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SPIN TRAPPING REACTIONS WITH NITRIC OXIDES II. ACYLALKYL NITROXIDES

A. Rockenbauer*, M. Győr, and F. Tüdős†

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest,
P.O.Box 17, Hungary
†also Eötvös Loránd University, Department of Chemical Technology, H-1088 Budapest, Múzeum
krt.6-8, Hungary

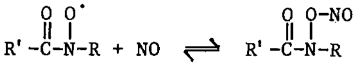
Abstract: Radical trapping by nitric oxide in the presence of oxygen has been studied by ESR spectroscopy. The oxygen was found to react much faster with alkyl radicals than nitric oxide, it suppresses formation of dialkyl nitroxides and initiates creation of acyl nitroxides through reactions between peroxy radicals and nitric oxide.

In paper I[1] we investigated the spin trapping properties of nitric oxide, when alkyl radicals were generated photochemically. It was found that at proper experimental conditions the signal of dialkyl nitroxides (R_2NO) can be detected in a number of solvents. In this paper we study the effect of oxygen, which can concur with nitric oxide, when the alkyl radicals are trapped.

The same nitric oxide saturated hydrocarbons (toluene, diphenylmethane, n-pentane, cyclohexane, ethylbenzene, cumene and 2-methylbutane) were studied as formerly, and the alkyl radicals were generated by photochemically initiated hydrogen abstraction, which was carried out either by triplet excited state anthraquinone or by t-butoxy radicals obtained from the photodecomposition of di-tert-butyl peroxide. Besides we also applied chloroform, carbon tetrachloride and their mixture, in which solvents the UV light can abstract chlorine without any photosenzitizers. The spectrometer, UV lamp and other experimental details are the same as in Paper I[1].

If oxygen is also present beside nitric oxide, the amount of dialkyl nitroxide formed is drastically changed; even trace amount of oxygen can reduce the yield, while in air saturated solvents no radicals of R_2NO type can be observed. In these experiments, however, a new type of signal appears, the ESR spectroscopic parameters of them are given in Table 1. On the basis of small a_N coupling and large g values, these radicals are inevitably of the type of acylalkyl nitroxides[2-4] (ARNO). The multiplicity of spectra is in accordance with the number of α hydrogens in the alkyl radicals generated from the respective solvents.

Even when oxygen is present only in traces, there is a convenient way of detecting the signal of acylalkyl nitroxides, since they are less sensitive to nitric oxide than R_2NO. If, e.g., when due to a prolonged UV irradiation the majority of nitric oxide is consumed and the dialkyl nitroxides are persistent, a subsequent nitric oxide bubbling can destroy the signal of R_2NO radical, while the signal of ARNO prevails. Interestingly, argon gas bubbling through the solvent causes the same effect. If the nitric oxide concentration is large and the oxygen concentration is small, a dominant signal of R_2NO can be seen after short irradiation at low temperature. After short warming up, however, the signal of R_2NO decays fast and the signal of ARNO builds up (Fig.1). This experiment shows the reversible nature of termination reaction between nitric oxide and acylalkyl nitroxide:



$$R'-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O^{\bullet}}{|}}{N}-R + NO \rightleftharpoons R'-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O-NO}{|}}{N}-R \qquad (1)$$

Table 1

Magnetic parameters for acylalkyl nitroxide radicals

Solvent	g	a_N	a_H^*
		in mT units	
Toluene	2.0067	0.728	0.463 (2)
Ethylbenzene	2.0066	0.743	0.286 (1)
Cyclohexane	2.0066	0.740	0.266 (1)
Diphenyl-methane	2.0067	0.736	0.193 (1)
n-Pentane	2.0067	0.742	0.155 (1)
Cumene	2.0066	0.789	-
2-Methyl-butane	2.0066	0.784	-
$CHCl_3$	2.0071	0.717	0.116 (1)
$CHCl_3/CCl_4$	2.0072	0.720	-

*The number of hydrogen coupling is given in parenthesis

It is not easy to suggest a straightforward mechanism for the formation of acylalkyl nitroxides, which can be applied for primary, secondary, and tertiary alkyl radicals, as well. The first step of this process should be the fast peroxy formation:

$$R^\bullet + O_2 \longrightarrow RO_2^\bullet \qquad (2)$$

which concurs with the trapping of $R^\bullet$ radicals by NO. The self-termination of peroxy radicals, particularly for primary and secondary alkyl peroxy radicals, yields to ketones[6], which may give $R'C^\bullet{=}O$ radicals due to the excitation of acyl group[7]. This could give an analogous mechanism of the formation of ARNO radicals suggested by Maruthamutu and Scaiano[8], who studied the biradical trapping in cycloalkanones. Even though, the ketones cannot play a dominant role in the formation of acylalkyl nitroxides, since the addition of different ketones (acetone, acetophenone) to the solvent does not improve the yield of ARNO formation in any cases. For this reason, it is more likely that some reactions between the peroxy radicals and nitric oxide, which can also be affected by the UV light, can yield to acyl nitroso compound, which can subsequently trap alkyl radicals.

This reaction mechanism was checked for tertiary alkyl peroxy radicals, where the singlet peak of peroxy radicals at g = 2.0150 can be easily recorded at low temperature during illumination[9] in cumene and 2-methyl-butane. By fixing the magnetic field at a value, where the signal has its maximum, we recorded the signal amplitude as a function of time. In air saturated cumene solution, which contained anthraquinone photosenzitizer, both the saturation of build up during irradiation and the decay in dark show second order kinetics (Fig.2a). When NO is also present the rate of initial build-up is the same, which shows that the rate of peroxy formation is much faster than the trapping of alkyl radicals by nitric oxide. The build-up, however, breaks and the concentration abruptly reaches a steady-state condition at a much lower value than without nitric oxide. Moreover, the initial rate of dark decay is faster in the presence of NO, but soon the rate of decay slows down into a second order kinetics (Fig.2b). The main features of the above kinetics can be explained by the assumption of a peroxy-nitroso adduct, which can react with peroxy radicals at a high rate:

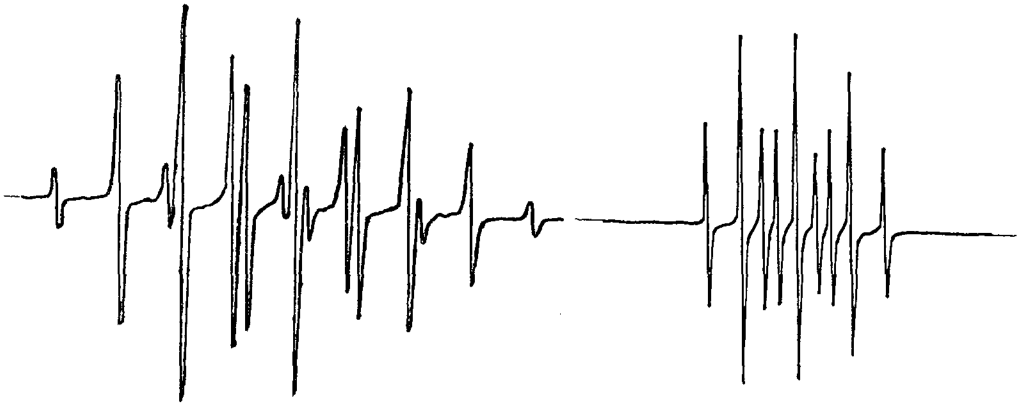


Fig.1. ESR spectra recorded at -50 °C in nitric oxide saturated toluene containing anthraquinone and trace amount of oxygen. Left: after a short irradiation; right: after a short warming up to room temperature.

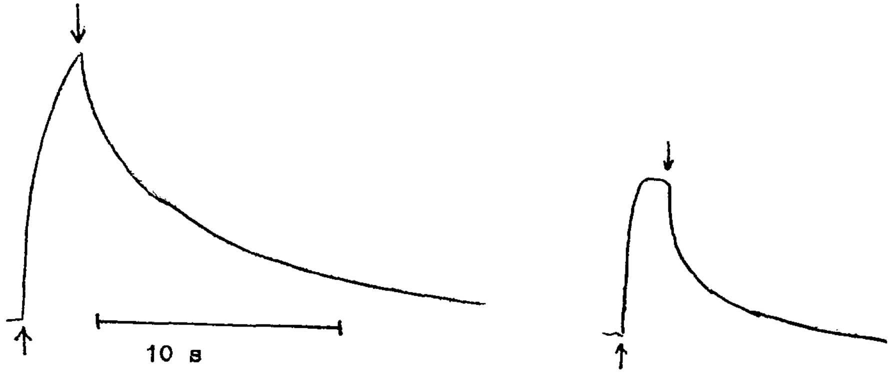
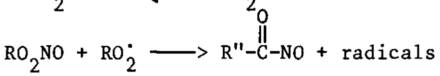


Fig.2. Kinetic ESR spectra of cumene containing anthraquinone photosenzitizer. Magnetic field was fixed, where the g = 2.0150 signal has maximum; temperature was -70 °C. Left: air saturated solvent; right: air and nitric oxide are also present. The arrows indicate the time of switch on and off of the irradiation.

$$RO_2^{\bullet} + NO \rightleftharpoons RO_2NO \qquad (3)$$



$$RO_2NO + RO_2^{\bullet} \longrightarrow R''\text{-}\overset{\overset{O}{\|}}{C}\text{-}NO + \text{radicals} \qquad (4)$$

Evidently, reaction (4) is not an elementary process and, presumably, the peroxy nitroso adduct can also decompose under the influence of light and one of the decomposition products can react with $RO_2^{\bullet}$ and yield the acyl nitroso scavenger. Additional work is required to clarify the details of the above mentioned processes.

It is interesting to note that no acylalkyl nitroxides are formed in CCl_4, but ARNO-type radicals can be observed in chloroform. The yield of ARNO formation is even larger in $CHCl_3/CCl_4$ mixtures, but the lack of hydrogen splitting shows that the acyl nitroso compound, which is formed from $\dot{C}HCl_2$ radicals, traps mainly $\dot{C}Cl_3$ radicals in this case.

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