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PHOTOSTABILIZING ACTIVITY OF STERICALLY HINDERED PIPERIDINES—I

PEROXIDE DECOMPOSING AND HYDROGEN DONATING ABILITY

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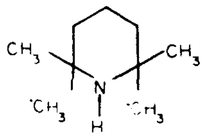
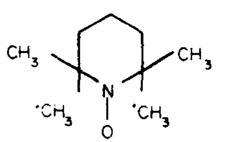
Abstract—Sterically hindered piperidine (I) and its corresponding nitroxyl have been examined for their ability to decompose hydroperoxides, donate hydrogen and influence the rate of photolysis of *t*-butylhydroperoxide in solution. None of these effects are significant. The formation of an adduct between hydroperoxide and I has been observed.

INTRODUCTION

Sterically hindered amines (HALS), such as those based on 2,2,6,6-tetramethylpiperidine (I), are known to be excellent light stabilizers for some plastics [1, 2, 4].

I





II

The mechanism by which these compounds operate is uncertain [2]. They certainly cannot act as light screeners since they exhibit no absorption above 280–290 nm.

Heller and Blattmann [2] as well as Felder and Schumacher [3] have shown that quenching of photoactive impurities by I appears not to be important in the photostabilizing process exhibited by HALS. This conclusion was corroborated by Allen *et al.* [4, 5] who did not observe carbonyl luminescence quenching in polypropylene samples containing HALS.

Belluš [6, 7] examined the quenching properties of I toward singlet oxygen Δ^1O_2. While the parent amine is rather a poor quencher of Δ^1O_2, the corresponding nitroxyl II is a very efficient quencher. In addition, the nitroxyl free radicals at high concentrations are excellent quenchers of excited carbonyls [2] and aromatics [8]. Moreover, they have been reported as efficient traps for $R^{\cdot}$ radicals [9–12]. The rate constant of this process was measured [13] to be 10^7–$10^8\,mol^{-1}\cdot l\cdot sec^{-1}$. On the other hand the nitroxyls seem not to react appreciably with $RO_2^{\cdot}$ radicals [10].

Amines of structure I are readily transformed to the corresponding nitroxyls II under conditions of mild oxidation [14, 15]. Schlyapintokh *et al.* [16] have observed the accumulation of paramagnetic nitroxyl free radicals in the early stages of polypropylene photooxidation when the polymer was stabilized by derivatives of I.

It seems plausible therefore that the high photoprotective efficiency of HALS night result predominantly from the presence of nitroxyls formed during photo-oxidation. The latter then might exhibit some of the above mentioned quenching or radical trapping properties.

According to Belluš [7] and Heller [2], singlet oxygen quenching seems not to be important during polyolefin photostabilization. As reported by Allen [4], the inhibition of carbonyl photolysis may however be significant in polypropylene stabilization. Radical scavening both by HALS and corresponding nitroxyls might be involved in photoprotection although the literature data are very scarce. No information is available about the ability of HALS to decompose hydroperoxides or to influence the quantum yield of ROOH photolysis. It was the purpose of this study to assess the above mentioned aspects.

EXPERIMENTAL

Chemicals

I and II were synthesized according to Rozantsev [15]. After purification, both substances had physical properties agreeing with literature data [15].

t-Butylhydroperoxide was synthesized [17] and then purified by preparative gas chromatography using all glass apparatus. The hydroperoxide was successfully separated on a 1 m column packed with 10% dioctylphthalate on Chromosorb W; the column temperature was 80° and N_2 flow-rate $360\,ml\,min^{-1}$. The purified hydroperoxide contained less than 0.25% of *t*-butyl alcohol. 2,4,6-Tri-*t*-butylphenoxy radical was prepared according to Müller and Ley [18].

An adduct of bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate and *t*-butylhydroperoxide was prepared thus: 8 g (0.0166 mol) of Tinuvin 770 (Ciba–Geigy) was dissolved in 30 ml of benzene; 3 g (0.0333 mol) of *t*-butylhydroperoxide dissolved in 10 ml of benzene were added dropwise to this solution with constant stirring. The mixture was left overnight and the solvent was then allowed to evaporate at room temperature. The resulting white crystalline powder was finally dried in a rotary evaporator at ambient temperature under vacuum. No condensate accumulated in a trap (−80°) positioned between the evaporator and pump. Yield 10.5 g (95.5% theor.); m.p. 83.5° (no difference from Tinuvin 770).

Powdered unstabilized polypropylene (Mosten) was compressed at 250° and 6.0 MPa between two Al sheets to give films 0.05 mm thick. Polypropylene hydroperoxide was obtained by exposing these films in Xenotest 150

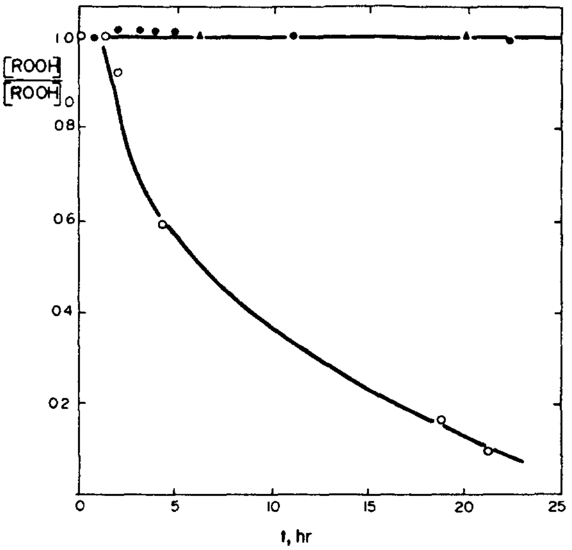


Fig. 1. Thermal reaction of *t*-butylhydroperoxide in the presence of **I**, **II** and dilaurylthiodipropionate (DLTP), in benzene at 60°. $[ROOH]_0 = 5.62 \times 10^{-2}\,mol \cdot l^{-1}$; (○) $6.17 \times 10^{-2}\,mol \cdot l^{-1}$ DLTP; (●) $6.20 \times 10^{-2}\,mol \cdot l^{-1}$ **I**; (▲) $6.10 \times 10^{-2}\,mol \cdot l^{-1}$ **II**.

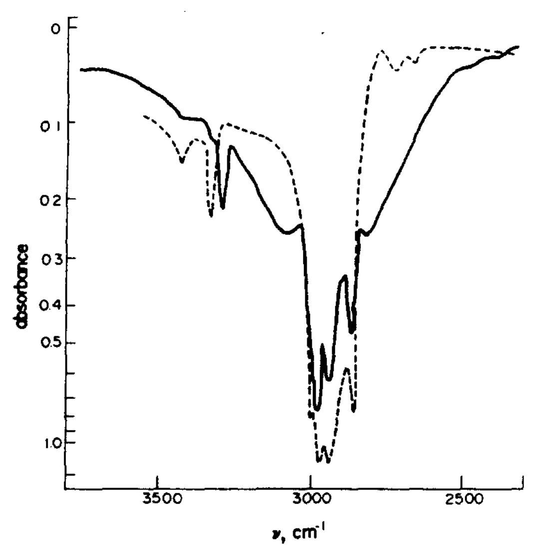


Fig. 2. i.r. Spectra of equimolar adducts of Tinuvin 770 and *t*-butylhydroperoxide (solid line); Tinuvin 770 (dashed line). Substances present in a KBr pellet (~2 mg/400 mg KBr).

apparatus for 100 hr. Commercial stabilizers, analytical reagents and solvents were used without further purification.

Analytical methods

GLC analyses of *t*-butylhydroperoxide were carried out on an F 11 Perkin–Elmer gas chromatograph at 55° using a 3 m glass column (o.d. 6 mm) packed with 1.5% fluorosilicone oil FS 1265 on Chromosorb W AW DMCS; argon was the carrier gas. i.r. Spectra were measured on a Perkin–Elmer 377 i.r. spectrometer; a u.v. spectrometer CF4 Optica Milano was employed. The peroxide concentrations in oxidized polypropylene films were determined using the method of Carlsson and Wiles [19].

Photo-oxidation

The irradiations were carried out on an optical train of our own design. The source of light was a high pressure xenon-lamp Tungsram XHP 1600; the light was filtered [20] to obtain the desired wavelength. The samples were irradiated in a quartz cylindrical cell equipped with a ground joint to attach an adaptor with septum so that samples could be taken during irradiation runs. The intensity of light flux was continuously monitored by a quantum counter [21] connected to a picoammeter. The instrument was calibrated by uranyl-oxalate actinometry [20]. The absolute values of intensities for 300–400 nm, 313 nm and 366 nm bands were 1.8×10^{-7}, 2×10^{-8} and 1.8×10^{-8} einstein $cm^{-2} \cdot sec^{-1}$ respectively.

RESULTS AND DISCUSSION

Hydroperoxide decomposing ability of HALS

In order to establish whether **I** or **II** are capable of decomposing peroxides, the thermal reaction of *t*-butylhydroperoxide in the presence of these compounds was examined. Results (Fig. 1) clearly indicate that **I**, when compared with a well known peroxide decomposer dilaurylthiodipropionate DLTP, does not appreciably affect the decomposition of *t*-butylhydroperoxide in benzene at 60°. **II** also exhibits no peroxide decomposing ability.

Similar results were obtained when oxidized polypropylene was used instead of *t*-butylhydroperoxide. The polypropylene samples were immersed at ambient temperature in 2% heptane solutions of reactants for a period and then analysed for peroxide. Here again **I**, unlike DLTP, did not decompose polypropylene hydroperoxides at ambient temperature.

Peroxide photolysis in the presence of 2,2,6,6-tetramethylpiperidine

The key role of peroxide decomposition during polyolefin photodegradation is generally recognized

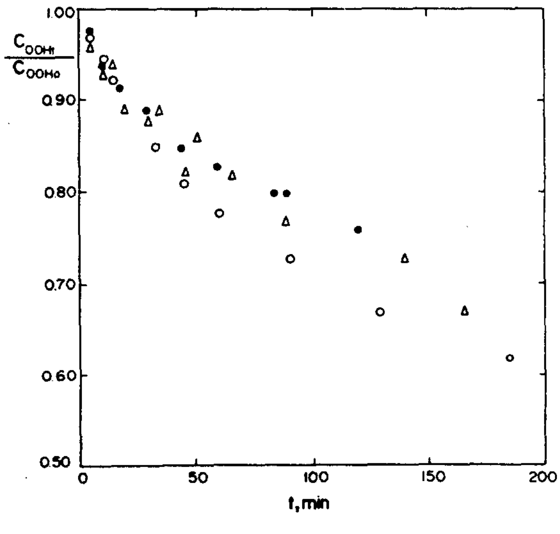


Fig. 3. Photolysis of *t*-butylhydroperoxide in *n*-heptane at 313 nm and 25°. $[ROOH]_0 = 0.25\,mol \cdot l^{-1}$; (○) $0.25\,mol \cdot l^{-1}$ of **I** present: photolysis in O_2; (●) photolysis of ROOH in Ar; (△) photolysis of ROOH in O_2.

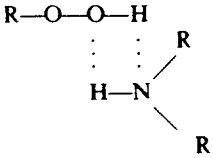
Table 1. Reaction of tri-*t*-butylphenoxy radical (**III**) with various hydrogen-containing substrates (SH). (In benzene at 25°, argon atmosphere)

[III] (mmol·l^{-1})	Substrate	[SH] (mmol·l^{-1})	[SH]/[III]	k (mol^{-1} l·sec^{-1})
0.694	**IV**	0.717	1.03	0.134
0.754	**V**	0.912	1.21	0.089
0.966	**I**	1.32	1.37	0.000
0.934	**I**	12.6	13.5	0.000
0.866	**I**	126	145	0.000
1.020	**VI**	1.25	1.23	270

I = 2,2,6,6-tetramethyl piperidine; **IV** = octyl mercaptan; **V** = dibutylamine; **VI** = 2,6-di-t-butyl-4-methylphenol.

[22]. Carlsson and Wiles [19] have pointed out that lowering the quantum yield of hydroperoxide photolysis might be one of the most efficient ways for polyolefin stabilization.

Amines are known to form hydrogen-bonded associates with hydroperoxides [23]:

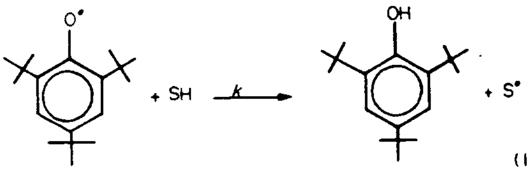


In the case of HALS, such associates have been prepared in this laboratory. Figure 2 shows the i.r. spectrum of an associate prepared from equimolar quantities of bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate (Tinuvin 770) and *t*-butylhydroperoxide.

In order to establish whether or not the quantum yield of peroxide photolysis is influenced by the presence of **I**, irradiations of *t*-butylhydroperoxide in heptane were carried out at 313 nm both in the absence and the presence of equimolar concentration of **I**. The rate of peroxide disappearance due to photolysis seems not to be influenced by the presence of **I** (see Fig. 3).

Hydrogen donating ability of HALS

The ability of a substrate SH to donate hydrogen was tested by means of its reaction with 2,4,6-tri-*t*-butyl-phenoxy radicals (**III**) in an inert atmosphere.



(1)

III

The changes of concentration of **III** could easily be followed spectrometrically at 625 nm ($\epsilon = 410$ mol^{-1} l·cm^{-1}). The rate constant of reaction (1) was calculated using the following relationship

$$-\frac{dx}{dt} = k(r - x)(s - x) \qquad (2)$$

where x represents the concentration decrease of **III**; r the initial concentration of **III**; s the initial concentration of substrate leading to

$$kt = (s - r)^{-1}\left(\ln\frac{s - x}{r - x} - \ln\frac{s}{r}\right) \qquad (3)$$

When the function on the right hand side is plotted against time, a linear relationship is obtained; in cases of slight curvature, the rate constant k was calculated from the initial rate.

Table 1 summarizes the results. Octyl mercaptan (**IV**), dibutylamine (**V**) and 2,6-di-*t*-butyl-4-methylphenol (**VI**) were selected as typical hydrogen donating substrates. Comparison was made with **I**. As shown in Table 1, **I** is not capable of hydrogen donation under conditions where phenols, non-hindered amines and mercaptans readily react. From these facts, there must be some doubt about the suggestion of Allen [4] on the ability of the hindered amine rapidly to donate a hydrogen atom to the photolytically severed C—H bond in $\alpha\beta$-unsaturated polypropylene macroketones before the hydrogen atom from that bond attaches itself to the α-carbon.

CONCLUSION

Neither in solution nor in polymers, are **I** and **II** capable of decomposing hydroperoxides at ambient and slightly elevated temperatures. The quantum yield for decomposition of ROOH is not influenced by the presence of **I** although an associate between the latter and ROOH was found. **I** cannot donate hydrogen under conditions where recognized hydrogen donors react readily.

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