

The Role of Hindered Piperidine (HALS) Compounds for the Stabilization of Polypropylene against Oxidation Reactions Caused by Ozone and Oxidative Products Formed During Photolysis of Ozone

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Synopsis

The role of hindered piperidine (HALS) photostabilizers for the photostabilization of polypropylene films against oxidative reactions caused by ozone and oxidative species formed during photolysis of ozone under UV irradiation (i.e., atomic oxygen and singlet oxygen) has been investigated and discussed. It has been found that ozonization and/or photoozonization of 2,2,6,6-tetramethyl-piperidine (I) and piperidinoxy radical (2,2,6,6-tetramethylpiperidino-1-oxy) (II) gives a high yield (91–98%) 2,6-dimethyl-2-hydroxy-6-nitro-heptane. Ozonization and/or photoozonization of HALS probably occur by a similar mechanism as reported for (I) and (II). HALS photostabilizer reacts with ozone and/or photolysis products of ozone (atomic oxygen and/or singlet oxygen) and loses its function in the photostabilization process. For that reason protection of polypropylene against photooxidative degradation and photoozonization is of great commercial importance.

INTRODUCTION

Ozone formed in the atmosphere is a result of atmospheric photochemical reactions and/or high-voltage discharges which occur between charged mass of air and earth.¹ Due to the large excess of energy of its molecule (143 kJ mol⁻¹) ozone is very reactive and also unstable during light irradiation. Ozone decomposition begins under irradiation in visible light and is very intense in the UV region. A number of active oxygen species such as atomic oxygen O (³P, ¹D, ¹S) and singlet oxygen ¹O₂ (¹Δ_g⁺, ¹Σ_g⁺) are formed during the ozone photolysis.^{2,3} All of these O₃, O, and ¹O₂ products are in the mixture with excess of molecular oxygen (³Σ_g⁻) and cannot be separated from one another.

Ozone reacts rapidly with polymers containing double bonds in the chain backbone, e.g., elastomers, and cleaves the chains under formation of aldehyde, ketone, and carboxylic groups.⁴⁻⁶ Ozone can also react with saturated polyolefins^{4,7-22} in reactions in which hydrogen abstraction is followed by rehybridization of the carbon sp³ to sp² state.^{23,24} Presence of different organic compounds (antioxidants) decreases the ozonization reactions. The most effective antioxidants are the *N,N*-disubstituted-*p*-phenylene-diamines.^{25,26}

Atomic oxygen reacts with polyolefins^{22,27} and with unsaturated polymers such as polydienes.^{28,29} The oxidation occurs only at or near the surface of polymers and causes changes in wettability and weight loss.^{27,30,31}

Stabilization of polymers against atomic oxygen oxidation has not been investigated yet.

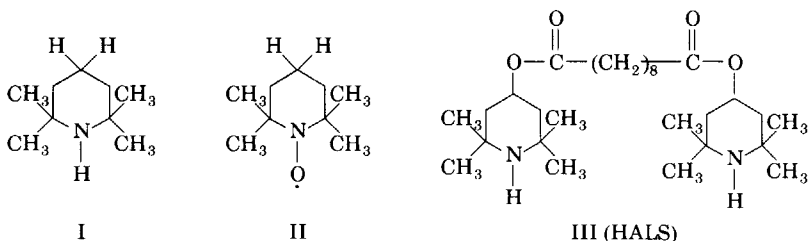
Reaction of singlet oxygen with different polymers and their stabilization against singlet oxygen has been presented in reviews³² and books.^{33,34} Singlet oxygen reacts mainly with double bonds in a polymer by the "ene" reaction to give allylic hydroperoxides. Hindered piperidines (HALS), which are effective stabilizers against photooxidation of polyolefins,^{33,34-37} react also with singlet oxygen.^{32,34}

Complex mechanistic chemistry is involved in the simultaneous oxidation of polypropylene by active species such as ozone and products of ozone photolysis, atomic oxygen, and singlet oxygen.²² The studies presented in this paper are undertaken to determine the role of HALS in the stabilization of a polymer against these agents. This work appears to be the first study of photoozonization of HALS and the consequences of these processes on the photostabilization of polypropylene in the presence of atmospheric ozone.

EXPERIMENTAL

Isotactic polypropylene (PP) was supplied by Polyscience Inc. Warrington (U.S.A.). Ozone was generated by an Ozone Generator Model 502 (Fischer Labor und Verfahrenstechnik, West Germany) equipped with an ozone concentration measuring device. A mixture of ozone and oxygen at a flow rate 500 mL/min and ozone concentration 2×10^{-3} or 4×10^{-3} g/L is passing through the quartz reactor, containing a PP film (50–70 μm). The PP samples can in addition be irradiated with a high pressure mercury lamp, type HPK 15, 1000 W or a low pressure mercury lamp (254 nm), type HPK, 125 W (both from Philips, Netherlands) at a distance of 30 cm.

The hindered piperidine (2,2,6,6-tetramethylpiperidine) (I) from Lanssen Chimica (Belgium), piperidinoxy radical (2,2,6,6-tetramethylpiperidino-1-oxy) (II) from Sigma Chemical Co. (U.S.A.) and HALS-Tinuvin 770 ((2,2,6,6-tetramethyl-4-piperidyl)sebacate) (III) delivered by Ciba-Geigy Corp. are used in these experiments:



Ultraviolet/visible (UV/VIS) and infrared (IR) absorption spectra are recorded with a Perkin-Elmer 575 UV/VIS spectrometer and a Perkin-Elmer 1710 IR Fourier transform spectrometer, respectively.

ESR spectra are determined with a Bruker ER-420 ESR spectrometer using accessories for solid samples in benzene solution irradiated with ultraviolet light at room temperature.

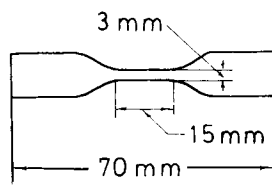
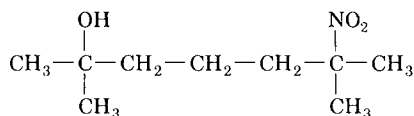


Fig. 1. Shape and dimension of the tensile bars used in testing.

The carbon NMR spectra are obtained on a Bruker NMR spectrometer B-SV7/BB 400 MHz. Deuteriochloroform is used as solvent, and the chemical shifts are recorded in parts per million from tetramethylsilane as internal standard.

Ozonization of piperidine (I) and piperidinoxy radical (II) are made with pure compounds (without solvents), exposing them to ozone (4 mg/L) for 1 h. The solid ozonization products are separated by thin layer chromatography (TLC) on precoated Silica Gel 60 plates, with benzene-ethanol (8:2) solution with a Camag HPTLC linear developing chamber 28510. The main product formed with a yield 91% (from I) and 98% (from II) is 2,6-dimethyl-2-hydroxy-6-nitro-heptane (IV): UV (NO_2) and 276 nm, $\epsilon_{276} = 28$ (Fig. 8); IR (NO_2) at 1537 cm^{-1} (asym. stretch) and 1397 cm^{-1} (sym. stretch); OH at 3400 cm^{-1} [Fig. 9(c)]; C-13 NMR (C2-OH 78.8/77.3179; C6- NO_2 94.8/88.1472). Other products were not identified.

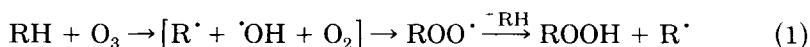


(IV)

For examination of the effect of ozonization on the tensile properties of the unstabilized and stabilized polymers, a sample sheet is cut using a template in the shape shown in Figure 1, sample thickness 0.2 mm. The tensile strength and elongation at break for these bars are determined using an Instron testing machine Model 1122, strained at the rate of 10 mm/min ($F = 1N$).

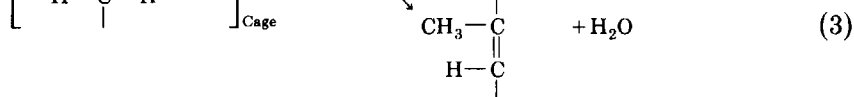
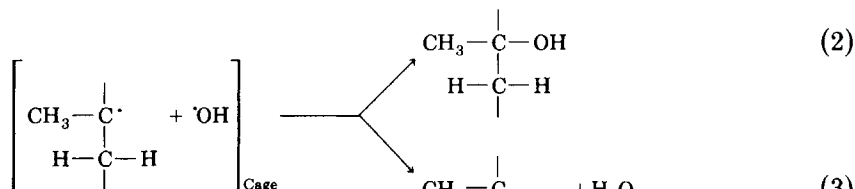
RESULTS AND DISCUSSION

Ozone can react with saturated hydrocarbons (RH) in reactions in which hydrogen abstraction is followed by rehybridization of the carbon atom from sp^3 to sp^2 state^{23,24}:

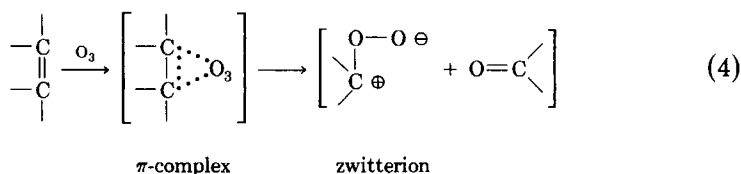


Similar reactions can also be considered in the case of ozonization of polyolefins. Polymer alkyl radicals formed during ozonization of PP (1) react immediately with molecular oxygen to polymer peroxy radicals and can be detected by ESR spectroscopy.^{12,15,22} The reaction rate and concentration of intermediate polymer peroxy radicals are proportional to the surface area and the square root of the ozone concentration.

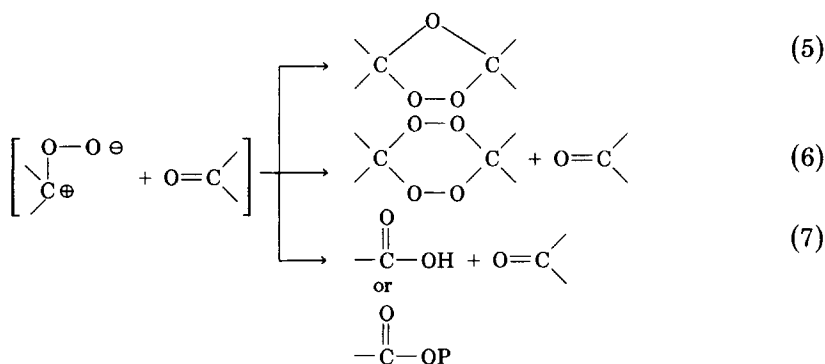
Hydroxyl radicals HO^\cdot formed in (1) can react with polymer alkyl radicals to polymer hydroxyl groups [(2)] or abstract hydrogen with formation of double bonds in polymer chain [(3)]:



The double bonds react with ozone to an unstable π -complex which rapidly decomposes to a zwitterion and an aldehyde or ketone group (4)³⁸⁻⁴⁰:



In further reactions crossozonide [(5)], dimeric peroxide [(6)], carboxylic, or ester groups [(7)] can be formed according to the following mechanisms³⁶⁻⁴²:



Increase of the ozonization temperature to 120°C (in the melt of low molecular PP) leads mainly to formation of carboxyl, ester, and aldehyde or ketone groups, while decrease of temperature leads to accumulation of peroxide and hydroperoxide groups.²¹ Reactions (1), (4), (6), and (7) cause chain scission in PP macromolecules.

Ozonization of PP films causes the formation of the following absorption bands in IR spectra: HOO/OH at 3500 cm^{-1} [Fig. 2(A)], CO at 1711 cm^{-1} and COOH at 1736 cm^{-1} [Fig. 3(A)]. The kinetics of the formation of these groups are shown in Figure 4. HOO/OH groups (3500 cm^{-1}) can be measured by IR after longer ozonization time (about 10 h) [Figs. 2(A) and 4] and their concentration increase slowly, whereas carbonyl CO (1711 cm^{-1}) and carboxyl

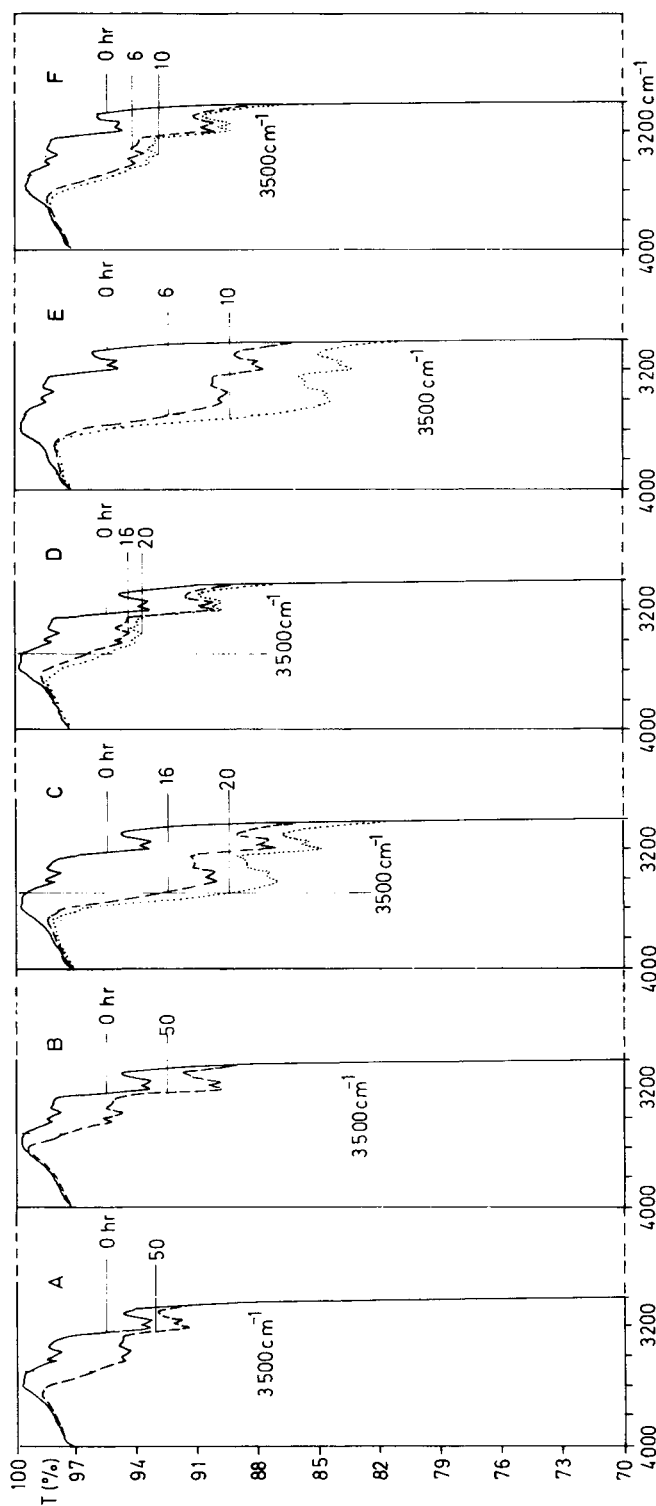


Fig. 2. Formation of hydroperoxy/hydroxyl groups on solid PP films during ozonization [(A) pure PP + O₃ (4 mg/L); (B) PP + HALS (III) + O₃ (4 mg/L)] and photoozonization process [(C) pure PP + O₃ (2 mg/L); (D) PP + HALS (III) + O₃ (2 mg/L)]; (E) pure PP + O₃ (4 mg/L) and (F) PP + HALS (III) + O₃ (4 mg/L). Content of HALS (III) = 0.6 wt %.

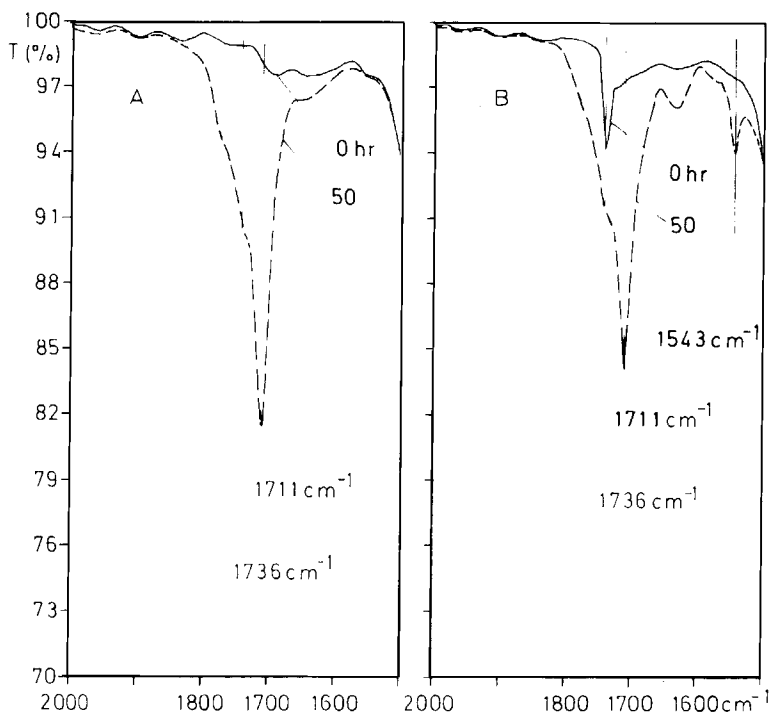
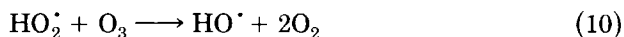
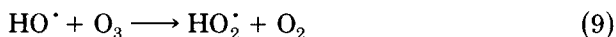


Fig. 3. Formation of carbonyl (CO), carboxyl (COOH), and nitro (NO₂) groups on solid PP films during ozonization [(A) pure PP + O₃ (4 mg/L); (B) PP + HALS (III) + O₃ (4 mg/L)] and photoozonization process [(C) pure PP + O₃ (2 mg/L); (D) PP + HALS (III) + O₃ (2 mg/L); (E) pure PP + O₃ (4 mg/L) and (F) PP + HALS (III) + O₃ (4 mg/L)]. Content of HALS (III) = 0.6 wt %.

groups COOH (1736 cm⁻¹) [Fig. 3(A)] form immediately (Fig. 4). The absorption band at 1711 cm⁻¹ in the IR spectrum is more intense than that of at 1736 cm⁻¹. These results confirm the generally accepted oxidation mechanisms of PP by ozone.^{4,7-17,20-22,41}

Ozone has UV absorption bands at 255 (strong), 305 (weak), and 340 (weak) nm and also at higher wavelengths (760, 670, 615, 510 nm), indicating that ozone may be degradable by absorption at several of these wavelengths.^{2,3} The main products formed from ozone photolysis are atomic oxygen (O) (³P, ¹D, ¹S) and singlet oxygen (¹O₂) (¹Δ_g⁺, ¹Σ_g⁺). Water vapor strongly affects the quantum yield of ozone photolysis, which rises from 6.7 to 130 in the UV region, since HO· radicals formed react efficiently with ozone¹:



These active species (O, ¹O₂, and O₂) may react with PP giving different products: alkyl radicals [(11)], hydroxyl groups [(12)], double bonds [(13)], and

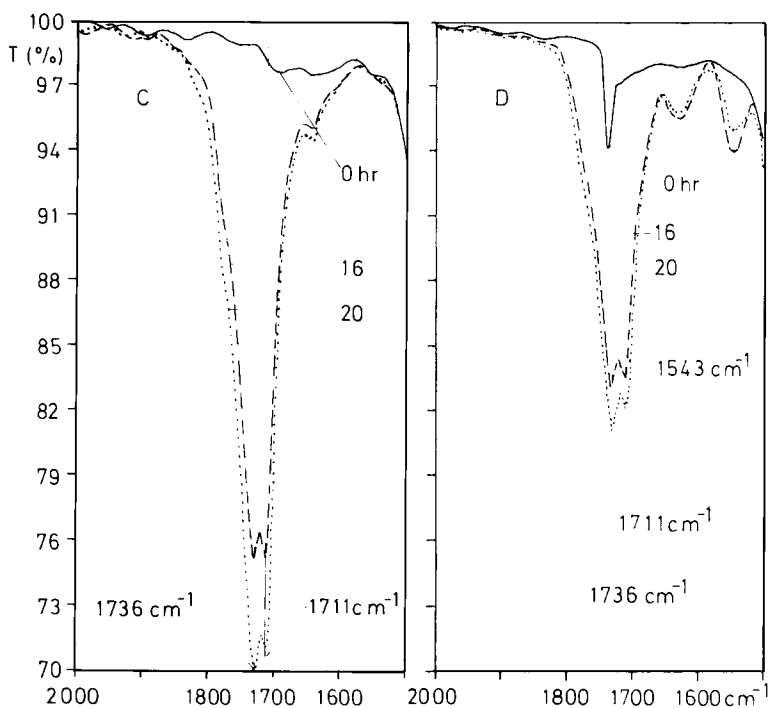
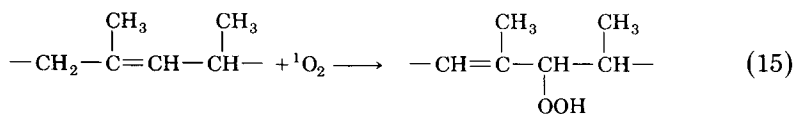
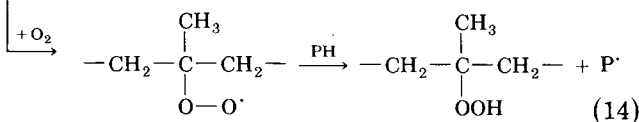
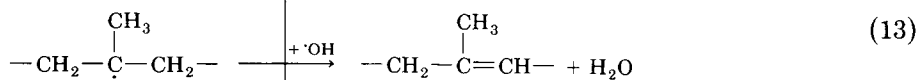
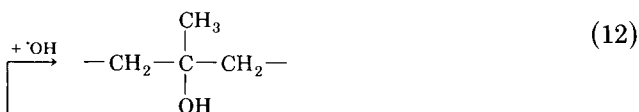
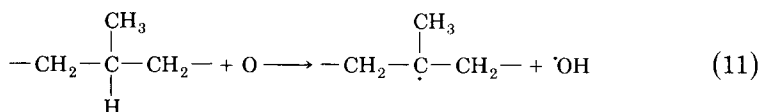


Fig. 3. (Continued from the previous page.)

hydroperoxides [(14), (15)]:



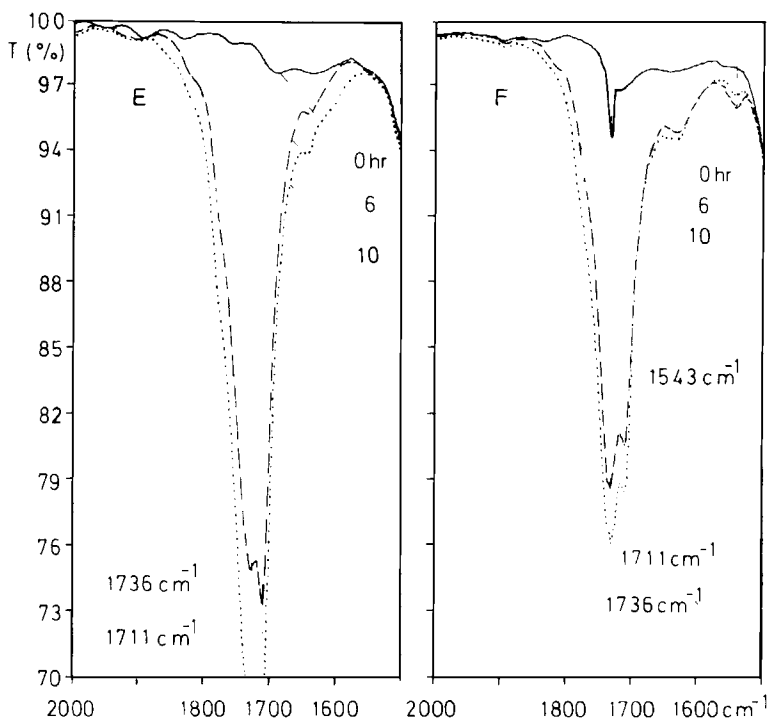


Fig. 3. (Continued from the previous page.)

Hydroperoxides can be further decomposed by UV irradiation to carbonyl or hydroxyl groups. Double bonds can also react with ozone according to the mechanisms (4)–(7).

UV irradiation activates the ozonization of low molecular organic compounds and produces a number of radical species and different oxidized

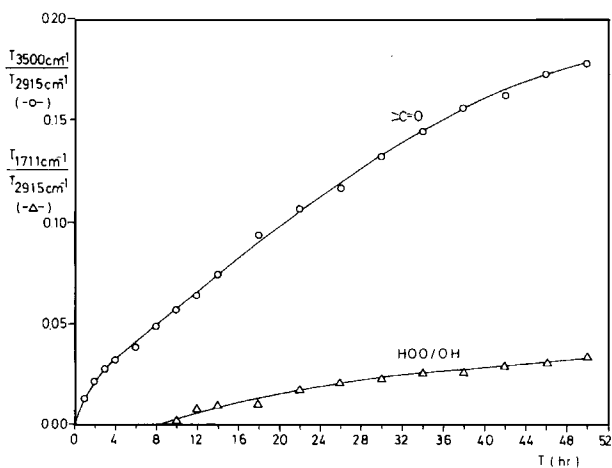


Fig. 4. Kinetics of carbonyl (CO) and hydroperoxy/hydroxyl (HOO/OH) groups formation on solid PP films during ozonization process (O_3 , 4 mg/L).

end-products.^{26,42,43} Ozonization in the presence of UV has been carried out only with water-soluble polymers.^{44,45}

Photoozonization of PP causes increase of the HOO/OH [Figs. 2(C, E)], CO, and COOH groups [Figs. 3(C, E)]. The amount of these groups formed depends on the ozone concentration: O₃, 2 mg/L [Figs. 2(C) and 3(C)] and O₃, 4 mg/L [Figs. 2(E) and 3(E)]. The kinetics of the formation of these groups are presented in Figs. 11(A) and (B). The PP samples become brittle after 20 h photoozonization at 2 mg/L O₃ and after 10 h at 4 mg/L O₃.

Addition of HALS (III) to PP decreases formation of HOO/OH, CO, and COOH groups both during ozonization [Figs. 2(B) and 3(B)] and photoozonization [Figs. 2(D, F) and 3(D, F)].

It is well known that aliphatic and aromatic amines react efficiently with ozone and give a number of oxidized products.⁵ The first step in the ozonization of amines is evidently the formation of amine-ozone adduct (R₂N⁺H—O—O—O⁻) or (R₃N⁺—O—O—O⁻).⁴⁶ The further step is formation of nitroxyl radical, which may be the main product of the reaction or may only be formed in appreciable amounts, depending on amine structure.⁴⁷ Aromatic amines and derivatives of *p*-phenylenediamine form nitroxyl radicals most readily.^{25,48}

When ozone reacts with di-*tert*-butylamine, the characteristic triplet in the ESR spectrum of nitroxyl radical has been observed.⁴⁹ Nitroxyl radicals are

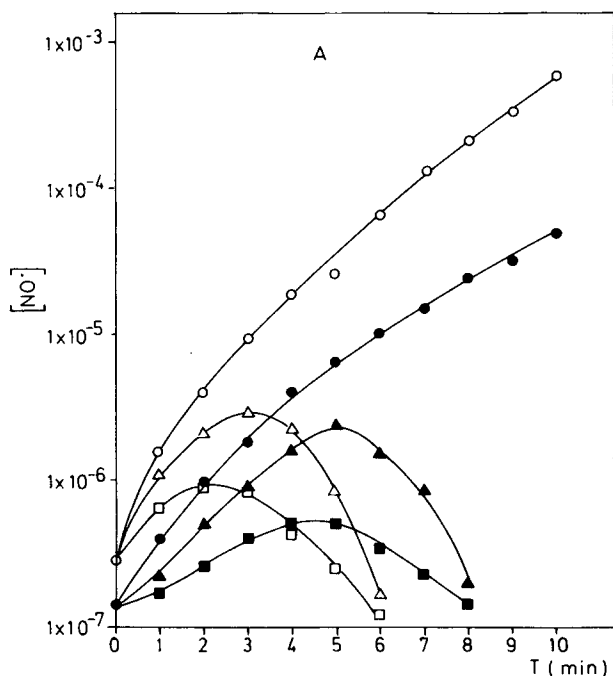
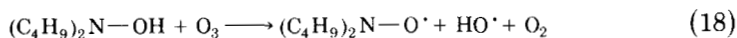
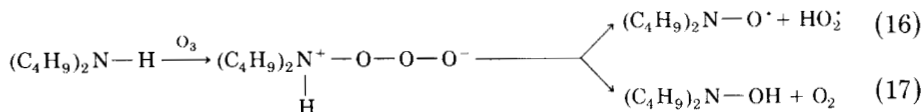
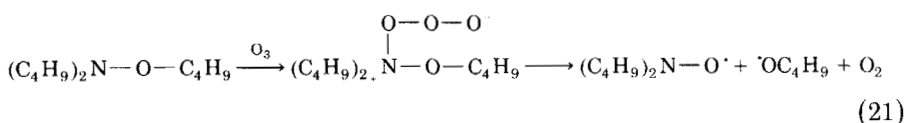
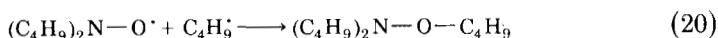
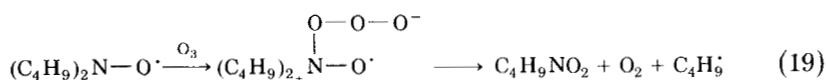


Fig. 5. Kinetics of the piperidinoxy radical formation from piperidine (I) and HALS (III), both in benzene solution ($1 \times 10^{-2} M$), measured by ESR spectroscopy during UV irradiation in air [(O) I; (●) HALS (III)], ozonization reaction [(Δ) I; (▲) HALS (III)], and photoozonization reaction [(□) I; and (■) HALS (III)]. Ozone concentration = 4 mg/L.

formed according to the reactions:



Ozone reacts also efficiently with nitroxyl radicals⁴⁶:



The major products are the same as those obtained from ozonization of di-*tert*-butylamine. The first step is addition of ozone to nitroxyl radical to give an unstable adduct [(19)]. This adduct decomposes into 2-methyl-2-nitropropane and *tert*-butyl radical [(19)]. A second molecule of nitroxyl

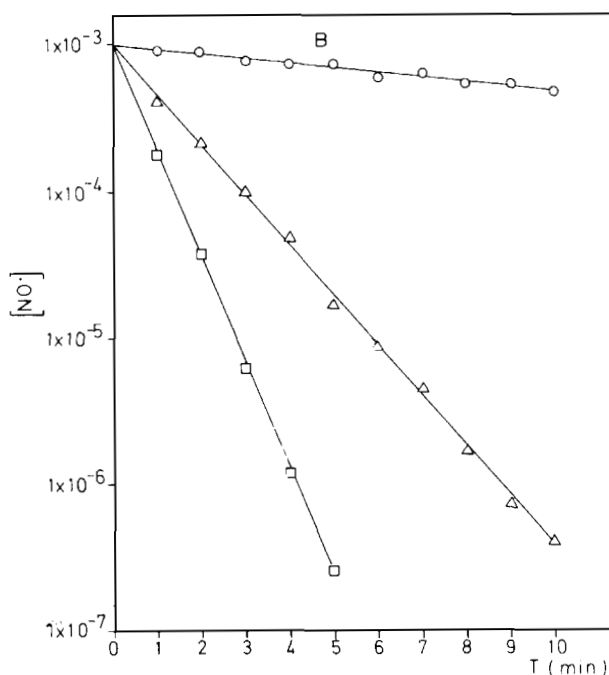


Fig. 6. Kinetics of the piperidinoxy radical (II) ($1 \times 10^{-3} M$ in benzene solution) disappearing, measured by ESR spectroscopy, during: (○) UV irradiation in air; (Δ) ozonization reaction; (□) photoozonization reaction. O_3 concentration = 4 mg/L.

radical may react further with *tert*-butyl radical to tri-*tert*-butyl nitroxide [(20)]. The latter reacts with ozone to produce nitroxyl radical [(21)].

During photooxidation, ozonization, and photoozonization of piperidine (I) and HALS (III) piperidinoxy radicals are formed (symmetrical triplet ESR signal). In the case of photooxidation of (I) and (III) the concentration of piperidinoxy radicals increases continuously with irradiation time. In the case of ozonization and photoozonization these radicals form and later disappear. Disappearing of radicals occurs faster during the photoozonization than during the ozonization process. The concentration change of radicals in the course of photooxidation, ozonization, and photoozonization is shown in Figure 5. A rapid decrease of these radicals has been also observed during ozonization and photoozonization of pure piperidinoxy radicals (II) (Fig. 6). The rate of disappearance of these radicals is faster in the case of photoozonization process. Radicals which were ozonized or photoozonized do not regenerate after 24 h in the dark in contrast to radicals which were only

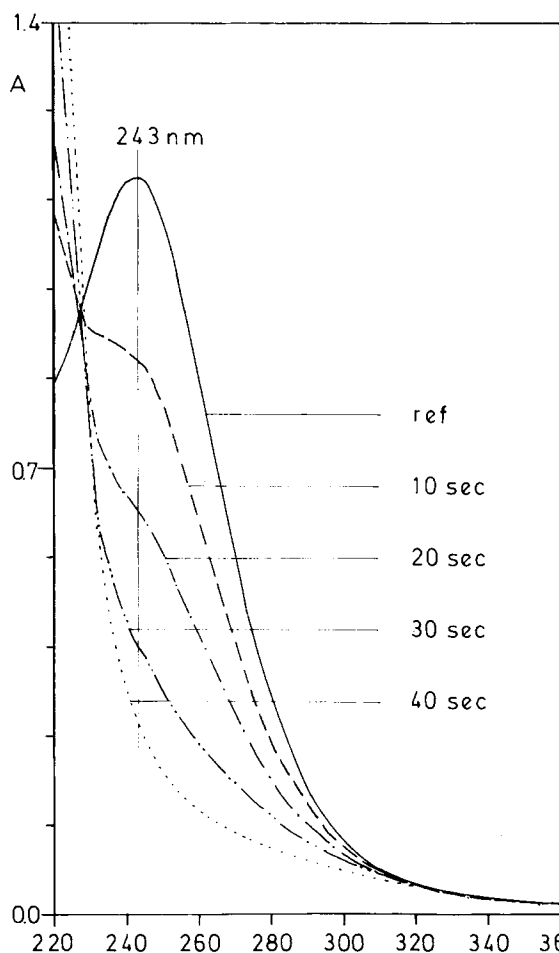


Fig. 7. UV/VIS absorption spectra of the piperidinoxy radical (II) in methanol solution ($5 \times 10^{-4} M$) after different times (s) of ozonization at ozone concentration 4 mg/L.

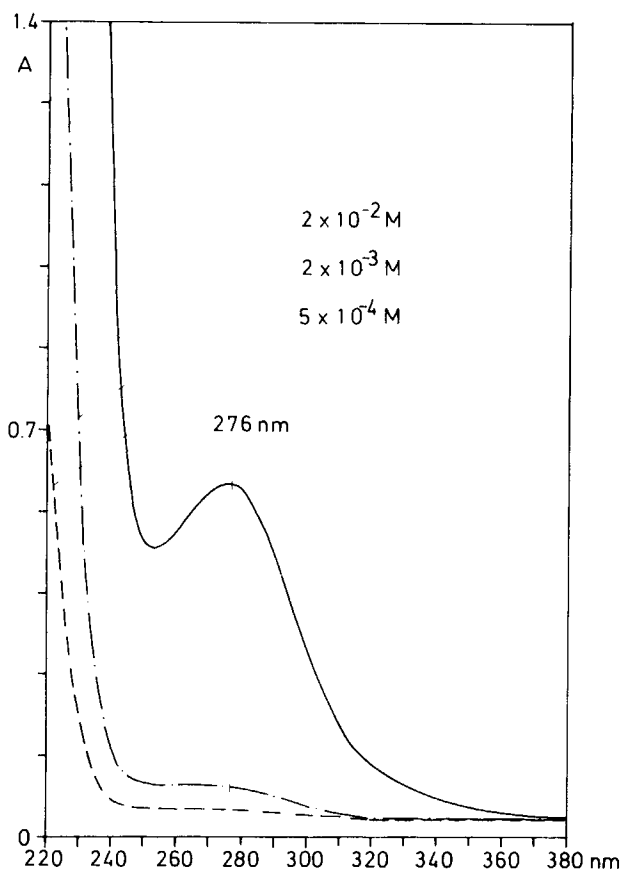


Fig. 8. UV/VIS absorption spectra of 2,6-dimethyl-2-hydroxy-6-nitro-heptane (IV) at different concentrations in methanol solution.

UV-irradiated in the absence of ozone. This means that these radicals are finally destroyed in the ozonization and photoozonization reactions. On the basis of ESR kinetics we can assume that when the first stage of the reaction is nearly ended the initial piperidine (I or III) is completely consumed. In the next stage, therefore, the reaction takes place only between piperidinoxy radicals and ozone (and/or products of ozone photolysis).

The disappearance of piperidinoxy radicals (II) during ozonization has also been measured as changes of its absorption spectra (Fig. 7). During the ozonization of (I) (liquid) or (II) (solid, strongly yellow) a similar major white solid product (IV) is formed. In the UV spectrum of this compound is a band at 276 nm with low extinction coefficient ($\epsilon_{276} = 28$) appears, which is characteristic for nitro group (NO_2) (Fig. 8).

The IR spectrum of this product [Fig. 9(C)] differs from the IR spectra of the original compounds (I) [Fig. 9(A)] or (II) [Fig. 9(B)]. In the spectrum of (IV) [Fig. 9(C)] two new bands characteristic for the presence of nitro group (NO_2) appear: 1537 cm^{-1} (asym. stretch) and 1397 cm^{-1} (sym. stretch). IR absorption bands for skeletal vibrations of saturated cyclic hydrocarbons, which are between 1250 and 910 cm^{-1} and absorption bands of secondary

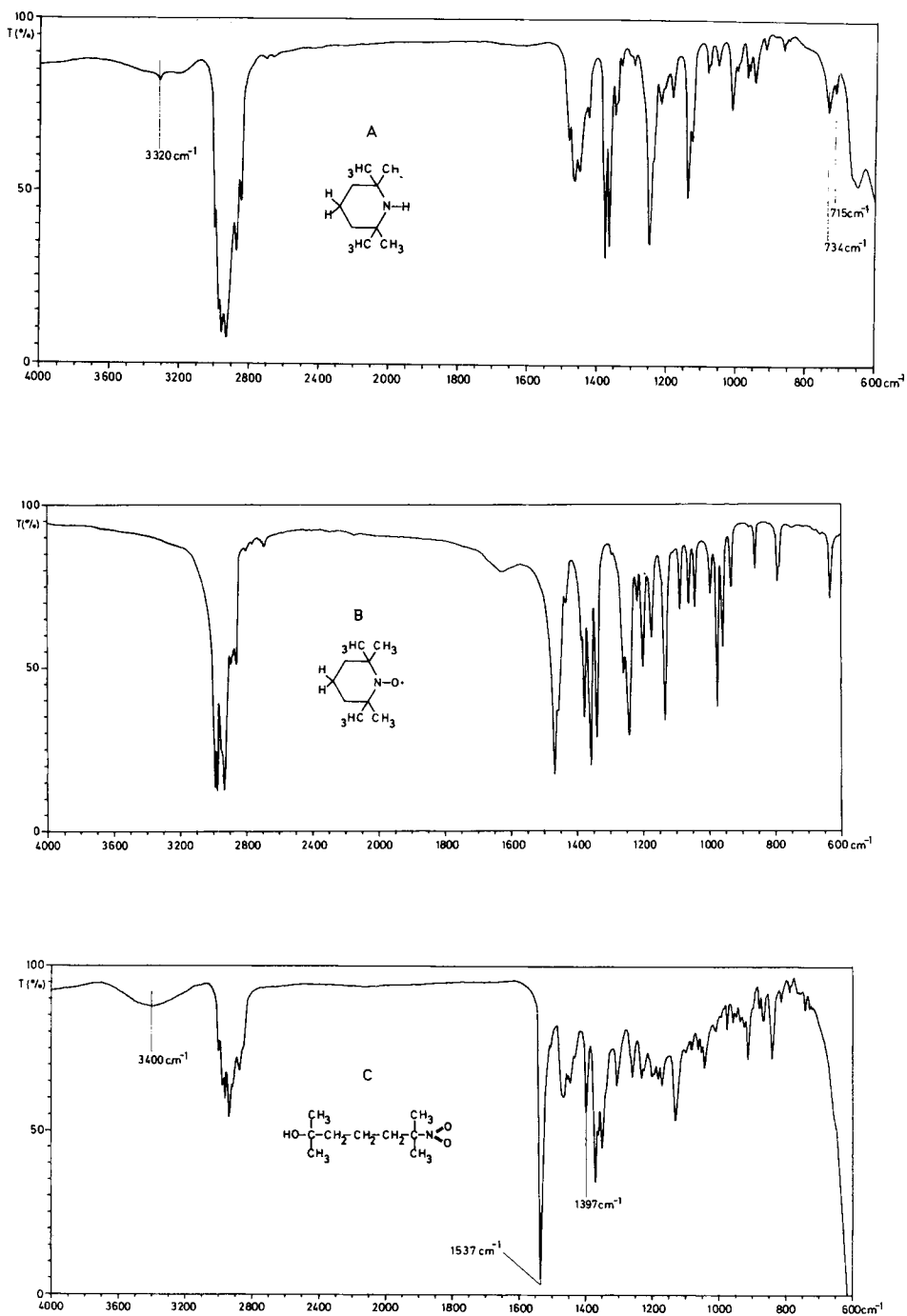
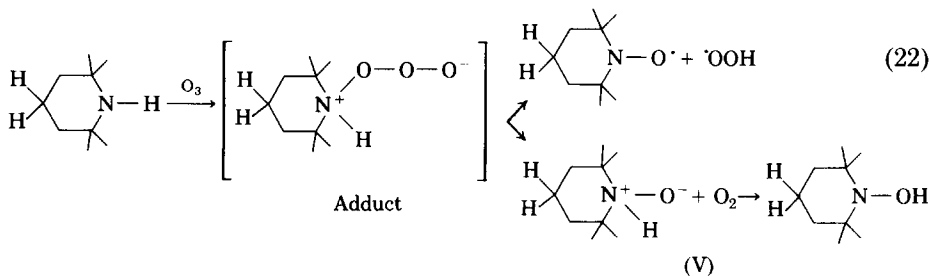


Fig. 9. IR spectra of: (A) piperidine (I) on NaCl plate; (B) piperidinoxy radical (II) from KBr pellet; (C) 2,6-dimethyl-2-hydroxy-6-nitro-heptane (IV) on NaCl plate.

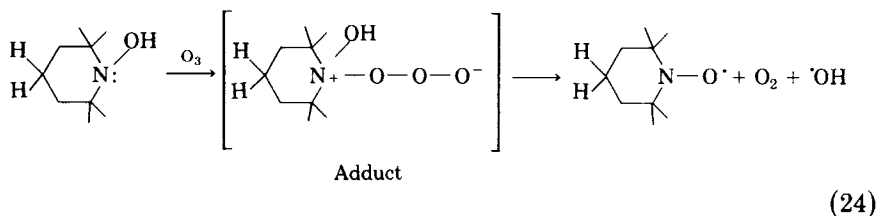
amines which are at 715 and 734 cm^{-1} , do not appear in the spectrum of (IV). A new band at 3400 cm^{-1} is attributed to the presence of OH groups.

All spectroscopical methods used (UV, IR, and C-13-NMR) indicate that ozonization and photoozonization of piperidine (I) and piperidinoxy radical (II) occur with opening of the heterocyclic ring and production of 2,6-dimethyl-2-hydroxy-6-nitro-heptane (IV) of high yield (91–98%), according to the following mechanism:

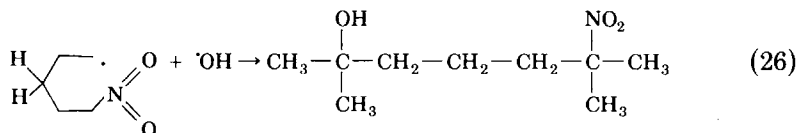
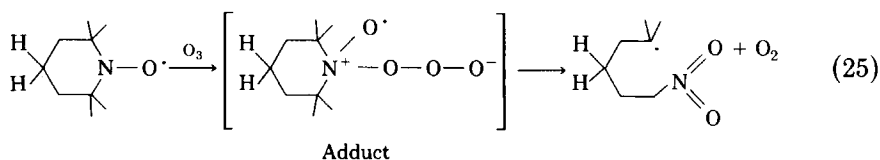
Step I:



(23)



Step II:



(IV)

Ozonization of piperidine (I) appears to occur via formation of piperidinoxy radical (II) (Step I) which is further ozonized to (IV) (Step II). We also consider the possibility of formation and disappearance of hydroxylpiperidine (V) (Step I), but this reaction has not been proven. In the case of HALS (III) ozonization and photoozonization in the PP matrix occur probably by the same mechanisms. IR spectra of PP films stabilized with III show, after ozonization and photoozonization, formation of a band at 1543 cm^{-1}

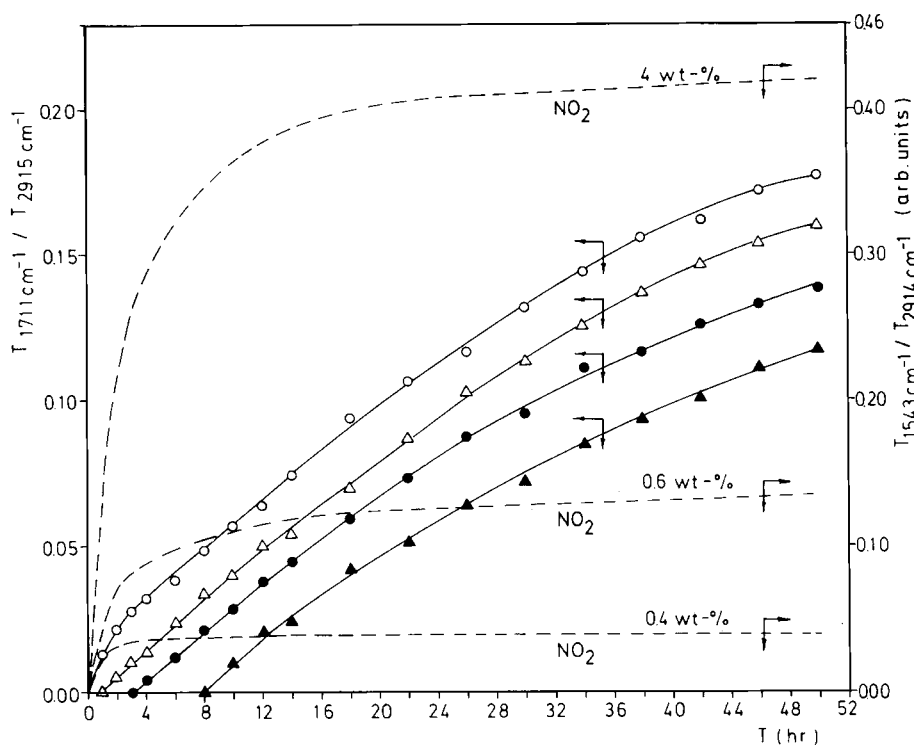


Fig. 10. Kinetics of carbonyl (—) and nitro (---) groups formation on solid PP with different amount of HALS (III): (Δ) 0.4 wt %; (\bullet) 0.6 wt %; (\blacktriangle) 4.0 wt %. Nitro groups formation was measured for PP samples with respective 0.4, 0.6, and 4.0 wt % of HALS (III).

[Fig. 3(B, D, and F)], which can be attributed to the NO_2 group. The kinetics of the formation of the nitroaliphatic compound during ozonization of HALS (III) in PP film is shown in Figure 10. The concentration of the nitro groups in PP film increases rapidly during the first 8 h of ozonization process and after this time does not change or increases slowly (Fig. 10). Kinetic measurements of the formation of carbonyl groups in PP containing different amounts of added HALS (III) (0.4, 0.6, and 4.0 wt %) (Fig. 10) show that ozonization of the polymer increases rapidly after consumption of HALS (III) in the ozonization reaction. The carbonyl group formation in PP with 0.4 wt % of HALS (III) starts after 1 h, with 0.6 wt % after 3 h and with 4.0 wt % after 8 h.

The kinetics of carbonyl (CO), HO/OOH, and NO_2 group formation in PP, unstabilized and stabilized with HALS (III) during photoozonization at different ozone concentration (2 and 4 mg/L) [Figs. 11(A) and (B)], show the very complicated mechanisms which occur. It probably depends on the reactive species from photolysis of O_3 (O , $^1\text{O}_2$, and O_2), which are present in excess in the ozone-oxygen mixtures, and take part in the oxidation of PP. The formation of HO/OOH groups in PP [Figs. 11(A) and (B)] starts immediately in contrast to the kinetics of the formation of these groups in ozonized PP (Fig. 4). The concentration of nitro groups (NO_2) increases at the beginning of the photoozonization, but later their concentration decreases and finally these groups disappear completely [Figs. 11(A) and (B)]. The kinetics of the forma-

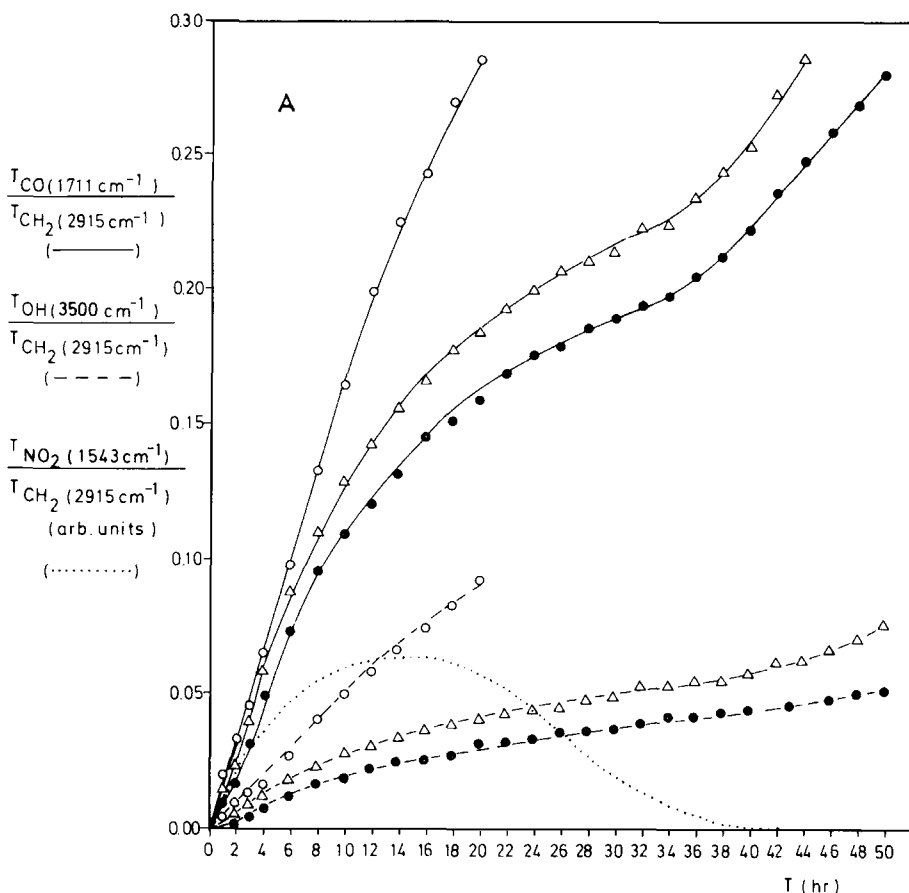


Fig. 11. Kinetics of carbonyl (—), hydroperoxy/hydroxyl (---), and nitro (···) groups formation on solid PP films during photoozone process at ozone concentration 2 mg/L (A) and 4 mg/L (B): (\circ) pure PP; and PP with different amount of HALS (III): (Δ) 0.4 wt % and (\bullet) 0.6 wt %. Nitro group formation was measured for PP samples with 0.6 wt % of HALS (III).

tion of CO and HO/OOH groups is evidently dependent on the formation and disappearance of NO_2 group. Intense formation of CO and HO/OOH groups occurs at the beginning of photoozone process and after disappearance of NO_2 groups. Prolonged UV irradiation photolyzes the nitroaliphatic compound, which forms from HALS (III), to nonidentified products. The primary photochemical reaction of simple nitroalkanes is the formation of alkyl, nitro, and nitroso radicals.⁵⁰

These results show that HALS are effective antiozonants and can protect PP against ozone oxidation. However, ozonization of HALS causes decreasing of its concentration in the PP matrix. In this way a polymer which was considered to be stabilized against photooxidative degradation by UV light by HALS becomes unprotected (unstabilized).

It seems desirable to consider the HALS ozone reaction not separately, but along with the reactions of piperidines with other oxidizing species such as atomic oxygen (O), singlet oxygen (1O_2),^{32,34} and a number of free radicals formed in this very complicated photochemical system.

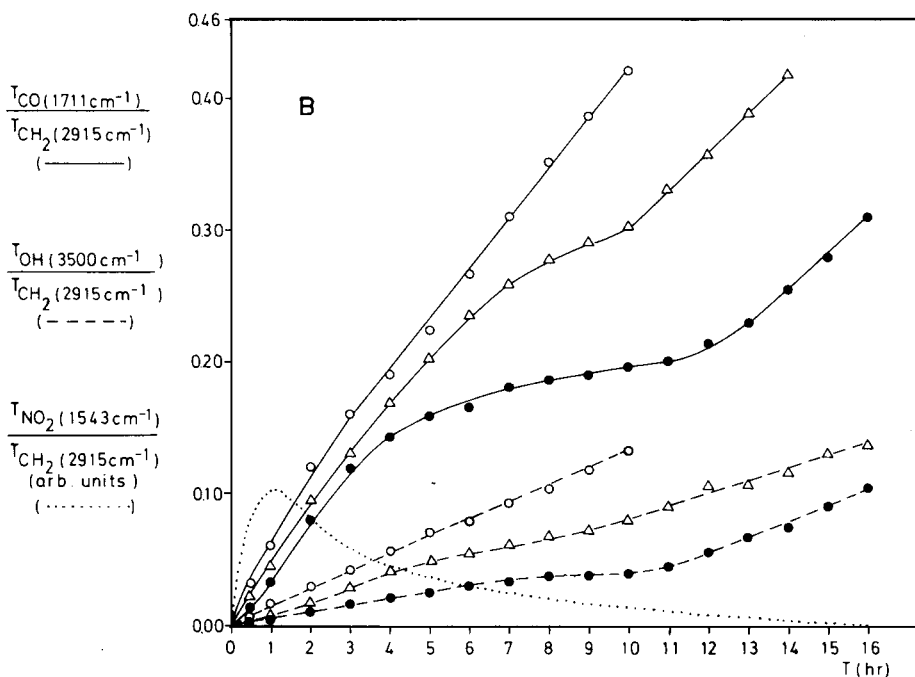


Fig. 11. (Continued from the previous page.)

The HALS at concentration 0.2 wt % (common used amount of HALS against photooxidative degradation) does not protect PP film against photoozonization with 254 nm light. The stress-strain curves in Figure 12 illustrate the effect of photoozonization of PP and PP in the presence of HALS (III). After 2-4 h of UV irradiation, PP samples are completely destroyed. The effect of HALS is visible only during first hour of irradiation.

In conclusion the overall consistency of the observed ozonization and photoozonization of HALS (III) and the proposed mechanism of ozonization is quite good. The wide variety of other products nonidentified can be explained

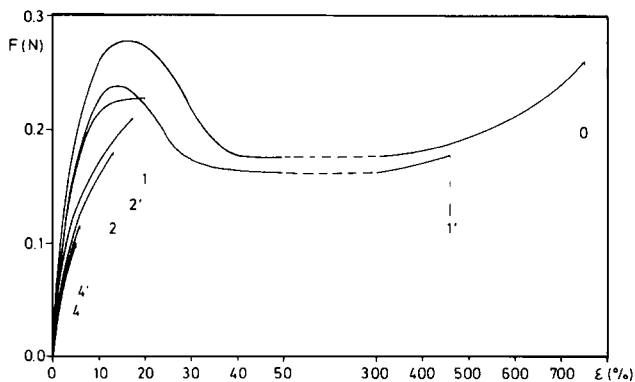


Fig. 12. Strain-stress curves for PP samples: (○) pure PP; and PP after different times of photoozonization (O₃, 4 mg/L): (1) 1 h; (2) 2 h; (4) 4 h. (1', 2', and 4') PP + HALS (III) (0.2 wt %).

well by extensions of ozonization mechanisms described in literature and photolysis of aliphatic nitro compounds. It would seem that a detailed investigation of ozonization and photoozonization products of a number of HALS stabilizers including derivative hydroxylamines would provide additional insight into the various mechanistic pathways.

The protection of PP against photoozonization is a problem of great commercial importance. If the added photostabilizer reacts with ozone and/or atomic oxygen (singlet oxygen), it loses its function in the photostabilization process.

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