J. Phys. Chem. A **1998,** *102,* 1457−1464

One-Electron Oxidation of Sterically Hindered Amines to Nitroxyl Radicals: Intermediate Amine Radical Cations, Aminyl, α-Aminoalkyl, and Aminylperoxyl Radicals

O. Brede,* D. Beckert, C. Windolph, and H. A. Göttinger

*University of Leipzig, Interdisciplinary Group for Time-Resolved Spectroscopy, Permoserstrasse 15,
D-04303 Leipzig, Germany*

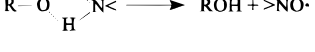
Received: November 5, 1997; In Final Form: December 26, 1997

Sterically hindered amines (2,2,6,6-tetramethyl-substituted piperidines) are easily oxidized (i) by electron transfer to parent cations in *n*-butyl chloride solution, (ii) by the sulfate radical anion in aqueous solution, and (iii) by sensitized electron transfer to carbonyl triplets. In nonpolar surroundings in the nanosecond time range, the radical cations of the tertiary piperidines have been directly observed by optical spectroscopy to exhibit absorption maxima below $\lambda = 300$ nm and around 550 nm. Subsequently, they deprotonate to α-alkylamine radicals, which are also the first observable products of oxidation with sulfate radical anions in water. In the case of secondary piperidines, the amine radical cations deprotonate to aminyl radicals in times < 10 ns. The triplet-sensitized electron transfer to the benzophenone as well as cyclohexanone triplet results in amine-derived and ketyl-type radicals formed at a nearly diffusion-controlled rate, which suggests an electron- and subsequent proton-transfer mechanism. In the presence of oxygen, the amine-derived radicals are oxidized to nitroxyl radicals by different pathways for secondary and tertiary piperidines. For the reaction of the nitroxyl radicals with other radicals, rate constants are found to be quite similar (about 5×10^8 M^{-1} s^{-1}) for several alkyl radicals and for the *tert*-butyloxyl radical and less than 10^5 M^{-1} s^{-1} for alkylperoxyl radicals. Because of the minor importance of radical reactions with the sterically hindered amines (HALS), the antioxidant effect of these compounds ought to be explained by oxidation, primarily via cationic and subsequently radical intermediates to the persistent nitroxyl radicals, which scavenge other radicals very efficiently.

Introduction

Although sterically hindered amines have long been used as stabilizers mainly against the light-induced degradation of polyolefins, the detailed mechanism of their action is still under discussion.[1] In a review of the mechanistic effects of photostabilization, Chirinos[2] emphasized the central role of alkylperoxyl radicals and alkylhydroperoxides within the process of the photooxidation of polymers. Hence in accordance with the classical philosophy of stabilization, the termination of the oxidation chain is explained to proceed by the deactivation of the alkylperoxyl radicals under amine radical formation (1) or by direct nitroxyl radical formation in a synchronous mechanism (2), as proposed by Geuskens[3] on the basis of a steady-state kinetic study.

$$\mathrm{ROO^{\bullet} + {>}NH \rightarrow [RO_2^{\,-} + {>}NH^{\bullet +}] \rightarrow RO_2H + {>}N^{\bullet}} \qquad (1)$$



$$\mathrm{R{-}O\overset{O^{\bullet}}{\cdots}\underset{H}{\cdots}N{<} \longrightarrow ROH + {>}NO^{\bullet}} \qquad (2)$$

Excited singlets act as quenchers without chemical consequence,[4] whereas in the case of triplet quenching radical products have been observed, which indicate electron transfer followed by proton transfer within the ion pair, or a hydrogen abstraction reaction[5,6] (eq 3).

$$\mathrm{A^{T1} + {>}NH \rightarrow [A^{\bullet -}\cdots{>}NH^{\bullet +}] \rightarrow AH^{\bullet} + {>}N^{\bullet}} \qquad (3)$$

Steady-state aging experiments with polyolefin matrixes containing HALS compounds resulted in complicated considerations concerning the antioxidant and photostabilizing effect of the sterically hindered amines that included the quenching of excited polymer−oxygen complexes.[7]

None of these indications gave a detailed picture of the stabilizing effect of HALS, and the following questions remained: Are the HALS themselves the stabilizers, and if so, what is the effective mechanism? Or do the HALS generate any products that are the species interrupting the oxidative degradation chain of the organic material?

The chief experimental problem is the difficulty of clearly detecting and identifying the radical intermediates. Most of the stationary experiments are based on the EPR spectroscopical observation of the stable nitroxyl radicals, which are involved in the HALS action mechanism, more or less as the final products of amine oxidation.[3]

To overcome the particular problems given in polyolefin systems such as no uniform molecular weight, high viscosity, and a multiphase system due to the semicrystallinity, time-resolved experiments on the HALS oxidation have been performed with low-molecular (liquid) systems.

Hence, triplet sensitized electron transfer (eq 3) enabled the observation of the acceptor radicals AH$^{\bullet}$ with optical spectroscopy,[8] whereas AH$^{\bullet}$ and >N$^{\bullet}$ have been detected by electron spin resonance spectroscopy.[5,9] Furthermore, amine radical cations have been detected in low-temperature and matrix isolation experiments.[8,10−12] Our own pulse radiolysis experiments on electron transfer from sterically hindered amines to

---

* Corresponding author.

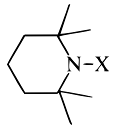
S1089-5639(98)00089-9 CCC: $15.00

solvent parent ions resulted in the case of secondary HALS in the optical detection of the corresponding amine radical cations.[6,8]

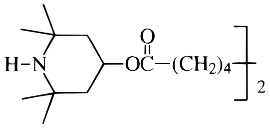
The aim of this paper is to give a detailed picture of the transient reactions and antioxidant action mechanism of sterically hindered amines. For this purpose we examined polar and nonpolar liquid and glassy model systems with stationary and pulsed radiolysis and laser flash photolysis combined with detection by both optical and electron paramagnetic spectroscopy.

Experimental Section

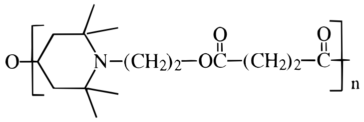
Chemicals. The following sterically hindered amines were used for our investigations:



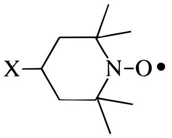
X = H, **1**
CH_3, **2**
OCH_3 **3**



4



5



X = H **6•**
OH **7•**

2,2,6,6-Tetramethylpiperidine (**1**), 1,2,2,6,6-pentamethylpiperidine (**2**), *N*-methoxy-2,2,6,6-tetramethylpiperidine (**3**), and the industrially used HALS compounds bis(2,2,6,6-tetramethyl-4-piperidinyl)sebaceate, Tinuvin 770 (**4**), and an oligomeric ester of butandioic acid with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol, Tinuvin 622 (**5**), were supplied by Ciba-Geigy. The piperidines were of analytical grade and in some cases purified by distillation in the presence of citric acid. 2,2,6,6-Tetramethylpiperidyl TEMPO (**6•**), and 2,2,6,6-tetramethyl-4-hydroxy-piperidyl radical, HO-TEMPO (**7•**), were obtained from Aldrich. *n*-Butyl chloride (spectroscopical grade, Merck) was dried by chromatography on A4 molecular sieves and then distilled under nitrogen flux. Cyclohexane (spectroscopical grade, Merck) and *n*-hexadecane (Erckner) were purified by treatment with oleum, washing with water, drying on an A4 molecular sieve, and distillation. Benzophenone, cyclohexanone, and potassium peroxidisulfate were used in commercial quality (p.a., Aldrich).

Pulse Radiolysis. Experiments were performed with a pulse transformer type accelerator ELIT (Institute of Nuclear Physics Novosibirsk, Russia) delivering 1-MeV, 16-ns electron pulses with a dose between 100 and 200 Gy. The optical detection system consisted of a pulsed 900-W xenon lamp (XBO 900, Osram), a Spectra Pro-500 monochromator (Acton Research Corp.), an 1P28 (RCA) photomultiplier, and a TDS 640 (500-MHz) Tektronics digitizing oscilloscope.

Laser Photolysis. Experiments were carried out with a perpendicular probe excitation arrangement. The solutions were photolyzed in a quartz cell connected to a flow system using the fourth (266-nm) or third (355-nm) harmonic of a Quanta Ray GCR-11 Nd^{3+}:YAG laser (Spectra Physics Inc.). Pulses 3 ns in length (fwhm) had an energy of 10−30 mJ. Optical detection was performed with equipment similar to that described for pulse radiolysis.

Steady-State Radiolysis Experiments. Solutions of the HALS compounds in the alkanes in the presence or absence of ketones and with well-defined oxygen concentration were prepared by the freeze−pump−thaw technique, gas introduction, and sealing. Irradiation was performed at room temperature in a ^{60}Co γ-ray source at doses up to 2 kGy. The nitroxyl yield of the samples was then analyzed by electron spin resonance spectroscopy.

Results and Discussion

To analyze the mechanism of the actual HALS antioxidant action, we studied those elementary reactions in detail that could be involved either in the radical reaction channel, the excited-state pathway, or the one-electron oxidation (ionization).

Radical Reactions. Pulse radiolysis enables the generation of different types of solvent radicals which could be considered as reaction partners of HALS. Hence, we studied the reactivity of the two basic HALS compounds **1** and **2** to OH, $c\text{-}C_6H_{11}^\bullet$, $c\text{-}C_6H_{11}OO^\bullet$, $^\bullet CH_2OH$, and other alkyl and alkylperoxyl radicals. As more or less expected, only in the case of OH did we observe a marked effect due to HALS radical formation (absorption tail in the UV) as formulated in eqs 4 and 5.

$$\mathbf{1} + OH \rightarrow {>}N^\bullet + H_2O \qquad k_4 = 5 \times 10^9\ M^{-1}\ s^{-1} \qquad (4)$$

$$\mathbf{2} + OH \rightarrow {>}N{-}CH_2^\bullet + H_2O \qquad k_5 = 4 \times 10^9\ M^{-1}\ s^{-1} \qquad (5)$$

In neither the pulse radiolysis of cyclohexyl chloride nor cyclohexane and methanol did we find any indication of the above-mentioned reactions of the various alkyl and alkylperoxyl radicals with HALS. Hence, only upper limits of the rate constants could be estimated, which differ owing to the different lifetime of the solvent radicals.

$$\mathbf{1}, \mathbf{2} + R^\bullet \rightarrow \text{products} \qquad k_6 < 10^6\ M^{-1}\ s^{-1} \qquad (6)$$

$$\mathbf{1}, \mathbf{2} + ROO^\bullet \rightarrow \text{products} \qquad k_7 < 10^4\ M^{-1}\ s^{-1} \qquad (7)$$

Summarizing these observations, it seems very unlikely that reactions of solvent or matrix radicals play an important role in the antioxidant action mechanism of sterically hindered amines during oxidative degradation.

Carbonyl Compounds as Sensitizers for HALS Reactions: Stationary Radiolysis. As reported in ref 3, γ-radiolysis of oxic solutions of some HALS compounds in cyclohexane yielded considerable amounts of nitroxyl radicals. If not of radical origin according to eq 2, the nitroxyls could also be formed by a much more complex mechanism involving the oxidation of cyclohexane to cyclohexanone,[15] followed by carbonyl triplet sensitized electron transfer with HALS and subsequent radical reactions as illustrated by the following

TABLE 1: Normalized Yields of Aminoxyl Radicals Determined by EPR Spectroscopy of γ-Irradiated (2-kGy) Solutions of 1 mM of the HALS Compound 5 in Cyclohexane under Various Oxygen Concentrations and the Addition of Ketones (0.1 M)

	normalized yield of $>NO^{\bullet}$		
sensitizer (0.1 M)	deaerated	air-saturated	O_2-saturated
without ketone	0.03	1.35	1.00
cyclohexanone	0.07	3.40	2.00
benzophenone	0.03	2.90	0.82

reaction sequence (eq 8).

$$c\text{-}C_6H_{12} \xrightarrow{\gamma} c\text{-}C_6H_{11}^{\bullet} \xrightarrow{+O_2} c\text{-}C_6H_{11}OO^{\bullet} \xrightarrow{2\times} c\text{-}C_6H_{10}O, \text{ etc.} \quad (8a)$$

$$c\text{-}C_6H_{10}O \xrightarrow[\text{by different ways, ISC}]{\text{radiation-chem. excitation}} c\text{-}C_6H_{10}O^{T1} \quad (8b)$$

$$c\text{-}C_6H_{10}O^{T1} + {>NH} \rightarrow [c\text{-}C_6H_{10}O^{\bullet -}\cdots{>NH^{\bullet +}}] \xrightarrow{\text{H+ transfer, diffusion}} c\text{-}C_6H_{10}OH^{\bullet} + {>N^{\bullet}} \quad (8c)$$

$$>N^{\bullet} + O_2 \rightarrow [\ \ ] \rightarrow {>NO^{\bullet}} \quad (8d)$$

To prove this hypothesis we undertook stationary γ-radiolysis experiments on solutions of **5** in cyclohexane (and n-heptadecane) with different oxygen concentrations and compared these measurements with those taken in the presence of an added ketone. The samples were irradiated with a dose of 2 kGy, and then the nitroxyl radical yield was determined by EPR spectroscopy integrating the three-line spectrum (Table 1). It can be seen that oxygen, of course, is necessary for nitroxyl formation and that in the presence of ketones the nitroxyl yield is about twice as high. Furthermore, in the air-saturated sample a markedly higher nitroxyl yield is found than in the oxygen-saturated one. Therefore, we suggest that in the case of cyclohexane-containing oxygen, its radiation-induced oxidation to carbonyl compounds initially takes place (cf. eq 8a), which then act as sensitizers for HALS oxidation (eqs 8b,c).

Oxygen dependence was studied systematically in the case of samples containing 0.5 mM **4** and 0.1 M cyclohexanone dissolved in n-hexadecane. Figure 1 shows the integral nitroxyl radical yield depending on the oxygen concentration of the solution. Corresponding to the finding given in Table 1, a yield dependence typical of triplet intermediates was observed, i.e., first increasing and at a higher oxygen concentration decreasing due to triplet quenching.

$$c\text{-}C_6H_{10}O^{T1} + O_2 \rightarrow c\text{-}C_6H_{10}O + O_2 \quad (9)$$

Considering the normalized nitroxyl yields (see Table 1) and the influence of oxygen (see Figure 1), the electron-transfer (eq 8) hypothesis seems to be favored.

Sensitization by Aromatic and Alicyclic Ketones: Time-Resolved Optical Spectroscopy. Because of its pronounced transient properties,[16,17] benzophenone is a very useful sensitizer. Hence its triplet has visible absorption with a maximum at λ = 530 nm, the radical anion absorbs with a maximum at around 600 nm, and the ketyl radical has an absorption maximum at 540 nm. Hence these species could be used as monitors for the reaction mechanism.[18] The amine species are not appropriate for this purpose because of their unfavorable absorption properties.

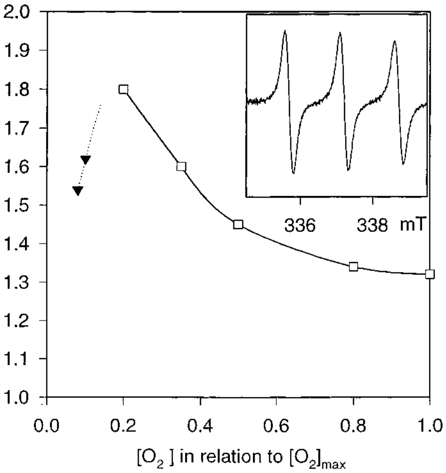


Figure 1. Yield of nitroxyl radicals (□) after γ-irradiation (4 kGy) of samples consisting of 0.1 M cyclohexanone and 0.5 mM **4** dissolved in n-hexadecane in the presence of different oxygen concentrations (relative concentration 1 equals oxygen-saturated solution) determined by EPR spectroscopy. (▼) and the dotted line indicate the estimated curve shape at essentially lower oxygen yield. The inset gives the EPR spectrum of the nitroxyl radical.

We performed 355-nm laser flash photolysis experiments with polyethylene (PE) doped with benzophenone (about 1 mM). As shown in Figure 2 after the flash we observed the first excited triplet state of the benzophenone. This triplet decayed by H abstraction from the surrounding PE, yielding the benzophenone ketyl radical. The spectra show the typical behavior also observed in the liquid state, and hence, particularly the spectral range at >530 nm could be used for kinetic analysis. H abstraction (eq 10) was found to proceed with $k_{11} = 10^6$ s^{-1}, as was estimated from the time profile in Figure 2a.

$$>CO^{T1} + PE \rightarrow {>C^{\bullet}{-}OH} + PE^{\bullet} \quad (10)$$

$$>CO^{T1} + {>NH} \rightarrow [{>CO^{\bullet -}}\cdots{>NH^{\bullet +}}] \rightarrow {>COH^{\bullet}} + {>N^{\bullet}} \quad (11)$$

Then we allowed both liquid piperidines **1** and **2** to diffuse into the foil, removed the residue on the surface, and performed flash photolysis. There was no indication for a benzophenone radical anion. Only its ketyl radical could be found. The changes in the time profile caused by the reaction of the piperidines (eq 11) analyzed at 600 nm can be seen in the insets of Figures 2 (b and c). Because of uncertainties in the distribution of the piperidines within the semicrystalline matrix, only the first-order rate was determined, $k_{11} = 1.2 \times 10^7$ s^{-1} for **1** and 6.2×10^6 s^{-1} for **2**. If nearly the same concentration of the two different amines is assumed, the reaction of the secondary amine seems to be faster than that of the tertiary one.

Because of the more qualitative character of the polymer photolysis experiment, we undertook liquid-state model experiments with ketones as sensitizers and different HALS compounds as electron donors. As a solvent we used benzene, which does not react in an H abstraction reaction, and so kinetic analysis becomes easier. The mechanism of the triplet sensitized reaction 11 was the same as in the case of PE; that is only the benzophenone triplet and the ketyl radical were observed as transients and there was no indication of the existence of the anion. Table 2 gives the rate constants of reaction 11 of various

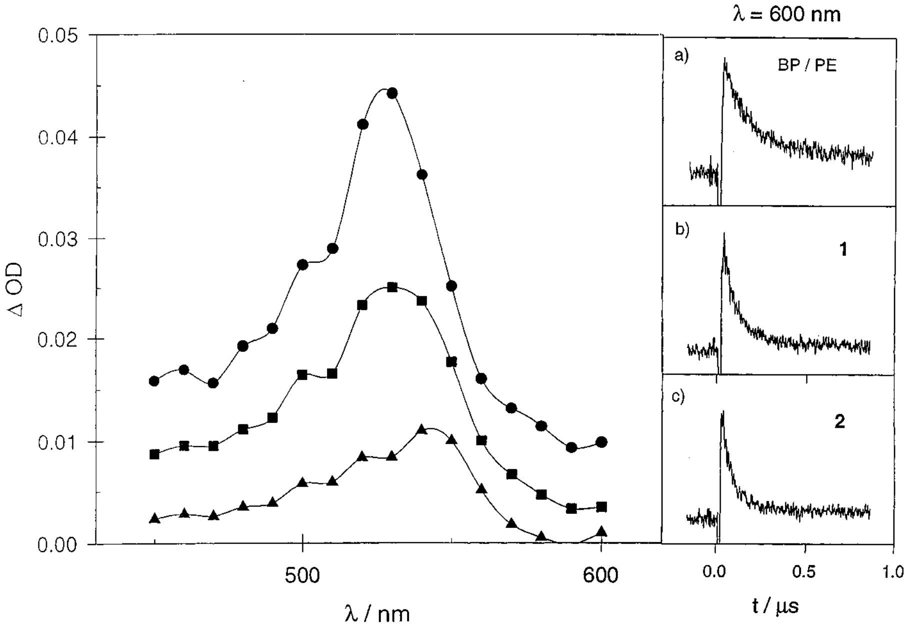


Figure 2. Time profiles (at 600 nm) taken during 355-nm laser photolysis of 1-mm PE foils doped with 1 mM benzophenone (BP) in this pure state (inset a) and after lying 10 h in the liquid piperidines **1** (inset b) and **2** (inset c). The optical absorption spectra were taken from the pure sample (a) and show the BP triplet (●, 50 ns after the flash) and the resulting BP ketyl radical absorption (■, 150 ns; ▲, 800 ns after the flash).

TABLE 2: Rate Constants of the Benzophenone Triplet Sensitized Reaction 10b with Different HALS Compounds Taken from Pulse Radiolysis[29] and Laser Photolysis Experiments in Benzene Solution at Room Temperature

electron donor	k/dm^3 mol^{-1} s^{-1}
4-hydroxy-2,2,6,6-tetramethylpiperidine	1.0×10^9
4-*n*-heptyl-2,2,6,6-tetramethylpiperidine	1.5×10^9
triacetonamine	7.5×10^8
5, Tinuvin 622 (oligomer, tertiary amine)	1.3×10^8
4, Tinuvin 770 (dimer, secondary amine)	1.3×10^9
1, 2,2,6,6-tetramethylpiperidine	2.0×10^9
2, 1,2,2,6,6-pentamethylpiperidine	$<10^9$

differently structured HALS compounds. Although the products are radicals,[5,6] owing to the nearly diffusion-controlled rate, the mechanism should be electron transfer followed by proton transfer within the ion pair. As a general observation, the overall rate constant of eq 11 is higher in the case of secondary HALS than in the case of tertiary piperidines.

Using a model system that is closer to the polymer than benzophenone, analogous experiments were performed with cyclohexanone as a sensitizer and acetonitrile as a solvent. Both HALS model compounds **1** and **2** quench the cyclohexanone triplet at a rate of $k_{12} = 10^8$ M^{-1} s^{-1}. The products could not be seen because they absorb within the UV range. Figure 3 shows the spectrum of the cyclohexanone triplet. The Stern–Volmer plot demonstrates the quenching influence of the secondary amine **1** and exhibits a nonlinear behavior, arguing for a complexed intermediate. In the case of the tertiary amine **2** (not shown here), this phenomenon was not observed and the Stern–Volmer plot fits well linearly.

$$c\text{-}C_6H_{10}O^{T1} + {>}NH \rightarrow [c\text{-}C_6H_{10}O^{\bullet -}\cdots{>}NH^{\bullet +}] \rightarrow \text{products (not observed)} \quad (12)$$

Amine Radical Cations as Intermediates of the HALS Oxidation. As already reported, because of the very rapid internal deprotonation, the ionic intermediates in the ion pair were not detected in the nanosecond time range. Hence the general question of the stability and reactivity of the HALS radical cations arose.

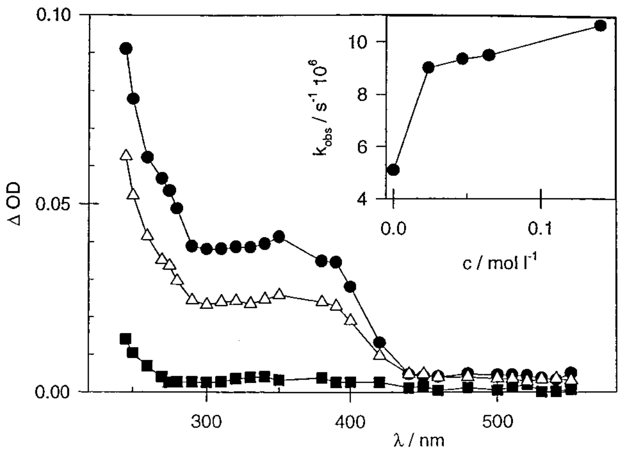


Figure 3. Optical absorption spectra taken after 266 nm flash photolysis of a solution of 0.1 M cyclohexanone in acetonitrile: (●) 30 ns, (△) 100 ns, and (■) 800 ns after the flash. The two absorption bands are assigned to the cyclohexanone triplet. The inset gives the Stern–Volmer plot due to reaction 12, i.e., the acceleration of the triplet decay in the presence of different concentrations of **1**.

The ion–molecule reaction of the HALS with radiolytically generated solvent parent ions ought to generate solute radical cations.[19,20] Hence we also performed pulse radiolysis experiments with solutions of the model HALS compounds **1**, **2**, and **3** in butyl chloride as solvent, reactions 13a,b.

$$n\text{-}C_4H_9Cl \xrightarrow{\text{radiolysis}} n\text{-}C_4H_9Cl^{\bullet +},\ Cl^-,\ n\text{-}C_4H_9^{\bullet},\ HCl, \text{ and other fragmentation products} \quad (13a)$$

$$n\text{-}C_4H_9Cl^{\bullet +} + {>}N{-}X \rightarrow n\text{-}C_4H_9Cl + {>}N^{\bullet +}{-}X, \quad X = H, CH_3, OCH_3 \quad (13b)$$

In this case the origin of the solute species is very clearly defined and radical reaction paths can be excluded for kinetic reasons (much lower rate). Figure 4a–c shows spectra taken in the pulse radiolysis of the mentioned three amines. All parts of the figure include also the spectrum of the parent ions taken in pure *n*-butyl chloride. In the presence of the amines, these species disappear. For all three amines, the rate constant k_{13b} amounts to 1.5×10^{10} M^{-1} s^{-1}, i.e., slightly higher than expected for diffusion control. This could be caused by an inhomogeneous spikelike part of the parent ion n-$C_4H_9Cl^{\bullet+}$ time profile.[19]

No amine radical cation absorption could be seen for **1** as a secondary amine after the disappearance of the solvent ion absorption in the vis range (Figure 4a). There is only very minor absorption of aminyl radicals around 500 nm. The UV part represents a superposition of solvent and solute radicals, including those partially of the aminyl type. These observations are interpreted in terms of rapid electron transfer (eq 13b), followed by an immediate deprotonation (eq 14) either by solvent proton stabilization or by Cl^- or HCl, respectively.

$$>N^{\bullet+}H \xrightarrow{\text{solvent, Cl}^- \text{ or HCl}} >N^{\bullet} + H^+(n\text{-}C_4H_9Cl), \text{ etc.} \qquad (14)$$

The tertiary amine **2** shows relatively stable cation absorption in the red range (Figure 4b), while that of the *N*-methoxy-substituted amine **3** is much more stable (Figure 4c). Considering the time profiles at 500 nm, the increasing part gives a kinetic indication of the product side of reaction 13b. These measurements argue for the actual existence of HALS radical cations and demonstrate their different kinetic stability. Radical cations were also visualized[21] by reaction 13b in the case of the technically used HALS compounds.

Subsequent Radical Reaction Resulting in Nitroxyl Radicals. Because of the different kinds of radicals produced in the pulse radiolysis of organic systems and their spectral superpositions, studying the fate of the HALS species is very complicated. Therefore we undertook oxidation of the amines **1**−**3** with the photolytically formed one-electron oxidant $SO_4^{\bullet-}$, ref 22. Hence we were able to selectively form the radicals derived from the HALS radical cation by deprotonation in the aqueous surrounding.

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\bullet-} \qquad (15a)$$

$$SO_4^{\bullet-} + {>}N{-}X \rightarrow SO_4^{2-} + {>}N^{\bullet+}X \qquad (15b)$$

$$>N^{\bullet+}X + H_2O \rightarrow H_3O^+ + \text{radicals}$$
$$>N^{\bullet} \text{ for } \mathbf{1},\ {>}N{-}CH_2^{\bullet} \text{ for } \mathbf{2},\ {>}N{-}OCH_2^{\bullet} \text{ for } \mathbf{3} \qquad (15c)$$

As shown in Figure 5, the 266-nm flash generates the known sulfate radical absorption with $\lambda_{max} = 450$ nm, which reacts with the amine **2** under the formation of solute radicals absorbing at the UV border. Apart from the substitution of the amine nitrogen, the spectrum for the solute N- and α-C-radicals looks quite similar. The reaction rate $k_{15b,c}$ amounts to 1.1×10^9 M^{-1} s^{-1} for **1**, 2.6×10^9 M^{-1} s^{-1} for **2**, and 2.5×10^8 M^{-1} s^{-1} for **3**, as was calculated from the time profiles. However, in the presence of oxygen, the fate of the HALS aminyl and α-aminomethyl radicals is very different. The decay of the α-methyl radical of **2** is accelerated by oxygen such that for low O_2 concentration the time profile decays faster in pseudo-first-order behavior ($k_{16a} = 3 \times 10^8$ M^{-1} s^{-1}), whereas with a higher oxygen level the signal becomes stable and has a fixed lifetime ($k_{16b} = 7 \times 10^4$ s^{-1}). This is shown in a Stern−Volmer plot given as an inset of Figure 5. We interpret this phenomenon as reaction 16a with the formation of an α-aminoalkylperoxyl, which has a shorter lifetime than the α-aminoalkyl radical and decays by fragmentation (eq 16b). The uncertainties in the Stern−Volmer plot and the apparently too slow rate constant k_{16a} could be explained by the superposition of the α-aminoalkyl

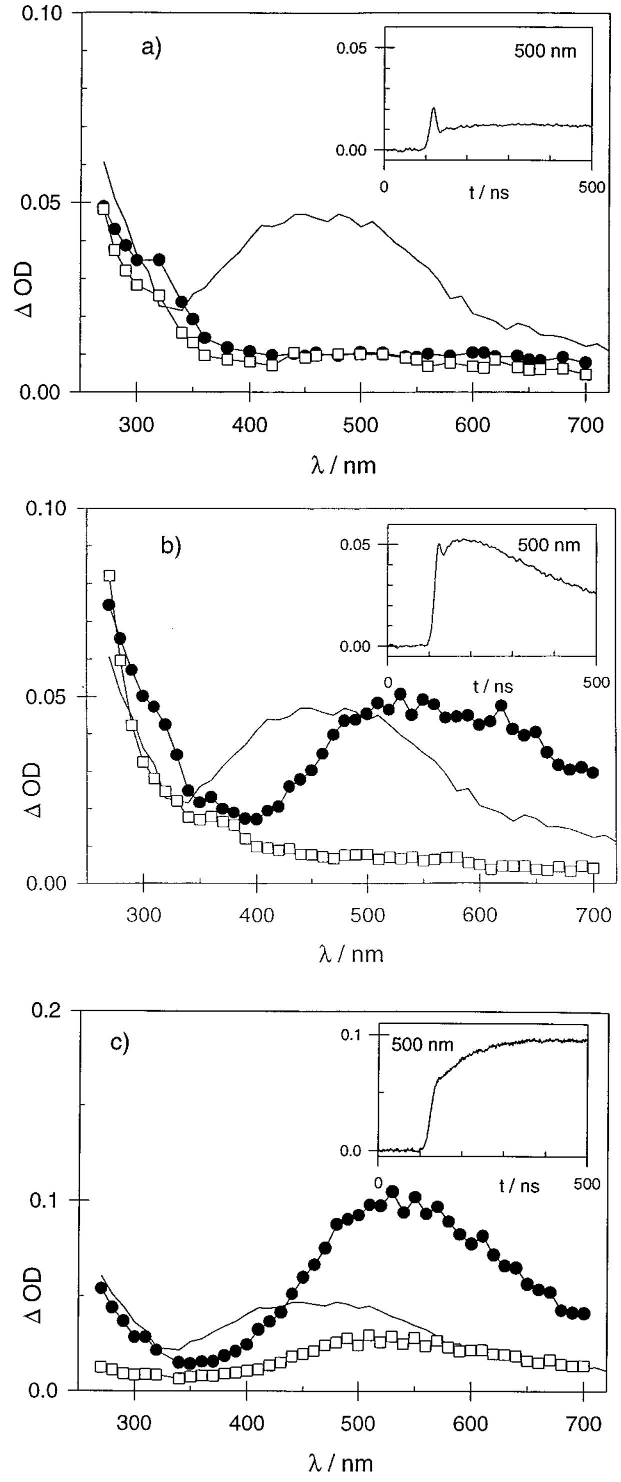


Figure 4. Transient absorption spectra taken in the pulse radiolysis of solutions of the piperidines in *n*-butyl chloride. The transient absorption of the *n*-butyl chloride parent radical cation (60 ns after the pulse) of the pure solvent is given as a solid line. (a) The sample contains 10 mM of **1**: (●) 60 ns and (□) 450 ns after the electron pulse. (b) The sample contains 10 mM of **2**: (●) 60 ns and (□) 1.5 μs after the electron pulse. (c) The sample contains 10 mM of **3**: (●) 60 ns and (□) 35 μs after the electron pulse. The insets give time profiles of the vis transient at λ = 500 nm and demonstrate the different stability of the amine radical cations.

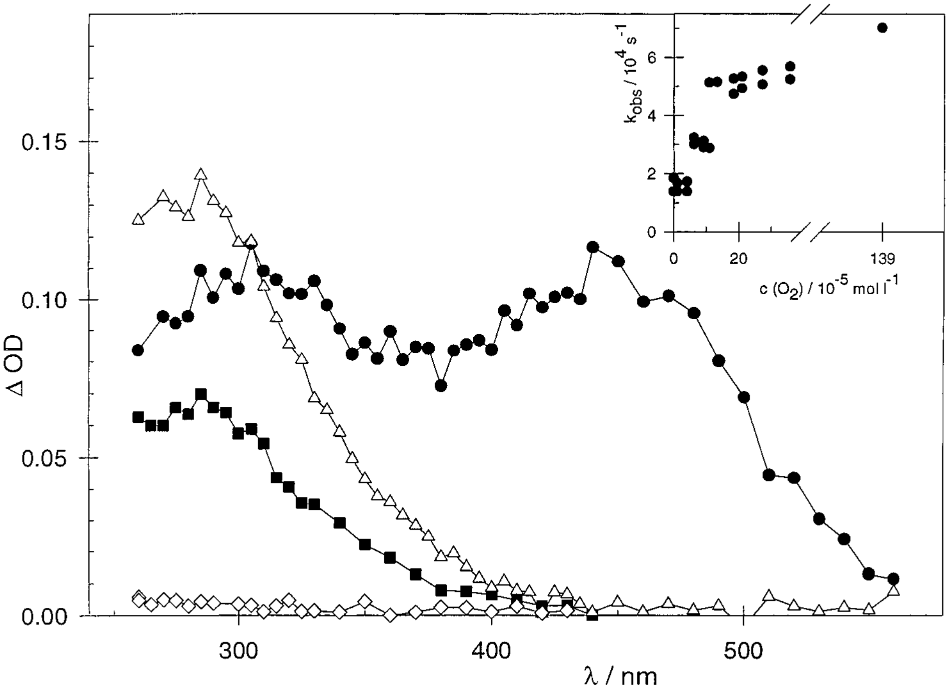


Figure 5. Transient absorption spectra taken in the 266-nm laser photolysis of a solution of 10 mM of **2** and 50 mM of potassium peroxidisulfate in water: (●) after 20 ns, caused by $SO_4^{\bullet -}$, and after (△) 750 ns and (■) 35 μs caused by α-alkyl radicals. In the presence of oxygen after 35 μs (□) this radical absorption is completely depleted. The inset shows the rate dependence of reaction 16 on the oxygen concentration.

and the α-aminoalkylperoxyl radicals within the UV spectral range.

In contrast to this, the kinetics of the aminyl radical of **1** is practically unaffected by oxygen ($k_{17} \leq 2 \times 10^6$ M^{-1} s^{-1}). This corresponds to previous findings about the low reactivity of aminyl radicals to oxygen, which has been estimated to have a rate constant of $k_{17} \leq 10^7$ M^{-1} s^{-1}, refs 23, 24. Low-temperature matrix isolation experiments with γ-irradiation and EPR detection confirm this assumption, identifying N-centered peroxyl radicals and giving grounds for interpreting the oxygen reaction as a loose equilibrium[11] (eq 17).

$$>\mathrm{N{-}CH_2^\bullet} + \mathrm{O_2} \xrightarrow{k_{16a}} >\mathrm{N{-}CH_2OO^\bullet} \xrightarrow{k_{16b}} >\mathrm{N{-}O^\bullet} + \mathrm{CH_2O} \qquad (16)$$

$$>\mathrm{N^\bullet} + \mathrm{O_2} \rightleftharpoons\ >\mathrm{N{-}OO^\bullet} \qquad (17)$$

Whereas reaction 16 gives a good hint for the mechanistic interpretation of nitroxyl radical formation (normally, alkylperoxyl radicals ought to survive much longer than alkyl radicals), the explanation of the formation of nitroxyls from aminyl radicals is somewhat speculative. CIDEP experiments on the triplet-sensitized electron transfer with carbonyls and HALS facilitated the time-resolved observation of the aminyl radicals by FT-EPR spectroscopy.[25] As expected, the aminyl radical of **1** exhibits spin polarization. By contrast, the nitroxyl radicals subsequently formed in the presence of oxygen do not show this polarization. This suggests that during the course of the transformation mechanisms a diamagnetic intermediate is crossed and the polarization is lost in this state.

Because of the above-mentioned low reactivity of aminyls with respect to oxygen (reaction 17), recombination reactions with alkyl peroxyl radicals have a chance to compete. Therefore, the reaction of the relatively persistent aminyl radicals with alkylperoxyl or other peroxyl radicals (eq 18) ought to be the main source of the nitroxyls rather than the more exotic-looking tetroxide mechanism (eq 19), which has been frequently proposed in analogy with hydrocarbon chemistry.

$$>\mathrm{N^\bullet} + \mathrm{ROO^\bullet} \rightarrow [>\mathrm{N{-}OO{-}R}] \rightarrow\ >\mathrm{N{-}O^\bullet} + \mathrm{RO^\bullet}, \quad \mathrm{R} = \text{alkyl} \qquad (18a)$$

$$>\mathrm{N^\bullet} + >\mathrm{NOO^\bullet} \rightarrow [>\mathrm{N{-}OO{-}N}<] \rightarrow 2 >\mathrm{N{-}O^\bullet} \qquad (18b)$$

$$2{>}\mathrm{NOO^\bullet} \rightarrow [>\mathrm{N{-}OOOO{-}N}<] \rightarrow 2{>}\mathrm{N{-}O^\bullet} + \mathrm{O_2} \qquad (19a)$$

$$>\mathrm{NOO^\bullet} + \mathrm{ROO^\bullet} \rightarrow [>\mathrm{N{-}OOOO{-}R}] \rightarrow\ >\mathrm{NO^\bullet} + \mathrm{RO^\bullet} + \mathrm{O_2} \qquad (19b)$$

Nitroxyl Radicals as Efficient Scavengers of Alkyl, Alkoxyl, and Alkylperoxyl Radicals. Generally speaking, nitroxyl radicals are very persistent species with only a slight dimerization tendency, as formulated in equilibrium 20.

$$2 >\mathrm{N{-}O^\bullet} \rightleftharpoons\ >\mathrm{N{-}OO{-}N}< \qquad (20)$$

In the case of sterical hindrance, this reaction can be completely neglected. In the presence of other radicals, however, they act as very efficient scavengers, forming neutral products.[27,28] To determine rate constants of the reactions of nitroxyl radicals, we performed pulse radiolysis experiments with the stable radicals TEMPO (**6**$^\bullet$) and HO-TEMPO (**7**$^\bullet$) and generated transient radicals as alkyl, alkoxyl, and alkylperoxyl radicals radiolytically. All these radicals have only small absorptions at $\lambda \leq 300$ nm, in the same spectral range in which the nitroxyl radicals also slightly absorb. Thus kinetic analysis of the time profiles must take this fact into account. Figure 6 (upper part) shows time profiles at $\lambda = 250$ and 280 nm taken in pure and oxygen-free cyclohexane compared to those taken in the presence of TEMPO (lower part). Considering the time axis, it can be seen that there is an important acceleration of the decay of the cyclohexyl radicals as well as a depletion effect caused by the consumption of the added nitroxyl radical. Analogous

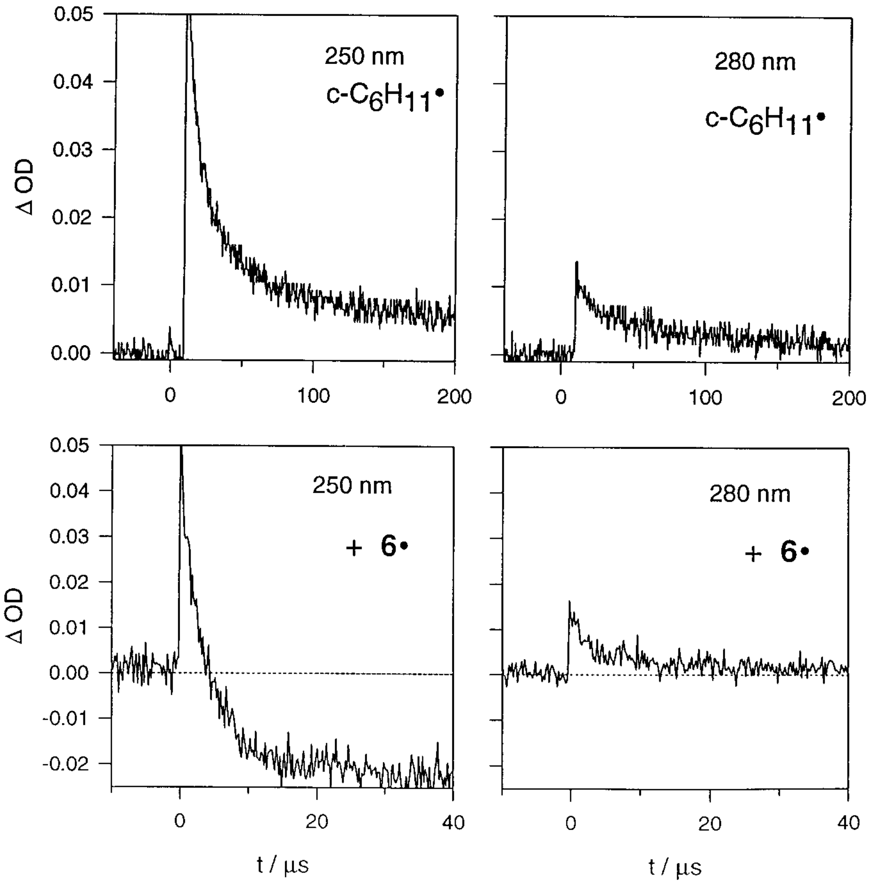


Figure 6. Time profiles of the cyclohexyl radical at $\lambda = 250$ and 280 nm obtained in the pulse radiolysis of pure deaerated cyclohexane (upper profiles) and in the presence of **6**$^\bullet$ (lower part).

TABLE 3: Rate Constants of the Reaction of the Stable Nitroxyl Radicals 6$^\bullet$ (TEMPO) and 7$^\bullet$ (HO-TEMPO) with Alkyl, Alkoxyl, and Alkylperoxyl Radicals

k (dm^3 mol^{-1} s^{-1})	**6**$^\bullet$	**7**$^\bullet$
c-$C_6H_{11}^\bullet$	6.3×10^8	6.0×10^8
i-$C_8H_{17}^\bullet$	2.6×10^8	3.1×10^8
n-$C_{17}H_{35}^\bullet$	8.0×10^8	
t-C_4H_9-$O^\bullet$	4.6×10^8	5.8×10^8
n-$C_{17}H_{35}OO^\bullet$	$<5 \times 10^5$	
other ROO$^\bullet$	$<10^5$	

experiments were also performed with n-heptadecane and isooctane and showed similar effects. The rate constants k_{21a} are on the order of some 10^8 M^{-1} s^{-1}, evidently exhibiting the impact of the structure of R$^\bullet$ (cf. Table 3). This corresponds well with data determined by other methods.[26,27]

$$\mathrm{RH} \xrightarrow{\text{irradiation}} [\mathrm{R}^\bullet + \mathrm{H}^\bullet] \rightarrow 2\mathrm{R}^\bullet + \mathrm{H}_2 \qquad (21a)$$

$$>\mathrm{N{-}O}^\bullet + \mathrm{R}^\bullet \rightarrow >\mathrm{N{-}O{-}R} \qquad (21b)$$

To check the case of the reaction of alkylperoxyl radicals, pulse radiolysis was carried out with oxic alkane samples in the absence and presence of **6**$^\bullet$. Under the given limitations of sensibility and long-term resolution for heptadecylperoxyl radicals (not of completely uniform structure), a rate constant of $k_{22} = 5 \times 10^5$ M^{-1} s^{-1} was estimated in an analogeous manner as described in the preceding paragraph. This rate seems to be similar for other alkylperoxyl radicals, but could hardly be detected.

$$>\mathrm{N{-}O}^\bullet + \mathrm{ROO}^\bullet \rightarrow \text{products} \qquad (22)$$

The situation is much more complicated for alkoxyl radicals, because of their limited lifetime due to their fragmentation. We generated the relatively stable $tert$-butoxyl radical in aqueous solution according to reaction 23.

$$(\mathrm{CH_3})_3\mathrm{COOH} + e_{aq}^- \rightarrow (\mathrm{CH_3})_3\mathrm{CO}^\bullet + \mathrm{OH}^- \qquad (23)$$

$$(\mathrm{CH_3})_3\mathrm{CO}^\bullet + >\mathrm{NO}^\bullet \rightarrow \text{products} \qquad (24)$$

Under our experimental conditions, we found a lifetime of about 600 ns for the $tert$-butoxyl radical. The decay of the alkoxyl radical was accelerated by adding increasing concentrations of **6**$^\bullet$, and hence, for reaction 24 a rate of $k_{24} = 4.6 \times 10^8$ M^{-1} s^{-1} was determined, i.e., a value quite similar to that for the alkyl radicals. Table 3 summarizes the rate parameters of the reaction of the different radicals with nitroxyl radicals.

Mechanism of HALS Stabilizer Action. In the foregoing sections we demonstrated that HALS compounds are much more succeptible to ionization than to undergoing radical or energy-transfer reactions. Now the question of the actual HALS antioxidant action mode should be discussed.

It is quite clear that the low reactivity against alkyl and similar radicals found in the pulse radiolysis experiments do not recommend the sterically hindered amines as stabilizers. By contrast, all ionization procedures such as direct biphotonic ionization, electron transfer with parent ions (eq 13b), one-electron oxidation with appropriate oxidants (eq 15b), and triplet-sensitized electron transfer (eq 3) first lead to amine radical cations, which were directly observed in certain cases. Particularly in polar surroundings and also under the conditions of sensitized electron transfer within the intermediate ion pairs, the piperidine radical cations rapidly deprotonate under the

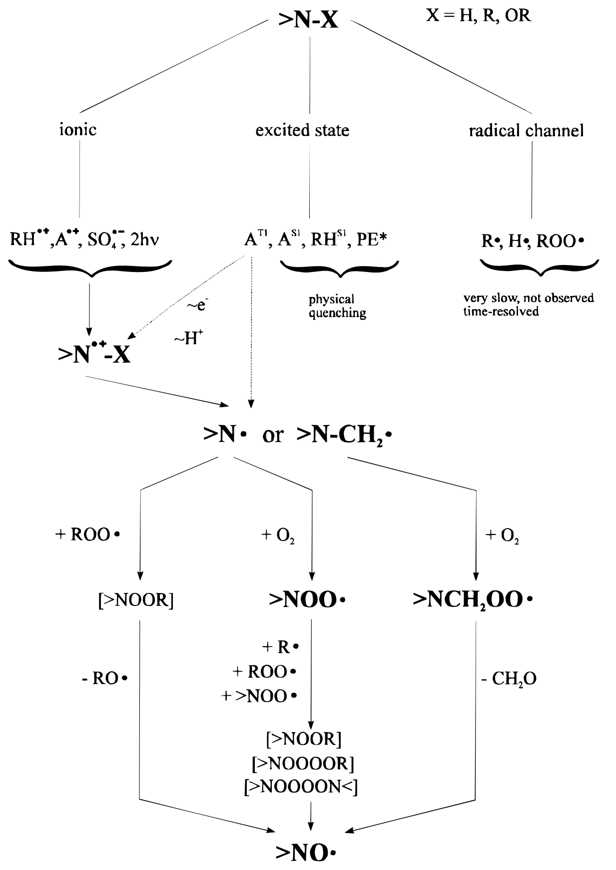


Figure 7. Reaction diagram describing the path of the (one-electron) oxidation of HALS compounds to nitroxyl radicals via intermediate amine radical cations, radicals and peroxyl radicals. In addition to the ionic pathway, the checked excited state and radical reaction channels are also mentioned.

formation of aminyl radicals (for secondary HALS) or α-aminoalkyl radicals (tertiary HALS). These radicals, however, exhibit different decay behavior: (i) the α-aminoalkyl radicals rapidly react with oxygen and fragment under the elimination of formaldehyde to nitroxyl radicals, whereas (ii) the aminyl radicals react slowly with oxygen and seem to prefer recombination with other radicals, which leads to aminoxyl and alkoxyl radicals in the case of the combination with alkylperoxyl radical (eqs 18a,b) via peroxides.

Because of the sterical hindrance, the 2,2,6,6-tetramethylpiperidyloxyl radicals are rather stable against recombining themselves. But with other types of radicals such as alkyl and alkoxyl and to a lesser extent alkylperoxyl radicals, they react relatively rapidly under product formation (eq 21). This has been demonstrated in the pulse radiolysis of TEMPO solutions in organic solvents, under which conditions the mentioned radicals are generated.

Hence, the conclusion seems to be justified that neither the HALS compounds nor the ionic and radical transients with amine function are the active antioxidants. The actual stabilizing species are the nitroxyl radicals formed in a sequence of reactions starting with amine ionization. This conclusion is illustrated by a reaction diagram (Figure 7) that shows a mechanism that ought to be generally valid for nitroxyl radical formation and its stabilizing effect.

Conclusions

By using direct transient detection and characterization techniques, in this paper we have demonstrated that the sterically hindered amines easily undergo one-electron oxidation under the formation of radical cations. This reaction seems to be a key reaction step in explaining the antioxidant activity of HALS compounds. Depending on the surroundings, the amine radical cations deprotonate to secondary amines under the formation of aminyl radicals and to tertiary amines of α-aminoalkyl radicals, which in the presence of oxygen are transformed via different peroxyl radical intermediates into nitroxyl radicals. These very persistent radicals react efficiently with alkyl and alkoxyl radicals, but less efficiently with alkylperoxyl radicals. This reaction of the aminoxyls interrupts the radical oxidation chain of organic material and therefore causes the actual antioxidant phenomenon of HALS. Under technical and natural conditions, the oxidation sequence of the HALS compounds seems to be mainly initiated by ketone triplet sensitized electron transfer.

References and Notes

(1) (a) Wiles, D. M.; Carlsson, D. J. In *New Trends in the Photochemistry of Polymers*; Allen, N. S., Rabek, J. F., Eds.; Elsevier Applied Science Publ.: New York, 1985; p 147. (b) Scott, G. In *Atmospheric Oxidation and Antioxidants;* Scott, G., Ed.; Elsevier: Amsterdam, 1993; Vol. I, p 121; Vol. II, p 385. (c) Gugumus, F. *Polym. Degrad. Stab.* **1993**, *40*, 167; **1994**, *44*, 299 and citations. (d) Step, E. N.; Turro, N. J.; Klemchuk, P. P.; Gande, M. E. *Angew. Makromol. Chem.* **1995**, *232*, 65. (e) Gugumus, F. In *Current Trends in Polymer Chemistry*; Allen, N. S., Edge, M., Bellobaro, I. R., Seli, E., Eds.; Ellis Horwood: Hampstead, 1995; p 257.

(2) Chirinos Padron, A. J. *J. Photochem. Photobiol., A: Chem.* **1989**, *49*, 1; *JMS*−*Rev. Macromol. Chem. Phys.* **1990**, *C30* (1), 107.

(3) Geuskens, G.; Nedelkos, G. *Polym. Degrad. Stab.* **1987**, *19*, 365. Geuskens, G.; Kanda, M. N. *Polym. Degrad. Stab.* **1996**, 5*1*, 227.

(4) Bortolus, N.; Flamingni, L.; Minto, F.; Monti, S.; Faucitano, A. *J. Photochem. Photobiol., A: Chem.* **1992**, *68*, 239.

(5) Step, E. N.; Turro, N. J.; Gande, M. E.; Klemchuk, P. P. *J. Photochem. Photobiol., A: Chem.* **1993**, *74*, 203.

(6) Brede, O. *Radiat. Phys. Chem.* **1997**, *49*, 39.

(7) Gugumus, G. *Makromol. Chem., Macromol. Symp.* **1989**, *27*, 25.

(8) Brede, O. *Macromol. Symp.* **1995,** *100*, 71.

(9) Beckert, D.; Fessenden, R. W. *J. Phys. Chem.* **1996**, *100*, 1622.

(10) Werst, D. W.; Trifunac, A. D. *J. Phys. Chem.* **1991**, *95*, 1268.

(11) Göttinger, H. A.; Zubarev, V. E.; Brede, O. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2167.

(12) (a) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 6400. (b) Shida, T.; Nosaka, Y.; Kato, T. *J. Phys. Chem.* **1978**, *82*, 695. (c) Eastland, G. W.; Rao, D. N. R.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1551. (d) Qin, X.-Z.; Williams, Ff. *J. Phys. Chem.* **1986**, *90*, 2292. (e) Shiotani, M.; Sjönqvist, L.; Lund, A.; Lunnel, S.; Erikson, L.; Huang, M.-B. *J. Phys. Chem.* **1990**, *94*, 8081.

(13) Gugumus, F. In *Current Trends in Polymer Chemistry*; Allen, N. S., Edge, M., Bellobaro, I. R., Seli, E., Eds.; Ellis Horwood: Hempstead, 1995; p 257.

(14) Das, S.; Schuchmann, M. N.; Schuchmann, H. P.; v. Sonntag, C. *Chem. Ber.* **1987**, *120*, 319.

(15) Wojnarovits, L. In *Radiation Chemistry of Hydrocarbons*; Földiak, G., Ed.; Elsevier Publ.: New York, 1981; p 201.

(16) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993.

(17) Brede, O.; Helmstreit, W.; Mehnert, R., *Z. Phys. Chem. (Leipzig)* **1975**, *256*, 505, 513.

(18) Brede, O.; Hermann, R.; Helmstreit, W.; Taplick, T.; Stephan, L. *Makromol. Chem., Macromol. Symp.* **1988**, *18,* 113.

(19) Mehnert, R.; Brede, O.; Naumann, W. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 525.

(20) Brede, O.; Mehnert, R.; Naumann, W. *Chem. Phys.* **1987**, *115*, 279.

(21) Göttinger, H. A.; Brede, O. To be published.

(22) (a) Deeble, J. D.; Schuchmann, M. N.; Steenken, S.; v. Sonntag, C. *J. Phys. Chem.* **1990**, *94*, 8186. (b) Brede, O.; David. F.; Steenken, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, *2*, 23.

(23) Hepp, M. G.; Kramer, H. E. A. *J. Photochem. Photobiol., A: Chem.* **1994**, *78*, 19.

(24) Schuchmann, H.-P.; v. Sonntag, C. In *Peroxyl Radicals*; Alfassi, Z. B., Ed.; Wiley: New York, 1997; p 439.

(25) Säuberlich, J. Ph.D. Theses, University of Leipzig, 1996.

(26) Arends, J. W. C. E.; Mulder, P.; Clark, K. B.; Wayner, D. D. M. *J. Phys. Chem.* **1995**, *99*, 8182.

(27) Nigam, S. N.; Asmus, K.-D.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2324.

(28) Brede, O.; Mehnert, R.; Naumann, W.; Teply, J. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1036.