Low-temperature EPR study of the reaction of the 2,2,6,6-tetramethylpiperidyl radical with molecular oxygen. Direct spectroscopic observation of an aminylperoxyl radical

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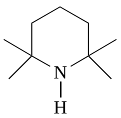
Gamma irradiation of a frozen solution of 2,2,6,6-tetramethylpiperidine in freon-113 at 77 K generates in the first step the piperidine radical cation 1$^{\bullet+}$ which deprotonates during annealing at 104 K under formation of the piperidyl radical 1$^\bullet$. After admission of oxygen at 113 K, the piperidylperoxyl radical 2$^\bullet$ appears, which is characterized by its EPR powder spectrum (fully anisotropic g-tensor with $g_1 = 2.0258$, $g_2 = 2.0066$ and $g_3 = 2.0022$ at 103 K). Upon warming, 2$^\bullet$ converts nearly quantitatively to the aminoxyl radical 3$^\bullet$.

Introduction

Sterically hindered amines are widely used as polymer stabilisers (HALS, hindered amine light stabilisers[1]). But until now, the stabiliser action of HALS compounds has not been understood in detail, although it is known that they act as quenchers of excited singlet or triplet molecules[2a,b] or react with oxidizing species such as $RO_2^\bullet$ radicals.[2c] As intermediates of radiation or light-induced oxidation, nitrogen-centered radical cations[3] and aminyl radicals[4] have been experimentally observed, detected by low temperature steady-state EPR or time-resolved spectroscopic techniques. The final product of stationary ageing experiments was found to be the aminoxyl radical, which is a very persistent species and can therefore be easily detected by EPR spectroscopy. The mechanism of the transformation of aminyl to aminoxyl radicals, however, has not been fully resolved in detail because the possible aminylperoxyl radical evades observation.

2,2,6,6-Tetramethylpiperidine (**1**) represents a basic model compound for studying the primary reactive steps in the antioxidant action of HALS compounds. Using this substance, the oxygen driven conversion of the piperidyl radical **1**$^\bullet$ into the aminoxyl radical **3**$^\bullet$ has been studied by Roberts and Ingold,[5a] who found a quantitative turnover. The mechanism can be summarized by reactions (1) and (2), *via* aminylperoxyl radicals.



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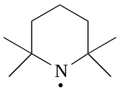

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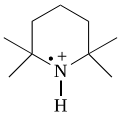

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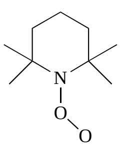

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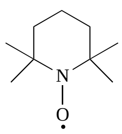

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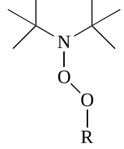

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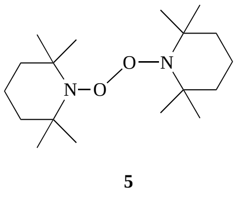

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$$\mathbf{1}^\bullet + O_2 \longrightarrow \mathbf{2}^\bullet \tag{1}$$

$$\mathbf{1}^\bullet + \mathbf{2}^\bullet \longrightarrow \mathbf{3}^\bullet + \mathbf{3}^\bullet \tag{2}$$

However, in the presence of alkylperoxyl radicals $RO_2^\bullet$, aminoxyl radical **3**$^\bullet$ should appear as a result of the reaction of the aminyl radical **1**$^\bullet$ with those radicals, *i.e.* not *via* a piperidylperoxyl radical **2**$^\bullet$ [see reaction (3)].

$$\mathbf{1}^\bullet + RO_2^\bullet \longrightarrow \mathbf{3}^\bullet + RO^\bullet \tag{3}$$

As already mentioned, the piperidylperoxyl radical **2**$^\bullet$ has not yet been detected directly even using time-resolved techniques.[4–6] In comparison with alkyl radicals, the reactivity of nitrogen centered radicals towards oxygen is much lower. Thus, for the simplest nitrogen-centered amine radical $H_2N^\bullet$ a rate constant of 1×10^7 dm^3 mol^{-1} s^{-1} in aqueous solution has been measured,[7a] and in the case of the 2,2,6,6-tetramethyl-4-hydroxy-1-piperidyl radical, a rate constant of 2.9×10^7 dm^3 mol^{-1} s^{-1} has been estimated from a non-direct measurement.[7b]

In a low-temperature EPR study by Faucitano *et al.*[8] an asymmetric EPR line (with $g_\parallel = 2.0333$ and $g_\perp = 2.0057$ at 77 K), observed in the EPR spectrum of UV-irradiated frozen polypropylene film enriched with a derivative of **1** (2,2,6,6-tetramethylpiperidin-4-yl hydrogen decandioate), has been assigned to a piperidylperoxyl radical similar to **2**$^\bullet$. However, no conclusive evidence was obtained either for the formation of the piperidyl radical **1**$^\bullet$ or for its reaction with molecular oxygen according to reaction (1). The $A_\parallel$ value of about 30 G given for the powder EPR spectrum of **1**$^\bullet$ seems to apply more for alkyl radicals of polypropylene (*cf.* ref. 9). Thus, it should be asked which kind of radicals really have been observed.[8]

From these considerations, and as an extension of our studies[10] on the primary reaction steps in the antioxidant action of HALS compounds, we performed a low-temperature matrix-isolation study on the reaction of the piperidyl radical **1**$^\bullet$ with molecular oxygen. The main goal of this work was to gain a deeper insight into the chemistry of the piperidyl radical **1**$^\bullet$ derived from the sterically hindered 2,2,6,6-tetramethylpiperidine. The direct spectroscopic detection of the piperidylperoxyl radical **2**$^\bullet$ is important for the elucidation of its structure, reactivity and the mechanism of its conversion into the aminoxyl radical **3**$^\bullet$.

Table 1 EPR parameters for the radicals involved in this work. All experiments made in freon-113 matrix unless otherwise stated.

Radical	g-Values	Hyperfine coupling/G^{a}	T/K	Ref.
$\mathbf{1}^{\bullet +}$	$g_{\parallel} = 2.0022$	$A_{\parallel} = 57$, $A_{\perp} = 2$, A_{iso}(H, N–H) = 23, A_{iso}(2H) = 11	77	
	$g_{\perp} = 2.0040$			
	$g_{iso} = 2.00382$	$a_N = 18.57$, a_H(H, N–H) = 21.35, a_H(12H) = 1.23	298	2a^{b}
$\mathbf{1}^{\bullet}$	$g_{\parallel} = 2.0026$	$A_{\parallel} = 43.0^{c}$, $A_{\wedge} = 5$, A_{iso}(2H) = 6	77	
	$g_{\perp} = 2.0054$			
	$g_{iso} = 2.0045$	$a_N = 14.65$, $a_H(CH_3) = 0.8$, $a(^{13}C) = 15.37^{d}$	243	
	$g_{iso} = 2.0048$	$a_N = 14.66$, $a_H(CH_3) = 0.82$	300	4^{e}
		$a_N = 14.6$, a_H(2H) = 4.6 G	133	4^{e}
$\mathbf{3}^{\bullet}$	$g_{iso} = 2.0060$	$a_N = 15.45$	243	
	$g_{iso} = 2.0064$	$a_N = 15.3$	173	4^{e}
$\mathbf{2}^{\bullet}$	$g_1 = 2.0258$		104	
	$g_2 = 2.0066$			
	$g_3 = 2.0022$			
	$g_{\parallel} = 2.0237$		123	
	$g_{\perp} = 2.0053$			
$RO_2^{\bullet}$	$g_{\parallel} = 2.0380$		77	
	$g_{\perp} = 2.0060$			
	$g_{iso} = 2.0167$		133	

[a] 1 G = 0.1 mT. [b] In CF_3COOH. [c] Compare with $A_{\parallel} = 44.5$ G for 2,2,6,6-tetramethyl-4-oxo-1-piperidyl radical in tetrahydrofuran, ref. 9. [d] From the computer fitting of the experimental spectrum. [e] In isopentane.

Experimental

Low-temperature EPR matrix-isolation experiments were performed as described in our previous work.[11] First derivative EPR spectra were obtained with an X-band (with 100 kHz field modulation) EPR spectrometer (ZWG, Berlin), with its own temperature control and data acquisition system. As a standard for g-value measurements the 2,2,6,6-tetramethylpiperidine aminoxyl radical [$g_{iso} = 2.0060$ at room temperature in freon-113($CF_2ClCFCl_2$)] was used. Irradiated samples were annealed at various temperatures using either a copper cryostat (in these cases after 10 min annealing they were recooled to 77 K for the EPR measurements) or they were annealed directly in the resonator of the EPR spectrometer using a temperature control system (variable temperatures above 103 K). This allowed us to observe the chemical reactions of the transient radicals directly during annealing.

A solution of piperidine **1** (5×10^{-2} mol dm^{-3}) in freon-113 ($CF_2ClCFCl_2$) was γ-irradiated at a dose of about 5 kGray. Powder EPR spectra were simulated using the program created by Ewert,[12] upgraded for the PC. Integration of the powder EPR spectra was carried out using the Bruker WIN-EPR program. Solution EPR spectra were analysed using a WIN-Simulation program developed by Duling (NIEHS, USA); in particular this allowed us to extract hyperfine coupling constants by fitting of experimental EPR spectra.

2,2,6,6-Tetramethylpiperidine **1** (Aldrich) already contained some aminoxyl radical **3**$^{\bullet}$ and, therefore, it was additionally purified (redistillation in vacuum with ascorbic acid). Freon-113 ('Genetron® 113', Fluka) was used as received.

Results and discussion

Table 1 shows the hyperfine coupling constants and the g-values for all radicals studied in this paper together with the available literature data.

Low-temperature matrix-isolation EPR study of piperidyl radical 1$^{\bullet}$

Generation of dissolved radical cations occurs by electron transfer from the solute to radiation-induced matrix parent cations.[13] Hence, γ-irradiation of piperidine **1** in frozen freon-113 matrices (RHal) resulted in the nitrogen-centered piperidine radical cation $\mathbf{1}^{\bullet +}$ *via* the electron-transfer reaction (4).

$$\mathbf{1} + RHal^{\bullet +} \longrightarrow \mathbf{1}^{\bullet +} + RHal \qquad (4)$$

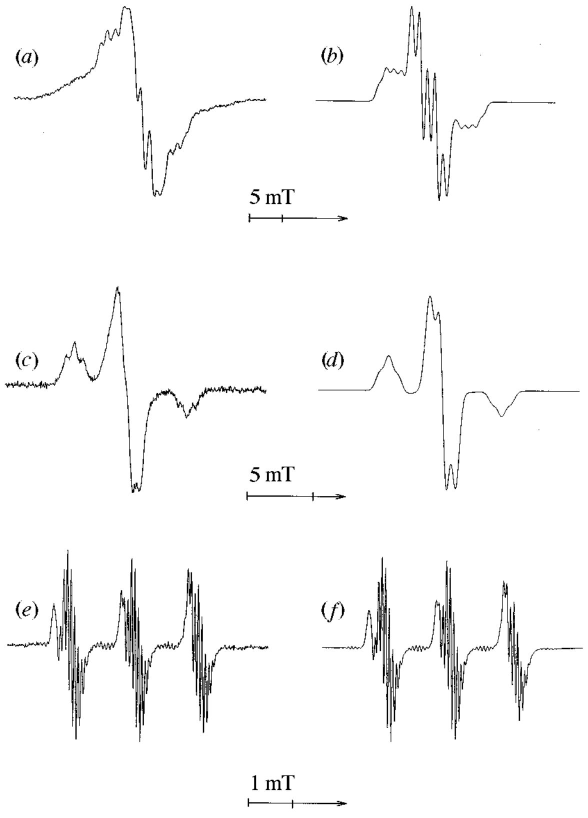

Fig. 1 First-derivative EPR spectra taken after γ-irradiation of piperidine **1**: (*a*) in frozen freon-113 matrix immediately after irradiation at 77 K, (*c*) after annealing of sample (*a*) at 130 K; (*e*) shows the solution EPR spectrum taken for the sample (*c*) at 243 K; spectra (*b*), (*d*) and (*f*) show the corresponding simulated EPR spectra. The contribution of piperidyl radical **1**$^{\bullet}$ and aminoxyl radical **3**$^{\bullet}$ to spectrum (*e*) was determined by computer fitting and found to be 91% and 9% respectively; multiplets of low intensity (0.87%) are clearly seen in both experimental (*e*) and simulated (*f*) spectra and are due to the splitting from ^{13}C in the piperidyl radical **1**$^{\bullet}$.

Electrons generated by γ-irradiation are completely scavenged by the matrix molecules and converted into matrix radicals as shown in reaction (5).

$$e^{-}_{solv} + CF_2ClCFCl_2 \longrightarrow CF_2ClCFCl^{\bullet} + Cl^{-} \qquad (5)$$

Fig. 1(*a*) shows the EPR spectrum of the radical cation $\mathbf{1}^{\bullet +}$ in frozen freon-113 matrix. At 77 K the intensity of the EPR signal of the matrix-derived $CF_2ClCFCl^{\bullet}$ radicals is low because of anisotropic line broadening[3b–e] and the main features of the EPR spectrum of the piperidine radical cation [*cf.* simulated spectrum in Fig. 1(*b*)] can be clearly observed. As a result of the deprotonation of the piperidine radical cation $\mathbf{1}^{\cdot +}$, the piperidyl radical $\mathbf{1}^{\cdot}$ appeared upon annealing of the irradiated frozen solutions. The solvent itself and the dissolved piperidine **1** and/or the matrix-derived anions Cl^- could be considered as deprotonation partners for the radical cation $\mathbf{1}^{\cdot +}$ as shown in reactions (6)–(8), (*cf.* ref. 3*d*).

$$\mathbf{1}^{\cdot +} + \mathrm{RHal} \longrightarrow \mathbf{1}^{\cdot} + \mathrm{H}^{+}(\mathrm{RHal}) \qquad (6)$$

$$\mathbf{1}^{\cdot +} + \mathbf{1} \longrightarrow \mathbf{1}^{\cdot} + \mathbf{1}\text{–H}^{+} \qquad (7)$$

$$\mathbf{1}^{\cdot +} + \mathrm{Cl}^{-} \longrightarrow \mathbf{1}^{\cdot} + \mathrm{HCl} \qquad (8)$$

Both the radical cation $\mathbf{1}^{\cdot +}$ and the matrix radical CF_2Cl-$CFCl^{\cdot}$ decayed upon annealing at and above 104 K. After the complete decay of the matrix radicals (which could be observed up to 140 K) only the piperidyl radical was present in the matrix. Its EPR spectrum is shown in Fig. 1(*c*). This EPR spectrum does not change upon melting of the sample. Double integration of the EPR spectra shows that nearly 70% of the initially formed piperidine radical cations are converted into the piperidyl radicals upon annealing of the irradiated solutions at 140 K.

The piperidyl radical $\mathbf{1}^{\cdot}$ is relatively persistent and could also be observed in solution at 238 K [see EPR spectrum in Fig. 1(*e*) and its simulation in Fig. 1(*f*)] for about 20 min until it decayed below the detection level of the EPR equipment (about 5×10^{-7} mol dm^{-3}). In the absence of oxygen, the main route of decay for the piperidyl radical in freon-113 could be abstraction of hydrogen atoms from the C–H bond of the piperidine ring.[5,9] Piperidine-derived cycloalkyl radicals, which are expected to be formed in that case, are too reactive to be directly observed under our experimental conditions.

The powder EPR spectrum of $\mathbf{1}^{\cdot}$ could be best simulated [Fig. 1(*d*)] assuming that the unpaired electron interacts with the nitrogen and two equivalent γ-hydrogen atoms (W-plane couplings with two axial hydrogen atoms at the 3- and 5-positions of the piperidine ring[5a,14]). The isotropic triplet subsplitting, which is clearly seen in the low and high field components of the EPR spectrum of $\mathbf{1}^{\cdot}$ are due to these two hydrogen atoms. Isotropic hyperfine splitting from the γ-hydrogen atoms of the two axial methyl groups[5a,9] is expected to be small at low temperatures and to contribute only to the linewidth of the powder EPR spectrum. The two axial hydrogen atoms at 3- and 5-positions of the piperidine ring have also been taken into account in the simulation of the powder EPR spectrum of the piperidine radical cation [see Fig. 1(*b*)], using the parameters shown in Table 1.

Thus, the piperidyl radical $\mathbf{1}^{\cdot}$ was clearly identified in a wide temperature range in the non-polar frozen and liquid matrices of freon-113 as the deprotonation product of the primary nitrogen-centered piperidine radical cation $\mathbf{1}^{\cdot +}$.

Reaction of piperidyl radical $\mathbf{1}^{\cdot}$ with molecular oxygen in a frozen freon-113 matrix

After γ-irradiation of an air-saturated frozen (77 K) pure freon-113 matrix and subsequent annealing at 92 K, the matrix-derived peroxyl radicals $RO_2^{\cdot}$ ($R = CF_2ClCFCl^{\cdot}$) are observed in the EPR spectrum (axially symmetric line with $g_{\parallel} = 2.0380$ and $g_{\perp} = 2.0030$ at 77 K, *cf.* parameters in ref. 15). Similar spectra were obtained upon admission of oxygen to the deoxygenated γ-irradiated frozen freon-113 matrix. The EPR spectrum of the matrix-derived peroxyl radical $RO_2^{\cdot}$ changes strongly and reversibly with the temperature, and at 140 K it is a symmetric singlet line (with peak-to-peak linewidth of 3.4 G and $g_{iso} = 2.0167$). This is due to averaging of the *g*-anisotropy by increased molecular motion indicating a high molecular mobility at this temperature.[15] Matrix-derived peroxyl radicals $RO_2^{\cdot}$ are persistent over a wide temperature range and only upon warming above 150 K do they decay completely.

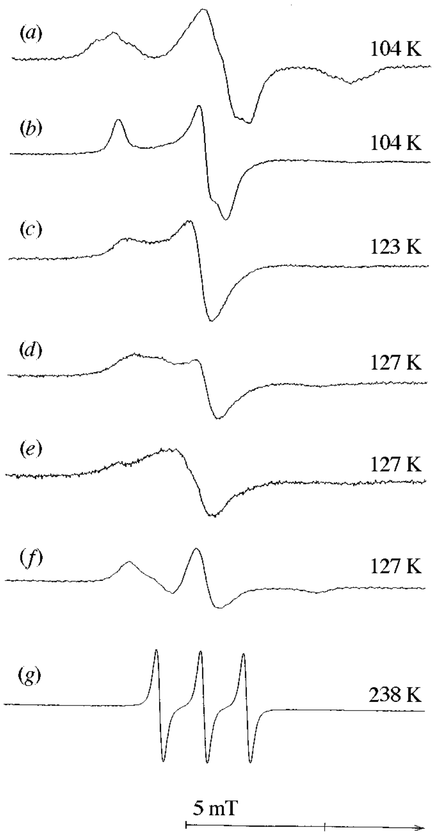

Fig. 2 First-derivative EPR spectra taken at different temperatures in a freon-113 matrix: (*a*) piperidyl radical $\mathbf{1}^{\cdot}$; (*b*), (*c*) and (*e*) piperidylperoxyl radical $\mathbf{2}^{\cdot}$; (*f*) and (*g*) aminoxyl radical $\mathbf{3}^{\cdot}$. Spectrum (*d*) was recorded during the decay of the piperidylperoxyl radical and consists of piperidylperoxyl and aminoxyl radicals. Spectrum (*e*) shows the piperidylperoxyl radical and is obtained by subtraction of spectrum (*f*) from spectrum (*d*).

After γ-irradiation of an air-saturated solution of piperidine in freon-113 frozen at 77 K and subsequent annealing above 92 K, matrix-derived peroxyl radicals $RO_2^{\cdot}$ strongly contribute to the composite EPR spectrum. Upon further warming of such samples up to 150 K, the peroxyl radicals $RO_2^{\cdot}$ decayed. In the course of annealing, piperidyl and aminoxyl radicals could be recognized in the composite EPR spectrum, and upon further warming above 150 K only aminoxyl radicals remained. Under such conditions, reaction (3), between the piperidyl radical and the matrix peroxyl radical, should be mainly responsible for the formation of aminoxyl radicals.

To avoid any interference with the matrix-derived peroxyl radicals, the piperidyl radicals were produced by prolonged annealing of the carefully degassed γ-irradiated solution of piperidine in a freon-113 matrix at 130 K. Under these particular conditions the piperidyl radical is the only radical species remaining in the matrix. Its EPR spectrum, shown in Fig. 2(*a*), is indistinguishable from that taken at 77 K [*cf.* Fig. 1(*c*)]. Taking into account the fact that the piperidyl radical $\mathbf{1}^{\cdot}$ is fairly stable in freon-113 far below the melting point of this matrix, we expect the main decay reaction of the piperidyl radical after admixture of oxygen to be with molecular oxygen.

Upon admission of oxygen (opening the samples in the air at 77 K) and annealing at 113 K , the piperidyl radical $\mathbf{1}^{\cdot}$ decays and simultaneously a novel radical species grows, which we assign to the piperidylperoxyl radical $\mathbf{2}^{\cdot}$. After 30 min annealing at 113 K the piperidyl radical $\mathbf{1}^{\cdot}$ contributes only slightly to the EPR spectrum [see Fig. 2(*b*)]. Double integration of the EPR spectra in Fig. 2(*a*) and (*b*) shows nearly quantitative conversion of the piperidyl radical into the piperidylperoxyl radical. Note that the relatively slow reaction of the piperidyl radical with molecular oxygen [reaction (1)] could not be due to restricted diffusion of oxygen in the matrix because under similar experimental conditions matrix-derived radicals are quickly and completely converted into the corresponding peroxyl radicals.

The reaction behavior of piperidyl radicals with molecular oxygen indicates either a low reactivity of piperidyl radicals towards molecular oxygen or reversibility of reaction (1), *i.e.* the peroxyl radical is formed in an equilibrium.

An asymmetric EPR line such as that of $\mathbf{2}^\bullet$ [Fig. 2(*b*)] is typical for a species having a fully anisotropic *g*-tensor with clearly defined g_1, g_2 and g_3 features.[16] As expected, no nitrogen hyperfine interaction has been observed in the EPR spectrum of the radical $\mathbf{2}^\bullet$ in the temperature range 77–123 K. The piperidylperoxyl radical $\mathbf{2}^\bullet$ has an intermediate $g_{\parallel}$-value of 2.0237 (measured at 123 K, see Table 1), which could be due to the weak overlap of the unpaired electron with the lone electron pair on the pyramidal nitrogen atom.

The piperidylperoxyl radical does not decay up to 123 K, and in the temperature range of 103–123 K its EPR spectrum changes reversibly [*cf.* Fig. 2(*b*) and (*c*)] due to the partial averaging of the *g*-anisotropy with increased molecular mobility. On warming the sample to 128 K, the piperidylperoxyl radical decays and simultaneously the aminoxyl radical $\mathbf{3}^\bullet$ appears. Both the piperidylperoxyl radical $\mathbf{2}^\bullet$ and the aminoxyl radical $\mathbf{3}^\bullet$ are observed in the composite EPR spectrum [Fig. 2(*d*)] taken after 3 min annealing at 128 K. Double integration of the EPR spectra in Fig. 2(*b*) and (*d*) shows that the overall radical concentration is nearly constant. Subtraction of the EPR spectrum of aminoxyl radical $\mathbf{3}^\bullet$ [separately shown in Fig. 2(*f*)] shows the EPR spectrum of the piperidylperoxyl radical $\mathbf{2}^\bullet$ at 128 K [Fig. 2(*e*)]. Upon further annealing at 128 K the piperidylperoxyl radical is converted into the aminoxyl radical $\mathbf{3}^\bullet$ [Fig. 2(*g*)]. This spectrum is broadened due to the dissolved oxygen. A quantitative treatment shows that *ca.* 80% of the peroxyl radical $\mathbf{2}^\bullet$ was converted into the aminoxyl radical $\mathbf{3}^\bullet$.

Considering the EPR properties of $\mathbf{2}^\bullet$ the piperidylperoxyl radical behaves like a typical peroxyl radical (see refs. 10, 11 and 17 for reviews).

Mechanism of conversion of the piperidyl radical into the aminoxyl radical

The net result of the reaction of piperidyl radicals with molecular oxygen is the formation of the aminoxyl radical. This is in agreement with steady-state[5] and time-resolved EPR results.[4,6] This could happen by reaction of aminyl radicals with alkylperoxyl [reaction (9)] or aminylperoxyl radicals [reaction (10)]

$$\mathbf{1}^\bullet + \mathrm{RO_2}^\bullet \longrightarrow \mathbf{4} \longrightarrow \mathbf{3}^\bullet + \mathrm{RO}^\bullet \qquad (9)$$

$$\mathbf{1}^\bullet + \mathbf{2}^\bullet \longrightarrow \mathbf{5} \longrightarrow \mathbf{3}^\bullet + \mathbf{3}^\bullet \qquad (10)$$

via the very unstable peroxides **4** and **5**. Under our experimental conditions (annealing of the degassed samples and the delayed addition of oxygen) only radicals derived from the piperidine could exist, *i.e.* $\mathbf{1}^\bullet$ and $\mathbf{2}^\bullet$ and at higher temperatures the product $\mathbf{3}^\bullet$. Hence, for the first time the piperidylperoxyl radical $\mathbf{2}^\bullet$ has been directly observed.

The coexistence of the aminyl and aminylperoxyl radicals observed in our experiments under various experimental conditions suggests possible reversibility of reaction (11), *i.e.* the formation of aminylperoxyl radicals in an equilibrium.

$$\mathbf{1}^\bullet + \mathrm{O_2} \rightleftharpoons \mathbf{2}^\bullet \qquad (11)$$

In the case of sterically hindered aminoxyl radicals, dimers such as **5** are not known, and if they are formed in reaction (10), they should decay highly exothermically.[18] In a recent time-resolved FTEPR study[6] the aminoxyl radical $\mathbf{3}^\bullet$ has been detected as the only radical product in the reaction of the piperidyl radical with molecular oxygen. Due to the loss of spin polarization during conversion of $\mathbf{1}^\bullet$ to $\mathbf{3}^\bullet$ its formation *via* a diamagnetic precursor was proposed. This supports our proposal of the existence of the very short-lived diamagnetic intermediate **5**.

Because of the low rate and the reversibility of the aminylperoxyl formation, recombination of these radicals is rather improbable. Hence, under our experimental conditions a mechanism analogous to tetroxide formation[5a] seems to be irrelevant.

Conclusions

In the reaction with molecular oxygen, the piperidyl radical is converted into the aminoxyl radical *via* the piperidylperoxyl radical $\mathbf{2}^\bullet$. Both, piperidyl and piperidylperoxyl radicals are important for the formation of aminoxyl radicals in a non-polar freon-113 matrix at low temperatures. Our observations suggest possible reversibility of the reaction of the piperidyl radical with molecular oxygen. Generally, depending on the reaction conditions (temperature, chemical and physical sample consistency) the reaction of aminyl radicals with aminylperoxyl radicals [reaction (2)] as well as with alkylperoxyl radicals [reaction (3)] should be taken into account in the mechanism of aminoxyl radical formation.

Acknowledgements

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