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C-NITROSO COMPOUNDS—VII

AN ESR STUDY OF ALKYLNITROXIDES[1]

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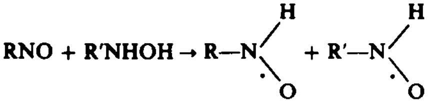
Abstract—It is demonstrated that alkylnitroxides can be generated from nitrosoalkanes by thermal reduction with hydroxylamines or by photoreduction with thiophenol. The solvent dependence of the ratio of the nitrogen and hydrogen splitting constants in t-butylnitroxide is explained on the basis of mesomeric contributions to the structure of the radical.

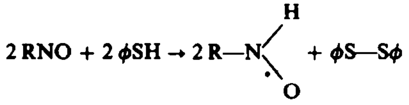
NITROXIDES with the general structure RR'NO· in which R'or R' = alkyl, phenyl, acyl and alkoxy have been described in the literature.[1–5] The combination R = alkyl and R' = H leads to relatively unstable *alkylnitroxides*, which have been investigated less broadly. Recent interest in these radicals[6–9] prompts us to report our results of an ESR study of these compounds.

Due to the instability of the alkylnitroxides they were only detected hitherto in flow systems by oxidation of aqueous solutions of hydroxylamines[6–8] and oximes.[9] This paper describes the formation of alkylnitroxides in a static system by reduction of nitrosoalkanes. The reduction was achieved by thermal reaction with a hydroxylamine:



$$\mathrm{RNO + R'NHOH \rightarrow R{-}N\!\!\begin{array}{l}\diagup H\\ \diagdown \dot{O}\end{array} + R'{-}N\!\!\begin{array}{l}\diagup H\\ \diagdown \dot{O}\end{array}}$$

or by photochemical reaction with thiophenol, which can be used as a (photo-) reducing agent:[10]



$$\mathrm{2\,RNO + 2\,\phi SH \rightarrow 2\,R{-}N\!\!\begin{array}{l}\diagup H\\ \diagdown \dot{O}\end{array} + \phi S{-}S\phi}$$

Hydroxylamines and diphenyl-disulfide are major products.[11]

When R is a *tertiary* group and R' a *secondary* one (e.g. cyclohexyl-) two alkylnitroxides may arise from the reaction of nitrosoalkanes with a hydroxylamine. However, the ESR spectrum of the t-alkylnitroxide is predominant, due to the greater stability of the radical. When both R and R' are t-alkyl groups radical-signals were found, which could not be interpreted up till now.

The ESR spectra of the alkylnitroxides are characterized by a nitrogen splitting $a_N \approx 13$ gauss and a large hydrogen splitting $a_{NH} \approx 10$–13 gauss, depending on the polarity of the solvent. The g-values are not significantly different from those of the dialkylnitroxides.

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The spectrum of a *secondary* alkylnitroxide (isopropyl instead of t-butyl) is given in Fig. 1b, which shows an additional hyperfine splitting by the H atom in β-position with respect to the N atom.

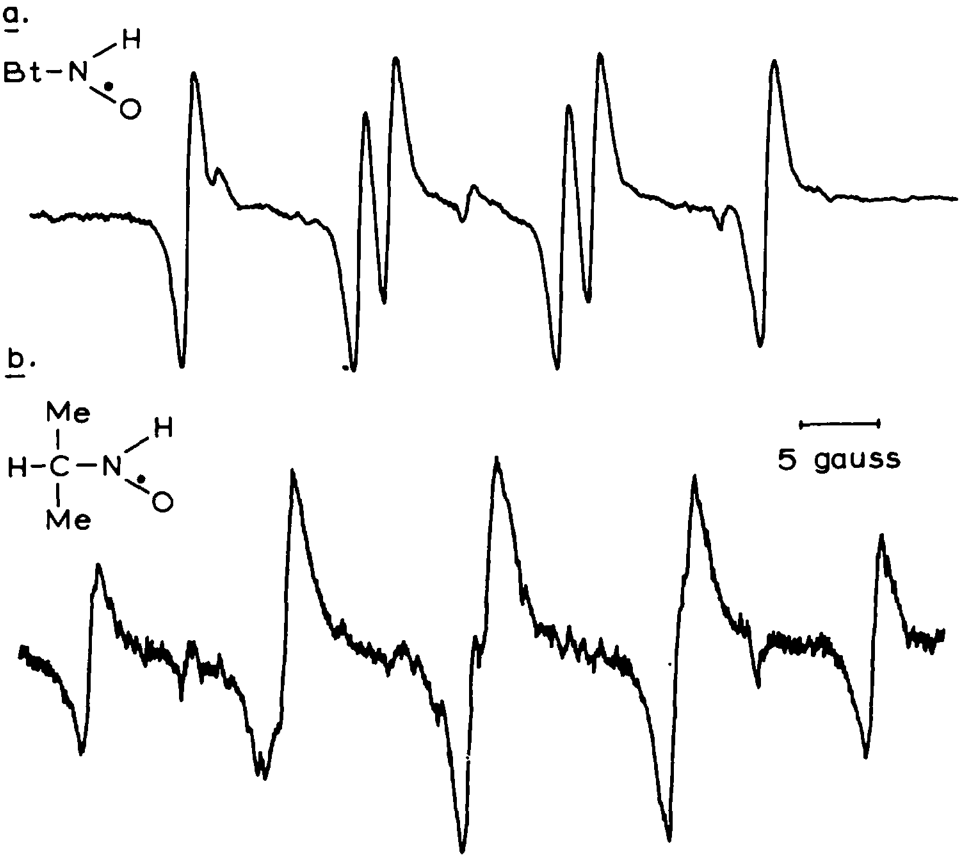


FIG. 1 ESR spectra of (a) t-butylnitroxide, (b) isopropylnitroxide.

The following considerations explain why the *secondary* nitroxide can not be formed under the same experimental conditions as the *tertiary* nitroxide. Nitroso compounds are known to exist in monomeric and dimeric forms, which are in equilibrium in solution. Solutions of *tertiary* nitrosoalkanes contain considerable amounts of the (blue) monomeric form whereas solutions of *primary* and *secondary* nitrosoalkanes contain at room temperature chiefly the (colourless) dimeric form.

Consequently the formation of an alkylnitroxide from solutions of a (largely monomeric) t-nitroso compound and cyclohexylhydroxylamine takes place already at room temperature. The dimeric sec-nitroso compound does not react at this temperature, but at higher temperatures monomer is generated and at about 60° nitrosocyclohexane (mixture of mono- and dimeric forms) and cyclohexylhydroxylamine yield cyclohexylnitroxide, clearly recognized by its characteristic ESR spectrum.

The same signal is present during photolysis ($\lambda > 320$ nm) of dimeric nitrosocyclohexane in thiophenol at room temperature. In this case monomer is generated photochemically from the dimer,[12, 13] and it is photoreduced by thiophenol; no thermal nitroxide formation is found. The dialkylnitroxide, which can be generated photochemically from a nitrosoalkane[14] is not stable under these experimental conditions.

With respect to the influence of the wavelength on the photoreduction we have found, that both UV light and red light (monomeric nitrosoalkanes absorb light of about 680 nm) accelerate the thermal reduction of monomeric nitrosoalkanes by thiophenol.[11] However, the alkylnitroxide is only detected during irradiation with UV-light, presumably because of the more intensive irradiation in the UV-region of the available light source (Philips SP 500 super high pressure mercury lamp). When in the photoreduction deuterated thiophenol (ϕSD) was used instead of the undeuterated compound the large a_{NH} was replaced by a small a_{ND}, a_{DH} = 0·15.[15]

The hyperfine splitting constants of the alkylnitroxides are listed in Tables 1 and 2.

The influence of the polarity of the solvent on the hfs constants of t-butylnitroxide is given in Table 3. For other nitroxides[16, 17] an increase in the nitrogen splitting constant with the polarity of the solvent has been found. For phenylnitroxide[17] the ratio a_{NH}/a_N is constant; on the contrary in t-butylnitroxide a_N/a_{NH} varies with the solvent. By plotting Reichardt's E_T-value[18] as a suitable criterion for solvent polarity a straight line is found for a_N/a_{NH} versus E_T (Fig. 2).

TABLE 1. HFS CONSTANTS OF ALKYLNITROXIDES (RNHO$^\cdot$) BY PHOTOREDUCTION IN THIOPHENOL AT 25°

R =	Splitting constants (in gauss)				g-value
	a_N	a_{NH}	a_{ND}	$a_{H\beta}$	
$—C(Me)_3$	13·1	11·2	1·81	—	2·0063
$—C(Me)_2CH_2Cl$	12·9	11·4	1·75	—	2·0063
$—C(Me)_2CH_2OAc$	13·0	11·4	1·75	—	2·0063
—cyclohexyl	12·8	11·5	—	11·8	2·0062
$—CH(Me)_2$	12·9	11·5	1·80	11·8	2·0062

TABLE 2. HFS CONSTANTS OF ALKYLNITROXIDES (RNHO$^\cdot$) FROM NITROSOALKANES AND CYCLOHEXYLHYDROXYLAMINE IN TOLUENE*

R =	Splitting constants (in gauss)		
	a_N	a_{NH}	$a_{H\beta}$
$—C(Me)_3$	13·0	10·6	—
$—C(Me)_2$-iPr	12·6	10·8	—
$—C(Me)_2CH_2OH$	12·4	10·6	—
$—C(Me)_2CH_2Cl$	12·8	10·5	—
$—C(Me)_2CH_2OAc$	12·8	10·8	—
—cyclohexyl	12·8	10·5	10·5

* For R = t-alkyl a small additional signal of the di-t-alkyl-nitroxide is found several times.

TABLE 3. VARIATION OF ESR DATA OF t-BUTYLNITROXIDE WITH SOLVENT-POLARITY

Solvent	Reichardts value E_T (cf ref. 18)	Splitting constants (in gauss)			g-value
		a_N	a_{NH}	a_N / a_{NH}	
Toluene	33·9	13·0	10·6	1·23	2·0060
Benzene	34·5	12·8	10·6	1·21	2·0060
Chloroform	39·1	13·2	11·3	1·16	2·0060
Methylenechloride	41·1	13·1	11·3	1·18	—
Acetone	42·2	12·8	11·0	1·16	2·0061
Acetonitrile	46·0	12·9	11·4	1·13	—
Nitromethane	46·3	13·1	11·5	1·13	—
Isopropanol	48·6	13·4	12·1	1·10	—
Ethanol	51·9	13·3	12·1	1·09	—
Methanol	55·5	13·4	12·5	1·07	—
Water	63·1	13·8	13·8	1·00	—

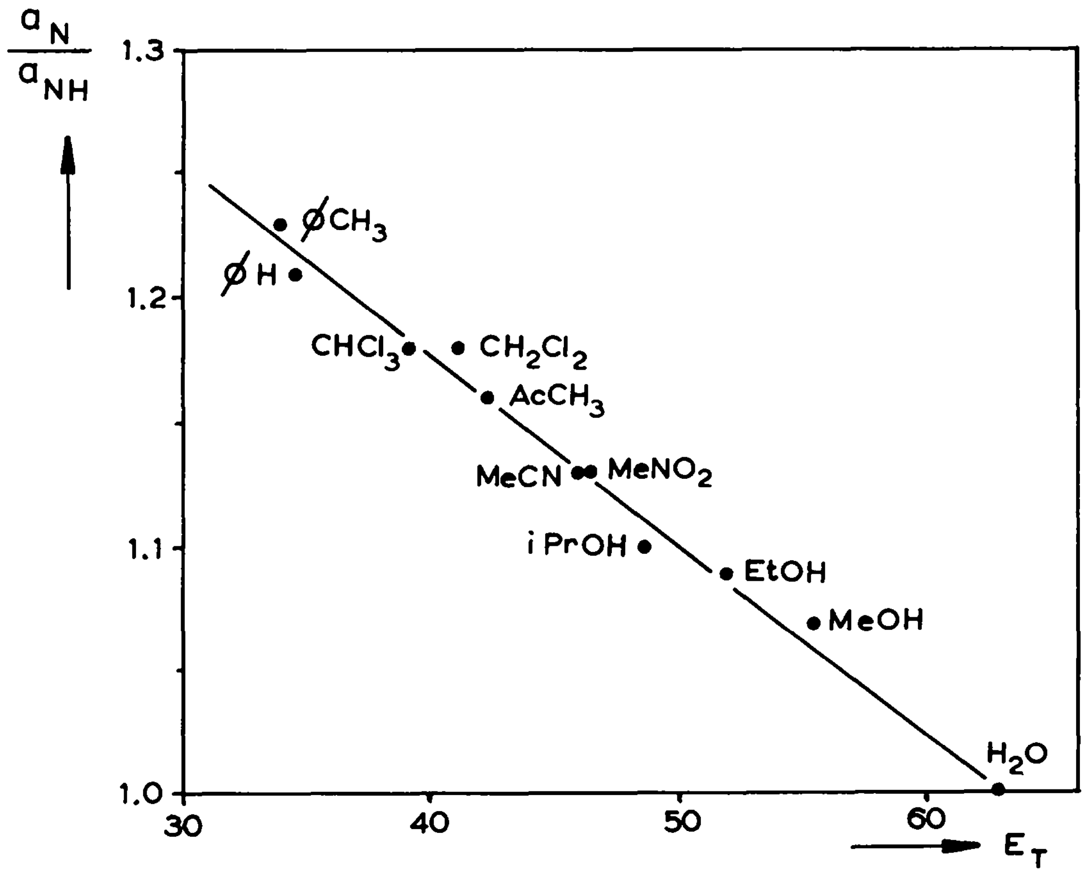


FIG. 2 Solvent dependence of a_N/a_{NH} for t-butylnitroxide. E_T is Reichardt's polarity parameter.[18]

To account for the influence of the solvent two formulae have to be considered for both the nitrogen and hydrogen splitting:[19]

$$a_N = Q_N \cdot \rho_N + Q_O \cdot \rho_O$$

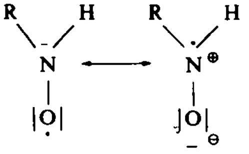
and

$$a_{NH} = Q_{NH} \cdot \rho_N$$

where ρ_N and ρ_O are the spin densities on the N and O atoms respectively, and Q_N and Q_O are parameters giving the contributions from the spin densities on the N and O atoms to the hyperfine structure. The a_{NH} is proportional to the spin density on the N atom if the hybridization of the N atom in the alkylnitroxides ls sp^2. From the formulae it follows that:

$$a_N/a_{NH} = \frac{Q_O}{Q_{NH}} \cdot \frac{\rho_O}{\rho_N} + \text{constant.}$$

Assuming that the Q-values are solvent independent[20] a decrease in the ratio a_N/a_{NH} is possible if ρ_N increases at the expense of ρ_O. So the decrease of this ratio for t-butylnitroxide with solvent polarity can be explained by a larger contribution of the polar mesomeric structure (b) to the resonance in the N—O bond.



(a) (b)

EXPERIMENTAL

All starting compounds were prepared following known methods.[14] Cyclohexylhydroxylamine was synthesized by reduction of nitrosocyclohexane.[21] Deuteration of thiophenol was achieved with D_2O in tetrahydrofuran. The ESR spectra were measured using a Varian E-3 spectrometer with 100 Kc/s field modulation along with a variable temp. accessory and optical transmission cavity. g-Values were determined, using solid diphenyl-dipicryl-hydrazyl (g = 2·0036) as a standard, with an accuracy of 0·0002.

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