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Polypropylene Photo-Stabilization by Hindered Secondary Amines. A Spectroscopic Investigation*†

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ABSTRACT

The conversion products from a commercially important photo-stabilizer based on 2,2,6,6-tetramethylpiperidine have been identified and quantified during the photo-oxidation of polypropylene. From a comparison with model compounds and model systems, direct evidence for the dominant involvement of grafted substituted hydroxylamine species was obtained by infra-red spectroscopy. Non-stabilizing conversion products, including N-*acyloxy compounds, were also identified and the overall mechanism of photo-protection by hindered amine stabilizers is discussed.*

INTRODUCTION

The success of hindered amines as highly effective photo-stabilizers for polymers which degrade by photo-oxidation has resulted in the publication of many investigations of the mechanisms by which this class of compounds photo-protects.[1-12] It is now clear that during photo-oxidation the 2,2,6,6-tetramethylpiperidine-based additives convert through a series of products, several of which are themselves stabilizers. In particular, grafted products (substituted hydroxylamines $>$N—O—C) have been suggested. These species are known to act as stabilizers in photo-oxidizing[1,5,7] and thermally oxidizing systems.[13]

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However, the presence and quantity of these products in polymers are usually inferred by indirect methods such as persistence of stabilization even after exhaustive extraction of the polymer[1,12] or generation of mobile (non-grafted) piperidyl species by chemical or photo-chemical attack on these polymer samples after extraction.[1,7,8]

Direct evidence for these grafted species is potentially possible by spectroscopic examination of stabilized polymer samples after UV exposure. Balint *et al.*[2] have attempted ultra-violet (UV) spectroscopy, but the method is not sufficiently definitive to discriminate between the weakly absorbing products. Hodgeman[7] has employed conventional transmission infra-red (ir) spectroscopy but was limited by absorptions from the host polymer (polypropylene) masking the additive spectrum below 1500 cm^{-1}. We report here results from analyses of products from a commercially important, hindered amine in photo-oxidizing polypropylene. The analyses are based on Fourier Transform (FT) infra-red (ir) spectroscopy with the use of spectral subtraction to remove the absorptions of the host polymer, coupled with electron spin resonance (esr) studies and selective chemical reactions. In FT infra-red spectroscopy, the high absorbance precision and (especially) the wavenumber precision and reproducibility (to $\pm 0{\cdot}01$ cm^{-1}) allow the use of spectral subtraction to remove the absorption of the host polymer.

EXPERIMENTAL

Materials

Bis (2,2,6,6-tetramethylpiperidyl) decanedioate (HN—NH Ciba Geigy) was found to be $\geq 99\%$ pure by gas chromatography (GC) and liquid chromatography (HPLC). Commercial polypropylene (PPH) film (25 μm, Hercules resin, largely unoriented) was acetone extracted for 48 h to remove processing aids and antioxidants.

For comparison with the infra-red spectra of expected products, the following series of compounds were prepared. [Composition and purity were established (where applicable) by liquid chromatography, esr, mass spectrometry and/or nuclear magnetic resonance.] The bis-*N*-oxyl (·ON—NO·) and mono-*N*-oxyl (·ON—NH) from HN—NH were prepared by treating the amine with *m*-chloroperbenzoic acid in hexane solution.[14] The bis-hydroxylamine (HON—NOH) was prepared from the bis-*N*-oxyl by reduction with diphenyl hydrazine.[15] Treatment of the bis-hydroxylamine with acetyl chloride gave a mixture of the bis-hydroxylamine hydrochloride and bis(1-acetoxy-2,2,6,6-tetramethylpiperidyl) decanedioate [CH_3—C(=O)—ON—NO—C(=O)—CH_3]. 4-Acetoxy-2,2,6,6-tetramethylpiperidine-1-oxyl was prepared from 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (Aldrich) and acetyl chloride.

The $>\mathrm{NO}\overset{|}{\underset{|}{\mathrm{C}}}-$ containing model compounds 1-(2′-cyano-2′-propoxy)-4-acetoxy-2,2,6,6-tetramethylpiperidine and 1-(2′-cyano-2′-propoxy)-4-oxo-2,2,6,6-tetramethylpiperidine were prepared by reaction of the respective *N*-oxyls with radicals generated by the thermal decomposition of α,α′-azo-bis-*iso*-butyronitrile, as described previously.[16] Syntheses of macro analogues of these $>\mathrm{NO}\overset{|}{\underset{|}{\mathrm{C}}}-$ species were attempted by γ-irradiating (AECL Gamma Cell, dose rate 800 rad min^{-1}) under vacuum PPH film containing either the acetoxy *N*-oxyl or ·ON—NO·. The former was apparently successful as the *N*-oxyl esr signal disappeared completely. With ·ON–NO·, some *N*-oxyl signal always persisted even after large doses. However, after a low dose of irradiation of an ON—NO containing film, exhaustive extractions gave a film with a residual *N*-oxyl signal typical of a spin label of the type PPON—NO·.

Infra-red spectra of reference compounds were measured on KBr discs, in hexane solution and, where possible, after diffusion into PPH film or pre-oxidized film.

Photo-oxidation

HN—NH was diffused into films from a solution of the amine in *iso*-octane or hexane for 15 h at 20 °C. After rinsing and vacuum drying, films were exposed in an Atlas xenon arc WeatherOmeter (6000 W). Most films were photo-oxidized in air prior to immersion in the HN—NH solution, using the same xenon arc system.

Spectroscopy

Infra-red spectra were obtained with a Nicolet 7199 FTIR spectrometer equipped with a broad band mercury cadmium telluride detector and a vertically aligned, gold wire grid polarizer. To eliminate interference fringes from film spectra, films (all with the machine direction vertical) were tilted at the Brewster angle as recommended by Harrick.[17] Because of a variable background absorption in the ~3400 cm^{-1} region at high expansions (apparently due to variable amounts of water absorbed on the optics and beam splitter depending on the spectrometer purge conditions), sample spectra were collected in groups of 50 with interleaved groups of 50 collected in the (empty) reference beam. Usually, 200 scans of the sample and 200 scans of the reference beam were separately averaged at 1·5 cm^{-1} resolution with Happ-Genzel apodization and then ratioed to give the stored spectrum.

Electron spin resonance (esr) spectra were recorded on a Varian E4 spectrometer, using a Nicolet 1170 data system to perform double integrations. Spectra were recorded on CH_2Cl_2 extracts from ~25 mg film samples and on the extracted film samples immersed in CH_2Cl_2, as well as both samples after treatment with *m*-chloroperbenzoic acid. Radical concentrations were estimated from a comparison of the integrated signals with those of a simultaneously measured ruby standard located in the cavity. The ruby was, in turn, calibrated with DPPH solutions and mono-*N*-oxyl solutions of known concentrations.

RESULTS

The dominant initial products from the photo-oxidation of unstabilized PPH are hydrogen-bonded hydroperoxide groups (PPOOH).[18,19] Pre-oxidized films containing HN—NH were irradiated in the xenon-arc WeatherOmeter and periodically withdrawn for analysis by FT infra-red and esr spectroscopy. The species formed and methods of identification are listed in Table 1.

FTIR spectroscopy

FT infra-red difference spectra at increasing ultraviolet irradiation times are compared in Fig. 1 for the 2000-500 cm^{-1} range. These spectra were obtained by subtracting the spectrum of unoxidized, additive-free PPH from that of each irradiated film sample. Spectral regions containing strong polymer infra-red absorptions cannot be meaningfully subtracted because of poor signal to noise ratio in these regions. In addition, Griffiths[20] has suggested that quantitative FT infra-red spectral

TABLE 1
Analyses of Species from HN—NH in PPOOH Film

Group	*Analysis technique*	
	Infra-red[a]	*Esr*
Solubles (*in* CH_2Cl_2 *extracts*)		
(a) >NO·	—	On extract
(b) >NOPP	((k)–(f))	—
(c) >NH + >NOPP	—	((d)–(a))
(d) Total extractable piperidyl	—	extract + per-acid
Grafted (*in extracted film*)		
(e) >NO·	—	film in CH_2Cl_2
(f) >NOPP	1 140 cm^{-1} ($\varepsilon = 240$)	—
(g) >NH + >NOPP	—	((h)–(e))
(h) Total grafted piperidyl	—	film in CH_2Cl_2 + per-acid
Totals		
(i) >NH	1 237 cm^{-1} on film ($\varepsilon = 150$)	—
(j) >NO·	—	((a) + (e))
(k) >NOPP	1 140 cm^{-1} on film ($\varepsilon = 240$)	—
(l) $>NO{-}C(=O){-}\overset{|}{\underset{|}{C}}{-}$	1 772 cm^{-1} on film ($\varepsilon = 470$)	—
(m) Total piperidyl ends	—	((d) + (h))
(n) Total stearoyl group	1 738 cm^{-1} on film ($\varepsilon = 350$)	—

[a] Extinction coefficients (ε) in $\text{M}^{-1}\,\text{cm}^{-1}$.

subtraction can only be performed in regions where band absorptions do not exceed 0·7; the spectra shown in Fig. 1 correspond to this criterion, gaps indicating missing data because of strong PPH absorptions in the 25 μm film. Difference spectra were optimized by adjusting the proportion of the stored PPH spectrum used in the subtraction until the weak and medium intensity PPH bands (e.g. at 1167, 997, 973, 898, 840 cm^{-1}) were suppressed closest to zero. The small positive and negative residual peaks at 898 cm^{-1} in Fig. 1 typify the problems of precisely suppressing all PPH peaks simultaneously to zero by spectral subtraction.

The —OH region (3500–3300 cm^{-1}) only showed a broad trough at

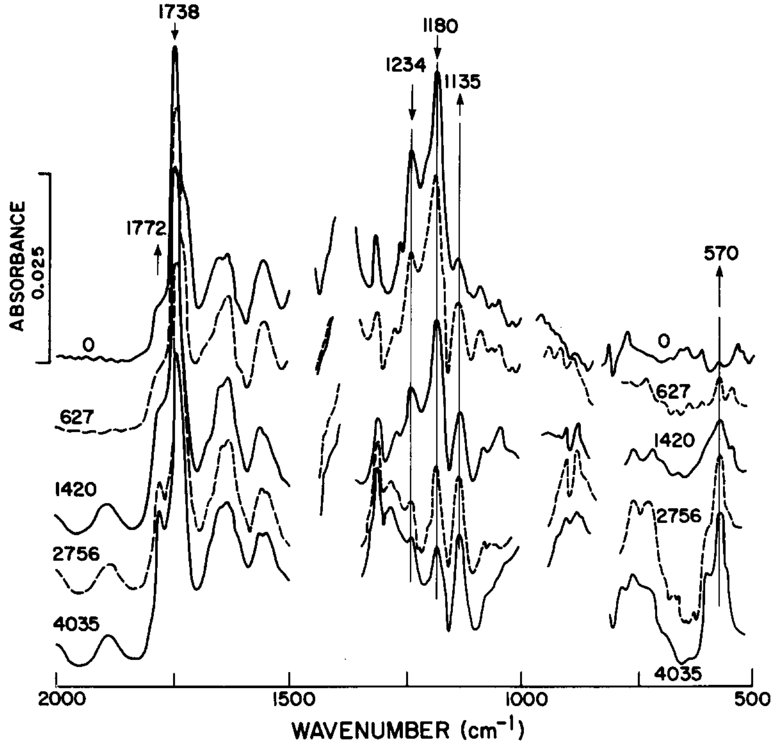


Fig. 1. FT infra-red difference spectra of polypropylene films. Times correspond to hours of xenon arc irradiation. Spectra obtained by subtracting a stored PPH spectrum from the collected spectrum of the PPOOH film with HN—NH, after designated irradiation time. Films studied as single layers in both cases. Arrows indicate key increasing and decreasing absorptions.

3400 cm^{-1} indicative of hydrogen bonded hydroperoxide and/or alcohol groups. Hydroperoxide was confirmed to dominate by iodometry[18] on extracted films. (OOH/OH initially ~10). Some piperidyl species (*N*-oxyls and amine oxides, for example) quantitatively oxidize I$^-$ and must be removed before —OOH analysis.[14] Hydroxylamine groups ($>$NOH) were confirmed to absorb at ~3420 cm^{-1} [21] but were not detected by nitroxide generation when films were treated with tert-butyl hydroperoxide.[22]

Infra-red spectra of several reference compounds in KBr discs were found to be markedly different from spectra of the same compounds in a low polarity environment (hexane or PPH). For example, a medium intensity band distinctive of $>$NH in HN—NH is a strong singlet at

1236 cm^{-1} when the amine is dispersed in hexane or PPH. This band is not present in the KBr disc spectrum but is apparently replaced by two bands at 1220 and 1242 cm^{-1}. Similarly, the ester band from HN—NH in KBr discs at 1720 cm^{-1} is shifted to 1738–1740 cm^{-1} when dissolved in an alkane matrix.

Precise estimation of the total stearoyl groups from the 1738 cm^{-1} absorption is complicated by the underlying carbonyl absorptions attributable to carbonyl products produced during xenon pre-oxidation.[18] However, the 1735 cm^{-1} absorption resulting from the oxidation products was only 20% of that resulting from the stearoyl groups. In addition, a broad, weak absorption at 1250–1150 cm^{-1} (possibly attributable to branched ethers formed during preoxidation) underlies the 1236 cm^{-1} $>$NH absorption.

Esr spectroscopy

No clear evidence of *N*-oxyl intermediates was obtained from FT infra-red spectroscopy, *N*-oxyls lacking useful infra-red absorption bands which distinctly differ from those of other piperidyl species. The technique of esr spectroscopy is, however, ideally suited for the identification and quantification of these groups, even in minute quantities. The esr spectra of various *N*-oxyls expected from HN—NH are shown in Fig. 2. In the dry solid state the highly anisotropic signal is uninformative as to the precise structure of the species and complicated by the degree of oxidation of the polymer.[23] Study of extracts or extracted films is more useful. The mono-grafted species PP—ON—NO· shows a distinctive esr in extracted films swollen with a solvent such as *iso*-octane or CH_2Cl_2; this spectrum is analogous to the spectra of spin labels in solvent-swollen polymers and indicates that rotation of the *N*-oxyl end can occur only about the N–O axis.[24] A similar spectrum for PPON—NO· has been reported by Hodgeman.[7] In the liquid phase it may be possible to discriminate between mono-*N*-oxyls (always triplets) and the bis-nitroxide ·ON—NO· (3-line or 5-line depending on the polarity of the medium).[25] However, we have found that the extractable oxidation products from PPOOH films are sufficiently polar to convert ·ON—NO· spectra to triplets even when *iso*-octane is used as the extraction (and esr) solvent. Thus, previous identifications of ·ON—NH from liquid phase esr measurements on species extracted from oxidizing polymers[4,7] are questionable. Nevertheless, from HPLC analyses of

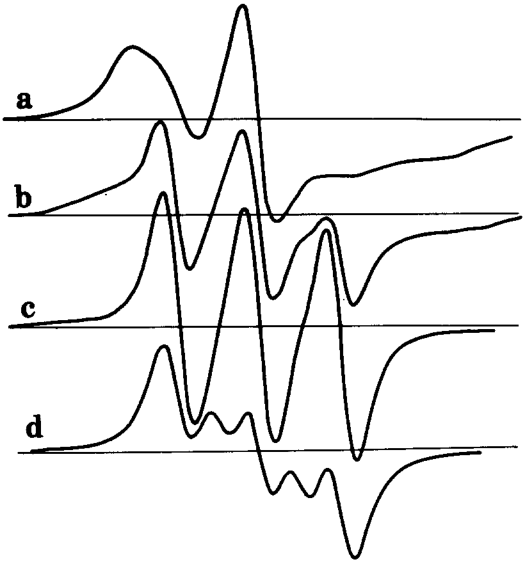


Fig. 2. Effects of environment on *N*-oxyl esr spectra. All samples under air at 22 °C.
a Solid state spectrum of ·ON—NO·, HN—NO· and PPON—NO· in PPH matrix.
b PPON—NO· in PPH film swollen with octane.
c ·ON—NH in all liquid solvents and ·ON—NO· in polar solvents (CH_2Cl_2, octane + extracted polymer oxidation products, etc.).
d ·ON—NO· in low polarity solvent (e.g. *iso*-octane).

extracts we have shown that HN—NO· is the dominant, extractable *N*-oxyl species (~10 times the concentration of ·ON—NO·) from HN—NH in irradiated PPH.[8] Methylene chloride was used in extraction experiments because of its speed of extraction of piperidyl species from films.

Several piperidyl species (>NH, >NOH, >NOC—>N—O—C(=O)—) have been shown to be quantitatively converted to >NO· groups by treatment with a solution of *m*-chloroperbenzoic acid[8] so that the total concentration of these species may also be estimated by esr.

Kinetic data for dominant species are collected in Fig. 3, based on the methods listed in Table 1 for the estimation of total concentrations.

Discussion

The high efficiency of hindered amines as uv stabilizers for PPH makes exposure experiments protracted unless low concentrations are employed

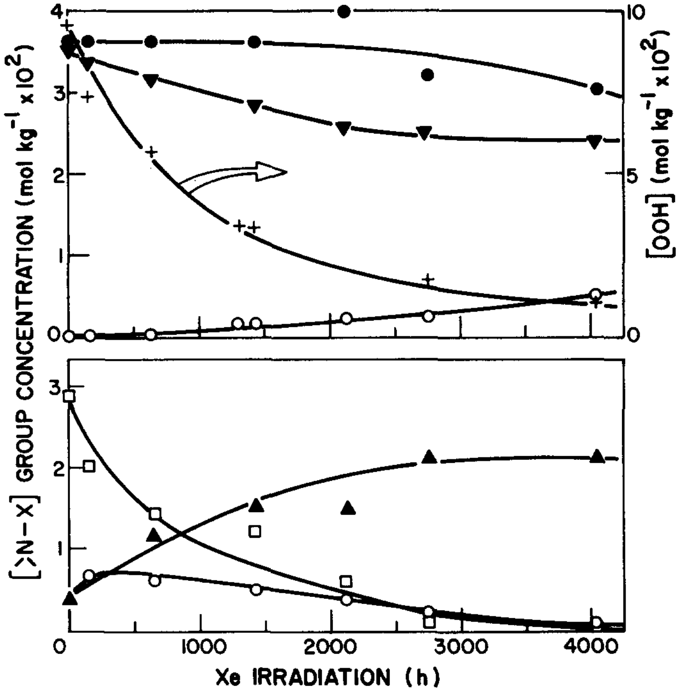


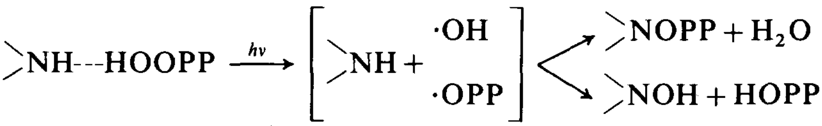
Fig. 3. Changes in piperidyl species during irradiation. Species estimated as shown in Table 1.

Upper Figure	+ PPOOH	● Total ~C(=O)—O~
	▼ Total piperidyl end groups	○ >NO—C(=O)—C—
Lower Figure	□ >NH	▲ >NOPP
	○ >NO·	

(when analyses are difficult and less definitive) or photo-chemistry can be augmented. FT infra-red can detect conversion products from HN—NH when initially at the $\sim 2 \times 10^{-2}\,\mathrm{M}\ \mathrm{kg}^{-1}$ level. To encourage rapid interconversion of stabilizing piperidyl species, films were pre-oxidized before incorporation of HN—NH. In addition, the presence of oxidation products also markedly increases the solubility of hindered amines.[26]

Interpretation of FT infra-red spectra

The difference spectra in Fig. 1 clearly show that several infra-red absorptions decrease, while others increase, during xenon irradiation. The unambiguous assignment of these changes is obviously essential for the interpretation of the HALS conversion products. The zero time spectrum is identical to that of the parent amine, in either non-oxidized film or in alkane solvents, with the 1738 cm^{-1} band attributable to the ester group in the backbone. The 1236 cm^{-1} band was not found in any of the other piperidyl species studied, and is used as a quantitative indicator of the concentration of >NH groups remaining in the polymer; this absorption decreases progressively towards zero upon ultraviolet exposure. Loss of >NH groups might result from the photo-cleavage of PPOOH which is associated with HN—NH as suggested by Sedlar *et al.*[10] (reaction (1)). From the known reactivity of HO· radicals



$$\mathrm{>NH{-}{-}HOOPP} \xrightarrow{h\nu} \left[\mathrm{>NH} + \begin{matrix}\cdot\mathrm{OH} \\ \cdot\mathrm{OPP}\end{matrix}\right] \begin{matrix} \nearrow \mathrm{>NOPP + H_2O} \quad (1(a)) \\ \searrow \mathrm{>NOH + HOPP} \quad (1(b)) \end{matrix}$$

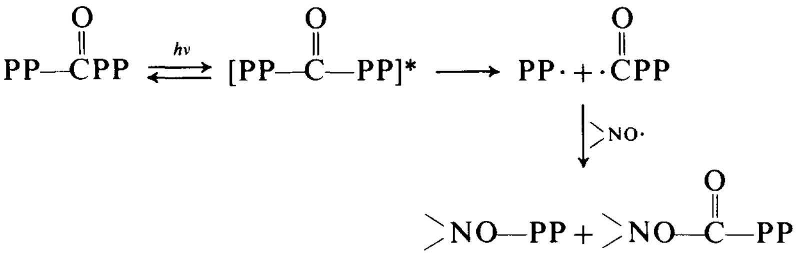
reaction (1(a)) can be expected to dominate. This expectation is consistent with the complete loss of the 3400 cm^{-1} —OH absorption of the pre-oxidized polymer (Fig. 3), whereas reaction (1(b)) would generate PPOH which absorbs more strongly at 3400 cm^{-1} than PPOOH.[18]

The respective products from the reactions of the acetoxy *N*-oxyl and the 4-oxo *N*-oxyl with 2-cyanoprop-2-yl radicals and the product from the reaction of the acetoxy *N*-oxyl with γ-irradiated PPH all showed an absorption at 1130–1150 cm^{-1}. Hence the 1135 cm^{-1} absorption in Fig. 1 is attributed to the $\mathrm{>NO{-}\overset{|}{\underset{|}{C}}{-}}$ absorption of the grafted piperidyl groups and increases progressively during irradiation. (The true location of the $\mathrm{>NO\overset{|}{\underset{|}{C}}{-}}$ absorption may, in fact, be slightly above 1135 cm^{-1} because of the problem of precisely subtracting the 1165 cm^{-1} absorption of PPH.)

Chakraborty and Scott[6] have suggested infra-red absorptions at ~1300 cm^{-1} (>NO—C—), ~1340 cm^{-1} (>NO·) and ~2765 cm^{-1} (>NOH) from a study of HN—NH in oxidizing polymers and model hydrocarbons. However, no clear evidence to support these assignments has yet appeared. The 2765 cm^{-1} band might, in fact, result from >NH--HOO-association[10] because >NOH normally absorbs weakly at ~3620 cm^{-1} (free >NOH) and ~3420 cm^{-1} (bonded >NOH).[21]

A band at 1180-1160 cm^{-1} was found in all 2,2,6,6-tetramethylpiperidyl species and provided no useful qualitative information.

Two other bands (1772 and 575 cm^{-1}) which clearly increase during irradiation (and cannot be confused with residual PPH bands) are much more difficult to assign. The 1772 cm^{-1} absorption could indicate the formation of a γ-lactone (at 1780-1790 cm^{-1}) as suggested by Adams[27] for highly oxidized PPH. However, the broad carbonyl absorption (1760–1705 cm^{-1}), due to the oxidation products in the pre-oxidized film, actually decreased during irradiation of the stabilized film. This was clearly shown when the stored spectrum of the pre-oxidized film was subtracted from the spectra of film irradiated for more than 1420 h. In particular, these difference spectra showed a clear negative absorption in the 1715 cm^{-1} region. Both changes (1772 increase and 1715 cm^{-1} decrease) may be explained by the formation of *N*-acyloxy species, which could result from the photo-cleavage of macro ketones, followed by *N*-oxyl scavenging of the fragments (reaction (2)). Felder *et al.*[9] have observed this scavenging of acyl radicals in model systems



$$\mathrm{PP{-}\overset{\overset{\displaystyle O}{\|}}{C}PP} \underset{}{\overset{h\nu}{\rightleftharpoons}} [\mathrm{PP{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}PP}]^* \longrightarrow \mathrm{PP}\cdot + \cdot\mathrm{\overset{\overset{\displaystyle O}{\|}}{C}PP} \xrightarrow{>\mathrm{NO}\cdot} >\mathrm{NO{-}PP} + >\mathrm{NO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}PP} \qquad (2)$$

but reported the $>$NO—C(=O)— absorption to be at 1748 cm^{-1} for 1-phenylacetoxy-4- benzoyloxy-2,2,6,6-tetramethylpiperidine in KBr discs. However, we find that the piperidyl $>$NO—C(=O)—CH$_3$ group absorbs at 1770 cm^{-1} in alkane media, consistent with the absorption in Fig. 1. Sedlar *et al.*[10] have suggested that a peak at ~1740 cm^{-1} from γ-irradiated PPH containing HN—NH results from $>$NO—C(=O)—PP. Their data appear to refer to extremely high degrees of oxidation and might reflect solely matrix effects on the ester absorption of HN—NH itself.

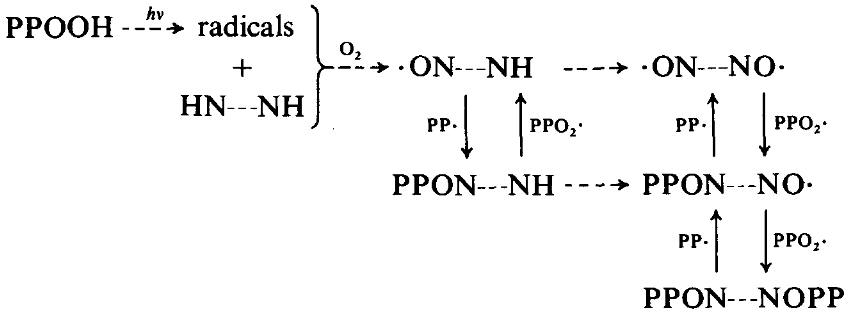
The origin of the 575 cm^{-1} absorption (which increases linearly above ~1500 h) is even less clear. Although this band is consistent with $-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{ONO}$ or $-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{NO_2}$ groups, the strong band expected at ~1600 cm^{-1} from such species was not observed. Neither $>\mathrm{NO}\underset{|}{\overset{|}{\mathrm{C}}}-$ nor

$>NO-C(=O)-\overset{|}{\underset{|}{C}}-$ model compounds displayed the 575 cm^{-1} absorption. Hodgeman[7] and Sedlar *et al.*[10] have observed the growth of absorptions at ~1630 and ~1540 cm^{-1} in irradiated PPH containing HN—NH; these absorptions might indicate the formation of a nitro compound, although quartenary ammonium groups ($>NH_2^+$) are another possibility.

In contrast to our previous study of HN—NH in photo-oxidizing PPH film, the pre-oxidized films gave quite complex results when extraction was used to partition products. For example, although $>NH$ groups had been largely consumed, as shown by infra-red (e.g. at 4035 h), extracts still contained species which reacted with per-acid to give ·ON—NO·. Extractable $>NOH$ species were not present in extracts, as shown by failure to quickly generate *N*-oxyl upon treatment with tert-butyl hydroperoxide (as does HON—NOH and other free hydroxylamines[22]). These extractable piperidyl species are most likely grafted products (PPON—NOPP) attached to low molecular weight PPH residues which have resulted from the extensive chain scission which accompanies PPOOH photo-cleavage.[18,19] This was confirmed by an examination of FT infra-red difference spectra corresponding to 4035 h irradiated films, both before and after extraction. A clear decrease to 60% of the pre-extraction value of the 1135 cm^{-1} band was observed. In addition, the 1772 and 575 cm^{-1} absorptions were reduced by about this same factor.

Hindered amine mechanisms

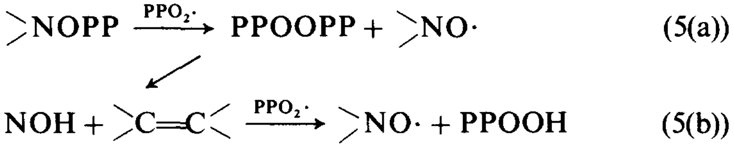
Data for the loss and accumulation of piperidyl species (Fig. 3) are, in general, consistent with the overall mechanism (reaction scheme (3)) which we have discussed previously for HN—NH in PPH film.[8] From the growth of the 1135 cm^{-1} absorption, the



(3)

reservoir of piperidyl species is directly confirmed to be the grafted species (>NOPP). However, the total concentration of piperidyl ends is below the concentration of ester groups estimated from the 1738 cm^{-1} absorptions at high irradiation times. This discrepancy may result from accumulated errors but might also be attributed to other uncounted piperidyl species such as the (possibly) nitro species (at 575 cm^{-1}). The >NOPP species may compete directly with the propagation reaction (4) via reaction (5(a)), although disproportionation via reaction (5(b)),[16] followed by a rapid peroxyl scavenging reaction[22] is also a

$$\mathrm{PPH} \xrightarrow{\mathrm{PPO_2\cdot}} \mathrm{PPOOH} + \mathrm{PP\cdot} \qquad (4)$$



$$>\mathrm{NOPP} \xrightarrow{\mathrm{PPO_2\cdot}} \mathrm{PPOOP} + >\mathrm{NO\cdot} \qquad (5(a))$$

$$>\mathrm{NOH} + >\mathrm{C{=}C}< \xrightarrow{\mathrm{PPO_2\cdot}} >\mathrm{NO\cdot} + \mathrm{PPOOH} \qquad (5(b))$$

possibility. However >C=C< accumulation (at ~1645 cm^{-1}) is not shown in the difference spectra (Fig. 2), although this has been reported by Hodgeman[7] and Chakraborty and Scott.[6] The >NOPP species are expected to be photo-stable to terrestrial sunlight, as our model compounds have no absorption above 250 nm.

Nitroxyl end groups (at maximum) account for only ~20% of the piperidyl species produced upon irradiation of PPOOH/HN—NH. Similar (or lower) concentrations have been reported by Russian workers[1,12] and Felder *et al.*[28] Baheri *et al.*[11] have also reported >NO· yields from HN—NH in photo-oxidizing PPH, but found very large >NO· levels (in fact, 1·5 times the initial >NH level). These values presumably result from the problems of quantifying products from the highly anisotropic, environment-dependent, solid state esr spectra of >NO· radicals. Despite their low concentration, >NO· species obviously occupy a pivotal roll in photo-stabilization by HN—NH. The low level is consistent with >NO· scavenging PP· radicals (reaction (6)) in competition with O_2 in the propagation reaction (7). Although $[>\mathrm{NO\cdot}]k_3/[\mathrm{O_2}]k_4$ is expected

$$\mathrm{PP\cdot} + >\mathrm{NO\cdot} \xrightarrow{k_3} >\mathrm{NOPP} \qquad (6)$$

$$\mathrm{PP\cdot} + \mathrm{O_2} \xrightarrow{k_4} \mathrm{PPO_2\cdot} \qquad (7)$$

to be small based on average concentrations,[3] association of piperidyl species with the oxidized domains[10,26] (i.e. radical generating centres) may compensate for the k_3/k_4 imbalance as will the long kinetic chain lengths expected in PPH photo-oxidation.[5]

Grafted, macro (i.e. nonextractable) *N*-oxyl species (presumably PPON—NO·) were detected by esr in all films, even before irradiation. However, these represented $\leq 2\%$ of piperidyl species at any one time and their slight growth during irradiation is not shown in Fig. 3.

Products absorbing at 1772 and 575 cm^{-1} have important implications for the ultimate longevity of the pre-oxidized film in that both indicate the accumulation of non-stabilizing species. Obviously, —NO_2 groups (if confirmed) imply opening of the piperidyl ring with complete loss of the stabilizing moiety and possibly photo-sensitizing reactions. The >NO—C(=O)—PP group is not attacked by peroxyl radicals[9] and so will neither scavenge nor reform >NO· to continue the stabilization cycle.

We have previously found that —OOH groups in pre-oxidized, stabilizer-free PPH film are destroyed quite rapidly under xenon arc irradiation ($\tau_{1/2} \sim 25$ h).[19] The very slow decrease to zero of the —OOH concentration (Fig. 3 $\tau_{1/2} \sim 600$ h) implies that the piperidyl species do not stop all oxidative chains and that an appreciable fraction of hydroperoxide photolized is regenerated through chain oxidation of PPH. In addition, the slow loss of >NH groups (Fig. 3) is unexpected in view of the very rapid loss ($\tau_{1/2} \sim 40$ h) of HN—NH (initially 0·03 w %) in non-oxidized PPH reported previously.[8] At the high initial HN—NH level used in the present work (~0·75 w %) some segregation of the amine may have occurred (although phase separation was not visible by optical microscopy). A slow re-solution of HN—NH into the PPH matrix could then occur as dissolved HN—NH is consumed by free-radical reactions.

Even before irradiation, HN—NH containing PPOOH films contained reacted piperidyl species (>NO· and >NOPP groups), as shown in Fig. 3. These species appeared to result from reaction even as the additive was diffused into the pre-oxidized film. Although the hindered amine does react slowly with —OOH groups in polypropylene,[26] the product generation appeared to be too rapid to attribute to this reaction. Possibly trapped free radicals remain from photo-oxidation, and are 'mobilized' in the presence of the hexane solvent so that reaction with HN—NH is then possible. A similar effect has been reported for γ-irradiated PPH.[29]

CONCLUSIONS

The infra-red spectroscopic evidence confirms that substituted hydroxylamines are the dominant reservoir of piperidyl species during the photo-oxidative degradation of PPH containing 2,2,6,6-tetramethylpiperidine additives. During ultraviolet exposure, non-stabilizing products are detected, including *N*-acyloxy compounds and (possibly) nitro compounds. The ultimate failure of articles photo-stabilized with HN—NH may in part result from this progressive deactivation of the piperidyl groups. Although we have employed rather high initial additive levels and pre-oxidized films, the results are quite consistent with our previous (indirect) studies at low concentrations of HN—NH in non-oxidized film.[8]

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