voltammetry were the same as already described.[14] Positive feedback compensation of the cell resistance[26] was used for sweep rates above 10 V s^{-1}. The working electrode was a mercury drop hanged at the tip of a gold disk of about 0.8 mm^2 surface area. The reference electrodes were Ag/Ag^+ (Ag^+ 10^{-2} M) in the used solvent (DMF, ACN, Me_2SO) or aqueous saturated calomel electrode. All the potentials were converted to values referred to the aqueous saturated calomel electrode in the corresponding medium.

Chemicals. The aromatic halides, catalysts, solvents, and supporting electrolytes were from commercial origin.[27]

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(20) The average value for the diffusion limit of usual aromatic molecules in DMF can be estimated at $5 \times 10^9\ M^{-1}\ s^{-1}$ from previous studies.[21] This figure is apparently in error by a factor of 2 since k_{dif} was taken as equal to $4\pi Dd$ (*D*, diffusion coefficient; *d*, diameter of the molecule) instead of $4\pi(2D)d$.[22] A more satisfactory value for DMF is then $10^{10}\ M^{-1}\ s^{-1}$. Taking into account the respective viscosities this would lead to $4 \times 10^9\ M^{-1}\ s^{-1}$ for Me_2SO and $2 \times 10^{10}\ M^{-1}\ s^{-1}$ for CH_3CN. The ratios between these k_{dif} values in is agreement with the peak heights obtained in cyclic voltammetry for the same compound, fluorenone, in the three solvents. Note also that a previous study by fluorescence quenching led to a value very close to $2 \times 10^{10}\ M^{-1}\ s^{-1}$ for CH_3CN.[23]

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N-tert-Butoxy-*N-tert*-alkylaminyls. A New Class of Persistent Radicals[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received August 16, 1979*

Abstract: *N-tert*-Butoxy-*N-tert*-butylaminyl (**1·**) and three related radicals have been generated from their parent hydroxylamines in hydrocarbon solution. In the absence of oxygen these radicals are extremely persistent. Their electronic structures, as indicated by their EPR parameters (a^{14N}, a^{17O}, and a^{13C}, all determined without isotopic enrichment) and the N-H bond strength in **1-H** (measured as 81.0 kcal/mol), show that the effectiveness of conjugative electron delocalization is reduced relative to that in the isomeric nitroxides. This effect is attributed to the greater electronegativity of oxygen compared with nitrogen.

We have been interested for many years in the rates and mechanisms of decay of four classes of isoelectronic radicals: alkylperoxyls (ROO·),[3] alkyl nitroxides (R_2NO·),[4] alkylhydrazyls ($R_2N\dot{N}R$),[5] and alkoxyaminyls ($R\dot{N}OR$).[6] Although persistent *N*-alkoxyarylaminyl radicals[6,7] and a persistent *N*-alkoxy-*N*-vinylaminyl[8] are known, there are no reports of a persistent *N*-alkoxy-*N*-alkylaminyl.[9] Tertiary alkyl groups dramatically increase the persistence of peroxyls, nitroxides, and hydrazyls. Unfortunately we were previously unable to explore this area of $RO\dot{N}R$ chemistry since all our attempts to synthesize *N,O*-di-*tert*-butylhydroxylamine were unsuccessful.[6] This problem has now been overcome since Meesters and Benn[11] have reported an elegant synthesis of this compound and of three other *N-tert*-butoxy-*N-tert*-alkylamines. They very kindly presented us with samples of their hydroxylamines and we have been able to show that the corresponding *N-tert*-butoxy-*N-tert*-alkylaminyl radicals are extremely persistent in solution under oxygen-free conditions.

Experimental Section

Sample Preparation. *N,O*-Di-*tert*-butylhydroxylamine (**1-H**) was prepared according to the procedure of Meesters and Benn[11] and purified by distillation and preparative GLC. *N-tert*-Amyl-, *N-tert*-octyl-, and *N*-(1-adamantyl)-*O-tert*-butylhydroxylamine (**2-H**, **3-H**, and **4-H**, respectively) were liberated from their hydrochlorides under oxygen-free conditions. Normally this reaction was carried out under vacuum directly in the EPR tube by distilling onto 5-25 mg of the solid hydrochloride thoroughly deoxygenated NH_3 and a hydrocarbon solvent (usually benzene or *n*-pentane).

Radical Generation. Radicals **1·**, **2·**, **3·**, and **4·** were generated in hydrocarbon solvents by one of the following methods: (a) UV photolysis of the hydroxylamine in the presence of di-*tert*-butyl peroxide; (b) UV photolysis of the hydroxylamine alone; (c) H abstraction by an inorganic oxidizing agent, e.g., PbO_2 and Ag_2O in the presence of a drying agent, usually $MgSO_4$, and $K_3Fe(CN)_6$ in 2 N NaOH.

If the foregoing procedures were carried out under oxygen-free conditions, using thoroughly degassed solvents and reagents, high concentrations of *N-tert*-butoxy-*N-tert*-alkylaminyl radicals could be generated. The radicals obtained in this way were extremely persistent, there being no detectable decay over very many days at room temperature. However, if oxygen was not carefully excluded, the radicals were very much less persistent, especially when they were generated by photolysis. Decay rates were not reproducible and, during photolysis, an intense spectrum of the corresponding *tert*-butoxy-

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tert-alkyl nitroxide, $Me_3CON(\dot{O})R$ ($a^N \sim 26$ G), could be observed. These radicals decayed rapidly when the light was cut off. Small amounts of di-*tert*-alkyl nitroxides were also formed in these experiments.

Higher radical concentrations could be obtained by chemical oxidation than by photolysis. Normally, a ca. 1 M solution of the hydroxylamine in benzene was stirred with PbO_2 or Ag_2O in the presence of $MgSO_4$ at 40-50 °C for 10-15 min. Traces of O_2 proved to be less of a problem than was the case with the photolytically generated radicals.

At concentrations of ca. 10^{-5} M in pentane the radicals showed no sign of dimerization to form a diamagnetic product at temperatures down to −80 °C.

EPR Measurements. Spectra were recorded on a Varian E 104 EPR spectrometer. Spectroscopic parameters for the radicals were obtained from measurements of the magnetic field positions and microwave operating frequencies. The EPR parameters showed no significant change over a range of temperatures from −80 to +60 °C.

The spectra of all radicals were sufficiently intense that a number of satellite lines could be observed. The radicals giving rise to these satellites contain ^{13}C, ^{15}N, and ^{17}O in natural abundance (^{13}C, 1.11%, $m_I = 1/2$; ^{15}N, 0.36%, $m_I = 1/2$; ^{17}O, 0.037%, $m_I = 5/2$; the intensities of the ^{17}O satellites are therefore only 0.006% of the intensities of the three central lines. To our knowledge, there is only one previous report on the detection of ^{17}O hyperfine splitting (hfs) from samples with ^{17}O in natural abundance and this was for a radical anion having one central line and four equivalent oxygens.[12]

From the remaining satellites, only the ^{13}C lines of **1·** were sufficiently well resolved to allow exact measurements of the coupling constants. The remaining ^{13}C and ^{15}N hfs could not be determined because of overlap among the various satellites.

Equilibrium Measurements. In order to obtain the N-H bond strength of **1**-H, we attempted to measure by EPR the equilibrium constant for H transfer between **1**-H and a persistent radical, R·, for which the bond strength for the parent compound R-H was already known.

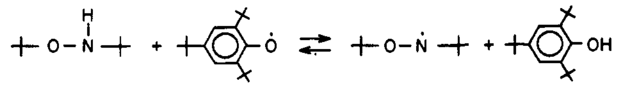
$$\mathbf{1}\text{-H} + R\cdot \rightleftharpoons \mathbf{1}\cdot + R\text{-H}$$

$$K = [\mathbf{1}\cdot][R\text{-H}]/[R\cdot][\mathbf{1}\text{-H}]$$

For this purpose, H transfer has to be the *only* reaction between the two species, and both radicals have to persist for the duration of the experiment.

Attempts to react **1**-H with bis(trifluoromethyl) nitroxide ($(CF_3)_2NO\cdot$) and with diadamantylketiminoxy ($(^1Ad)_2C{=}NO\cdot$) were unsuccessful. These compounds reacted with **1**-H by pathways other than purely an H exchange. The mechanism of these other reactions was not investigated. However, the appropriate conditions for determining the **1**-H bond strength were met with 2,4,6-tri-*tert*-butylphenoxyl (**5·**).

Samples for equilibrium measurements were prepared by mixing benzene solutions of **1**-H and **5·** of known concentrations. Radical **5·** was prepared in essentially quantitative yield by stirring a benzene solution of the corresponding phenol, **5**-H, with $PbO_2/MgSO_4$. All operations were carried out under oxygen-free conditions (either vacuum or under an argon atmosphere). The concentrations of solutions of **5·** were checked against DPPH as standard and were found to equal the starting concentration of **5**-H within the limits of accuracy of this procedure. The overall radical concentration did not change upon mixing the solutions of **1**-H and **5·**. The equilibrium constant, *K*, was evaluated by measuring the relative intensities of **1·** and **5·** by double integration of their first-derivative EPR spectra. Knowledge of this ratio and the starting concentrations of **1**-H and **5·** allows *K* to be calculated.



1-H **5·** **1·** **5-H**

Results and Discussion

All four *tert*-butoxy-*tert*-alkylaminyl radicals could be generated by direct photolysis of their parent hydroxylamines. The anticipated mechanism for their formation is

$$Me_3CONHR \xrightarrow{h\nu} Me_3C\dot{O} + H\dot{N}R$$

$$\left.\begin{matrix} Me_3CO\cdot \\ R\dot{N}H \end{matrix}\right\} + Me_3CONHR \rightarrow \left.\begin{matrix} Me_3COH \\ H_2NR \end{matrix}\right\} + Me_3CO\dot{N}R$$

This mechanism is supported by the detection (by GLC) of traces of *tert*-butyl alcohol and *tert*-butylamine in an EPR sample of $Me_3CONHCMe_3$ after prolonged irradiation.

Table I. EPR Parameters for $Me_3CO\dot{N}R$ Radicals[a]

radical	R	g	$a^{^{14}N}$	$a^{^{17}O}$	a^{other}
1·	Me_3C	2.0049	14.1	11.4	9.1 (1 ^{13}C)[b] 7.0 (3 ^{13}C)[b,c]
2·	$Et(Me)_2C$	2.0050	14.1	11.5	*c, d*
3·	$Me_3CCH_2(Me)_2C$	2.0049	14.5	11.4	*c, d*
4·	1-adamantyl	2.0049	14.1	11.6	*c, d*

[a] In *n*-pentane or benzene at 24 °C. Hyperfine splittings are given in gauss. [b] Assigned to *N*-*tert*-butyl group. [c] ^{15}N hfs insufficiently resolved. [d] ^{13}C hfs insufficiently resolved.

The EPR parameters for the four radicals studied in this work are listed in Table I. Their *g* values and nitrogen hfs require no comment since they are similar to those reported for other alkoxyalkylaminyls.[6,7] The ^{13}C hfs observed with **1·** can be assigned to the *N*-*tert*-butyl group. The hfs of the *N*-alkyl groups and the *O*-*tert*-butyl groups are not resolved, because of the large EPR line widths (ca. 1.0 G). Only in the case of *N*-(1-adamantyl)-*O*-*tert*-butoxyaminyl (**4·**) could an incompletely resolved hydrogen hfs be observed. An attempt to measure a^H for **1·** by the NMR method[13] was unsuccessful because the radical could not be generated in sufficiently high concentration (>0.1 M).

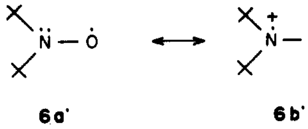
A simple relationship between the isotropic ^{17}O hfs, $a^{^{17}O}$, and the π-spin density at the oxygen nucleus, ρ_O, has been developed by Silver[14] through an investigation of the ^{17}O hfs of organic and inorganic oxygen-containing radicals.[15]

$$Q^O = a^{^{17}O}/\rho_O = 41 \text{ G}$$

It is presumed that any spin polarization at the oxygen nucleus is completely dominated by the π-spin density on the oxygen so that the effect of the spin on neighboring atoms can be ignored. If Silver's equation is applied to **1·**, the π-spin density on oxygen will be ca. 0.30. This leaves a spin density for nitrogen, ρ_N, of ca. 0.70, provided that delocalization into the alkyl substituents can be neglected. A ρ_N value for **1·**, significantly greater than the value of ca. 0.5 which has been generally accepted[16,17] for di-*tert*-butyl nitroxide (**6·**) and related radicals, is also indicated by the magnitude of the *N*-*tert*-butyl ^{13}C hfs for these two radicals in benzene, viz., $a^{C}_{CMe_3} = 9.1$ G for **1·**, 4.38 G for **6·**;[18] $a^{C}_{C(CH_3)_3} = 7.0$ G for **1·**, 4.35 G for **6·**.[18]

When comparing the spectroscopic or chemical properties of isomeric alkoxyaminyl and nitroxide radicals the greater electronegativity of oxygen compared with nitrogen should always be kept in mind. This difference in electronegativity implies, for example, that the dipolar canonical structure **1b·** will contribute less to the resonance hybrid of **1·** than does the corresponding dipolar canonical structure **6b·** to the hybrid of

1a· **1b·**



6a· **6b·**

6·. Conjugative electron delocalization is therefore less important in **1**· than in **6**·. This led us to conclude that the N–H bond strength in **1**-H should be greater than the O–H bond strength in **6**-H—which is known to be ca. 70 kcal/mol.[19] To check this prediction the equilibrium constant, $K = ([\mathbf{1}\cdot][\mathbf{5}\text{-H}]/[\mathbf{5}\cdot][\mathbf{1}\text{-H}])$, was measured in benzene. At 24 °C, K is 1.48 ± 0.30 (mean of five separate determinations) and hence $\Delta G = 0.2$ kcal/mol. A calorimetric measurement of the O–H bond strength for **5**-H gave 81.2 kcal/mol in benzene.[20] Provided that solvent effects are essentially the same for the **1**·/**1**-H pair as for the **5**·/**5**-H pair and that ΔS for H-atom transfer is negligible, the N–H bond strength for **1**-H will be 81.0 kcal/mol.

The great persistence of the *tert*-butoxy-*tert*-alkylaminyls stands in interesting contrast to the behavior of the (unknown) trialkylsilyltrialkylsiloxyaminyls.[21] Hydrogen-atom abstraction from *N,O*-bis(trimethylsilyl)hydroxylamine yields only bis(trimethylsilyl)nitroxide, even at temperatures as low as −80 °C.[21]

$$\mathrm{Me_3SiONHSiMe_3} \xrightarrow{(-\mathrm{H}\cdot)} [\mathrm{Me_3SiO\dot{N}SiMe_3}]$$

$$[\mathrm{Me_3SiO\dot{N}SiMe_3}] \xrightarrow{\circlearrowleft} \mathrm{(Me_3Si)_2NO}$$

Intramolecular radical rearrangements occurring by 1,2 migration of silicon-centered groups between two heteroatoms are well documented.[22] However, analogous processes do not occur with sp^3-hybridized carbon-centered groups because sp^3 carbon has no orbital which is sufficiently low lying to accept the unpaired electron in the transition state. (In contrast, silicon has fairly low-lying vacant d orbitals.) The lowest energy pathway by which an alkoxyalkylaminyl could rearrange to a nitroxide would involve the elimination and readdition of the *O*-alkyl group, i.e.

$$\mathrm{Me_3CO\dot{N}CMe_3} \xrightarrow{\beta} \mathrm{Me_3\dot{C}} + \mathrm{O{=}NCMe_3} \rightarrow \mathrm{(Me_3C)_2NO\cdot}$$

From the observed persistence of these radicals we estimate that the activation energy for this β-scission must be ≥28 kcal/mol.

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