Polymer Degradation and Stability **20** (1988) 1–35

Mechanism of Synergistic Stabilization by Hindered Amines

Xun-Zhuan Yang,* Yanmo Chen,‡ L. Charles Dickinson & James C. W. Chien§

Department of Polymer Science and Engineering, University of Massachusetts,
Amherst, MA 01003, USA

(Received 2 July 1987; accepted 18 July 1987)

ABSTRACT

Tetramethyl piperidine (TMP) and several derivatives have been studied for their activities in various modes of polymer stabilization. The derivatives are tetramethyl piperidinoxyl (TMPO˙), N-*hydroxy tetramethyl piperidine (TMPOH),* N-*butoxy tetramethyl piperidine (TMPOR) where R is* n-*butyl and* t-*butyl, and* N-*methyl tetramethyl piperidine (TMPMe moiety of Tinuvin 292) as well as some commercial HALS (hindered amine light stabilizer). Inhibition of AIBN initiated cumene oxidation was used to determine free radical scavenging activity; decomposition of* t-*BuOOH was monitored by iodimetry, gas chromatography, and high pressure liquid chromatography; the rate constant for quenching of carbonyl excited states was measured by inhibition of diethyl ketone initiated photo-oxidation of propylene tetramer; singlet oxygen quenching was determined from the fluorescence intensity of rubrene; the effect on photo-oxidation initiated by photolysis of di-*t-*butyl peroxide was also studied. TMPOH and TMPMe each scavenges about one peroxyl radical, a combination of the two is strongly synergistic in this action. Further inclusion of TMPO is beneficial. The activity of hydroxyperoxide decomposition decreases in the order TMPOH > TMP > TMPO˙ > TMPMe. Evidence for Cope reaction between TMPMe and ROOH was seen by ESR. The combination of TMP/TMPO˙ shows high efficiency in the quenching of diethyl ketone excited states. Other synergistic systems for this process are TMPO˙/TMPMe and TMPO˙/TMPOR. TMPOH quenches singlet oxygen*

---

* On leave from the Research Institute of Synthetic Materials Aging, Guangzhou, China.

‡ On leave from the China Textile University, Shanghai, China.

§ To whom correspondence should be addressed.

Polymer Degradation and Stability 0141-3910/88/$03·50

*with an efficacy comparable to that of nickel chelates; it also interferes with di-*t*-butyl peroxide initiated photo-oxidation. TMPOR shows little or no activity in any of the above tests though it has been proposed to be a key ingredient in a well-known catalytic stabilization mechanism. The results showed that all the TMP derivatives, with perhaps the lone exception of TMPOR, exhibit individually only modest stabilization of some kind. For certain stabilizer functions there are combinations of compounds which are strongly synergistic. If these derivatives were produced during processing or aging of polyolefins containing HALS, their combined actions could explain the outstanding effectiveness of HALS.*

1 INTRODUCTION

A degradable polymer can be stabilized significantly and made useful in numerous applications. For instance, polyolefins are particularly susceptible to degradation by thermal and photochemical oxidations. Their wide usage under various environmental conditions is testimony to the effectiveness of stabilizer systems developed for specific applications.

With the exception of mechanical and thermal degradations during processing, all other degradations of polyolefins are the direct results of autoxidation. The elementary processes for autoxidation can be written as[1]

$$\mathrm{POOH} \longrightarrow \mathrm{P}^{\cdot} \qquad R_i \tag{1}$$

$$\mathrm{P}^{\cdot} + \mathrm{O}_2 \longrightarrow \mathrm{PO}_2^{\cdot} \tag{2}$$

$$\mathrm{PO}_2 + \mathrm{PH} \longrightarrow \mathrm{POOH} + \mathrm{P}^{\cdot} \qquad k_p \tag{3}$$

$$2\mathrm{P}_2^{\cdot} \longrightarrow \text{products} \qquad k_t \tag{4}$$

where PH represents a polyolefin which is understood to be poly(propylene) in the present discourse, and $P^{\cdot}$ and $PO_2^{\cdot}$ are the corresponding macroalkyl and macroperoxyl radicals. The rate of oxidation with an abundance of oxygen is:

$$-\frac{\mathrm{d}[\mathrm{O}_2]}{\mathrm{d}t} = \frac{k_p}{k_t^{1/2}}[\mathrm{PH}]R_i^{1/2} = R_0 \tag{5}$$

If the system is oxygen starved, eqn (5) can be modified[2] to include dependences on the oxygen pressure. The kinetic chain length $(-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t)/R_i$, is a function of temperature, and also of light intensity in the case of photo-oxidation.

It is generally accepted that hydroperoxides are the initiation species in hydrocarbon autoxidation,[1] which are regenerated during chain propagation (eqn (3)). In the case of polypropylene, PP, sequences of adjacent hydroperoxides[3] are produced which decompose with a faster rate at lower temperatures than ordinary hydroperoxide,[4] i.e. *t*-BuOOH. This largely accounts for the marked oxidative instabilities of all poly(α-olefins).[5] The above simple reaction sequence (eqns (1) to (4)) adequately describes the autoxidation of PP from low temperatures[1,5] to moderate[1] and very high temperatures.[6]

A synergistic stabilizer system against thermal oxidation of polyolefins should scavenge the peroxyl radicals and decompose the hydroperoxides by molecular processes.[7,8] The alkyl radicals are usually thought to be oxygenated too rapidly under atmospheric condition to be scavenged. Hindered phenols are very effective radical scavengers; phosphites and sulfides are transformed under aging conditions to various acids which decompose hydroperoxides catalytically.[8] A very important consideration is the volatility of a stabilizer which usually limits its usefulness.[9]

There are several photo-initiation pathways (*vide infra*). Several classes of UV stabilizer have been used to protect PP in outdoor applications, such as hydroxy benzophenones, hydroxyphenyl benzoates, nickel chelates, phosphites, cyanurates, phosphonates, and others. Synergistic systems derived from them have afforded modest UV stabilization of PP. Therefore, it is a significant discovery[10] that a small amount (*ca.* 0·1%) of tetramethylpiperidiene compounds, TMP, imparted several fold longer UV lifetime than previous systems at ten times higher concentrations. A family of TMP compounds are now used commercially as light stabilizers, they are referred to collectively as hindered amine light stabilizers, HALS, even though a compound may contain other moieties such as hindered phenol or phosphite which act differently from the TMP-type functional groups.

An intriguing and challenging aspect of HALS is that the TMP moiety does not appear to be chemically equipped for actions against the various elementary reactions in a photo-oxidation. In their original paper, Usilton and Patel[10] suggested that HALS scavenges radicals and quenches singlet oxygen but wisely left open other possible modes of action. It was soon noticed that the TMP moiety disappeared at very early stages of aging,[11,12] and that PP containing HALS kept in a drawer for several months has markedly improved weather-o-meter lifetimes. Polymer processing conditions were also found[13] to influence strongly the effectiveness of HALS. Therefore, TMP is acknowledged to be only a precursor of some other active species.

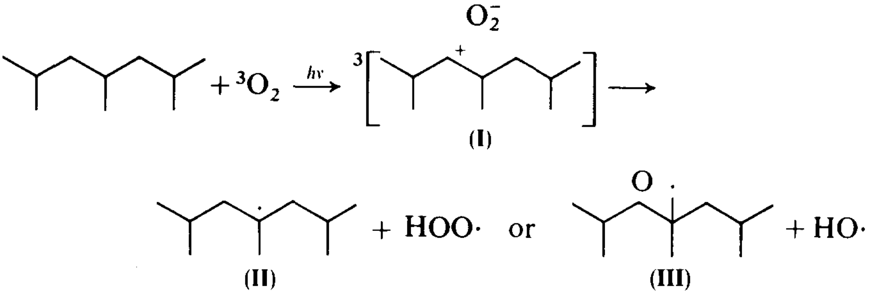
There have been many investigations on light stabilizations by TMP derivatives, often with contradictory results. Rather elaborate catalytic schemes (*vide infra*) have been proposed involving cyclic reactions of $TMPO^{\cdot}$/TMPOR and TMPOH/$TMPO^{\cdot}$ where $TMPO^{\cdot}$, TMPOR, and TMPOH are the nitroxyl radical, alkoxyl and hydroxyl derivatives of TMP, respectively.

The central purpose of this research is to investigate the efficiencies of a number of compounds, which can be conceivably produced from TMP under thermal, oxidative, photolytic and processing conditions, in the inhibition of various elementary processes of photo-oxidation of PP. This investigation makes no presumptions of stabilizing actions for any particular TMP derivative. A particular emphasis is the elucidation of synergistic effects.

2 INITIATION PROCESSES IN THE PHOTO-OXIDATION OF POLYOLEFINS

To understand the action of a stabilizer one must know the mechanism of degradation. An outline of the elementary processes in photo-oxidations of polyolefins would facilitate the rationalization of experimental objectives and discussion of results.

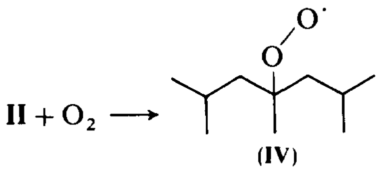
Saturated hydrocarbon molecules, which alone do not absorb UV photons, exhibit charge transfer absorption in the presence of oxygen.[14]



(6)

Radicals are produced by this charge transfer excitation.[14] Though the above process has only low efficiency because of its small absorption coefficients and quantum yields, it nevertheless provides a photo-initiation pathway in the absence of any impurity chromophores for an ideally pure PP.

The dominant fate of **II** is oxygenation to form peroxyl radical (**IV**) which occurs with a diffusion limited rate constant[15] of *ca.* 10^9 (M s)$^{-1}$.

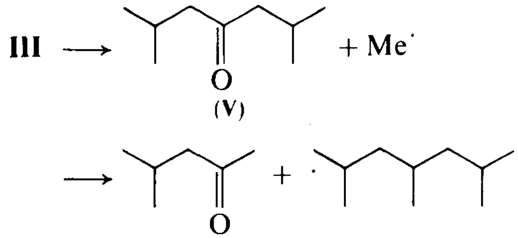


(7)

This is also true for the terminal alkyl radical **II′** produced in reaction (9).

The alternative pathways of chain scission or hydrogen abstraction are energetically less favorable.

There are at least three reaction pathways for the alkoxyl radical **III**. The dominant one is hydrogen abstraction; for instance, the rate constant of this process for cyclohexane at 24°C is 3×10^4 (M s^{-1}).[16] They can combine with high probability; the rate constant of the reaction for *t*-BuO˙ radical is about 10^5 $(\text{M s})^{-1}$. Finally, the β scission of **III** is the the main source of ketonic compounds **V** and **V′**:

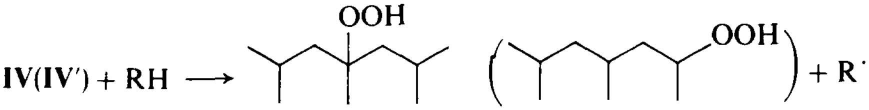


(V) (8)

(V′) (II′) (9)

In these equations and elsewhere the prime is used to distinguish the chain-end species from the corresponding backbone species. The rate constant for reaction (8) should be comparable to the room temperature values of 10 to $300\,\text{s}^{-1}$ estimated for the β-scission of *t*-BuO˙ radical[17,18] with an activation energy of 13 to 14 kcal mol^{-1}. Main chain scission (reaction (9)) should be appreciably faster than reaction (8), but unfortunately, there are no estimates for its rate constant.

Peroxyl radical is the chain propagating species:



(VI) (VI′) (10)

The rate constant of hydrogen abstraction by **IV** is much smaller than that by **III** because of their differences in bond strengths,[19] viz., D(RO—H) = 104 kcal mol^{-1} and D(ROO—H) = 90 kcal mol^{-1}. As pointed out above the structures of **VI** (**VI′**) include —OOH, —OH and $\rangle$C═O functionalities on adjacent tertiary carbon atoms.

When the substrate possesses tertiary hydrogens, i.e., PP, the propagating species is the tertiary peroxyl radicals. This is both due to the ease of abstraction of the hydrogen on tertiary carbon, and also, if any *p*- and *s*-ROO˙ radicals are formed, they terminate with rate constants which are orders of magnitude greater than those between *t*-ROO˙ radicals.[20]

As soon as some ketones (**V**) or hydroperoxides (**VI**) are formed, their photolysis becomes the dominant initiation processes and the charge transfer excitation, reaction (6), no longer has much significance. The former have much larger extinction coefficients for photon absorption and higher quantum yields of photolysis than the latter.

Predissociation occurs with the absorption of an UV photon by hydroperoxides:

$$\mathrm{VI(VI')} \xrightarrow{h\nu} \mathrm{III(III')} + \mathrm{HO}^{\bullet} \tag{11}$$

The quantum yield of this process for alkyl hydroperoxides in the condensed phase is near unity. However, there are present a variety of hydroperoxides. In addition to those mentioned above there may also be allylic hydroperoxides produced by singlet oxygen (*vide infra*). These substances can be present in different concentrations C_i for the ith species each with extinction coefficients $\varepsilon_{i,\lambda}$ at wavelength λ, and quantum yields of photolysis, $\phi_{i,\lambda}$. At an incident light intensity I_0, the overall rate of initiation will be:

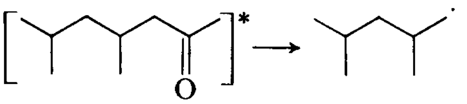
$$R_i(\mathrm{POOH}) = I_0 x_i \sum_i \int \phi_i \exp(-\varepsilon_{i,\lambda} C_i l)\, \mathrm{d}\lambda \tag{12}$$

Here x_i is the fraction of I_0 absorbed by the ith species in the presence of other chromophores:

$$x_i = \frac{[1 - \exp(-C_i l \int \varepsilon_{i,\lambda}\, \mathrm{d}\lambda)]}{\sum_i [1 - \exp(-C_i l \int \varepsilon_{i,\lambda}\, \mathrm{d}\lambda)]} \tag{13}$$

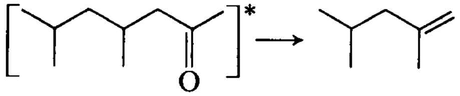
It is evident that quantitation of initiation rates by the photolysis of hydroperoxides is insurmountably difficult because of the number of different kinds of hydroperoxides present and their $C_i(t)$, and $\varepsilon_{i,\lambda}(t)$ are all unknown. The same difficulties also hold true for the photo-initiation by all the other chromophores discussed below.

The photochemistry of ketones has been extensively investigated. The excited singlet and triplet states can dissociate by a Norrish type I process:



$+ \mathrm{CO} + \mathrm{Me}^{\bullet}$ (14)

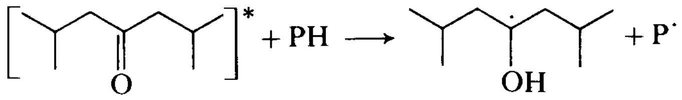
or undergo Norrish type II rearrangement:



$+ \mathrm{MeCOMe}$ (15)

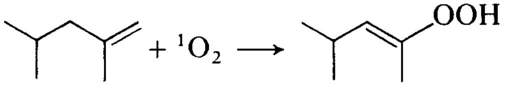
The former is important for small aliphatic ketones; for instance, the quantum yields are 1·0 and 0·84 for type I decomposition of acetone and methyl ethyl ketone, respectively. As the size of the alkyl group increases, type I quantum yield becomes very small (it is only 0·04 for methyl neopentyl ketone) and the type II process becomes increasingly important to about sixfold greater in this example.

The triplet state of ketone in fact reacts like a diradical and can abstract a labile hydrogen to produce two radicals:



(16)

There are other reaction pathways for excited ketones such as fluorescence, phosphorescence, and quenching by solvent, light stabilizer, and oxygen. The last process is the main source of singlet oxygen. Trozzolo & Winslow[21] proposed that $^1O_2$ may react with the olefins produced by the Norrish II process (eqn (15)) via an 'ene' reaction to form allylic hydroperoxide:



(VII)

(17)

Aside from the above initiation processes, the remainder of the reactions in photo-oxidation are similar to those of the autoxidation (eqns (2)–(4)).

3 EXPERIMENTAL

3.1 Materials

Most of the materials were purchased from Aldrich Chemical Company unless otherwise stated. The following initiators were used. α,α'-Azobis(isobutyronitrile) (AIBN) was recrystallized thrice from methanol. Diethylketone (DEK), di-*t*-butylperoxide (DBP), and *t*-butylhydroperoxide (TBHP) were purified by distillation under reduced pressure and inert atmosphere. Rubrene was used as received.

Cumene was distilled under reduced pressure and used as the substrate in thermal autoxidation. Hydrogenated propylene tetramer (PT) from ESSO Chemicals was the substrate in photo-oxidation because of its optical transparency. It was treated with concentrated sulfuric acid repeatedly until no color developed after overnight stirring. This treatment serves to remove olefinic impurities. The PT was then washed thrice with 10% H_2SO_4, thrice with saturated solution of $KMnO_4$ in 10% H_2SO_4, and repeatedly with distilled water to neutrality. It was dried over anhydrous $MgSO_4$ and distilled.

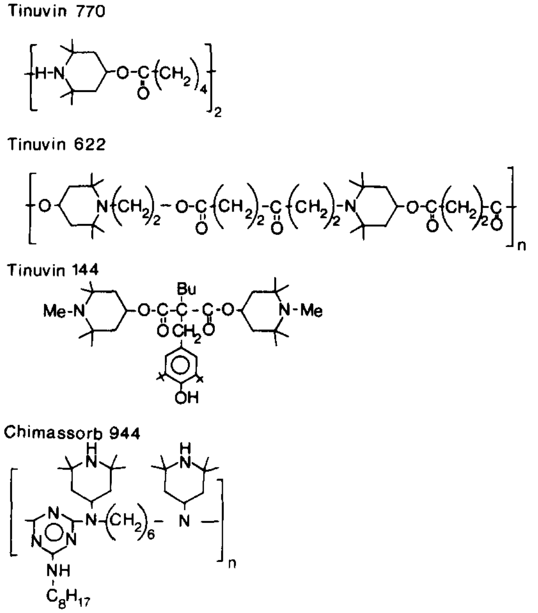


Fig. 1. Structures of commercial HALS.

Chlorobenzene was distilled under reduced pressure. Ultra pure hexane and methyl-*t*-butyl ether from Fischer Chemical were used as received for high pressure liquid chromatography (HPLC).

The starting materials for TMP derivatives were 2,2,6,6-tetramethyl piperidine (TMP) and 2,2,6,6-tetramethylpiperidinoxy free radical (TMPO$^{\cdot}$) from Aldrich Chemicals. *N*-hydroxyl-2,2,6,6-tetramethyl piperidine (TMPOH) was prepared by the reduction of TMPO with ascorbic acid. This hydroxy amine is a white crystalline hygroscopic solid which readily oxidizes to TMPO$^{\cdot}$ upon exposure to air. It is stored under N_2 at 0°C. *N*-*n*-butoxy-2,2,6,6-tetramethyl piperidine (TMPO-*n*-Bu) and *N*-*t*-butoxy-2,2,6,6-tetramethyl piperidine (TMPO-*t*-Bu) were synthesized by reacting the corresponding lithium alkyl with TMPO$^{\cdot}$. The products were chromatographed with an Al_2O_3 column and recrystallized. These compounds all have the correct elementary analysis and proton NMR spectra.

Several commercial HALS compounds were included in this study: bis(2,2,6,6-tetramethyl-4-piperidenyl) sebacate (Tinuvin® 770), bis(1,2,2,6,6-pentamethyl-4-piperidenyl)sebacate (Tinuvin® 292, abbreviated as TMPMe), Tinuvin® 622, which is a moderate molecular weight tertiary hindered amine, Tinuvin® 144, which contains a hindered phenol moiety, and Chimasorb® 944, which has a cyanurate nucleus with TMP pendant groups. All these stabilizers were obtained from Ciba-Geigy Corporation, their structures are given in Fig. 1.

3.2 Autoxidation

Autoxidation of cumene was monitored by an automatic oxygen uptake apparatus.[23] The reactor, containing a 10 ml solution of 1:2, cumene: chlorobenzene with dissolved stabilizer, was cooled to −78°C, evacuated and filled with oxygen thrice, then brought up to 62·5°C. After thermal equilibration, AIBN dissolved in a small amount of chlorobenzene was introduced. The volumetric consumption of oxygen was continuously recorded at a constant oxygen pressure of 760 torr.

3.3 Photo-oxidation

Photo-oxidation of propylene tetramer was continuously recorded by a similar automatic oxygen uptake apparatus[9] except that the UV source was a 6 W RPR-350 nm lamp. The light was filtered by the pyrex glass of the reactor. Five millilitres of propylene tetramer containing the stabilizer and either DEK or DBP initiator was irradiated under 1 atm of oxygen at *ca.* 38°.

3.4 Hydroperoxide decomposition

A chlorobenzene solution of TBHP and stabilizer was evacuated and filled with argon at −78°C. The solution was brought to the reaction temperature; samples were withdrawn periodically and assayed for hydroperoxide concentration by one of three methods. For iodimetry, KI was added to the sample and the iodine liberated was titrated with standard sodium thiosulfite. Both TMPO$^\cdot$ and TMPOH react with I_3^- thus interfering with iodimetric analysis. In these cases [THBP] was determined by either GC or HPLC. A Varian Aerograph 2400 series instrument equipped with a FFAP column (Analab) was used for GC, and a Varian 4000 series chromatograph using a silica gel column equipped with a refractive index detector and a 15% methyl -*t*-butyl ether/*n*-hexane moving phase for HPLC.

3.5 Singlet oxygen quenching

A methylene chloride solution of rubrene (tetraphenyl naphthacene) and stabilizer was saturated with air. A Perkin-Elmer MPF-44 spectrophotometer was used to excite fluorescence at 520 nm and the emission intensity at 545 nm was recorded.

3.6 Spectroscopies

Electron spin resonance spectra (ESR) of free radicals were recorded with a Varian E-9 spectrometer. The radical concentration was determined by comparison with a standard solution of TMPO˙ at the same klystron frequency and leakage current for the diode detector.

A Perkin-Elmer K-12A instrument was used for proton NMR.

Electronic spectra were obtained with a Beckman model MVII spectrometer using ethanol as the solvent. Stabilizer solutions were purged at $-78°C$ with prepurified argon before bringing up to room temperature for spectral recording.

Fluorescence spectra was recorded with a Perkin-Elmer MPF-49 spectrometer. The methylene chloride solution of rubrene and stabilizer was saturated with air before measurement.

4 RESULTS

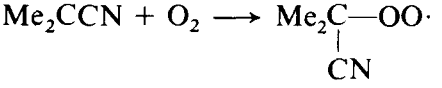
4.1 Electronic spectra

Electronic spectra of TMP derivatives have been obtained for TMP derivatives. Table 1 summarizes the absorption parameters.

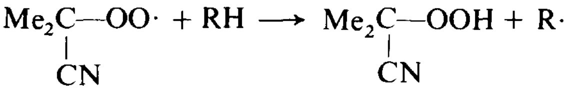
4.2 Inhibition of autoxidation

AIBN dissociates at 62·5°C with a rate constant $k_d = 1{\cdot}54 \times 10^{-5}\,\text{s}^{-1}$, a fraction ($\alpha = 0{\cdot}65$) of the cyano-*i*-propyl radicals escaping from the primary cage to initiate autoxidation of cumene.[22] In place of eqn (1) we can write specifically for the initiation processes:

$$\text{AIBN} \rightarrow \text{Me}_2\dot{\text{C}}\text{CN} + \text{N}_2 \qquad 2\alpha k_d \tag{18}$$



$$\text{Me}_2\dot{\text{C}}\text{CN} + \text{O}_2 \longrightarrow \text{Me}_2\underset{\substack{|\\ \text{CN}}}{\text{C}}\text{—OO}\cdot \tag{19}$$



$$\text{Me}_2\underset{\substack{|\\ \text{CN}}}{\text{C}}\text{—OO}\cdot + \text{RH} \longrightarrow \text{Me}_2\underset{\substack{|\\ \text{CN}}}{\text{C}}\text{—OOH} + \text{R}\cdot \tag{20}$$

followed by eqns (2) to (4). Specifically, the R_i in eqn (5) is:

$$R_i = 2\alpha k_d[\text{AIBN}]_0 \exp(-k_d t) \tag{21}$$

where $k_p/k_t^{1/2} = 4{\cdot}5 \times 10^{-3}\,(\text{Ms})^{-1/2}$ for cumene[22] at 62·5°C. The initial rate of oxidation, R_0, for 10 mM AIBN, is $3{\cdot}8 \times 10^{-6}\,\text{Ms}^{-1}$ in agreement with the calculated value of $4{\cdot}8 \times 10^{-6}\,\text{Ms}^{-1}$.[23]

In the presence of an effective inhibitor, In, its scavenging of $\text{RO}_2^{\cdot}$ competes with, or supersedes, the termination reaction 4.

$$\text{In} + n\text{RO}_2^{\cdot} \rightarrow \text{products} \qquad k_{\text{inh}} \tag{22}$$

TABLE 1
Electronic Spectra of TMP Derivatives

Compound	λ_{max} *(nm)*	ε_{max} $(Mcm)^{-1}$	*Transition*
TMP	<210	—	$n\sigma^*$
TMPOH	212	930	$n\sigma^*$
TMPO-*n*-Bu	<210	—	$n\sigma^*$
	280	31	$n\pi^*$
TMPMe	<210	—	$n\sigma^*$
TMPO˙	242	2 200	$n\rho^*$
	450	12	$n\pi^*$

The resulting induction period, t_{ind}, is related to the number of radicals, n, which are scavenged by In.[8,23]

$$t_{ind} = n[\text{In}]/R_i \tag{23}$$

The reduced rate of initiation is given by:

$$R_i = R_0^2 k_t (k_p[\text{RH}])^{-2} + nk_{inh}[\text{In}]R_0(k_p[\text{RH}])^{-1} \tag{24}$$

Usually the amount of inhibitor employed in such studies is less than $2\alpha n$[AIBN]. However, if the additive caused no induction period then a large quantity of it is used to bring out any retardation effect through reduction in R_0 (eqn (24)). If the observed R_0 is the same as the uninhibited rate of eqns (5) and (21), then the additive is without any radical scavenging activity.

TMP, TMPO˙ and TMPOR are all without any effect on autoxidation either singly at 0·01 M concentration or in pairs at 0·01 M each (Table 2). There was neither an induction period nor a decrease of R_0.

TABLE 2
TMP Derivatives Without Radical Scavenging Activity

TMP derivatives[a]	$R_0 \times 10^6$ Ms^{-1}
None	3·85
TMP	3·42
TMPO˙	2·92
TMPO-*t*-Bu	3·50
TMPO-*n*-Bu	3·42
TMP + TMPO˙	3·33
TMP + TMPO-*n*-Bu	4·0
TMP + TMPO-*t*-Bu	4·0
TMPO˙ + TMPO-*n*-Bu	2·92
TMPO˙ + TMPO-*t*-Bu	2·92

[a] The concentrations are 10 mM for all compounds.

TABLE 3
Effect of TMPOH Systems on Cumene Oxidation

Compounds				t_{ind} (*min*)	$R_o \times 10^6\ Ms^{-1}$
A	*Conc.* (*m*M)	*B*	*Conc.* (*m*M)		
TMPOH	1·9	None		125	2·70
TMPOH	1·9	TMP	10	100	2·70
TMPOH	1·9	TMPOBu	10	100	2·70
TMPOH	1·9	TMPO˙	10	185	2·60

Among the TMP derivatives only TMPOH and TMPR show some radical scavenging activity. Using 1·9 mM of TMPOH, which is one-fifth the amount of the other additives used in the experiments of Table 2, one finds a 125 min induction period which corresponds to the scavenging of 0·8 radicals. Addition of either TMPH or TMPOBu to TMPOH caused a slight decrease of t_{ind}. On the other hand, the addition of TMPO˙ resulted in a slight increase of t_{ind}. But since the latter was added in 10 mM quantity the small effect on cumene autoxidation is not significant. These results are summarized in Table 3.

Among the commercial HALS one expects good radical scavenging activity for Tinuvin 144 due to the hindered phenol moiety. It was found to scavenge 1·2 radicals, which is less than the expected value of $(2 + 1)/2 = 1{\cdot}5$ radicals. Rather unexpectedly, Tinuvin 292 was found to possess a similar activity. The result in Table 4 showed that each TMPMe group scavenges one peroxyl radical. The antioxidant activity of TMPMe was not seen with other tertiary amines. Tinuvin 622, which is said by the manufacturer to have ethyl and oxyethylene groups on the tertiary nitrogen atom (Fig. 1), showed no activity.

During cumene oxidation in the presence of Tinuvin 292, an ESR signal characteristic of nitroxyl radical was observed. The increase of ESR

TABLE 4
Effect of HALS on Cumene Oxidation

Compound[a]	t_{ind} (*min*)	*n*	$R_o \times 10^6\ Ms^{-1}$
None	None		3·85
Tinuvin 622	None		4·0
Chimassorb 944	None		3·22
Tinuvin 292	820	1·0	1·57
Tinuvin 144	1 000	1·2	0·98

[a] Conc. 6·8 mM of functional moiety.

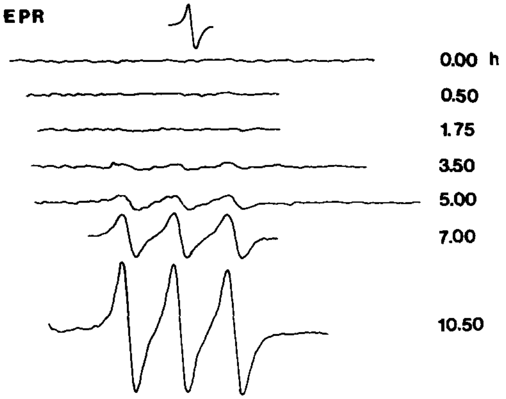


Fig. 2. Increase of TMPO˙ ESR signal intensity during the induction period in the thermal oxidation of cumene: [AIBN] = 0·01 M, [cumene] = 2·4 M; [Tinuvin 292] = 0·0034 M; PO_2 = 740 torr, temperature = 62·5°C for time in hours indicated on the right.

intensity with time during the induction period is shown in Fig. 2. Figure 3 shows that the concentration of nitroxyl radical is proportional to the quantity of oxygen consumed but the former is only about 0·3% of the latter. At the end of t_{ind}, 4×10^{-5} M of nitroxyl radicals was formed, which corresponds to *ca.* 1% of the Tinuvin 292. Therefore, the nitroxyl radical is only a minor oxidation product of this HALS.

The synergistic effect of TMP derivatives was investigated in detail. The

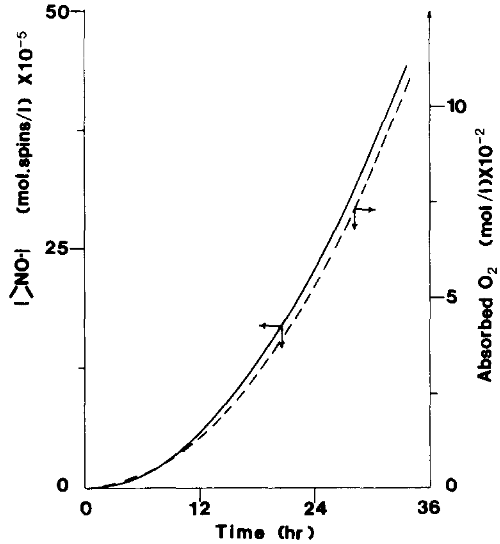


Fig. 3. Change in nitroxyl radical concentration and oxygen consumed with time of cumene oxidations; conditions are the same as in Fig. 2. (——) [TMPO˙]; (– – – –) [O_2].

TABLE 5
Effect of Synergistic HALS Systems[a] on Cumene Oxidations

Component 2	*Conc. (m*M*)*	*Component 3*	*Conc. (m*M*)*	t_{ind} *(min)*	$R_o \times 10^6$ Ms^{-1}
None				820	1·57
TMP	10			800	1·64
TMP-*t*-Bu	10			930	1·16
TMPO-*n*-Bu	10			715	0·53
TMPO˙	10			—	0·35
TMPOH	1·9			—	0·11[b]
TMP	10	TMPOH	1·9	700	2·69
TMPO˙	10	TMPOH	1·9	—	0·03[b]

[a] HALS is 3·4 mM of Tinuvin 292.
[b] Initial $R_0 = 3{\cdot}3 \times 10^{-7}\,\mathrm{Ms}^{-1}$.

results are shown in Table 5 and Fig. 4. TMP is without any effect on Tinuvin 292 inhibited cumene oxidation. The alkyl ethers showed slight beneficial effects of reducing the rates of oxidation following t_{ind}. When 10 mM of TMPO˙ is added to 3·4 mM of Tinuvin 292 there is a positive synergistic effect which increases the induction period to longer than 3000 min. However, it is the TMPOH/TMPOMe which is the most effective synergistic combination; the rate of oxidation was only $1{\cdot}1 \times 10^{-7}\,\mathrm{Ms}^{-1}$ with 1·9 mM of TMPOH and 3·4 mM of Tinuvin 292. The amount of oxygen consumed in 3000 min of autoxidation was 10 mM as compared to 12 mM of cyano-*i*-propyl radicals generated by the dissociation of AIBN during this period. The results suggest that the cyano-*i*-propyl radicals are immediately oxygenated upon

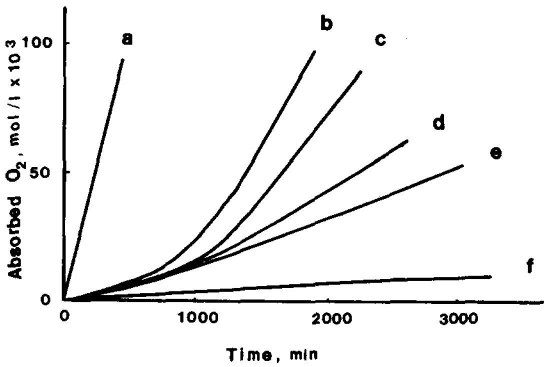


Fig. 4. Effect of synergistic systems containing Tinuvin 292 on cumene oxidations; experimental conditions are the same as in Fig. 2: (a) no additive; (b) Tinuvin 292 alone; (c) with TMPO-*t*-Bu (0·01 M); (d) with TMPO-*t*-Bu (0·01 M); (e) with TMPO˙ (0·01 M); (f) with TMPOH (0·0019 M). The concentration of Tinuvin 292 in (b)–(f) is 0·0034 M.

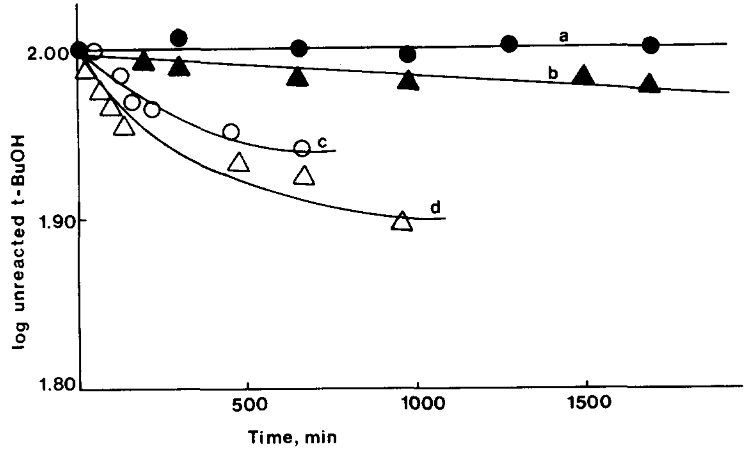


Fig. 5. Decomposition of *t*-BuOOH in chlorobenzene under N_2: (a, ●) 1 M *t*-BuOOH at 40°C; (b, ▲) 0·25 M TMPO˙ in 1 M *t*-BuOOH at 40°C; (c, ○) 1 M TMP in 1·5 M *t*-BuOOH at 25°C; (d, △) 1 M TMPOH in 1·5 M *t*-BuOOH at 25°C.

leaving the solvent cage and the resulting cyano-*i*-propylperoxyl radicals were all scavenged in these experiments. One significant observation is that the rate of oxidation during the initial 40 min is about $3{\cdot}3 \times 10^{-7}\,\mathrm{M s^{-1}}$ which decreases steadily to one-third of that value. This suggests that the best synergistic system may involve a third substance readily formed by the oxidation of TMPOH, which is most likely to be TMPO˙ (*vide infra*).

Two ternary systems were investigated by adding a third additive to the synergistic TMPOH/Tinuvin 292 system. 10 mM of TMP effectively negated the positive synergism of TMPOH which has rate of cumene oxidation nearly the same as with Tinuvin 292 alone. On the other hand, TMPO˙ exhibits some beneficial effect, lowering the oxidation rate to only $3 \times 10^{-8}\,\mathrm{M s^{-1}}$. Therefore, the TMPOH/TMPMe/TMPO˙ is the most synergistic ternary system.

4.3 Hydroperoxide decomposition

Decomposition of *t*-BuOOH by TMP derivatives was investigated in chlorobenzene solution at 40°C or lower temperatures in an inert atmosphere. Under such conditions *t*-BuOOH is stable over a long time (Fig. 5, line a). TMPO˙ showed a slight activity for hydroperoxide decomposition. The data is linear in a first order plot (Fig. 5, line b) to give a rate constant of about $5{\cdot}1 \times 10^{-6}\,\mathrm{s^{-1}}$. However, since less than 5% of the *t*-BuOOH was decomposed in the experiment, the results did not provide a real determination of the kinetic order of the reaction.

The decomposition of *t*-BuOOH by TMP is faster than by TMPO˙. Figure

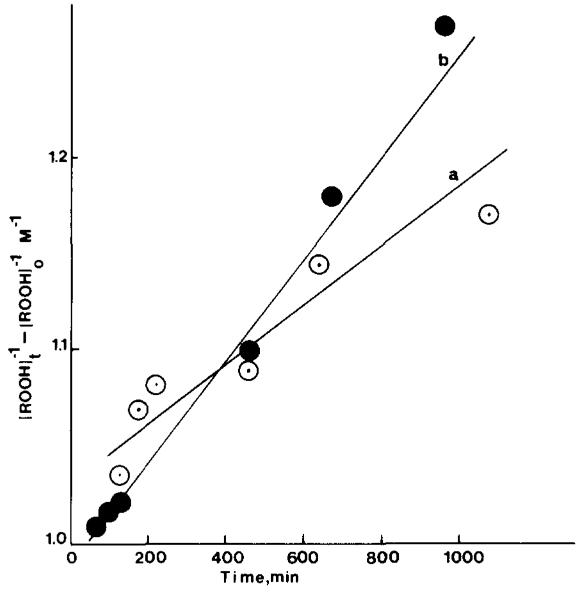


Fig. 6. Second order plots of decomposition of 1·5 M *t*-BuOOH at 25°C by (a, ○) 1 M TMP and (b, ●) 1 M TMPOH (data from Fig. 5).

5, line c showed this reaction to be definitely not first order; it is better approximated by the second order plot of Fig. 6, line a. The latter may be expected for bimolecular reactions of equimolar amounts of *t*-BuOOH and TMP. However, the results of experiments in which [TMP] was varied while keeping *t*-[BuOOH] constant showed the process to be more complicated. The rate of *t*-BuOOH decomposition (amount decomposed in 24 h) is proportional to $[TMP]^2$ as shown in Fig. 7. The decomposition rate was much faster at 40°C than at 30°C consistent with an activation energy of about 19 kcal mol^{-1}.

The decomposition of *t*-BuOOH by TMPOH was monitored by chromatographic techniques (see section 3). The HPLC retention times for *t*-BuOOH, TMPOH and TMPO˙ are 13 min 10 s, 7 min 24 s and 6 min 15 s, respectively (Fig. 8). The reaction product of TMPOH and *t*-BuOOH is TMPO˙; Fig. 9 plots the consumption of TMPOH and the production of TMPO˙. The retention time of *t*-BuOOH did not remain constant as it does for the other two compounds, but increases during the course of the reaction. A possible explanation is that the *t*-BuOOH monomer has longer retention time than its dimer. At the beginning of a reaction the [*t*-BuOOH] is high; the compound is largely present as dimers having short HPLC retention time. As [*t*-BuOOH] decreases during the course of the reaction, the dimers are dissociated into monomers resulting in broadening of the HPLC peak toward longer retention time.

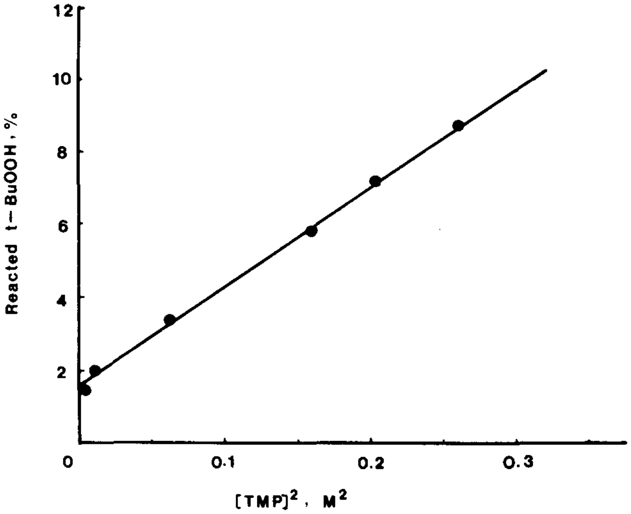


Fig. 7. Effect of concentration of TMP on decomposition of *t*-BuOOH plotted as per cent *t*-BuOOH reacted versus $[TMP]^2$ after 24 h at room temperature.

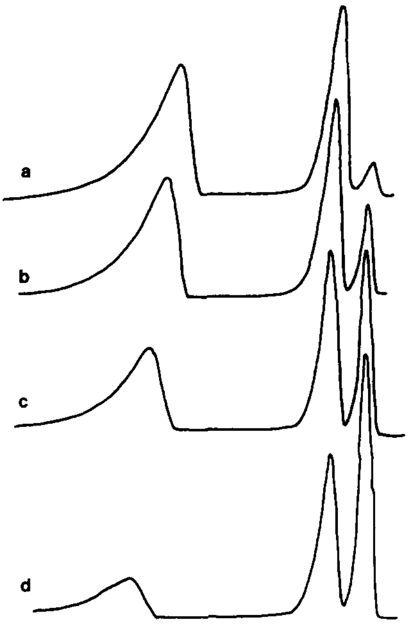


Fig. 8. HPLC monitoring of the decomposition of 1·5 M *t*-BuOOH by 1 M of TMPOH (1·0 M) at room temperature under N_2: (a) 15 min; (b) 90 min; (c) 430 min; (d) 1685 min. The elution peaks from left to right are those of TMPOH, *t*-BuOOH and TMPO$^\cdot$.

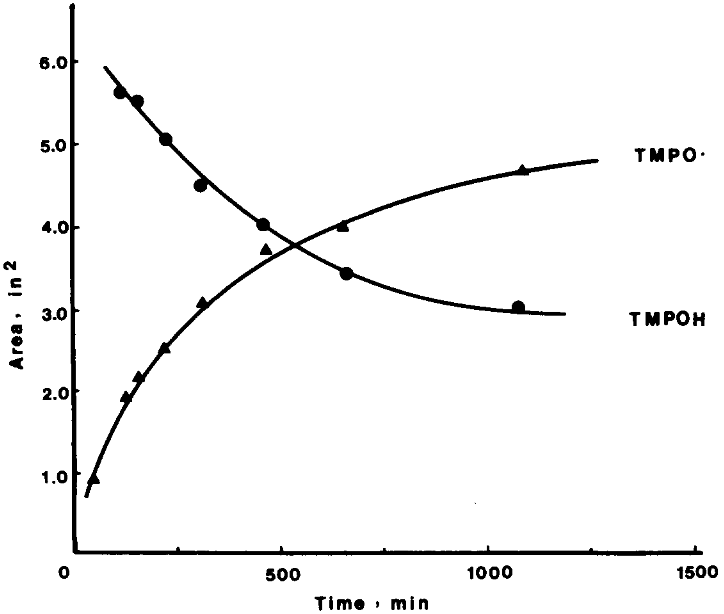
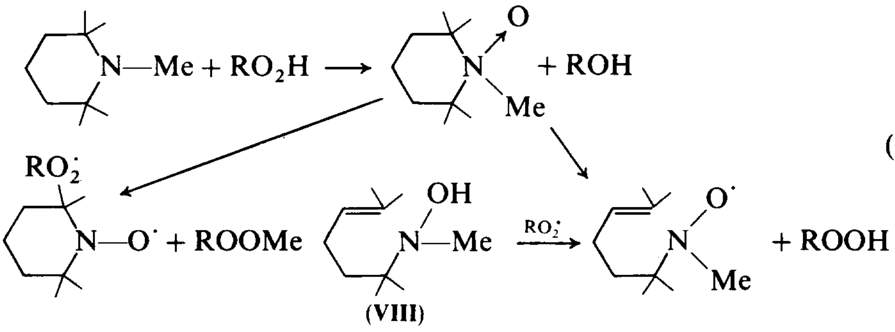


Fig. 9. Changes in the integrated areas of [TMPOH] and [TMPO·] with time for the HPLC data of Fig. 8.

The rate of decomposition of *t*-BuOOH by TMPOH can also be followed by GC. Figure 10 shows the results for a 0·70 M *t*-BuOOH reaction with 0·99 M TMPOH. A first order plot of the data gives a first-order rate constant of $5{\cdot}6 \times 10^{-6}\,\mathrm{s}^{-1}$. A similar value of $5{\cdot}4 \times 10^{-6}\,\mathrm{s}^{-1}$ was obtained by HPLC for the same reaction.

Tinuvin 292 reacts very slowly with *t*-BuOOH. The initial product is a nitroxyl radical (Fig. 11), but a more complicated ESR spectrum was observed after several hours (Fig. 12). A probable source is the reaction of a small number of $RO_2^{\cdot}$ radicals with Tinuvin 292, which produces the ring opened species **VIII** via Cope rearrangement:



(25)

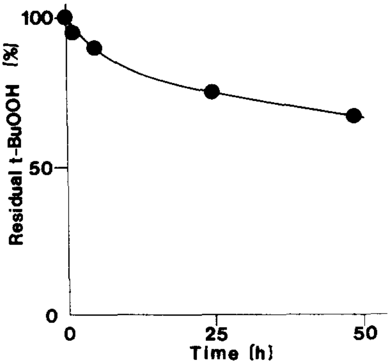


Fig. 10. GC monitoring of the decomposition of *t*-BuOOH (0·70 M) by TMPOH (0·99 M) at room temperature under N_2.

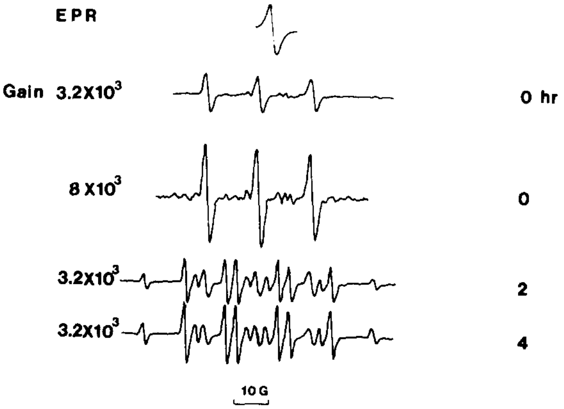


Fig. 11. Changes in the ESR signal with time of reaction of Tinuvin 292 with *t*-BuOOH at 40°C under argon.

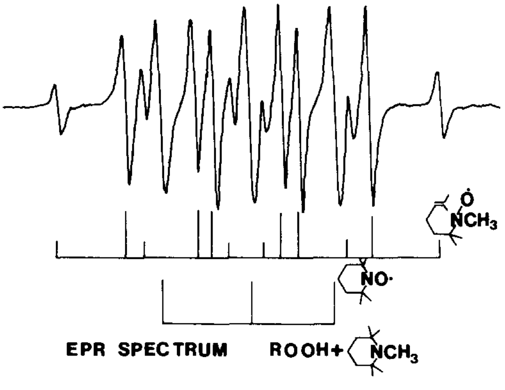


Fig. 12. ESR of the radical after long reaction time of Tinuvin 292 with *t*-BuOOH.

4.4 Singlet oxygen quenching

Rubrene has long been used to sensitize the formation of singlet oxygen:[24]

$$\mathrm{Ru}^* + {}^3\mathrm{O}_2 \rightarrow \mathrm{Ru}^0 + {}^1\mathrm{O}_2 \tag{26}$$

Rubrene also reacts readily with ${}^1\mathrm{O}_2$ to form endoperoxide:[25]

$$\mathrm{Ru} + {}^1\mathrm{O}_2 \rightarrow \mathrm{RuO}_2 \qquad k_{ox} \tag{27}$$

These reactions reduce the fluorescence emission of Ru* at 545 nm:

$$\mathrm{Ru}^* \rightarrow \mathrm{Ru}^0 + h\nu \tag{28}$$

Quenching of ${}^1\mathrm{O}_2$ by an additive, Q,

$${}^1\mathrm{O}_2 + \mathrm{Q} \rightarrow {}^3\mathrm{O}_2 + \mathrm{Q} \qquad k_q^0 \tag{29}$$

can compete with reaction (27). This increases the fluorescence intensity:

$$k_q^0 = \frac{k'_{ox}[\mathrm{Ru}] + k_d}{[\mathrm{Q}]}\left[\frac{(\mathrm{d}[\mathrm{Ru}]/\mathrm{d}t)}{(\mathrm{d}[\mathrm{Ru}]/\mathrm{d}t)_q} - 1\right] \tag{30}$$

where k_d is the rate constant for radiationless decay of ${}^1\mathrm{O}_2$. The values of k_{ox} and k_d in methylene chloride are known to be $7 \times 10^7\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $7{\cdot}3 \times 10^3\,\mathrm{s}^{-1}$, respectively.

The k_q^0 values of TMP derivatives are compared with that of nickel acetylacetonate in Table 6 determined at the concentrations given and $[\mathrm{Ru}] = 1{\cdot}65 \times 10^{-5}\,\mathrm{M}$. TMPOH quenches ${}^1\mathrm{O}_2$ almost as effectively as Ni acetylacetonate. The k_q^0 value for TMPO˙ is only about 1/50 as large as TMPOH. The other two compounds, TMP and TMPO-*n*-Bu, are virtually inactive.

4.5 Quenching of carbonyl excited states

Carbonyl chromophores are usually formed during processing of polyolefins, the photochemistry of which was discussed above. The

TABLE 6
Singlet Oxygen Quenching

S	*Conc.* (*m*M)	$k_q^0 \times 10^{-8}$ $\mathrm{M}^{-1}\,s^{-1}$
Ni acetylacetonate	0·87	1·8
TMPOH	1·47	1·5
TMPO˙	1·15	0·028
TMP	7·94	0·004
TMPO-*n*-Bu	4·69	0·003

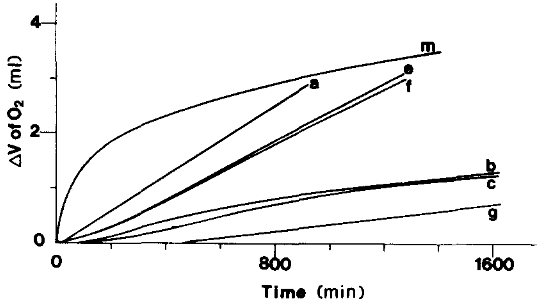


Fig. 13. Photo-oxidation of propylene tetramer initiated by diethyl ketone (1·0 M) using 350 nm light at 38°C, 1 atm. of O_2 and 0·06 M of additives: (a) no additive; (b) TMPO$^{\cdot}$; (c) TMP; (e) Tinuvin 292; (f) TMP-O-*t*-Bu (m) TMPOH; (g) substrate alone.

metastable species of carbonyl can be quenched via a long range dipolar radiationless energy transfer process,[26-28] if the quencher has a strong allowed absorption spectrum which overlaps with the emission spectra of the excited carbonyl compounds. Even if this condition is not met, very efficient quenching of the triplet state of the carbonyl occurs if the quencher has a triplet state comparable to, and lower in energy than, the former.

In this study, diethylketone, DEK, was used as a model initiator and propylene tetramer as a model substrate. Photo-oxidation of propylene tetramer was initiated by the photo-excitation of DEK. A good quencher would significantly inhibit this oxidation.

Irradiation of propylene tetramer alone in the Rayonet reactor consumes a negligible amount of oxygen during the first 480 min, after which there is a slow rate of oxidation (Fig. 13, Table 7). The photo-oxidation is probably initiated by the photolysis of hydroperoxides produced during the induction period as a result of charge transfer excitation (eqn (6)).[14] Addition of DEK initiated rapid photo-oxidation without an induction period. TMPO-*t*-Bu and Tinuvin 292 caused a short t_{ind} with slow oxygen uptake followed soon

TABLE 7

Effect of Single Component Stabilizers on DEK[a] Initiated Photo-oxidation

Stabilizer[b]	t_{ind} *(min)*	$R_m \times 10^7\ Ms^{-1}$
No DEK	480	0·9
Control (no stabilizer)	0	5·1
TMP	180	2·0
TMPO$^{\cdot}$	160	2·1
TMPO-*t*-Bu	100	3·8
Tinuvin 292	95	4·9

[a] $[\text{DEK}]_0 = 1$ M; [b] $[S]_0 = 60$ mM.

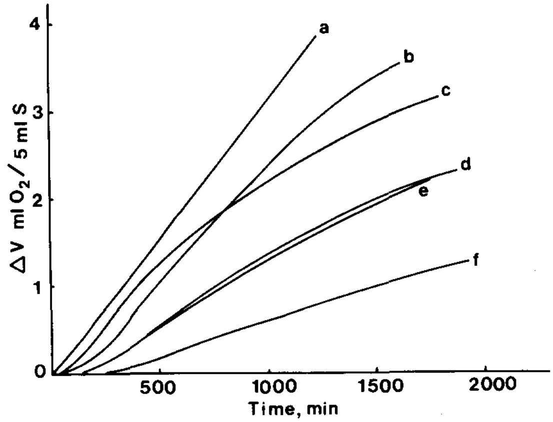


Fig. 14. Effect of HALS on the photo-oxidation of propylene tetramer. Conditions are the same as in Fig. 10: (a) no additive; (b) Tinuvin 292; (c) Tinuvin 144; (d) Tinuvin 770; (e) Chimassorb 944; (f) Tinuvin 292 (0·01 M) + TMP (0·02 M) + TMPO$^{\cdot}$ (0·02 M).

by more rapid oxidation with rates comparable to the control. It seems that both compounds are rapidly consumed by photo-oxidation. It is worthy of note that the two compounds behave very similarly even though Tinuvin 292 is an excellent radical scavenger whereas TMPO-*t*-Bu is not (*vide supra*). Thus, the comparative measure of excited state quenching is not significantly affected by radical scavenging.

Another kind of behavior is shown in Fig. 13 for TMPOH. There is a rather rapid initial consumption of oxygen which declines with irradiation time. After about 400 min the rate of oxidation is only about two-fifths of the rate without stabilizer. During the initial stage the amount of oxygen reacted is about 0·01 M which corresponds to *ca.* 15% of the TMPOH present. Therefore, up to about 0·01 M of some active species may be generated early during the process.

The two most active quenchers (Table 7, Fig. 13) are the TMP and TMPO$^{\cdot}$. In the presence of TMP the photo-oxidation curve is sigmoidal. In the case of TMPO$^{\cdot}$ the oxidation following t_{ind} has continuously decreasing rates suggestive of the formation of another more active quencher.

The effects of commercial HALS on DEK initiated photo-oxidations are shown in Fig. 14. They are consistent with the results of the model compounds that TMP is the most effective moiety. The retardation of photo-oxidation increases in the order of Tinuvin 292 < Tinuvin 144 < Tinuvin 770 ~ Chimasorb 944.

Two component systems were also investigated; the results are summarized in Table 8. The most effective combination is TMPO$^{\cdot}$ + TMP; in fact, the photo-oxidation with these two additives is not appreciably greater than that of propylene tetramer alone. It appears that most of the

TABLE 8

Effect of Two Component Stabilizers on DEK[a] Initiated Photo-oxidation

Stabilizers[b]		t_{ind} *(min)*	k_0 *Ms*$^{-1}$	*Synergism*[c]
A	*B*			
TMP	TMPOH	None	3·7	– –
TMPO$^{\cdot}$	TMPOH	80	1·6	—
TMP	TMPO-*t*-Bu	150	2·9	○
TMP	Tinuvin 292	230	2·5	○
TMPO$^{\cdot}$	TMPO-*t*-Bu	240	1·8	+
TMPO$^{\cdot}$	Tinuvin 292	320	1·6	+
TMPO$^{\cdot}$	TMP	300	0·92	+ +

[a] $[\mathrm{DEK}]_0 = 1$ M.

[b] $[\mathrm{S}] = 0{\cdot}03$ M each.

[c] Antisynergistic, (— —); weakly antisynergistic, (—); neutral, (○); weakly synergistic, (+); strongly synergistic, (+ +).

excited states of DEK were quenched by this system. On the other hand, the photo-oxidation behavior with the TMP + TMPOH system is quite similar to that with DEK alone. Therefore, TMPOH is an antisynergist in this reaction.

The activity of TMPO$^{\cdot}$ is not as greatly reduced by the presence of TMPOH. Its activity is also more readily enhanced by other additives, i.e. by TMPO-*t*-Bu and Tinuvin 292. In contrast, these same derivatives have neither positive nor negative effects on TMP.

4.6 DBP initiated photo-oxidation

Absorption of a UV photon by DBP leads to predissociation without the intermediacy of metastable excited states (*vide supra*). In an earlier study,[28] parallel photo-oxidations by 313 nm radiation were conducted at concentrations of DBP and DEK such that they have comparable initiation rates in the absence of stabilizers. Reduction of DBP photo-oxidation was attributed to UV screening and the additional reduction of DEK photo-oxidation rate was attributed to quenching of excited states.

In the present study 350 nm light of Rayonet lamps was used to photolyze DBP for the initiation of propylene tetramer oxidation. At 0·1 M DBP the oxidation rate was $2{\cdot}9 \times 10^{-6}\,\mathrm{Ms}^{-1}$ without stabilizer.

It was found (Table 9) that only TMPOH is effective against the DBP initiated photo-oxidations. The other compounds show only small reduction of rates. The effect of [TMPOH] on the DBP initiated photo-oxidation is shown in Fig. 15. The induction period was found to increase

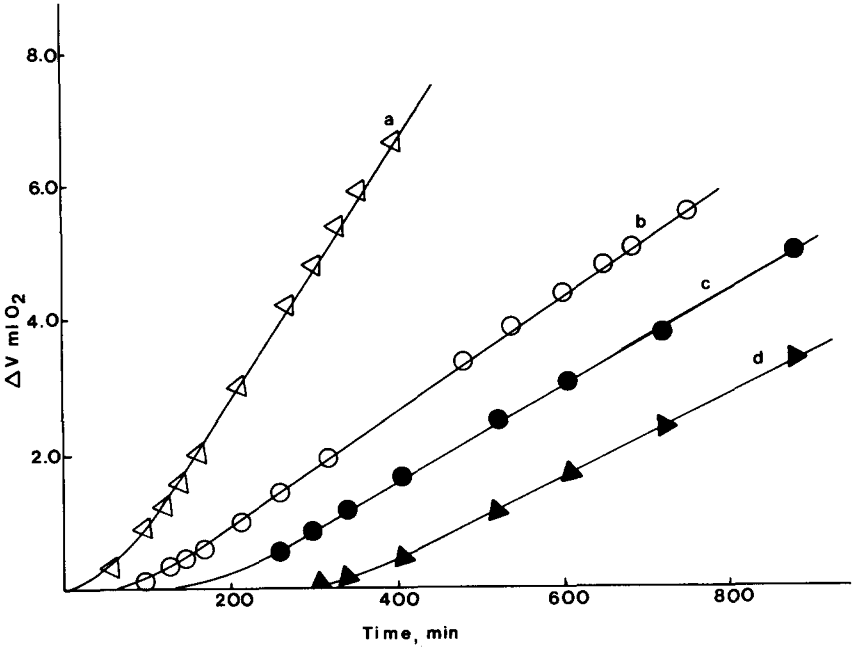


Fig. 15. Effect of TMPOH in photo-oxidation of propylene tetramer initiated by DBP (0·1 M) at 38°C plotted as volume of O_2 consumed per 5 ml of substrate for [TMPOH]: (a, △) 0 M, control; (b, ○) 6 mM; (c, ●) 15 mM; (d, ▲) 30 mM.

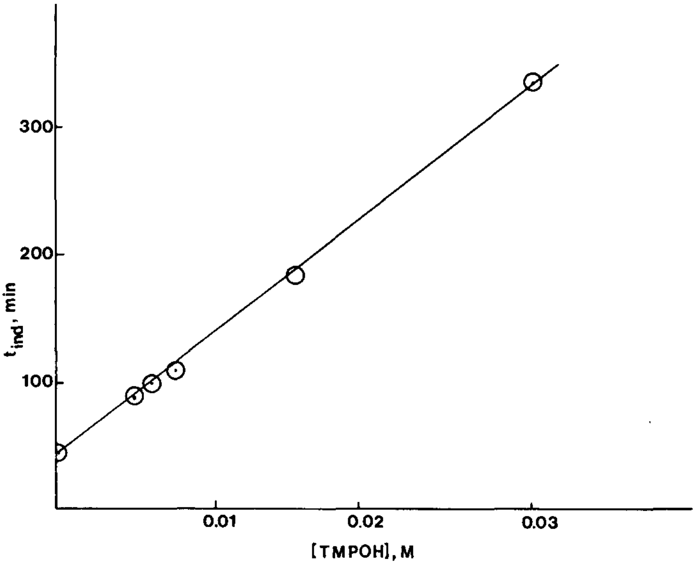


Fig. 16. Dependence of induction period on [TMPOH] for the data of Fig. 15.

TABLE 9
Effects of TMP Derivatives on DBP Initiated Photo-oxidation of Propylene Tetramer[a]

Compound	t_{ind} *(min)*	$R_m \times 10^7$ Ms^{-1}
None	none	2·90
TMP	none	1·64
Tinuvin 292	none	1·48
TMPO-*n*-Bu	none	1·30
TMPO-*t*-Bu	none	1·30
TMPO˙	none	1·16
TMPOH	185	1·08

[a] Photo-oxidations initiated by 0·1 M of DBP by Rayonet source with λ_{max} = 350 nm at 38°C; additive concentrations are 0·015 M.

linearly with [TMPOH] (Fig. 16). This stabilization cannot be attributed to the scavenging of radicals by TMPOH because a better radical scavenger, Tinuvin 292, does not inhibit this photo-oxidation.

Experiments were also carried out to find synergistic effects but without success. Photolysis in the presence of TMPOH/TMPO˙, or TMPOH/Tinuvin 292, or TMPOH/Tinuvin 292/TMPO˙ all have the same photo-oxidation rates as with TMPOH alone. Thus, there is neither positive nor negative synergism.

5 DISCUSSION OF RESULTS

5.1 Brief review of proposed mechanism for HALS

It is generally recognized that TMP cannot be the main active species responsible for the effectiveness of HALS. Two catalytic mechanisms have been proposed, both of which assigned a central role to TMPO˙. This is understandable because TMPO˙ is the most easily identifiable product from TMP by ESR. It has been shown to be formed in the reaction of TMP with $^1O_2$,[11] $RO_2^\cdot$,[29] and ROOH.[30]

The first catalytic mechanism involves TMPO˙ and TMPOR.[31-34] TMP is said to be converted by radicals to TMPO˙; the radical may be generated, for instance, by the photolysis of polymer hydroperoxide. Then TMPO˙ scavenges a macro carbon radical P˙:

$$\text{TMPO}^\cdot + \text{P}^\cdot \rightarrow \text{TMPOP} \qquad k_{\text{NO}^\cdot} \tag{31}$$

The TMPO$^{\cdot}$ radical is regenerated by reaction with peroxyl radical:

$$\text{TMPOP} + \text{POO}^{\cdot} \rightarrow \text{TMPO}^{\cdot} + \text{POOP} \qquad k_{\text{NOR}} \qquad (32)$$

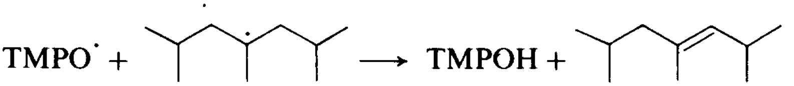
One notes that this is basically a mechanism of stabilization by radical scavenging. It differs from the usual mechanism of radical scavenging by hindered phenols in that both carbon radicals and peroxyl radicals are scavenged and that the TMPOR/TMPO$^{\cdot}$ mechanism is cyclic. However, reactions (31) and (32) must be able to compete with reactions (2) and (3), respectively, if there is to be effective stabilization. The values of rate constants $k_{\text{NO}^{\cdot}}$ and k_{NOR} have been estimated[35] to be 4×10^{8} $(\text{Ms})^{-1}$ and 0·3 to 3 $(\text{Ms})^{-1}$, respectively. The values of k_o^{16} and $k_p^{1,5}$ for the oxidation of polypropylene are estimated to be 7×10^{9} $(\text{Ms})^{-1}$ and $1{\cdot}6 \times 10^{-2}$ $(\text{Ms})^{-1}$, respectively, at 25°. Therefore, the TMPO$^{\cdot}$/TMPOR mechanism is valid if $[\text{TMPO}^{\cdot}]/[\text{O}_2] > 20$ and $[\text{TMPOR}]/[\text{RH}] > (0{\cdot}5 - 5) \times 10^{-3}$. In fact, for polypropylene film containing 5×10^{-3} M of TMP the amount of TMPO$^{\cdot}$ produced by xenon arc irradiation is only about 10^{-4} M. The concentration of TMPOP is not known but is probably smaller than that of [TMPO$^{\cdot}$], whereas the tertiary hydrogen concentration in polypropylene is about 10 M. Finally, the secondary and tertiary alkoxyl amines are unstable and readily converted to the corresponding nitroxyl radicals in the presence of air.[36]

An ingenious proposal has been advanced[37] that TMPO$^{\cdot}$ is associated with the hydroperoxides. Photolysis of the latter produces alkyl radical in close proximity to the former and the two react immediately. However, the equilibrium constant for association of TMPO$^{\cdot}$ and ROOH has been estimated[37,38] to be 25 M^{-1}. Therefore, one objection to the TMP/TMPOP mechanism is that less than 0·25% of POOH may be complexed with TMPO$^{\cdot}$. This objection should be tempered for polymeric systems. In the case of PP the hydroperoxide groups are formed in blocks and the commercial HALS are polyfunctional. Association between them will be greatly strengthened because of multiple hydrogen bonding interactions.

Another point of interest is the relative concentrations of alkyl and peroxyl radicals and whether the alkyl radicals are converted so rapidly by O_2 to peroxyl radical so that the former species need not be considered in stabilization. The mechanism above and the one below both propose the scavenging of alkyl radicals. This is justifiable for polymeric systems. In autoxidizing polypropylene the ratio of $[\text{P}]/[\text{POO}^{\cdot}]$ has been estimated[39] to be 2×10^{-3} at 100°C as compared to $[\text{R}^{\cdot}]/[\text{ROO}^{\cdot}] = 5 \times 10^{-6}$ for isopentane. Therefore, the importance of scavenging of alkyl radicals may be greater in polypropylene stabilization than in liquid hydrocarbon.

A second mechanism involving TMPO$^{\cdot}$TMPOH has been proposed by Scott and his coworkers.[40-42] They argued that reaction (32) is inherently reversible, particularly in the presence of light. Instead of the combination of

TMPO˙ with macroradical (eqn (31)), it was postulated to abstract the hydrogen next to the free radical, the C—H bond being weakened by hyperconjugation:



(33)

The nitroxyl radical is then regenerated by:

$$\mathrm{TMPO} + \mathrm{PO}^{\cdot}(\mathrm{PO}_2^{\cdot}) \longrightarrow \mathrm{TMPO}^{\cdot} + \mathrm{POH(POOH)} \qquad (34)$$

IR evidence[40,43] for the formation of olefins and TMPOH (2765 cm^{-1} band) in photo-oxidizing polypropylene containing HALS was cited to support this mechanism. However, other investigators found neither olefin production[34] nor the 2765 cm^{-1} absorption.[44] One notes that this TMPOH/TMPO˙ mechanism also deals primarily with the thermal autoxidative reactions as the TMPOR/TMPO˙ mechanism.

Fairgrieve and MacCallum[38] proposed HALS to act mainly as metal ion deactivator. HALS was assumed to be complexed to metal ions so that, instead of the usual redox reaction with ROOH to produce radicals:

$$\mathrm{M}^{+n} + \mathrm{ROOH} \rightarrow \mathrm{M}^{+n+1} + \mathrm{HO}^{-} + \mathrm{RO}^{\cdot} \qquad (35)$$

or

$$\mathrm{M}^{+n} + \mathrm{ROOH} \rightarrow \mathrm{M}^{+n-1} + \mathrm{H}^{+} + \mathrm{ROO}^{\cdot} \qquad (36)$$

the metal ion–TMP complex reacts to form inert products:

$$\begin{tikzcd}
\mathrm{M}^{+n} \arrow[r, shift left, "\mathrm{HALS}"] \arrow[d, shift left, "\mathrm{ROOH}"] & \mathrm{M}^{n+}\cdots\mathrm{HALS} \arrow[l, shift left] \arrow[d, shift left, "\mathrm{ROOH}"] \\
\mathrm{M}^{n+}\cdots\mathrm{ROOH} \arrow[u, shift left] \arrow[r, shift left] \arrow[d] & \begin{array}{c}\mathrm{M}^{n+}\cdots\mathrm{HALS}\\ \diagdown\quad\diagup\\ \mathrm{ROOH}\end{array} \arrow[l, shift left] \arrow[u, shift left] \arrow[d] \\
\text{radicals} & \text{non-radical products}
\end{tikzcd} \qquad (37)$$

However, if the fraction of ROOH complexed with HALS is small, as estimated by these authors in their objection to the proposal of Gratten *et al.*,[37] then the significance of the ternary complexation of metal ion, HALS and ROOH is even more remote. In fact, metal ion deactivator such as oxanilide finds usage only in wire-coating applications.

5.2 Single species stabilization

Let us consider how individual TMP derivatives act in various tests for stabilization.

TMP has no absorption > 210 nm so it cannot act as UV screener. It does not have any low lying excited states, thus cannot be effective in ${}^1O_2$ quenching. In the presence of oxygen there will be charge transfer excitation as had been reported for amines;[45] TMP can be a photo-initiator in analogy to reaction (6):

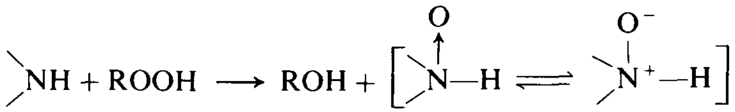
$$\rangle NH + {}^3O_2 \xrightarrow{h\nu} \left[\rangle NH^+O_2^-\right] \longrightarrow \rangle NO^{\cdot} + HOO^{\cdot} \qquad (38)$$

All these considerations apply similarly to TMPOR and TMPMe.

It is not surprising that TMP does not inhibit autoxidation. Even though TMP will react with peroxyl radical, the resulting species can participate in chain propagation.[29,46]

$$\begin{aligned} \rangle NH + ROO^{\cdot} &\longrightarrow \rangle N^{\cdot} + ROOH \\ \rangle N^{\cdot} + O_2 &\longrightarrow \rangle NOO^{\cdot} \\ \rangle NOO^{\cdot} + RH &\longrightarrow \rangle NOOH + R^{\cdot} \end{aligned} \qquad (39)$$

TMP has been reported to react slowly with polypropylene hydroperoxides.[30,47] The present study found TMP to be active in the decomposition of hydroperoxide. The process is noncatalytic, which may be simply accounted for by:



$$\rangle NH + ROOH \longrightarrow ROH + \left[\rangle \overset{O}{\overset{\uparrow}{N}}{-}H \rightleftharpoons \rangle \overset{O^-}{\overset{|}{N^+}}{-}H\right] \qquad (40)$$

There is a claim[48] that TMP quenches excited chromophore but there are also claims to the contrary.[38,49–51] Based on the observed inhibitory effect of TMP on DEK* initiated photo-oxidation, TMP is apparently quite effective in quenching DEK*. The activity of TMP cannot be attributed to its conversion to TMPO˙ by photo-oxidation. First, this conversion occurs only to a slight extent. Secondly, TMP exhibits slightly better quenching inhibition of photo-oxidation than TMPO˙. Finally, TMP/TMPO˙ is an excellent synergistic system (Table 8).

TMPO˙ had been the focus of research and discussion on HALS action. Though it has strong UV absorption (Table 1), it lies at too short a wavelength to be of value as a UV absorber. The visible absorption of

TMPO˙ has a very small extinction coefficient. Previously TMPO˙ has been said both to be active[51,52] and inactive[38,53] in quenching $^1O_2$. The present study (Table 6) found it to be only moderately effective. The energy transfer process between $^1O_2$ and ^{2}TMPO˙ is not a forbidden one:

$$^1O_2 + {}^2\text{TMPO}^\cdot \rightarrow {}^3O_2 + {}^2\text{TMPO}^{\cdot *} \qquad (41)$$

The process probably has very low transition probability because the excitation energy of $2{\cdot}22 \times 10^4\,\text{cm}^{-1}$ for TMPO˙ is much greater than the energy of $^1O_2$. Weak quenching may occur via paramagnetic perturbed singlet–triplet transition for oxygen.

TMPO˙ has only a slight effect of 20% rate reduction in cumene oxidation (Table 2). There may be a small contribution from the following reaction:

$$\text{TMPO}^\cdot + \text{ROO}^\cdot \rightleftharpoons [\text{TMPOOOR}] \rightarrow \text{TMPOR} + O_2 \qquad (42)$$

The equilibrium favors the left-hand-side because TMPO˙ has been said not to react with peroxyl radicals.[31,54] Alternatively, if not all the cyanoisopropyl radicals are oxygenated, they may react with TMPO˙.[31,54]

$$\text{TMPO}^\cdot + \text{R}^\cdot \rightarrow \text{TMPOR} \qquad (43)$$

Reports on quenching of excited states by TMPO˙ have been contradictory.[38,51,52,55] The results on inhibition of DEK* initiated photooxidation suggests TMPO˙ to be capable of quenching DEK*.

TMPO˙ possesses some activity in the decomposition of ROOH. However, it is probably a transfer reaction:

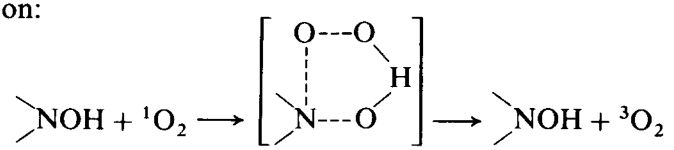
$$\text{TMPO}^\cdot + \text{ROOH} \rightarrow \text{TMPOH} + \text{ROO}^\cdot \qquad (44)$$

Since an ROO˙ is formed, the process should not contribute toward stabilization.

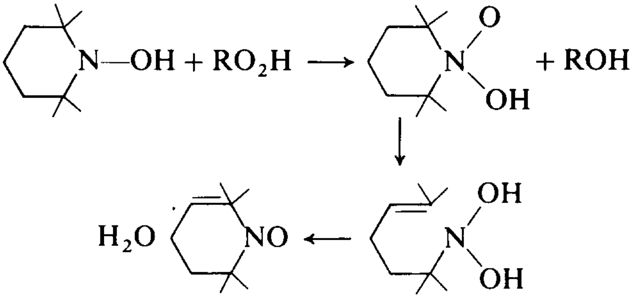
TMPOR has been reported as a radical scavenger,[31–33,35] and proposed to be mainly responsible for the activity of HALS.[33,34,43,56,57] Evidence for the formation of TMPOR in oxidizing polypropylene is available.[34] According to reactions (31) and (32) TMPOR should be a good synergist for TMPO˙. The experimental results do not bear out this expectation; there is no inhibition of cumene oxidation by TMPOR alone or together with TMPO˙. From the above discussion of competing oxidation and radical scavenging reactions, very large amounts of TMPOR ($>0{\cdot}11$ M) are required to affect observable inhibition of oxidation. Finally, TMPOR has only limited stability in the presence of oxygen.[12,36] It is unlikely that the TMPOR/TMPO˙ radical scavenging mechanism is operative in actual UV stabilization of polyolefins.

TMPOR is without activity in the quenching of either $^1O_2$ or carbonyl excited states.

The radical scavenging activity of TMPOH can be simply attributed to reaction (34). It is by far the most efficient $^1O_2$ quencher among the TMP derivatives. A plausible explanation is deactivation via complexation and dissociation:


(45)

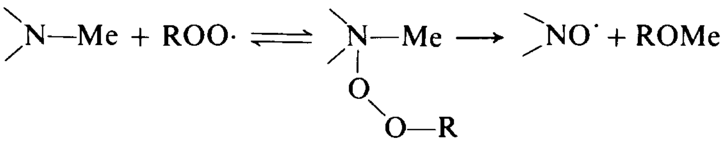
The decomposition of hydroperoxide by TMPOH is probably analogous to reaction (25) for TMPME:


(46)

The difference is that nitroso compound is the product instead of a nitroxide radical of Fig. 12.

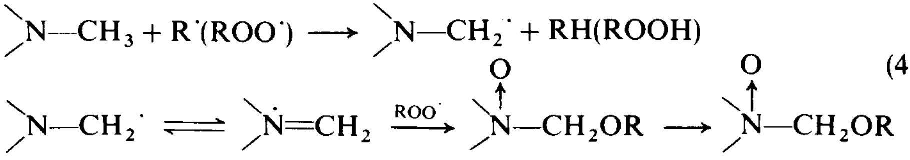
The inhibition of DBP initiated photo-oxidation by TMPOH is unexpected. This effect cannot be attributed to radical scavenging because TMPMe does not cause inhibition. It is possible that there is complexation between DBP and TMPOH and that the complex does not undergo predissociation. In addition, the inhibition was observed at [TMPOH] only one-tenth of [DBP]. This requires a greater absorbance by the complex than the very weak DBP absorption at 340 nm.

The radical scavenging by TMPMe was quite a surprising finding. A possible reaction is:



$$>N{-}Me + ROO\cdot \rightleftharpoons >\underset{\substack{|\\ O\\ \diagdown\\ O-R}}{N}{-}Me \longrightarrow >NO^{\cdot} + ROMe \qquad (47)$$

The occurrence is supported by the observation of $TMPO^{\cdot}$ by esr. Hydrogen abstractions commonly found for aromatic amines may also occur for TMPMe:



$$\begin{aligned} &>N{-}CH_3 + R^{\cdot}(ROO^{\cdot}) \longrightarrow >N{-}CH_2^{\cdot} + RH(ROOH) \\ &>N{-}CH_2^{\cdot} \rightleftharpoons >\dot{N}{=}CH_2 \xrightarrow{ROO^{\cdot}} >\overset{\substack{O\\ \uparrow}}{N}{-}CH_2OR \longrightarrow >\overset{\substack{O\\ \uparrow}}{N}{-}CH_2OR \end{aligned} \qquad (48)$$

Table 10 summarizes the observed stabilization activities of TMP

TABLE 10
Stabilization Activities of TMP Derivatives

Mode of action	*Active species*
Radical scavenging	TMPMe/TMPOH > TMPMe ~ TMPOH
ROOH decomposition	TMPOH > TMP > TMPO$^{\cdot}$ > TMPMe
DEK* quenching	TMP/TMPO$^{\cdot}$ > TMPO$^{\cdot}$/TMPMe ~ TMPO$^{\cdot}$/TMPO-*t*-Bu > TMP ~ TMPO$^{\cdot}$
$^1O_2$ quenching	TMPOH

derivatives. Apparently, TMP, TMPO$^{\cdot}$, TMPOH and TMPMe can act to inhibit or retard different processes in the photo-oxidations.

5.3 Synergistic mechanisms for HALS

The best explanation for the extreme effectiveness in prolonging the outdoor lifetime of polypropylene by a very small amount of HALS is through extensive synergism which interferes with all the photoactive and chain propagating species. This is in contrast with previously proposed cyclic mechanisms involving only two TMP intermediates and the propagating species for a thermal oxidation.

The simplest scheme for photo-oxidation of polypropylene in the absence of HALS is given in Scheme 1. Scheme 2 gives the reactions for stabilization by HALS. Those synergistic combinations have their components in square brackets. In the case of hydroperoxide decomposition, TMPOH and TMPR are also active though only TMP is used in the derivation of rate laws.

Let us denote all quantities in experiments without or with stabilizers by subscripts *o* and *s*, respectively; then the relative rates of oxygen uptake for the two conditions are:

$$\frac{-(\mathrm{d}[O_2]/\mathrm{d}t)_o}{-(\mathrm{d}[O_2]/\mathrm{d}t)_s} = \frac{[\mathrm{POOH}]_o}{[\mathrm{POOH}]_s}\left(1 + \frac{k_{11}[\mathrm{TMPO}^{\cdot}]}{k_6[O_2]}\right) \tag{49}$$

The reduction of R_0 is attributable mainly to the smaller $[\mathrm{POOH}]_s$ in the presence of HALS than without it. Their expressions are quite complicated.

$$[\mathrm{POOH}]_o = \frac{k_3\phi' I_0\varepsilon'[\mathrm{PCOR}]_o}{(k_3 + k_4[O_2])\phi I_o\varepsilon} + \frac{k_p[\mathrm{PH}]}{\phi I_o\varepsilon}\left\{\frac{-k_p[\mathrm{PH}]}{2k_t} + (k_p^2[\mathrm{PH}]^2 + 4k_t k_6[O_2]\phi I_o\varepsilon[\mathrm{POOH}]_o(k_1 + k_2[\mathrm{PH}]))^{1/2}\right\} \tag{50}$$

$$[\mathrm{POOH}]_s = \frac{k_3\phi' I_0\varepsilon'[\mathrm{PCOR}]_s}{(k_3 + k_4[O_2] + k_{10}[\mathrm{TMP/TMPO}^{\cdot}])(\phi I_0\varepsilon + k_9[\mathrm{TMP}])} + \left(\frac{k_p[\mathrm{PH}]}{\phi I_0\varepsilon + k_9[\mathrm{TMP}]}\right)\left(\frac{k_6[O_2]\phi I_0\varepsilon[\mathrm{POOH}]_s}{(k_1 + k_2[\mathrm{PH}])(k_p[\mathrm{PH}] + k_9[\mathrm{TMPOH/TMPR}]}\right) \tag{51}$$

$\mathrm{POOH} + h\nu \rightarrow \mathrm{PO}^{\cdot}$	$\phi I_0 \varepsilon[\mathrm{POOH}]$
$\mathrm{PO}^{\cdot} \rightarrow \mathrm{PCOR} + \mathrm{P}^{\cdot}$	k_1
$\mathrm{PO}^{\cdot} + \mathrm{PH} \rightarrow \mathrm{POH} + \mathrm{P}^{\cdot}$	k_2
$\mathrm{PCOR} + h\nu \rightarrow \mathrm{PCOR}^*$	$\phi' I_0 \varepsilon'[\mathrm{PCOR}]$
$\mathrm{PCOR}^* \rightarrow \mathrm{PCOR} + \text{olefin}$	k_3
$\mathrm{PCOR}^* + \mathrm{O}_2 \rightarrow \mathrm{PCOR} + \mathrm{O}_2^*$	k_4
$\mathrm{O}_2^* + \text{olefin} \rightarrow \mathrm{POOH}$	k_5
$\mathrm{P}^{\cdot} + \mathrm{O}_2 \rightarrow \mathrm{PO}_2^{\cdot}$	k_6
$\mathrm{PO}_2^{\cdot} + \mathrm{PH} \rightarrow \mathrm{POOH} + \mathrm{P}^{\cdot}$	k_p
$2\mathrm{PO}_2^{\cdot} \rightarrow \text{products}$	k_t

Scheme 1. Elementary processes in the photo-oxidation of polypropylene.

Stabilization can be measured also by the formation of carbonyls or decrease in molecular weight; expressions for these can also be written based on the above schemes. All the expressions will contain the effect of reactions in Scheme 2 in suppressing the oxidation. However, the POOH and PCOR concentrations are time dependent and are significantly different with and without HALS. The concentrations of the TMP derivatives are unknown and they also vary with time. With the exception of TMPMe, all the other TMP derivatives studied in this work had been postulated to be produced during the photo-oxidation of TMP containing systems. Maybe there is an equilibrium such as:

$$\mathrm{TMP} + \mathrm{ROO}^{\cdot} \rightleftharpoons \mathrm{TMPR} + \mathrm{HOO}^{\cdot} \qquad (52)$$

based on the stronger O—H versus NH bonds. If this reaction does not occur naturally, then Tinuvin 292 can be added to other HALS as a synergist.

Table 10 did not contain UV screening. Therefore, it may be beneficial to include some hydroxyl benzophenones or hydroxy phenyl benzoate as additional synergist. If there is a need for metal deactivation in some application, one can introduce oxanilide for that purpose. Incidentally, oxanilide had also been said to be a UV absorber.[58] Finally, polymer MW loss may be reduced by the presence of a phosphite stabilizer to couple those polymeric radicals produced by photo-oxidation.

A most important finding of this work is that some TMP derivatives show

$\mathrm{PO}_2^{\cdot} + [\mathrm{TMPOH/TMPR}] \rightarrow \text{inactive products}$	k_7
${}^1\mathrm{O}_2 + \mathrm{TMPOH} \rightarrow \text{inactive products}$	k_8
$\mathrm{POOH} + \mathrm{TMP}\ (\text{or TMPOH or TMPR}) \rightarrow \text{inactive products}$	k_9
$\mathrm{PCOR}^* + [\mathrm{TMP/TMPO}^{\cdot}] \rightarrow \text{inactive products}$	k_{10}
$\mathrm{P}^{\cdot} + \mathrm{TMPO}^{\cdot} \rightarrow \text{inactive products}$	k_{11}

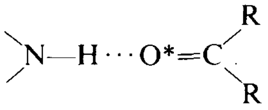
Scheme 2. Mechanism of synergistic stabilization by HALS.

strong synergism even in experiments designed to determine activities for a single mode of stabilizer action. One may call this homotropic synergism.

In the case of excited state quenching, the observed activities are in the order $\mathrm{TMPO}^{\cdot}/\mathrm{TMP} > \mathrm{TMPO}^{\cdot}/\mathrm{TMPMe} \sim \mathrm{TMPO}^{\cdot}/\mathrm{TMPO}\text{-}t\text{-Bu}$, all of which are more effective in quenching carbonyl excited states than either $\mathrm{TMPO}^{\cdot}$ or TMP alone. The other two derivatives, TMPMe and TMPO-*t*-Bu, have no activity by themselves. A rational explanation is available in this instance because excited singlet, $^{1}\mathrm{DET}^{*}$, and triplet, $^{3}\mathrm{DEK}^{*}$, states are formed. Each component of the homotropic synergistic system may be deactivating one of the two metastable species. Because of conservation of spin multiplicity, it is probably the $^{3}\mathrm{DEK}^{*}$ which is quenched by $\mathrm{TMPO}^{\cdot}$:

$$^{3}\mathrm{DEK}^{*} + {}^{2}\mathrm{TMPO}^{\cdot} \rightarrow {}^{1}\mathrm{DEK}^{0} + {}^{2}\mathrm{TMPO}^{\cdot *} \qquad (53)$$

This leaves the $^{1}\mathrm{DEK}^{*}$ to be deactivated by the second synergistic component. The excitation energies of the TMP derivatives are too great to quench $^{1}\mathrm{DEK}^{*}$ by resonance dipolar energy transfers.[26-28] De-excitation probably occurs via a collisional process. A weak complex may be envisaged as an intermediate in the case of TMP:



The homotropic TMPOH/TMPMe synergism toward radical scavenging is unexpected. The results suggest the possibility that TMPOH and TMPMe can scavenge different radicals or scavenge the same radical via dissimilar reaction pathways (eqns (34), (47), (48)).

Finally, there may be other homotropic synergisms not revealed in this study such as the synergistic effect in ROOH decomposition, $^{1}O_2$ quenching, and DTP photo-oxidations.

ACKNOWLEDGEMENT

This work was supported by a CUMIRP grant at the University of Massachusetts.

REFERENCES

1. J. C. W. Chien and C. R. Bass, *J. Polym. Sci., A1*, **5**, 3091 (1967).
2. L. Reich and S. S. Stivala, *Autoxidation of Hydrocarbon and Polyolefins*, Dekker, NY (1969).

3. J. C. W. Chien, E. J. Vandenberg and H. Jabloner, *J. Polym. Sci. A1*, **6**, 381 (1968).
4. J. C. W. Chien and H. Jabloner, *J. Polym. Sci. A1*, **6**, 393 (1968).
5. J. C. W. Chien and D. S. T. Wang, *Macromolecules*, **8**, 920 (1975).
6. J. C. W. Chien and J. K. Y. Kiang, *Makromol. Chem.*, **181**, 47 (1979).
7. J. C. W. Chien and C. R. Boss, *J. Polym. Sci. A1*, **5**, 1683 (1967).
8. J. C. W. Chien and C. R. Boss, *J. Polym. Sci. A1*, **10**, 1579 (1972).
9. M. Blumberg, C. R. Boss and J. C. W. Chien, *J. Appl. Polym. Sci.*, **9**, 3837 (1965).
10. J. J. Usilton and A. R. Patel, *Am. Chem. Soc. Polym. Prepr.*, **18**, 393 (1977).
11. V. B. Ivanov, V. Y. Shlyapintokh, O. M. Khoostach, A. B. Shapiro and E. G. Rozantsev, *J. Photochem.*, **4**, 313 (1965).
12. D. J. Carlsson, D. W. Grattan, T. Suprunchuk and D. M. Wiles, *J. Appl. Polym. Sci.*, **22**, 2217 (1978).
13. (a) N. S. Allen, A. Parkinson, J. L. Gardette and J. Lemaire, *Poly. Deg. and Stab.*, **5**, 135 (1983); (b) F. P. LaMantia, *Poly. Deg. and Stab.*, **15**, 283 (1986).
14. J. C. W. Chien, *J. Phys. Chem.*, **69**, 4317 (1965).
15. K. U. Ingold, *Acc. Chem. Res.*, **2**, 1 (1969).
16. J. A. Howard, *Adv. Free Radical Chem.*, **4**, 49 (1972).
17. P. Gray, R. Shaw and J. C. J. Thyme, *Prog. React. Kin*, **4**, 63 (1967).
18. D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **89**, 489 (1967).
19. S. W. Benson and R. Shaw, *Adv. Chem. Ser.* (**75**), 288 (1968).
20. G. H. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).
21. A. M. Trozzolo and F. H. Winslow, *Macromolecules*, **1**, 98 (1968).
22. G. S. Hammond, J. N. Sen and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955).
23. C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3233, 3238 (1955).
24. C. S. Foote, *Science*, **162**, 963 (1968).
25. B. A. Schmuriger, J. Boundon and J. Bedu, *Photochem. Photobiol.*, **8**, 361 (1968).
26. The Forster, *Disc. Faraday Soc.*, **27**, 7 (1959).
27. D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).
28. J. C. W. Chien and W. P. Connor, *J. Am. Chem. Soc.*, **90**, 1001 (1968).
29. V. Ya. Shlyapintokh, E. V. Bystritzkaya, A. B. Shapiro, L. N. Smirnov and E. G. Rozantsev, *Izv. Akad. Nauk. SSSR, Ser. Khim*, 1915 (1973).
30. K. Muroyama, S. Marimura and J. Yoshioka, *J. Bull. Chem. Soc. Japan*, **42**, 1640 (1969).
31. M. S. Khlplyankina, A. L. Buchachenko, M. B. Neiman and A. G. Vasileva, *Kin. i Kat.*, **6**, 394 (1965).
32. M. V. Sudnik, M. F. Rozantsev, A. B. Shapiro and E. G. Rozantsev, *Bull. Acad. Sci. USSR*, 2702 (1976).
33. T. A. B. M. Bolsonan, A. P. Blok and J. H. G. Frijins, *Rec. Trav. Chim. Pays. Bas.*, **97**, 313 (1978).
34. D. J. Carlsson and D. M. Wiles, *Poly. Deg. and Stab.*, **6**, 1 (1984).
35. D. W. Grattan, D. J. Carlsson and D. M. Wiles, *Poly. Deg. and Stab.*, **1**, 69 (1979).
36. D. J. Carlsson, A. Garton and D. M. Wiles, *Developments in Polymer Stabilization.* Vol. 1 (Scott, G. (Ed.)), Elsevier, London, 219 (1979).
37. D. W. Grattan, A. H. Reddoch, D. J. Carlsson and D. M. Wiles, *J. Polym. Sci. Polym. Lett. Ed.*, **16**, 143 (1978).
38. S. P. Fairgrieve and J. R. MacCallum, *Poly. Deg. and Stab.*, **8**, 107 (1984).
39. E. T. Denisov, in *Developments in Polymer Stabilization.* Vol. 5. (Scott, G. (Ed.)), Elsevier, London, 23 (1982).

40. K. B. Chakraboty and G. Scott, *Polym.*, **21**, 252 (1980).
41. R. Bagheri, K. B. Chakraborty and G. Scott, *Poly. Deg. and Stab.*, **4**, 1 (1982).
42. G. Scott, *Poly. Deg. and Stab.*, **10**, 97 (1985).
43. D. K. C. Hodgeman, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 807 (1981).
44. N. S. Allen, J. L. Kotecha, J. L. Gardette and J. Lemaire, *Poly. Deg. and Stab.*, **11**, 181 (1985).
45. H. Tsubomura and R. S. Milliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960).
46. N. S. Allen, *Poly. Deg. and Stab.*, **2**, 129 (1980).
47. D. J. Carlsson, K. H. Chan, J. Durmis and D. M. Wiles, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 575 (1982).
48. A. S. Takikolova and V. A. Kuzmin, *Doklady Acad. Nauk. SSSR*, **232**, 860 (1977).
49. N. S. Allen, K. O. Fatinikun, J. L. Gardette and J. Lemaire, *Poly. Deg. and Stab.*, **3**, 243 (1981).
50. D. Bellus, H. Lind and J. F. Wyatt, *J.C.S. Chem. Commun.*, 1199 (1972).
51. B. Felder and R. Schumacher, *Angew. Makromol. Chem.*, **31**, 34 (1973).
52. R. Ballardini, G. Beggiato, P. Bortolus, A. Faucitano, A. Buttafava and F. Gratani, *Poly. Deg. and Stab.*, **7**, 41 (1984).
53. M. Norwakowska, *Poly. Deg. and Stab.*, **7**, 193 (1984).
54. Y. B. Shilov and E. T. Denisov, *Vysokomol. Soed.*, **A16**, 2313 (1974).
55. A. R. Watkins, *Chem. Phys. Lett.*, **29**, 526 (1974).
56. J. Sedlar, J. Petring, J. Pac and A. Zahradnikova, *Eur. Polym. J.*, **16**, 659, 663 (1980).
57. N. S. Allen and A. Parkinson, *Poly. Deg. and Stab.*, **4**, 161 (1982).
58. M. Allan, T. Billy, E. Haselback and P. Suppan, *Poly. Deg. and Stab.*, **15**, 311 (1986).