitatively formed. Irradiation in O_2-free, alkane solvents containing tert-butyl hydroperoxide (not shown) also caused the loss of St--NCH_3 at the same rate as in air or O_2 saturated solutions but the expected piperidyl products (St--NH, St--NO•, St--NOS, etc.) were not observed. Without the deliberate addition of a photo-initiator, St--NCH_3 in air saturated hexane was destroyed 10-20 times slower by Xe irradiation than is shown in Figure 2. Amine oxide was not detected in any of our irradiated solutions. In addition formaldehyde was not detected by the sensitive pararosaniline test. This is not conclusive however because of the speed with which formaldehyde is oxidized to formic acid. In irradiations of air saturated St--NCH_3 solutions initially spiked with formaldehyde (2 x 10^{-3}mol.dm^{-3}), none was detectable after ~ 1 h.

To examine the effects of carbon centered radicals in St--NCH_3, O_2-free alkane solutions containing α,α'-azo-bis-iso-butyronitrile were heated at 80°C. No loss of the amine was observed even after several half lives of the initiator. Hydroperoxide or peroxide solutions containing St--NCH_3 were found to be indefinitely stable if stored in the dark.

St--NCH_3 Photo-Stabilization Mechanisms

From both the model liquid phase systems and from the polypropylene film experiments, the St--NCH_3 compound is converted into the secondary amine in quite high yield, with the associated detection of formate anion in the liquid system. The oxidation of aliphatic tertiary amines has been extensively studied and although secondary amine formation is well documented (SCHMITZ 1960, HOWARD, YAMADA 1981, KARNOJITZKY 1977), the observed products and conclusions are complex. In the presence of O_2 an α-hydroperoxy amine ($>NCH_2OOH$) can be expected to result from free radical attack on the α CH group of a tertiary amine (reaction 3a, SCHAEFER, ZIMMERMANN 1970, HOWARD, YAMADA 1981, KARNOJITZKY 1977). Hydrogen abstraction from a C-H group α to an amine-group is known to be much faster than attack on a similar C-H group in a saturated alkane for alkoxyl and peroxyl radicals [x 10^3 faster for alkoxyl attack, x 10^4 faster for peroxyl attack (GRILLER et al 1981)]. It is possible that the α-hydroperoxy amine is attacked by unoxidized tertiary amine [as suggested by HOWARD, YAMADA, 1981 and SCHULZ et al 1976] to give an alcohol and an amine oxide, followed by formaldehyde elimination (reaction 3a).

Although the separately synthesized St--N(→O)CH_3 was found to confer photo-stability on PPH films [and is expected to be an antioxidant (SCHULZ et al 1976)] it was not detected either in extracts from St--NCH_3 stabilized films or in model



liquid systems. This is however inconclusive because separate experiments showed that the amine oxide is unstable in alkanes (half life at 20°C ~ 10h). The octadecanoate amine oxide gave a complex sequence of decomposition products in alkane solvents. These products did not include St--NH but possibly did include St--NCH_2OH (based on CI-MS). None of these amine oxide products was observed in model liquid oxidations of St--NCH_3 in alkanes.

α-Hydroperoxy amines are notoriously unstable (SCHAEFER, ZIMMERMANN 1970, SCHMITZ 1960) but the fate of tertiary α-hydroperoxy amines is as yet unclear. However as an alternative to the amine oxide reaction 3a it is tempting to suggest a direct isomerization of the α-hydroperoxy amine to the observed formate salt (reaction 3b). Similarly the α-hydroperoxy amine could undergo amine induced fragmentation via reaction 3c to give the detected N-formyl product (SCHAEFER, ZIMMERMANN 1970, KARNOJITZKY 1977) rather than generation from the self reaction or cross-reaction of peroxyl radicals (reaction 3d). This latter process should have generated an equivalent yield of St--NCH_2OH.

SAHYUN and CRAM (1963) have shown that amine oxides are very much more stable in hydrogen bonding solvents such as methanol. Nevertheless, when St--NCH_3 was photo-oxidized in methanol, amine oxide was not detected by HPLC and in addition high yields (~ 90%) of St--NH and formic acid were detected (based on St--NCH_3 loss) rather than the 50% yield expected from reaction 3a. Direct alkoxyl attack on the St--NCH_3 may be the dominant source of tertiary amine destruction in the presence of peroxides or hydroperoxides, especially when the possibility of strong hydroperoxide-amine association is considered (SEDLAR et al 1982). In the PPH film however, where only ~ 1 x 10^{-4}mol dm^{-3} -OOH groups are detected (largely resulting from in-process oxidation and shelf storage), another alternative source of St--NCH_3 loss could be photolysis of the expected amine-O_2 charge transfer complex as suggested by KULEVSKI et al (1973).

Based upon the observed products from St--NCH_3 both in photooxidizing PPH and in model liquid phase oxidations, we draw the following conclusions. The parent amine undergoes attack by an oxygen centered radical to generate an α-hydroperoxy amine as the most likely intermediate. This intermediate rearranges to St--NH with the associated formation of formic acid, but without the intermediacy of an amine oxide. The secondary amine and/or its weak formate salt then take part in the usual cascade of stabilization reactions and intermediates (St--NO•, St--NOPP,etc.) which have been previously observed for secondary hindered amines (DURMIS et al 1981, CARLSSON and WILES, in press).

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