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SPIN TRAPPING REACTIONS WITH NITRIC OXIDES,I. DIALKYL NITROXIDES

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Abstract: Dialkyl-nitroxide radicals formed from nitric oxide, which trapped two alkyl radicals in consecutive steps, have been detected by Electron Spin Resonance spectroscopy. The structure of radicals was found independent of the way of alkyl radical generation. Stereoselectivity of radical trapping was observed for secondary alkyl radicals with chiral carbons.

Though investigation of nitric oxide forms a classical chapter in the history of radical chemistry[1], the possibility of applying nitric oxide as a versatile spin trapping agent has not been exploited so far. As to our knowledge only Maruthamutu and Scaiano[2] used nitric oxide in order to trap biradicals produced by photocleavage of cycloalkanones. They recorded Electron Spin Resonance spectra of cyclic acyl-nitroxides by using flow system, as the life-time of radicals was only a few seconds.

The properties which make nitric oxide a prospective spin trap are the large rate of its addition reaction to alkyl radicals, when nitroso compound is formed[3] and the radical scavenging properties of nitroso compounds, which yield to persistent nitroxide radicals[4]. Since in these processes the nitric oxide reacts with two radicals subsequently a great variety of nitroxide radicals can be synthesized, and special spin labelling methods can also be achieved, e.g., when the NO group is directly linked to the main chain of polymers, or when it forms a crosslink in the polymer network. In the first part of these applications we demonstrate formation of dialkyl nitroxide radicals, when the alkyl radicals are photochemically generated.

In all samples hydrocarbon solvents saturated with freshly made nitric oxide were applied. NO gas was formed by dropping cc. sulphuric acid into saturated water solution of $NaNO_2$. The reactor, where the nitric oxide was generated, was flushed with argon prior to adding H_2SO_4, the solvents were purified from oxygen by argon gas bubbling. In this work we studied only those radicals that were not affected by the presence of trace amounts of other compounds of nitrogen and oxygen. High pressure mercury lamp was used for the irradiation in quartz sample tubes.

The alkyl radicals have been generated either by hydrogen abstraction from different solvents, or by photolysis of compound containing alkyl groups (e.g. 1-azo-bis-1-phenylethane, dibenzylmercury). The hydrogen abstraction was initiated either by the triplet state anthraquinone or t-butoxy radicals obtained from the decomposition of di-tert-butyl peroxide.

The ESR spectra were recorded by a JEOL-FE-3X spectrometer using a microwave power of 1 mW, modulation frequency and width of 100 kHz and 0.05 mT, respectively.

In all cases the photoirradiation of samples containing nitric oxide yields to the formation of nitroxide radicals with different structure. It was possible to apply conditions, however, when exclusively dialkyl nitroxides were formed by two subsequent radical addition processes

$$R^{\cdot} + NO \rightarrow RNO \qquad (1)$$

$$R^{\cdot} + RNO \rightarrow R_2NO^{\cdot} \qquad (2)$$

where the R alkyl group is primary in toluene and hexamethylbenzene; secondary in diphenylmethane, n-pentane, cyclohexane and ethylbenzene, and tertiary in cumene and 2-methylbutane, respectively.

The spectroscopic parameters of radicals given in Table 1 agree well with those of dialkyl nitroxide radicals synthesized by other techniques[5,6,7]. The crucial factor influencing the stability of dialkyl nitroxide radicals is the reaction with nitric oxide:

$$R_2NO^{\cdot} + NO \rightarrow R_2NONO \qquad (3)$$

Even for tertiary alkyl nitroxide the signal disappears in dark at room temperature within a few seconds if the nitric oxide concentration is large. If we apply long irradiation, however, when the majority of NO is consumed, the nitroxide radicals are persistent after stopping the irradiation. After bubbling NO through the sample again the signal disappears.

Reaction (3) was found strongly temperature dependent: below -50 °C the dialkyl nitroxides are stable even in NO-saturated solvents. After warming up the sample for a few seconds the signal disappears again. At low temperature short lived methyl-alkyl nitroxide can also be detected in ethylbenzene (VIII) and cumene (XII) showing methyl radical formation in these cases. After prolonged irradiation lines of a new nitroxide radical (VII) containing a secondary and a tertiary alkyl group appears in ethylbenzene. The intensity of these lines increases if the solvent was irradiated both before and after the NO bubbling. Consequently, the source of tertiary alkyl group is the termination product of secondary alkyl radicals. A spectrum of similar pattern can also be observed in cumene-ethylbenzene mixture (XIII). If first the cumene solvent containing nitric oxide and photosensitizer was irradiated, then the NO was removed by argon bubbling and ethylbenzene was added, in this case the second irradiation resulted in exclusively the signal of mixed-alkyl nitroxide. In 2-methylbutane, besides the main triplet a six-line pattern also appears (X) showing the formation of secondary and tertiary alkyl radicals due to the hydrogen abstraction from the solvent.

In the case of ethylbenzene the trapping of secondary alkyl radicals yields to the formation of diastereomers due to the chirality of α-carbons. In this case the spectra were always a superposition of two signals with markedly different intensity (Fig.1). The spectral parameters were not affected by the way of radical generation (hydrogen abstraction by anthraquinone or tert-butoxy radicals, or decomposition of the azo-bis compound). The two radicals can be distinguished by their different hydrogen coupling constants (VIa and VIb). This coupling is a measure of restriction for the rotation of N-alkyl group: the smaller is a_H the more

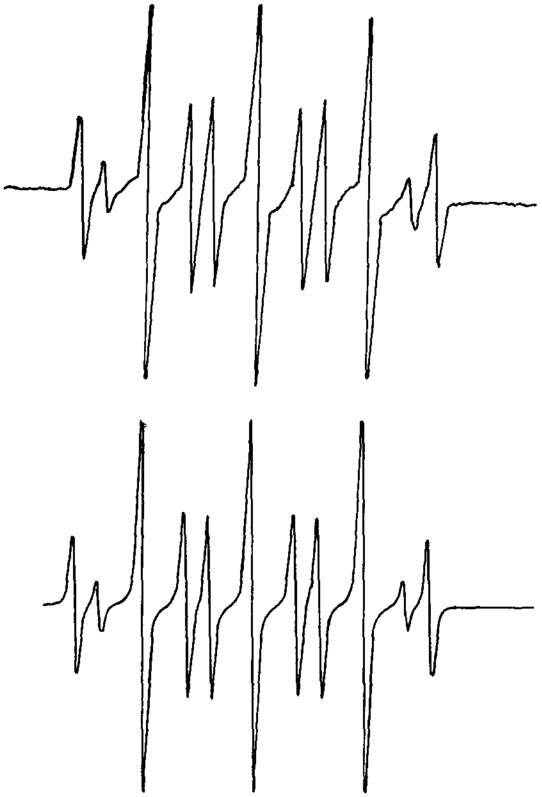
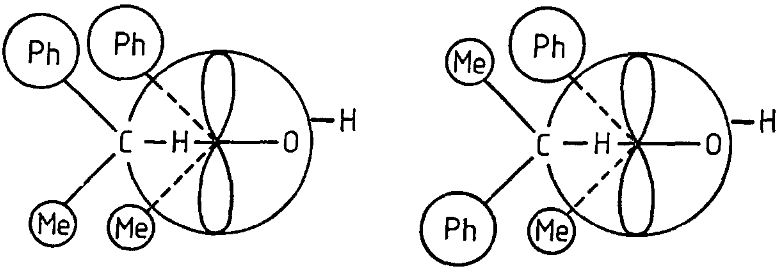


Figure 1
ESR spectra detected after UV irradiation in ethylbenzene containing nitric oxide and anthraquinone.
Top: experimental, bottom: computer simulated spectrum with parameters
a_N = 1.500 mT, a_{2H} = 0.908 and 0.577 mT, a_{6H} = 0.023 mT, line width 0.04 mT, ratio of superposition 1:0.37.

preferential is the eclipsing position of NO and CH bonds[7,8]. If the steric interaction between the two alkyl groups is large this conformation is less favoured or more strongly distorted, which results in larger hydrogen coupling. This trend can be seen from the data of Table 1, too. As in the case of ethylbenzene the larger steric interaction is expected for the radical with opposite chiral centers (see Fig.2), we assign the larger coupling to this diastereomer (VIa). There is a remarkable stereoselectivity of reaction (2), and possibly (3) since the concentration of radical VIb is much lower than that of the radical VIa. The relative concentration is typically 0.37 if the irradiation is carried out at room temperature, at higher temperature it can increase to 0.60 (80 °C) and at lower temperature (-50 °C)



opposite chirality identical chirality

Figure 2: Newman diagram for dialkyl nitroxide radicals in ethylbenzene.

Table 1

Magnetic parameters of dialkylnitroxide radicals

Radical	Solvent	g	a_N (mT)	a_H(mT)*
I	hexamethylbenzene	2.0061	1.581	1.34 (4)
II	toluene	2.0061	1.525	0.860 (4)
III	diphenylmethane	2.0060	1.456	0.593 (2)
IV	cyclohexane	2.0060	1.450	0.410 (2)
V	n-pentane	2.0060	1.427	0.395 (2)
VIa	ethylbenzene	2.0060	1.500	0.908 (2)
VIb		2.0060	1.500	0.577 (2)
VII		2.0059	1.495	0.275 (1)
VIII**		2.0059	1.571	1.167 (3), 0.778 (1)
IX	2-methylbutane	2.0060	1.523	-
X		2.0060	1.455	0.110 (1)
XI	cumene	2.0059	1.497	-
XII**		2.0060	1.584	1.159 (3)
XIII	cumene/ethylbenzene	2.0059	1.505	0.275 (1)

*The number of hydrogen couplings is given in parenthesis

**Measured at -50 °C

it is about 0.15. There is some dependence on the irradiation time as well. At the beginning this ratio is somewhat larger, but later reaches a constant value. The smaller rate of radical build up for molecules, where the chirality of carbons is identical, can be rationalised by the stronger locking of alkyl group in this case, which complies to more strict geometrical conditions for the "successful" encountering of R$^\cdot$ and RNO molecules, when the addition reaction can take place.

References

1. W.A.Waters: The Chemistry of Free Radicals, Oxford, Clarendon Press, 1948, p. 62-79
2. P.Maruthamuthu and J.C.Scaiano: J.Phys.Chem., 82, 1588 (1978)
3. M.I.Christie and J.S.Frost: Trans.Farad.Soc., 61, 468 (1965)
4. M.J.Perkins: Advances in Phys.Org.Chem., 17, 1 (1980)
5. G.Chapelet-Letourneux, H.Lemaire, R.Lenk, M.A.Marechal and A.Rassat: Bull.Soc.Chim. France, 3963 (1968)
6. Th.A.J.Wajer, A.Mackor, Th.J.de Boer and J.D.W. van Voorst: Tetrahedron, 23, 4021 (1967)
7. A.Rockenbauer, S.A.Abdel-Monem, G.Móger and L.Sümegi: J.Mol.Struct., 46, 169 (1978)
8. E.W.Stone and A.H.Maki: J.Chem.Phys., 37, 1326 (1962)

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