SPIN TRAPPING REACTIONS WITH NITRIC OXIDES. III. ALKOXYALKYLNITROXIDES AND NEW NITROGEN CEN-
TERED RADICALS

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Abstract: Subsequent trapping of photochemically generated alkyl and alkoxy radicals by
nitric oxide yields alkoxyalkylnitroxide radicals. New types of nitrogen centered radicals
have been detected and tentatively explained by reactions of nitrogen oxides N_2O, NO, NO_2,
N_2O_3, N_2O_4 with alkyl and peroxide radicals.

In the preceding papers we investigated the spin trapping reactions of nitric oxide when
alkyl radicals are generated photochemically[1], and when peroxy radicals are formed by oxida-
tion of alkyl radicals[2]. In the present paper we account for our results of trapping alkoxy
radicals with nitric oxide. We also report observation of a few other non-stable nitrogen cen-
tered radicals formed by scavenging alkyl and peroxy radicals with different compounds of nit-
rogen and oxygen, like N_2O, NO_2, N_2O_3, N_2O_4 etc., which can be present in the course of gener-
ation of nitric oxide[3], particularly, when oxygen is not completely purged out of the reactor.

The same experimental apparatus (JEOL-JES-FE-3X spectrometer) and the same technique of
generating nitric oxide was applied as earlier[1]. Radicals were generated in hydrocarbon sol-
vents (RH) by anthraquinone (AQ) in its photoexcited triplet state and by photolysis of di-t-
butylperoxide (DTBP). Electron Spin Resonance spectra were recorded both in the course of ir-
radiation and thereafter at low temperature (between -50 $^{\circ}$C and -80 $^{\circ}$C).

At low temperature and in deaerated solvents containing dissolved nitric oxide and DTBP,
the characteristic signal[4] of alkoxyalkylnitroxide radicals (AANO) can be observed during ir-
radiation. The spectroscopic parameters of radicals are given in Table 1. The intensity of
this signal is significantly larger than that of the dialkylnitroxides (R_2NO) during irradia-
tion, but in the dark this signal disappears fast.

After an induction period, the build up of AANO and R_2NO is accelerated, which shows the
formation of alkylnitroso scavenger:

$$DTBP \xrightarrow{h\nu} t-BuO^{\cdot} , \tag{1}$$

$$t-BuO^{\cdot} + RH \rightarrow R^{\cdot} + t-BuOH , \tag{2}$$

$$R^{\cdot} + NO \rightarrow RNO , \tag{3}$$

$$RNO + t-BuO^{\cdot} \rightarrow t-BuO(R)NO^{\cdot} , \tag{4}$$

$$RNO + R^{\cdot} \rightarrow R_2NO^{\cdot}, \tag{5}$$

where BuO' stands for the butoxy radical.

Table 1. Spectroscopic parameters of radicals detected by applying nitric oxides as scavengers

Solvent	Radical	g	a_N	a_H	a'_N
toluene	I	2.0055	2.668	0.642 (2)	
ethylbenzene	II	2.0055	2.668	0.432 (1)	
n-pentane	III	2.0056	2.671	0.16 (1)	
cumene	IV	2.0054	2.752	–	
ethylbenzene*	Va	2.0040	2.978		
	Vb	2.0042	2.978		
cumene*	Va	2.0040	2.983		
	Vb	2.0042	2.983		
cumene	VI	2.0042	2.999		0.098
ethylbenzene	VII	2.0039	3.031	0.134 (1)	0.066
ethylbenzene	VIII	2.0049	3.374	0.170 (1)	0.044
cumene	IX	2.0063	1.179	1.055 (1)	0.695

*A doublet structure of 0.041 mT was detected, which was interpreted as a superposition of two signals with different g values due to the asymmetry of signal.

The decay rate of AANO was found to decrease in dark if the NO concentration is small, i.e., the nitric oxide can react with the nitroxide radicals:

$$t\text{-BuO(R)NO}^{\cdot} + NO \; \rightleftharpoons \; t\text{-BuO(R)NONO} . \tag{6}$$
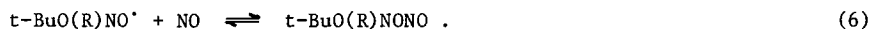
In the experiments, where radicals were generated by AQ, AANO signal was not detected. If oxygen was admitted into the reactor, when nitric oxide was formed, and this gas mixture was admitted into previously degassed ethylbenzene and cumene solvents containing either AQ or DTBP, new types of signals could be detected at low temperature after short UV irradiation. The spectral parameters are also given in Table 1 for radicals V-VIII. These radicals are not stable under UV irradiation and disappear after a few minutes. In dark, however, these radicals are more persistent than the AANO radicals.

An additional type of radical (IX in Table 1) was also observed in cumene if nitric oxide is admitted into air saturated solvent containing either AQ or DTBP. In this case the large oxygen concentration converts all alkyl radicals into peroxides, which prevents formation of R_2NO and acylalkylnitroxides (ARNO), and after prolonged UV irradiation a spectrum of 18 lines with identical intensity appears. This signal is rather stable below -50 $^{\circ}$C in dark. If only trace amount of oxygen is present, this signal also appears, but its intensity is much smaller than that of the ARNO radical.

In order to assign tentatively the above radicals, we made a compilation of literature data for the g values and a_N hyperfine constants of different nitrogen centered radicals[4-18] (we use the term "nitrogen centered" for radicals, where a significant portion of spin density is localized on the nitrogen atom). The most characteristic values in organic solvents are given in Table 2. According to this Table, the nitroxide and aminyl (or amidyl) radicals of similar structure can be easily distinguished by their g values. The small g values of radicals V-VII, e.g., are typical for aminyl radicals, but the a_N values are much larger than

Table 2. Compilation of spectroscopic parameters for different nitrogen centered radicals in organic solvents

Compound	g	a_N (in mT)	a''_N	Ref	Compound	g	a_N (in mT)	a'_N	Ref
$R\dot{N}R$	2.0048	1.5		(5)	$R\dot{N}R$ with $\overset{O^{\cdot}}{\vert}$	2.0060	1.5		(6)
$\overset{O}{\overset{\Vert}{-C}}-\dot{N}R$	2.0052	1.5		(7)	$\overset{O\ O^{\cdot}}{\overset{\Vert\ \vert}{-C}}-\dot{N}R$	2.0066	0.7		(8)
$R\dot{N}OR$	2.0040	1.5		(9)	$R\dot{N}OR$ with $\overset{O^{\cdot}}{\vert}$	2.0052	2.7		(4)
$\overset{O}{\overset{\Vert}{-C}}-\dot{N}OR$	2.0058	1.1		(10)					
$>C=\dot{N}$	2.0030	1.0		(11)	$>C=\dot{N}$ with $\overset{O^{\cdot}}{\vert}$	2.0062	3.0		(12)
$RN=\dot{N}$	2.0005	2.2	1.0	(13)	$RN=\dot{N}$ with $\overset{O^{\cdot}}{\vert}$	2.0015	3.0	0.2	(14)
$>C=N-\dot{N}R$	2.0035	1.1	0.75	(15)					
$R'_2N-\dot{N}R$	2.0038	1.1	0.9	(16)	$R'_2N-\dot{N}R$ with $\overset{O^{\cdot}}{\vert}$	2.0052	1.2	0.2	(17)
					$RN-NO$ with $\overset{O^{\cdot}}{\vert}$	2.0058	1.0	0.35	(18)

Here R stands for alkyl, aryl groups or for hydrogen atom.

was measured for aminyl radicals. We think the large a_N value can occur, when two oxygens are bonded to the nitrogen, which can give significant contribution to the s-p hybridization of nitrogen orbitals. At least, it is the case both for AANO and $RNO_2^{\cdot -}$ anion radicals[19]. Namely, radical V can be interpreted as a dialkoxyaminyl radical. As the same spectrum was obtained for radical V in cumene and ethylbenzene and no additional hyperfine splitting was observed except an asymmetric doublet with 0.041 mT separation (it was assigned to a superposition of radicals Va and Vb), we assign radical V to diacyloxyaminyl radical, where the two ground conformations have slightly different parameter sets:

$$\text{Va} \qquad\qquad \text{Vb}$$
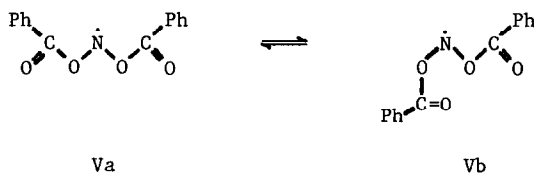
Analogous reactions between NO_2 and peroxide radicals, that we observed between NO and peroxide[2], can yield to the formation of radical V.

In the case of radicals VI and VII, additional hyperfine splittings were observed from a second nitrogen and a hydrogen. These radicals can be formed either by addition reaction of NO and an NO_2-alkyl adduct (alkylnitrite):

$$RONO + NO \longrightarrow R\dot{N}ONO \qquad\qquad\qquad (7)$$

or by alkyl radical trapping of N_2O_3

$$R^{\cdot} + N_2O_3 \longrightarrow R\overset{\cdot}{N}ONO \ . \tag{8}$$

According to Table 2, the $\underline{g}$ values are typically larger by 0.001 for nitroxides, than for the analogous aminyls, thus radical VIII can be a nitroxide analogue of VII, which can be formed by two ways:

$$RONO + NO_2 \longrightarrow RON\overset{\overset{\displaystyle O^{\cdot}}{|}}{O} \tag{9}$$

or

$$R^{\cdot} + N_2O_4 \longrightarrow RON\overset{\overset{\displaystyle O^{\cdot}}{|}}{O} \tag{10}$$

In the spectrum of radical IX, two nitrogens give comparable splitting, which is typical for hydrazyls, but the $g = 2.0063$ value shows this radical should be an aminonitroxide. The large hydrogen coupling can be assigned to an NH hydrogen of the NO group and the lack of additional splitting makes it probable, that the amino group is substituted by two acyl groups:

IX
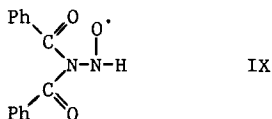
The two acyl substituents can strongly modify the spin distribution of the two nitrogen atoms, which can explain the anomalous ratio of nitrogen couplings. The precursor of radical IX may be an aminonitroso formed by a reaction of peroxy radicals and N_2O, which can abstract hydrogen in its excited triplet state from the solvent.

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