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Mechanism of Polymer Stabilization by Hindered-Amine Light Stabilizers (HALS). Model Investigations of the Interaction of Peroxy Radicals with HALS Amines and Amino Ethers

E. N. Step and N. J. Turro*

Department of Chemistry, Columbia University, New York, New York 10027

M. E. Gande and P. P. Klemchuk

Additives Division, CIBA-GEIGY Corporation, Ardsley, New York 10502

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ABSTRACT: Peroxy radicals, when generated in the presence of hindered-amine light stabilizers (HALS), oxidized HALS to produce nitroxides. This reaction, in addition to the scavenging of alkyl radicals by nitroxides, forms a cycle describing HALS as a class of excellent polymer stabilizers. As model systems for the mechanism of the oxidation of HALS, both alkyl peroxy and acyl peroxy radicals were produced by photolyzing the photoinitiators, ketones 2,4-diphenylpentan-3-one and 1-benzoyl-1-hydroxycyclohexane, in oxygen-saturated hexane in the presence of HALS amine **I** and amino ethers **II–V**. Significant yields of the nitroxide **VI** were observed in these reactions. Product analysis shows that the chemical yields of nitroxide **VI** are dependent on the HALS structure and on the electronic properties of peroxy radicals, being substantially higher for acylperoxy radicals than for alkyl peroxy radicals. ESR analysis shows that the oxidation of HALS amine **I** to **VI** was much less temperature dependent than the oxidation of the HALS amino ether **III**. A mechanism for the efficient production of **VI** from HALS with peroxy radicals is proposed.

1. Introduction

The high efficiency of hindered-amine light stabilizers (HALS, the amine and amino ether derivatives of 2,2,6,6-tetramethylpiperidine) as inhibitors of polymer photooxidation is considered to be determined primarily by a complex set of reactions involving the scavenging of active alkyl and peroxy radicals formed during oxidation.[1–6] During polymer exposure, both amine and amino ether derivatives of HALS produce nitroxides which can intercept alkyl radicals to yield amino ethers which, in turn, can react with peroxy radicals to destroy the latter and to regenerate nitroxides which are then returned to the alkyl radical scavenging pool. Therefore, HALS of different structures are able to interconvert in cyclic pathways, destroying species which could lead to polymer degradation and creating species which protect the polymer against degradation. In seeking a partial understanding of HALS polymer stabilization, model systems emphasizing specific features of the solution chemistry of HALS are often examined and the results are offered as potentially relevant to certain aspects of the complex mechanism which occurs in the polymers. We report such a model investigation of the peroxy radical-induced oxidation of HALS to nitroxides in solution.

A number of quantitative measurements relevant to the steps involving the scavenging of alkyl radicals and peroxy radicals are available from solution studies and are pertinent to any mechanistic analysis of HALS stabilization in polymers. For example, the bimolecular rate constants of the reactions of alkyl radicals with nitroxides to form amino ethers in nonviscous solvents are generally high,[7] ca. 10^7–10^9 M^{-1} s^{-1}. In solid polymers the rate of scavenging of alkyl radicals associated with the polymer is probably controlled only by molecular diffusion of the nitroxide. Peroxy radicals, on the other hand, are known to be much less reactive than alkyl radicals in the reaction with nitroxides;[8] therefore, nitroxide scavenging of peroxy radicals is not considered an important reaction in the stabilization by HALS.

HALS amines and amino ethers are not effective alkyl radical scavengers, but are believed to be effective in scavenging and pacifying the oxidative ability of peroxy radicals. For example, it has often been proposed in the literature that peroxy radicals react with HALS amino ethers to yield nitroxides along with peroxides, although until recently[3,5] no detailed mechanistic studies have been reported. In the recent work, the reactions of peroxy radicals of different structure (both alkylperoxy and acylperoxy) with HALS amino ethers in chlorobenzene at 60 °C were shown to yield, depending on the structure of peroxy radicals, nitroxides, ketones, alcohols, and carboxylic acids, but not peroxides.[3] In oxidation of cyclohexane with isotopic labeling (molecular oxygen-18), the label was found to incorporate into the nitroxide and alcohol formed from cyclohexylperoxy radicals, but no label was incorporated into the ketone formed from the amino ether.[3] These model results place serious constraints on any acceptable mechanism for the oxidation of amino ether HALS in the presence of peroxy radicals.

In a previous paper[9] we reported that triplet benzophenone, which is considered to be a powerful organic one-electron acceptor, is not quenched by HALS amino ethers in organic media, but is quenched by HALS amines. Since the mechanism of triplet benzophenone quenching by amines as well as by other organic substrates containing heteroatoms is generally considered to involve charge transfer or electron transfer as a primary photochemical process, the failure of amino ethers to quench benzophenone triplets implies that peroxy radicals, which are relatively weak electron acceptors in organic media, almost certainly would not be capable of an effective electron-transfer interaction with amino ethers in polymers. This conclusion leaves open the question of the possible mechanisms of interaction of amino ethers and peroxy radicals and the oxidation of amino ethers to nitroxides in the presence of peroxy radicals, and serves as a stimulus for the present model studies which were undertaken with the objectives of investigating (1) the efficiency and

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Chart 1

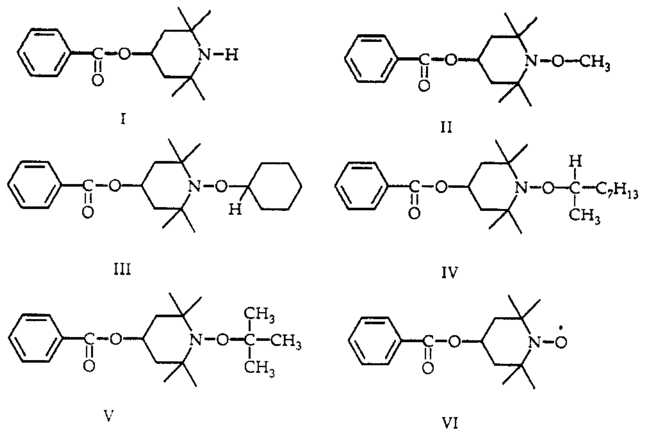
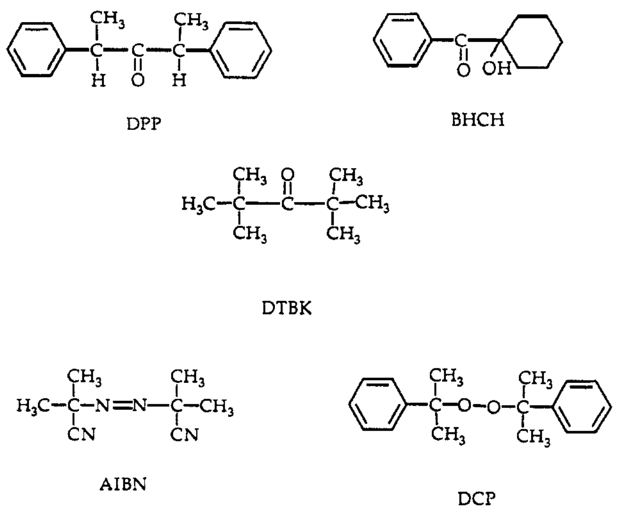


Chart 2



mechanism of the generation of nitroxide in the putative reaction of peroxy radicals with HALS amino ethers in solution; (2) the comparison of this reaction with the formation of nitroxides from the interaction of peroxy radicals with HALS amines; (3) the determination of the factors which control the efficiency of the reaction of amino ethers with peroxy radicals (in particular, structures of peroxy radicals and amino ethers); (4) the elucidation of the possible mechanisms of oxidation of amino ethers to nitroxides in the presence of peroxy radicals.

To achieve these objectives the following sets of experiments have been carried out. First, by steady-state photolysis of two ketones (used as photoinitiators to produce alkyl and acyl radicals) in oxygen-saturated solutions, peroxy radicals of various structures were generated (in the presence of HALS amines or amino ethers). The chemical yields of nitroxides and other products formed in these photolyses were determined. For comparison, the yields of nitroxide were also determined in the reaction of HALS with alkylperoxy radicals, generated from azobis(isobutyronitrile) photolysis in oxygen-saturated benzene and with alkoxy radicals generated in the photolysis of dicumyl peroxide. Second, peroxy radicals were generated by the same procedure within an ESR cavity, and the ESR spectra of both the peroxy radicals and the nitroxides were monitored. Finally, the temperature effect on the efficiency of nitroxide formation in the reaction of peroxy radicals with HALS amines and amino ethers was also investigated by ESR.

One HALS amine (**I**) and four amino ethers (**II–V**) were used in this work. When peroxy radicals of different structures were generated in the presence of these HALS, the same nitroxide **VI** was formed from each of the precursors.

2. Experimental Section

HALS compounds (**I–VI**) (see Chart 1) were obtained from CIBA-GEIGY.

Photoinitiators. 2,4-Diphenylpentan-3-one (DPP) was synthesized according to a literature procedure[10] and 1-benzoyl-1-hydroxycyclohexane (BHCH, Irgacure 164) was obtained from CIBA-GEIGY; di-*tert*-butyl ketone (DTBK) and dicumyl peroxide (DCP) were purchased from Aldrich and used as received; azobis(isobutyronitrile) (AIBN) was purchased from Janssen and was used as received.

Photolyses of DPP, BHCH, and DCP in hexane (or heptane) in a quartz cell were carried out on a Rayonet photochemical reactor equipped with a set of 300-nm lamps at room temperature. Due to its low solubility in hexane AIBN was photolyzed in benzene; lamps emitting at 350 nm were used in this photolysis. In each case solutions were bubbled with oxygen (or argon) before and during photolysis. Concentrations of photoinitiators were 5–6 mM for ketones, 50 mM for DCP, and 14 mM for AIBN and the concentrations of HALS were ca. 30 mM, unless specified.

The products of the photolyses were identified on the basis of the comparison of their GC retention times compared with the compounds of the known structure. Yields of products and conversions of photoinitiators were measured by gas chromatography employing a Hewlett Packard 5890 capillary GC with a 25-m Carbowax 20 M column; dibenzyl was used as an internal standard. The data on the yields of the products are based on the averaging of the data of 2–3 photolyses for each HALS or photoinitiator, and in each photolysis the yields are measured for several conversions of the used photoinitiator or HALS.

ESR spectra were recorded on a Bruker ESP 300 spectrometer with ESP 1600 data system and ER 4111 VT temperature controller. Photolyses of DTBK in toluene were carried out at different temperatures directly in the ESR cavity with constant bubbling of oxygen. Emission from a Xe–Hg 1-kW lamp (Hanovia), passed through an aqueous filter, was used for the photolyses.

3. Results

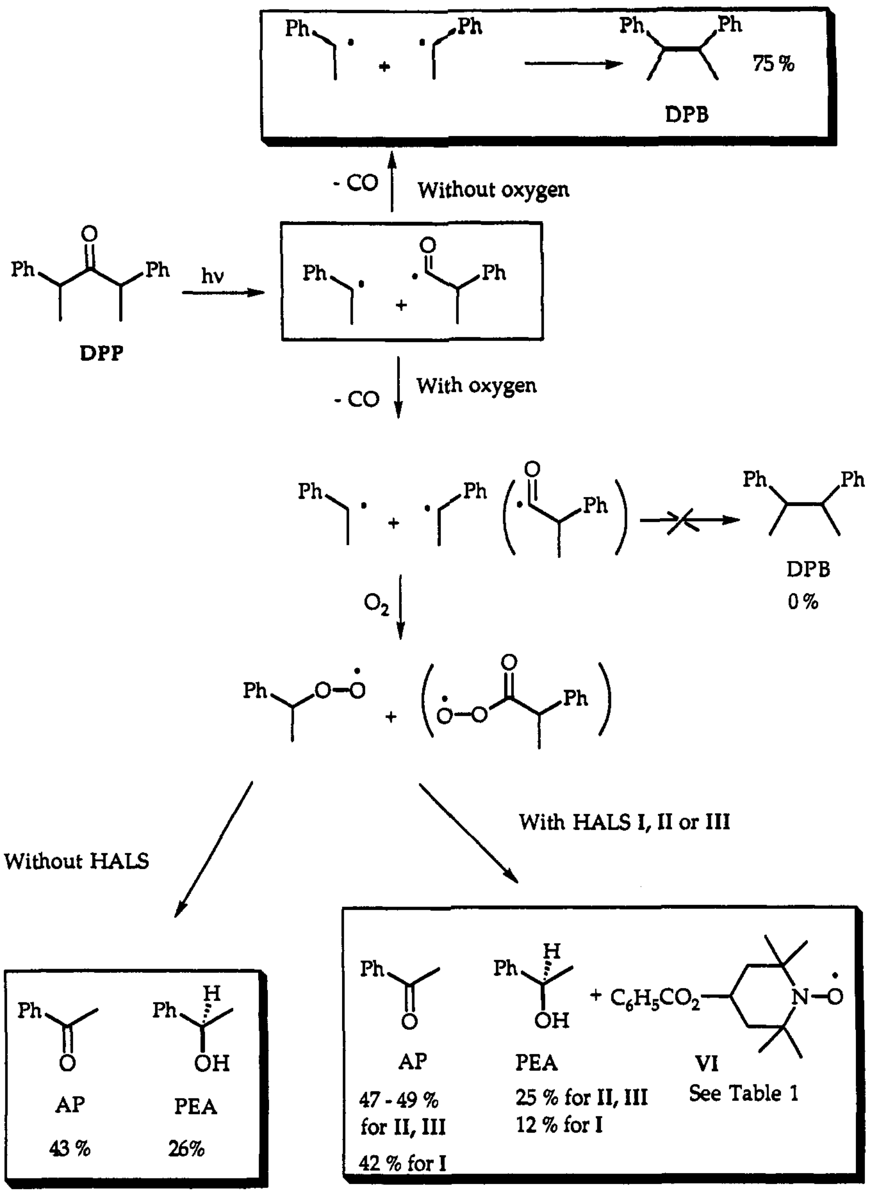
3.1. Photolysis of Ketones in the Presence of HALS; Product Analysis.

Peroxy radicals of different structures were generated by the photolysis of ketones (photoinitiators) DPP and BHCH in oxygen-saturated hexane. HALS compounds used in these experiments were the amine **I** and the amino ethers **II–V**. For both DPP and BHCH, control photolyses were carried out in deoxygenated solutions. Control photolyses of photoinitiators in oxygen-saturated solutions without HALS were used to show that in the presence of oxygen all primary carbon-centered radicals formed in the photolyses are converted into peroxy radicals. Photolyses of photoinitiators with HALS in the absence of oxygen allowed the evaluation of the possible interaction of primary carbon-centered radicals formed in the photolyses with HALS, and it was found (*vide infra*) that the carbon radicals generated from photolysis of DPP and BHCH do not react with the amino ethers **II** and **III**.

Photolysis of DPP and BHCH in solution proceeds through primary photochemical α-cleavage (the cleavage of the C–C bond at the carbonyl group).[10,11] DPP and BHCH were selected as photoinitiators because they undergo exclusive α-cleavage and their excited triplet states are so short-lived (1 ns or less) that they are not quenched by oxygen. Schemes 1 and 2 summarize the mechanisms of the photolysis of DPP and BHCH in solution.

3.1.1. Photolysis of DPP. Photolysis of DPP (2,4-diphenylpentan-3-one) yields the *sec*-phenethyl/*sec*-phenethylacyl radical pair as the primary intermediate from

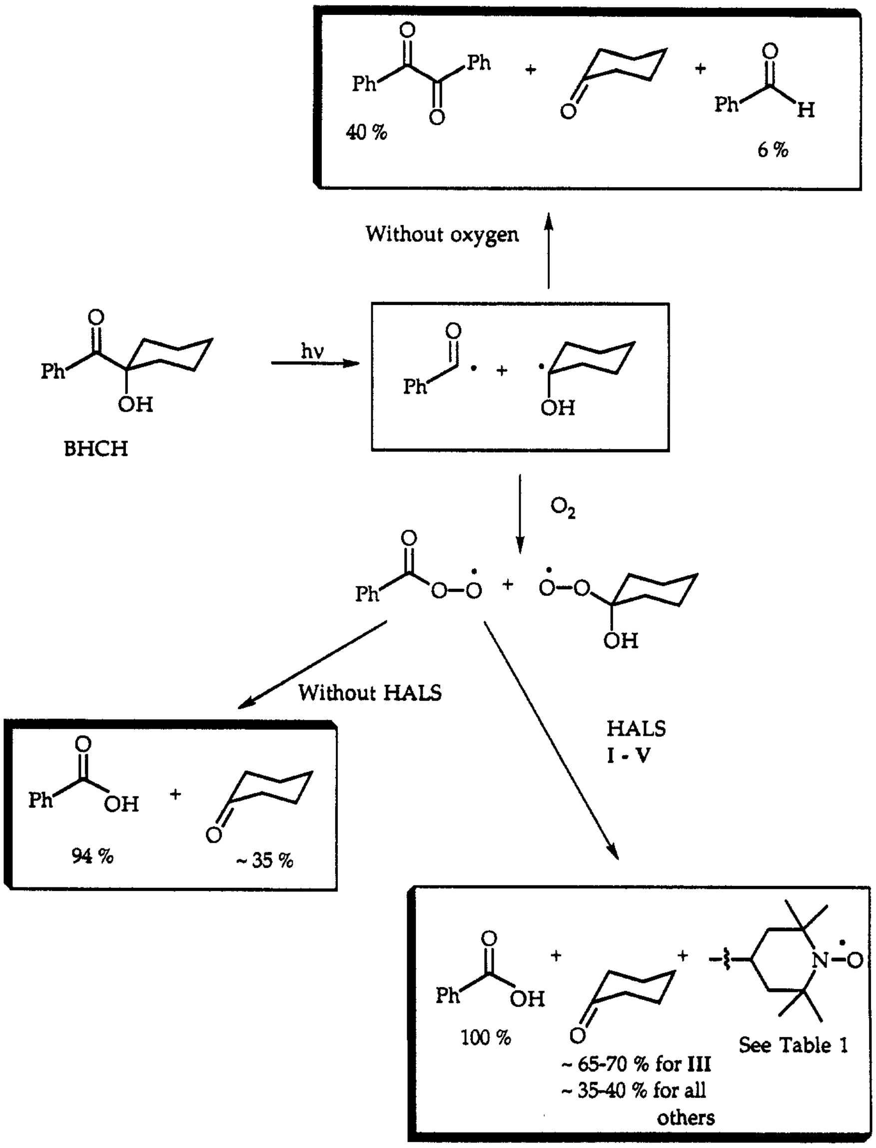
Scheme 1



α-cleavage of the excited triplet molecule.[10] The main product of the photolysis of DPP in deoxygenated solution is 2,3-diphenylbutane (DPB). The chemical yield of DPB in the photolysis of DPP in hexane without oxygen was about 75% (see Scheme 1). In the presence of oxygen, no DPB was formed. On the basis of the following kinetic considerations it may be safely assumed that the absence of DPB is due to the fact that all of the *sec*-phenethyl radicals were scavenged by oxygen and converted into alkylperoxy radicals, R_1OO (R_1 = *sec*-phenethyl radical). The quantum yields of disappearance of DPP in photolysis with and without oxygen are the same based on the rate of photolysis under low conversion, i.e., oxygen has no effect on the primary α-cleavage which leads to products and does not quench the triplet excited state of DPP, so that the absence of DPB is not simply the result of the quenching of the triplet of the photoinitiator. It has been reported[12] that *sec*-phenethylacyl radicals have a very short lifetime at room temperature due to decarbonylation (k_{-CO} = 4.9×10^7 M^{-1} s^{-1}, τ = 20 ns). By taking into account the solubility of oxygen in hexane near ambient temperatures (14.8 mM)[13] and the expected rate constant for the reaction of *sec*-phenethylacyl radical with oxygen ($k_{O_2} \approx 2 \times 10^9$ M^{-1} s^{-1}),[14] the lifetime of *sec*-phenethylacyl radicals *versus* the addition of oxygen is expected to be about 30–35 ns. This estimation allows the conclusion that, under oxygen, alkylperoxy radicals R_1OO (R_1 = *sec*-phenethyl radical) have a higher probability of formation and that the relative formation of acylperoxy radicals ($R_1C(O)OO$) is probably small because of the rapid unimolecular decarbonylation of the acyl radicals. However, acylperoxy radicals should be definitely formed in some amount (ca. 20–25%, on the basis of the rate constants and solubility of oxygen mentioned above and 1:1 primary ratio *sec*-phenethyl to *sec*-phenethylacyl radicals).

The main products which are formed during the photolysis of DPP in an oxygen-saturated hexane solution are acetophenone (AP) and *sec*-phenethyl alcohol (PEA) (see Scheme 1). They are the products of the termination of *sec*-phenethylperoxy radicals. The total chemical yield of these products is about 65–70% based on consumed DPP, and the ratio AP/PEA ≈ 1.6. The high chemical yield of AP and PEA, the termination products of *sec*-phenethylperoxy radicals, and the absence of other products in substantial amounts (in particular, hexanones or hexanols) demonstrates that the reaction of primary peroxy radicals with the solvent (hexane) is not important under our conditions. We may assume that the remaining 30–35% of unidentified products are formed through peroxy radicals formed from *sec*-phenethylacyl. The latter estimation of the yield of acylperoxy radicals is slightly higher than one based on the rate constants presented above (20–

Scheme 2



25%), although the agreement is quite good, taking into account that the values of the rate constants may have a 20–40% error and mass balance during photolyses almost never is 100%.

Photolysis of DPP in the presence of HALS I–III in *deoxygenated* solution proceeded in the same manner as that for photolysis of DPP without HALS. No new products were formed, the rate of decomposition of the starting material was the same, and the yield of DPB was similar to that without HALS for II and III. However, the yield of DPB was reduced about 55–60% when DPP was photolyzed in the presence of I. Evidently, hydrogen abstraction (NH) from I by *sec*-phenethyl radicals occurs to a certain extent. Therefore, we may conclude that there were no reactions of *sec*-phenethyl radicals with amino ethers II and III, and relatively slow reaction with amine I, which competes with recombination of *sec*-phenethyl radicals. The important result is that the amino ethers do not react significantly with the alkyl radicals generated, so that the interaction of alkyl radicals with HALS can be ruled out in the mechanisms involving the formation of nitroxides.

Photolysis of DPP in *oxygen-saturated* hexane with I–III showed the same rate of disappearance of DPP with or without HALS. However, in each case a new product, the nitroxide VI, was formed. The chemical yield of VI (the molar ratio of nitroxide formed in the photolysis to starting ketone decomposed) for each HALS was not changed during the photolysis at least up to 40–50% conversion. This confirms the fact that nitroxides are not very active as chemical interceptors of peroxy radicals.

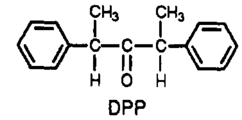
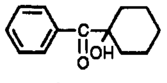
The chemical yields of nitroxide VI formed during the photolysis of DPP in oxygen-saturated hexane with different HALS are presented in Table 1. Since all the conditions in the photolysis of DPP with the different HALS were similar, we consider the data on nitroxide yields as representative of the relative activity of the HALS toward *sec*-phenethylperoxy radicals and/or (*sec*-phenethylacyl)peroxy radicals.

A control experiment, the photolysis of an oxygen-saturated hexane solution of III without DPP under similar conditions did not yield any nitroxide VI.

The product composition from the photolysis of DPP under oxygen with different HALS was generally similar, but photolysis with III gave cyclohexanone with a yield of about 30–40% as an additional product (however, cyclohexanol formation was not detected). Under photolysis with I, the ratio of AP/PEA was 3.6 in comparison to 1.6 without HALS and 1.9 with II or III.

3.1.2. Photolysis of BHCH in the Presence of HALS. Photolysis of BHCH in deoxygenated solution yields a benzoyl and hydroxycyclohexyl radical pair[11] which recombine and/or disproportionate giving benzil (40%), benzaldehyde (6%), and cyclohexanone (see Scheme 2).

Table 1. Chemical Yields of Nitroxide VI (%) under Photolysis of Ketones with HALS (30 mM) in Oxygen-Saturated Hexane[a]

photoinitiator	I >N—H	II >N—OCH$_3$	III >N—OC$_6$H$_{11}$	IV >N—OC$_8$H$_{17}$	V >N—OC(CH$_3$)$_3$
 DPP	23	15	40		
 BHCH	91	50	64	60	9

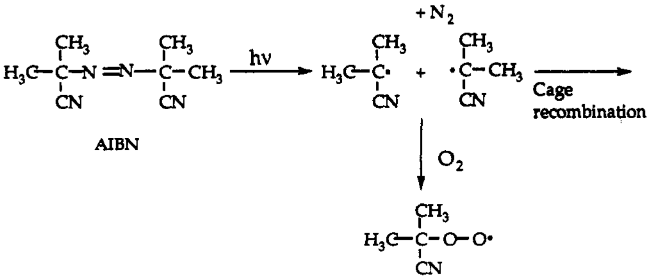
[a] The chemical yield is calculated as a ratio (in percent) of moles of nitroxide formed to moles of ketone disappeared.

Under photolysis with oxygen, benzoic acid was formed in 94% yield, showing that essentially all benzoyl radicals were converted into benzoylperoxy radicals. The presence of oxygen increased the yield of cyclohexanone from hydroxycyclohexyl radicals and no other new products were formed in significant amounts relative to the deoxygenated solution.

The addition of amino ether III in the absence of oxygen did not give any new products in the photolysis of BHCH in hexane, nor did addition of III cause changes in the chemical yields of the products produced from the photolysis of DPP.

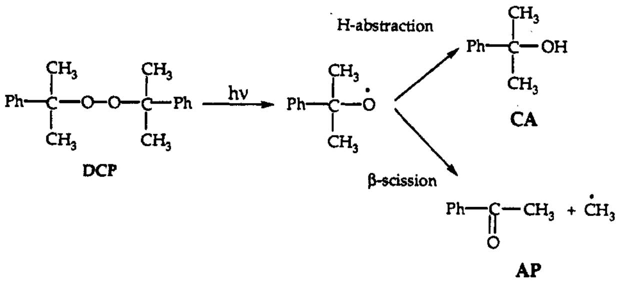
Photolysis of BHCH with HALS I–V in hexane saturated with oxygen gave nitroxide VI with higher yields than in the case of DPP (see Table 1). Only in the presence of V did the photolysis of BHCH in hexane saturated with oxygen generate a small yield of nitroxide (about 9%). Photolysis of BHCH with a low concentration of III (3.2 mM) gave almost the same (within the experimental error) high yield of VI (71% *versus* BHCH disappearance). In addition, under these conditions we were able to monitor the disappearance of III during the photolysis and to calculate that the efficiency of nitroxide VI formation from amino ether III was 96% (based on HALS), indicating very high efficiency of nitroxide formation.

3.2. Photolysis of AIBN with HALS. Photolysis of AIBN in deoxygenated solution is known to yield 2-cyanoisopropyl radicals.[15,16] As any unstable carbon-centered free radicals, 2-cyanoisopropyl radicals should react with oxygen to produce peroxy radicals with the rate of the order 10^9 M^{-1} s^{-1} [14] and the experimental observations support the observation that AIBN decomposition in solution in the presence of oxygen gives various oxygen-containing products.[15c,17,18] On the basis of these data we used the photolysis of AIBN in benzene in the presence of oxygen as a clean and unambiguous source of alkyl (2-cyanoisopropyl)peroxy radicals.



Photolysis of AIBN in oxygen-saturated benzene in the presence of III gave only a small amount of nitroxide (about 5% yield on the basis of AIBN decomposed).

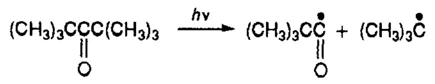
3.3. Photolysis of DCP in the Presence of HALS. Photolysis of dicumyl peroxide (DCP)[19,20] was employed as a source of alkoxy (cumyloxy) radicals.



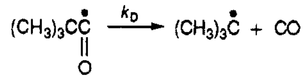
In heptane, due to the fast reaction of cumyloxy radicals with solvent, cumyl alcohol (CA) was the only detectable product. The addition of III to the system did not yield nitroxide or II (see below). In benzene, during DCP photolysis, CA and acetophenone (AP) are formed with competing rates (about 1:4). The addition of nitroxide VI to the DCP in benzene under photolysis in the absence of oxygen results in the formation of II, since nitroxide is an excellent scavenger of methyl radicals which are produced during β-scission of cumyloxy radicals. Therefore, the formation of nitroxide in the DCP photolysis in benzene with III in deoxygenated solution may be monitored by measuring the formation of II in the secondary reaction. The chemical yield of nitroxide in the reaction of cumyloxy radicals with III (30 mM) estimated in this manner is only about 1–2% on the basis of the decomposition of DCP.

3.4. ESR Studies of the Reaction of Peroxy Radicals with HALS. For steady-state ESR experiments peroxy radicals were generated by the photolysis of di-*tert*-butyl ketone (DTBK) in an oxygen-saturated toluene solution with constant bubbling of oxygen. DTBK was selected because under photolysis in oxygen it yields *tert*-butylperoxy radicals, which due to their relative stability, are very convenient to monitor by ESR.[21] The sequence of reactions which yields peroxy radicals during the photolysis of DTBK is shown in eqs 1–4.

The rate constants of the decarbonylation reaction of *tert*-butylacyl radicals have been measured previously[22] to be $k_D = 1.6 \times 10^3$ s^{-1} at −40 °C and $k_D = 1.2 \times 10^5$ s^{-1} near room temperature (25 °C). The solubility of oxygen in toluene is approximately the same as in benzene,[13] 9.2×10^{-3} M at 25 °C. The rate constant for the reaction of *tert*-butyl radicals with oxygen at room temperature has been measured to be diffusion controlled,[14] $k_1 = 4.9 \times 10^9$ M^{-1} s^{-1}. Therefore, the pseudo-first-order effective rate constant for the reaction of *tert*-butyl radicals with oxygen

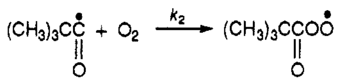


$$(CH_3)_3C\underset{\underset{O}{\|}}{C}C(CH_3)_3 \xrightarrow{h\nu} (CH_3)_3C\underset{\underset{O}{\|}}{\dot{C}} + (CH_3)_3\dot{C} \tag{1}$$



$$(CH_3)_3C\underset{\underset{O}{\|}}{\dot{C}} \xrightarrow{k_D} (CH_3)_3\dot{C} + CO \tag{2}$$

$$(CH_3)_3\dot{C} + O_2 \xrightarrow{k_1} (CH_3)_3CO\dot{O} \tag{3}$$



$$(CH_3)_3C\underset{\underset{O}{\|}}{\dot{C}} + O_2 \xrightarrow{k_2} (CH_3)_3C\underset{\underset{O}{\|}}{C}O\dot{O} \tag{4}$$

in toluene saturated with oxygen at room temperature is ca. $k_{eff} = 4.5 \times 10^7$ s^{-1}. Even if we assume that the rate constant for the reaction of *tert*-butylacyl (pivaloyl) radicals with oxygen, k_2, is several times less than that of *tert*-butyl radicals (the only rate constant of an acyl radical with oxygen, which to the best of our knowledge is available in the literature, is the rate constant of the reaction of *p*-chlorobenzoyl radical, $k_{O_2} = 2 \times 10^8$ M^{-1} s^{-1} [14b]), the estimation indicates pivaloyl radicals should react faster with oxygen than they eliminate carbon monoxide. This analysis leads to the conclusion that under experimental conditions at room temperature pivaloyl radicals are converted to the corresponding acylperoxy radicals, and the ratio of alkyl (*tert*-butyl) peroxy radicals to acylperoxy radicals formed during photolysis of DTBK in oxygen-saturated toluene is expected to be close to 1:1.

At lower temperatures the difference between the rates of decarbonylation and the addition of oxygen to pivaloyl radicals should probably be even larger, since the activation energy of diffusion (the addition of oxygen to nonstabilized carbon-centered radicals is close to diffusion control) is in the range of 5–6 kcal/mol which is less than the 9.3 kcal of decarbonylation.[22] In addition to this effect, the solubility of oxygen increases with decreasing temperature. Therefore, both *tert*-butylperoxy and (*tert*-butylacyl)-peroxy radicals are expected to be formed during the photolysis of DTBK in oxygen-saturated toluene. If the concentration ratio of the two peroxy radicals is close to 1:1 at room temperature, the ratio should not change substantially with change in temperature.

The photolysis of DTBK in toluene directly in an ESR cavity was employed to generate two types of peroxy radicals (*tert*-butyl and pivaloyl) and the ESR signal of peroxy radicals was monitored in neat solution along with the formation of nitroxide VI in the presence of amine I and amino ether III.

Figure 1 shows the spectra, monitored during the photolysis of 0.1 M DTBK (a) in oxygen-saturated toluene at -40 °C and (b) in oxygen-saturated toluene containing 0.03 M of I at -40 °C. The former spectrum contains the signal of the peroxy radical only and the latter spectrum is the superimposition of the characteristic nitroxide three-line spectrum with a smaller amount of the peroxy radical signal. The latter contributes mainly to the lowest field nitroxide peak, which is visually larger than the other two peaks. The photolyses of a DTBK solution with I at temperatures above -40 °C gave only nitroxide spectra without any indications of the peroxide. The intensity of the nitroxide ESR signal was not significantly changed by change in temperature.

In contrast to these results, the ESR spectrum obtained by photolysis of a DTBK solution with 0.03 M of III in oxygen-saturated toluene at -40 °C (Figure 2a) did not show any sign of nitroxide formation. However, under photolysis at -20 °C, the ESR spectrum of the DTBK solution with III showed the presence of nitroxide as a minor component, and under photolysis at 0 °C the nitroxide contribution to the spectrum was considerable (Figure 2b). At 20 °C, the contribution of peroxy radicals to the resulting spectra was minor, and intensive nitroxide spectra were observed (Figure 2c). Moreover, if the solutions photolyzed at low temperature were warmed up without further irradiation, intense ESR spectra of nitroxide were observed.

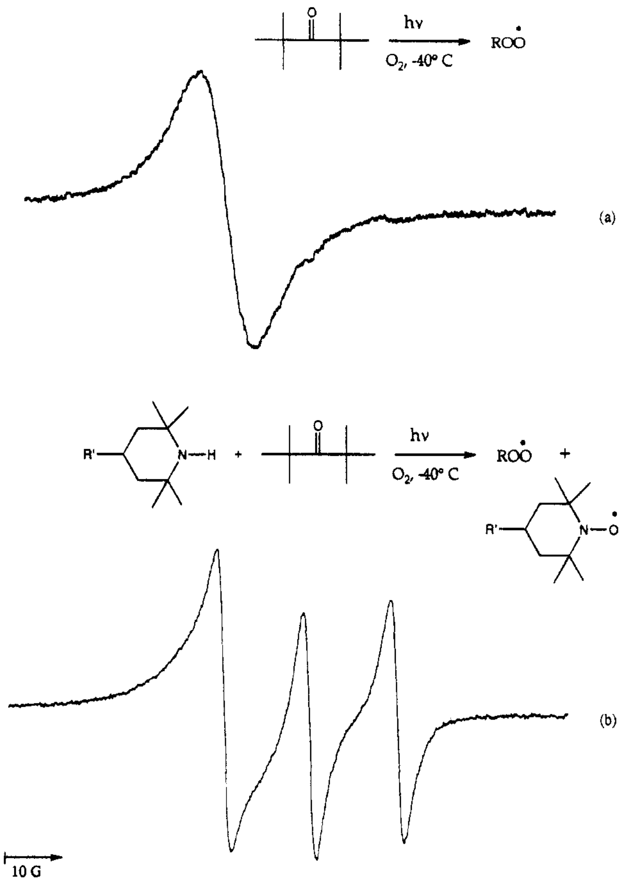


Figure 1. ESR spectra monitored during the photolysis of 0.1 M of DTBK in oxygen-saturated toluene (a), and during the photolysis of the same solution containing 0.03 M of amine **I** (b) at -40 °C.

Different effects of temperature were observed in the reactions of *tert*-butylperoxy radicals with amine I and amino ether III to form nitroxide VI. The reaction with I was only slightly temperature activated; the reaction with III was crucially dependent on the temperature. At -40 °C the reaction of peroxy radicals with III to form a nitroxide was very slow, but at room temperature it had about the same efficiency as the reaction with I (less efficient for peroxy radicals from BHCH and more for those from DPP; see the results of the yields of VI in Table 1). Therefore, we conclude that these two reactions might follow different mechanisms. The reaction of peroxy radicals with 2,2,6,6-tetramethylpiperidine and its derivatives as well as with other secondary aliphatic amines has been proposed[2,3,23] to follow the pathway which includes primary hydrogen abstraction with the formation of aminyl radical, which is converted to nitroxide in reaction with oxygen. The mechanism of the reaction of peroxy radicals with HALS amino ethers is therefore assumed to be different from that for amines and it is now considered in the discussion.

4. Discussion

4.1. The Nature of Oxidizing Species. Although the formation of a nitroxide in the peroxide-generating photolysis of DPP and BHCH in the oxygen-saturated

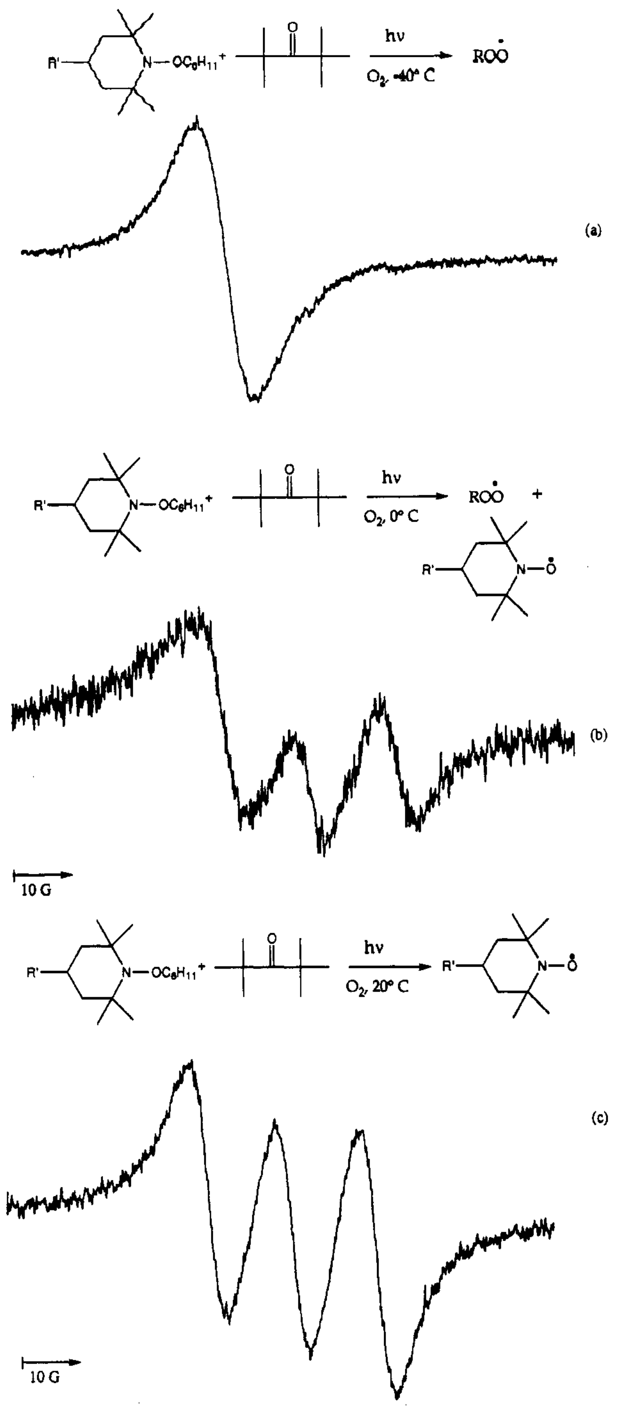


Figure 2. ESR spectra monitored during the photolyses of 0.1 M of DTBK and 0.03 M of III in oxygen-saturated toluene at -40 °C (a), at 0 °C (b), and at 20 °C (c).

solution in the presence of HALS amino ethers does not necessarily require that a nitroxide be formed in a direct reaction of peroxy radicals with an amino ether, we will show that this is probably the actual mechanism of nitroxide formation and that other possibly active species formed in the system are not able to produce nitroxide with high yield in the reaction with amino ethers. We will also show that acylperoxy radicals are much more effective than alkylperoxy radicals in forming nitroxide from amino ethers. Finally we will propose the mechanism of the reaction of peroxy radicals with amino ethers, involving primary electrophilic attack of a peroxy radical on the nitrogen atom of amino ether that both fits all experimental observations and possesses good theoretical support.

The photolysis of ketones, DPP, BHCH, and DTBK, in oxygen-saturated solution provides a clean and convenient method from producing alkyl- and acylperoxy radicals as shown in Schemes 1 and 2 and eqs 1–4. Since the rates of photolysis (disappearance) of DPP and BHCH are the same in the presence or absence of oxygen, we conclude that there was no significant oxygen quenching of the excited triplet states of ketones under the reaction conditions. Due to the relatively large solubility of oxygen in hexane (ca. 10^{-2} M) and to the high (close to diffusion control) rate constants for reactions of carbon-centered radicals with oxygen in solution, alkyl and acyl radicals are converted into peroxy radicals within a few tens of nanoseconds under the photolysis conditions. As evidence of the rapid formation of peroxy radicals, the photolysis of DPP under oxygen yielded no DPB (Scheme 1), the major product of the reaction of *sec*-phenethyl radicals. Thus, we conclude that the steady-state concentration of the *sec*-phenethyl radicals was very low due to efficient and rapid oxygen scavenging. The control photolyses of both DPP and BHCH in deoxygenated solution showed that alkyl and acyl radicals do not yield nitroxide in the reaction with amino ethers. Amino ethers were also found to be stable toward direct photolysis at 300 nm (both in the presence and absence of oxygen), employed in this investigation. Therefore, either peroxy radicals or the oxidizing products derived from them are the most likely candidates responsible for the nitroxide formation in the reaction with amino ethers.

The different yields of nitroxide **VI** produced may be due to variability in the concentrations of the effective oxidizing agents which are formed in the peroxy radicals' termination reactions which convert the HALS to **VI**. For example, eqs 5–7

$$2\mathrm{R{-}O_2} \rightleftharpoons \mathrm{R{-}O{-}O{-}O{-}O{-}R}\ (<-90\ ^\circ\mathrm{C}) \qquad (5)$$

$$\mathrm{R{-}O{-}O{-}O{-}O{-}R} \rightarrow \mathrm{R{-}\dot{O}} + \mathrm{O{=}O} + \mathrm{\dot{O}{-}R} \qquad (6)$$

$$\mathrm{R{-}\dot{O}_2} + \mathrm{\dot{O}{-}R} \rightleftharpoons \mathrm{R{-}O{-}O{-}O{-}R}\quad (-80\ ^\circ\mathrm{C} < t < -30\ ^\circ\mathrm{C}) \qquad (7)$$

summarize some of the important species that may be derived from peroxy radicals and may be involved in the oxidation. These species are termed oxidizing equivalents of the peroxy radical because they may behave kinetically in the same manner as peroxy radicals (if appropriate rapid equilibria exist) and may be the species that are involved in the initial oxidizing attack on a HALS molecule. It is well established[21,24] that peroxy radicals undergo second-order termination to form a tetroxide ($\mathrm{RO_4R}$), which may exist in an equilibrium (eq 5) with peroxy radicals at low (-90 °C) temperature. At higher temperatures the tetraoxide reacts irreversibly to form alkoxy radicals and molecular oxygen (eq 6) or to yield stable molecular products. At temperatures near -30 °C, the pool of alkoxy radicals from step 6 may combine with the peroxy radicals from step 5 to form a trioxide ($\mathrm{RO_3R}$), which, depending on conditions, may be in equilibrium with the pool of peroxy and alkoxy radicals. At temperatures about 0 °C and higher, trioxides irreversibly decompose to form molecular products.[24] Thus, it is chemically reasonable that a tetraoxide or trioxide could react with an amino ether to cause the formation of a nitroxide. In step 6, the product molecular oxygen may be produced in an excited state (singlet molecular oxygen), but we do not consider this species as an important oxidizing equivalent because of results in the literature which show that the maximum yield of singlet oxygen during termination of different peroxy radicals does not exceed 10–15%.[25]

With eqs 5–7 in mind, let us summarize the salient experimental observations concerning the reaction of amino ether **III** in the presence of peroxy radicals which any working mechanism must accommodate. At room temperature the yield of nitroxide **VI** in this reaction was relatively high (ca. 40–60%, see Table 1). An important observation is that at low temperature (−40 °C) no nitroxide was detected by ESR under the photolysis conditions (see Figure 2a). However, when the reaction mixture was warmed up to room temperature after the end of the reaction (complete disappeerence of peroxy radicals) at −40 °C, nitroxide radicals at modest concentration were detected by ESR. The amount of nitroxide monitored by ESR was increased with the increase in the temperature of the reaction from −40 °C to +20 °C. The yield of nitroxide in the reaction of peroxy radicals from DPP with **III** was almost twice as large at room temperature as those with **I**, but was also negligible at low (−40 °C) temperature.

These observations are consistent with the conclusion that the reactions of peroxy radicals with amino ethers at −40 °C proceeded through the formation of a transient species, which was both relatively stable and ESR silent, but which began to decompose with increasing temperature. A similar temperature effect of the rate of nitroxide formation during the photooxidation of isooctane (also a tertiary peroxy radical is formed) in the presence of a HALS amino ether was recently reported,[5] so that the observation is not unique to the systems investigated in this report.

On the basis of our ESR results, we propose that the ESR-silent oxidizing intermediate is relatively stable at −40 °C and is involved in our studies is di-*tert*-butyl trioxide and that its formation from peroxy radicals and alkoxy radicals[24] (eq 7) successfully competes with the reaction of peroxy radicals with HALS amino ethers at low temperatures. The possibility that the ESR-silent species is the tetroxide is ruled out by the known instability[21] of dialkyl tetraoxides at temperatures above −80 °C.

At low temperature (−40 °C) where trioxides are expected to be stable and their concentration is expected to be the highest no nitroxide is formed on the basis of ESR spectra. On the other hand, carrying out the reaction at 0 °C, a temperature at which a trioxide is considered to be unstable and therefore its concentration is lowest, the formation of nitroxide is clearly established by ESR (Figure 2b). On the basis of these arguments we rule out the possibility of the nitroxide formation in the reaction of HALS amino ethers with dialkyl trioxides. The alkoxy radicals generated in the photolysis of dicumyl peroxide give a very low yield of nitroxide in the reaction with HALS amino ethers. This experimental observation rules out alkoxy radicals, which may be formed during the decay of peroxy radicals, as a significant oxidizing equivalent in nitroxide formation from HALS amino ethers.

From these arguments, we consider working mechanisms including only peroxy radicals as the species which oxidizes amino ethers directly.

Now we will extend this conclusion and will show that only *acylperoxy* radicals give a high chemical yield of nitroxide in the reaction with HALS amines and amino ethers.

(1) The data in the Table 1 show that for amino ethers **II** and **III** and for amine **I**, for which the yield of nitroxide formation was measured for both DPP and BHCH photolysis, the yield of **VI** is higher for peroxy radicals from BHCH. Photolysis of BHCH in oxygen-saturated solution gives a theoretical 1:1 ratio of acyl- and alkylperoxy radicals. In the case of DPP photolysis, as has been discussed above, due to fast decarbonylation of *sec*-phenethylacyl radicals, only ca. 20–30% of all peroxy radicals generated are acylperoxy radicals. The higher yields of nitroxide **VI** from the photolysis of BHCH are consistent with a higher reactivity of acylperoxy radicals in the oxidation of HALS.

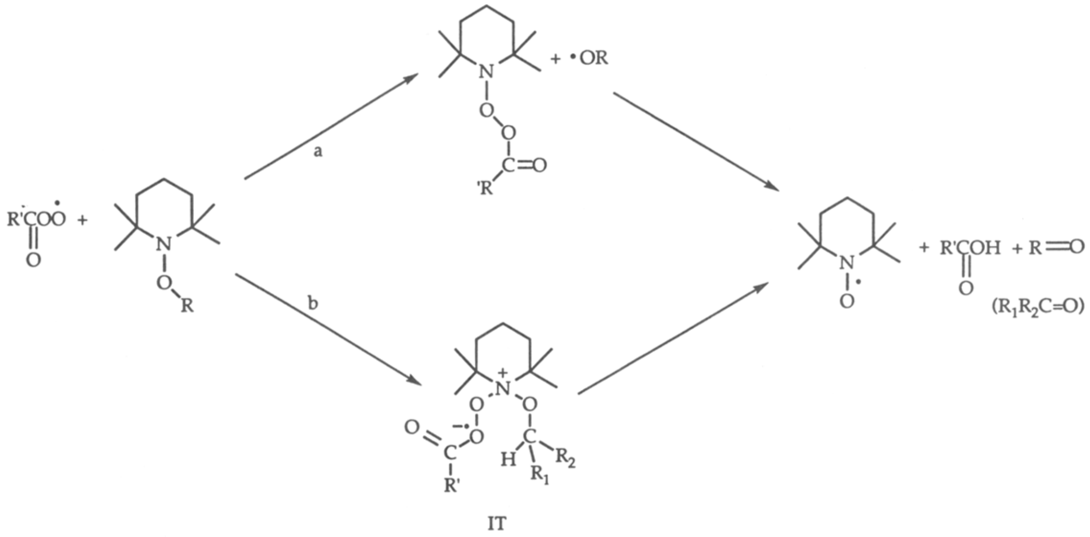
(2) The minor participation of *sec*-phenethyl peroxy radicals in the reaction with amino ethers **II** and **III** comes from the observation that the yields of AP and PEA in the reaction of photolysis of DPP in oxygen-saturated hexane with and without HALS (Scheme 1) are identical. Since both AP and PEA are the products of termination of *sec*-phenethylperoxy radicals, if these radicals participated in the oxidation of **II** or **III** to nitroxide, the yields of AP and PEA would be changed, which is not the case. Therefore, we may conclude that *sec*-phenethylperoxy radicals play at best a minor role in the reaction with amino ethers to yield nitroxide. It is not possible to make such a firm conclusion for the reaction of *sec*-phenethylperoxy radicals with amine **I**, since the decrease in the yield of PEA in the reaction of DPP photolysis with **I** is probably induced by aminyl radicals, which can abstract hydrogen from PEA, an excellent hydrogen donor.

(3) A final piece of evidence of the inefficiency of the reaction of alkyl peroxy radicals with amino ethers comes from an experiment of AIBN photolysis in oxygen-saturated solution with **III**. The latter photolysis clearly produces 2-cyanoisopropylperoxy radicals, yet the nitroxide **VI** is only formed in a yield of a few percent. From the above results, we assume that only acylperoxy radicals form nitroxide in the reaction with HALS aminoethers with a high yield.

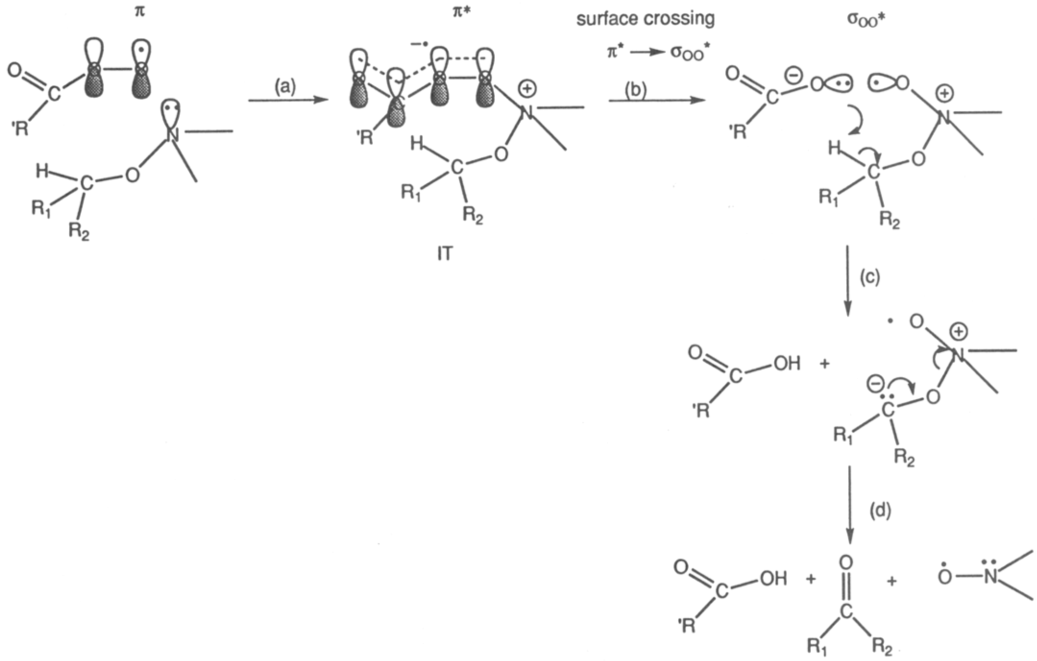
4.2. The Mechanism of the Reaction of Peroxy Radicals with HALS Amino Ethers To Produce Nitroxide. Under photolysis, the addition of HALS (**I**–**IV**) to oxygen-saturated hexane solutions of DPP and BHCH resulted in the formation of the same nitroxide **VI** with yields which were dependent on the structure of both the ketone and the HALS. These and other presented results, as it has been unambiguously shown in the previous part of the paper, are qualitatively consistent with a mechanism involving the direct interaction of peroxy radicals (and preferentially acylperoxy radicals) with amino ethers to yield nitroxide and the corresponding ketone (from the ether portion of the amino ether) and alcohol or acid (from the peroxy radicals). Recent quantum-chemical calculations support the energetic feasibility of radical attack of a peroxy radical on an amino ether nitrogen to yield nitroxide along with alcohol and ketone.[26] Acylperoxy radicals were found to have a remarkably lower barrier (ca. 8.5 kcal/mol) in the reaction pathway than alkylperoxy radicals.[26a] In addition to these theoretical considerations, a working mechanism of this reaction must be consistent with the labeling results from previous studies from one of our laboratories[3] which showed that the oxygen in the nitroxide formed comes from a peroxy radical and not from the amino ether. Therefore, an acceptable mechanism requires the formation of a *new* N–O bond where nitrogen is from the amino ether and oxygen is from the peroxy radical.

A recently proposed mechanism[3] of the reaction of peroxy radicals with amino ethers assumed radical attack of peroxy radicals on the nitrogen atom of amino ether, but it did not provide a detailed pathway for the formation of the products. In addition, the formation of free alkoxy anion is problematic in the nonpolar environment of a polymer or hydrocarbon solvent. Therefore, we reconsider the detailed mechanism of peroxy radicals–HALS amino ethers interaction, taking into account the new results obtained in this work.

Scheme 3



Scheme 4



We propose two mechanisms for the reaction of peroxy radicals with HALS amino ethers to produce the nitroxide. The first one is a direct, concerted electrophilic radical substitution[27] at the nitrogen atom of the amino ether (Scheme 3, route a). This reaction is postulated to yield amino peroxide NOOR′ as an intermediate. The formation of analogous amino peroxide intermediates, which decompose giving nitroxide with a relatively high yield, was assumed to be involved in the reactions of peroxy radicals with aromatic aminyl radicals.[28,29] The absence of an ESR signal of the alkoxy radical $R'O^\bullet$ resulting from the reaction is still consistent with this mechanism, because alkoxy radicals are known to be ESR silent as a result of fast spin relaxation.[30a,b] However, a concern about this proposed mechanism is that alkoxy radicals, which are highly reactive in hydrogen abstraction are formed, so that their formation might be expected to promote the degradation, rather than the stabilization of polymers. This objection can be overcome if it is proposed that the reactive alkoxy radicals which are formed in pathway a in Scheme 3 do not leave the primary cage but induce decomposition of the amino peroxide with the formation of nitroxide and other stable products. However, a possible objection to this postulate is that it is difficult to imagine why the reaction of alkoxy radical $RO^\bullet$ with NOOR′ yields R=O and R′OH so selectively.[3]

An alternative mechanism for the reaction of peroxy (acylperoxy) radicals with amino ethers is a full peroxy radical addition at the nitrogen center instead of radical substitution (pathway b in Scheme 3). In this mechanism the reaction of peroxy radicals with amino ethers proceeds through an intermediate (**IT**) with the subsequent breakage of the O–O bond and/or a concerted intramolecular hydrogen atom transfer to yield nitroxide and molecular products. The proposed mechanism is fully supported by our experimental results and by the relevant theoretical and experimental data in the literature.[31–33]

The primary step (Scheme 4, step a) of this mechanism, an electrophilic attack of a peroxy radical on the electron-rich nitrogen of an amino ether, may initially appear to be unusual, so we consider its plausibility in more detail. An analogous reaction to yield a pentavalent structure is well known for the addition of oxygen radicals at a phosphorus center.[33] However, since nitrogen does not have d orbitals, an odd ninth electron cannot be localized on the nitrogen atom of **IT**, but more probably in the peroxy O–O group and/or carbonyl group. From the view point of electron distribution, this process is similar to the reaction of free radical-induced decomposition of peroxides[31] and electron transfer-activated decomposition of acyl peroxides or peroxy esters followed by chemiluminescence.[34] Formally, the peroxide group in the latter reactions has a resonance formed with an odd electron delocalized over the peroxy O–O bond and conjugated carbonyl group[32,34] (in the case of acylperoxy radicals), which is similar to the assumed electron distribution in **IT**. Therefore, on the basis of these two precedents we propose that in the reaction of peroxy radicals with HALS amino ethers, an odd electron is delocalized over the O–O bond, and obviously, the additional conjugation with the carbonyl group in the original acylperoxy radical should decrease the resonance energy of the intermediate (or transitional state) **IT** formed in the initial step (Scheme 4, a) of the reaction. In the case of radical-induced decomposition of peroxides,[32] it is known that in acyl peroxides, and particularly in dibenzoyl peroxide, the singly occupied molecular orbital (MO) of the attacking radical and the 2pσ^* antibonding orbital of the peroxy oxygen atoms interact in a way that electron transfer from the radical to the peroxide is important in the transition state, preceding O–O bond cleavage and decreasing the activation energy of this process.[32] We propose that **IT** also cleaves by a similar mechanism which possesses low activation energy. The low activation energy is the result of a surface crossing of the π^* orbital of the delocalized electron in **IT** and low-energy σ^* dissociating orbital of O–O bond during the reaction (step b). The subsequent (or alternatively concerted) proton transfer to form an acid (step c) through a six-membered transitional state and the scission of the counter species to yield ketone and nitroxide (step d) are well precedented within the framework of conventional organic reaction mechanisms.

An important point in the proposed mechanism of peroxy radicals–amino ethers reaction is the role of the α-hydrogen atom of amino ethers in the efficiency of nitroxide production. The formation of a ketone and an acid in addition to nitroxide in this reaction requires "intramolecular" proton transfer at some point during the reaction pathway. If this hydrogen atom is an α-hydrogen of amino ether, the proton transfer can readily proceed through a favorable six-membered transition state (steps b and c in Scheme 4) and is expected to proceed faster than, say, five- or seven-membered transition states. The six-membered transitional state, which includes α-hydrogen atom transfer has been already proposed as a possible mechanism in the reactions of peroxy radicals with HALS amino ethers.[35] Our experimental results support this idea; HALS amino ether **V** (*tert*-butyl) which does not possess an α-hydrogen gives only about 9% yield of nitroxide in the reaction with peroxy radicals from BHCH photolysis *versus* 50–64% yield for amino ethers where α-hydrogen is available (see Table 1).

The different yields of nitroxide in the reactions of peroxy radicals, formed in the photolyses of DPP and BHCH, with HALS are in line with the proposed mechanism. Since the chemical yields of nitroxide in the reactions of HALS with peroxy radicals were calculated on the basis of the amount of ketone which disappeared and hence on the amounts of peroxy radicals formed, the amount of nitroxide formed in the reactions of the same peroxy radical with different HALS as well as the same HALS with different peroxy radicals will depend on the rates of competing reactions. For example, the increase in the chemical yields of nitroxide in the reactions of **III** with peroxy radicals from ketones is in the order BHCH > DPP (Table 1) that can be rationalized by the larger amount of acylperoxy radicals produced during photolysis of BHCH. Since both ketones give two peroxy radicals as a result of α-cleavage and radical reaction with oxygen, the maximum chemical yield of nitroxide in the reaction with HALS may be 200% on the basis of ketone disappearance. In the case of BHCH half of all peroxy radicals formed are acyl (benzoyl) peroxy radicals so that the percentage of the nitroxide yield provides information on the relative efficiency of nitroxide formation *versus* acylperoxy radicals disappearance. In the photolysis of DPP, where acylperoxy radicals are formed in low yield due to fast decarbonylation, the yields of nitroxide are smaller (see Table 1). In fact, a major part of nitroxide formation in the reaction of peroxy radicals from DPP with HALS might be ascribed to the reaction of acylperoxy radicals with HALS. The similar chemical yield of AP and PEA (the products of termination of *sec*-phenethylperoxy radicals) in the photolysis of DPP with **II** and **III** and without HALS in oxygen-saturated solution supports this hypothesis.

A factor which might explain the increase in the reactivity of acyl peroxy radicals with HALS is the increase of relative electron-accepting ability of the acylperoxy radicals *versus* alkylperoxy radicals. It is known that the electron-accepting substituents increase the spin density on the terminal oxygen of peroxy radicals,[36] making them more active in radical reactions. Since the first step in the proposed mechanism (Scheme 4, step a) is an electrophilic attack of a peroxy radical on nitrogen, the rate of this reaction of acylperoxy radicals should be faster than with alkylperoxy radicals. This feature is probably coupled with the facilitation of cleavage of the O–O bond as the N–O bond is formed due to population of the σ_{OO}^* orbital.

The reaction of *tert*-butylperoxy and (*tert*-butylacyl)peroxy radicals with amine **I** in oxygen-saturated solution to form nitroxide was found in this work to be much less temperature dependent than the reaction with amino ether **III**. Thus, **I** may follow a different mechanism which does not include the formation of the transient similar to **IT**, or if an intermediate related to **IT** is formed from **I** (**IT–I**), it may possess pathways for decomposition unavailable to the intermediates formed from amino ethers. One obvious possibility for a unique mechanism would be an initial hydrogen (N–H) atom abstraction by peroxy radicals. The kinetics and mechanism of hydrogen abstraction of peroxy radicals were studied in detail for different aromatic amines.[37] This reaction was found to have a very low activation energy, E_A = 1–5 kcal/mol and a large deuterium isotope effect, which were attributed to the formation of hydrogen-bonded peroxy radical–aromatic amine complex followed by the transfer of a hydrogen atom within the complex.[37a] The small temperature dependence of the efficiency of nitroxide formation in the reaction of peroxy radicals with **I** is thus consistent with the mechanism of this reaction including hydrogen atom abstraction to form an aminyl radical of **I** at a primary stage.[2,3,23] This aminyl radical should be very reactive with oxygen to yield an amino peroxide at an initial stage and nitroxide as a final product.[9,38]

Although a hydrogen abstraction mechanism is possible, we cannot exclude a mechanism involving the reaction of peroxy radicals with amines which does not include hydrogen abstraction to form aminyl radical and hydroperoxide. For example, one can imagine a mechanism of this reaction for acylperoxy radicals with **I** which in its primary step is similar to the mechanism for amino ethers (Scheme 4). The transition state or intermediate **IT–I** can then yield nitroxide and acid through O–O cleavage and proton transfer to the carbonyl oxygen through a six-membered transition state. A detailed investigation of this reaction mechanism will be the subject of future work.

5. Conclusions

Reactions of photochemically generated peroxy radicals of different structure with HALS amines (in the presence of oxygen) and amino ethers in solution at room temperature give nitroxides with significant yields. The chemical yields of nitroxide in these reactions are dependent both on the HALS and peroxy radicals' structures. It is concluded that for acylperoxy radicals the yields of nitroxide were found to be much higher than for alkylperoxy radicals. A mechanism of the reaction of acylperoxy radicals with HALS amino ethers to yield nitroxide along with ketones and acids is proposed.

Finally, we would like to mention that there is one more type reaction which can take place in the investigated systems and which should not be completely excluded from the consideration. If one assumes that the rate of hydrogen abstraction by acylperoxy radicals (from some unspecified sources) is fast enough to compete with the reaction of acylperoxy radicals with HALS amino ethers (and amines) so that substantial amount of peracids are formed, peracids formed in high concentration may oxidize HALS to form nitroxides. As a result of a reviewer's comment, this possibility was checked by reacting a prototypical peracid, 3-chloroperbenzoic acid, with **III** in hexane in a control experiment. Indeed, nitroxide is formed, but at a substantially slower rate (a few orders of magnitude slower) experimentally observed during photoinitiators photolysis in the presence of HALS. Therefore, even if peracids are formed with high yield from acyl peroxy radicals (no reliable data on the rate constants of acylperoxy radicals hydrogen abstraction is available to the best of our knowledge, and there is no indication that this reaction should be substantially faster than that of alkyl peroxy radicals[39]), their reaction with HALS amino ethers to form nitroxide is much slower, than observed during photolysis of employed photoinitiators. As a result of this discussion we disregard a reaction of peracids with HALS a major contribution to nitroxide formation.

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