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C-NITROSO COMPOUNDS.

PART I. THE FORMATION OF NITROXIDES BY PHOTOLYSIS OF NITROSO COMPOUNDS AS STUDIED BY ELECTRON SPIN RESONANCE.

by
A. Mackor, Th.A.J.W. Wajer and Th.J. de Boer
Laboratory for Organic Chemistry,
University of Amsterdam, Nieuwe Achtergracht 129,
Amsterdam, The Netherlands.

and

J.D.W. van Voorst
Laboratory for Physical Chemistry,
University of Amsterdam, Nieuwe Prinsengracht 126,
Amsterdam.

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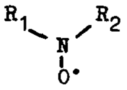
It has recently been reported, that upon irradiation of nitrosobenzenes in tetrahydrofuran or methanol stable diphenylnitroxide radicals are formed among the reaction products (1, 2).

While investigating photochemical and thermal reactions of nitroso compounds we have found by e.s.r. that the formation of nitroxides

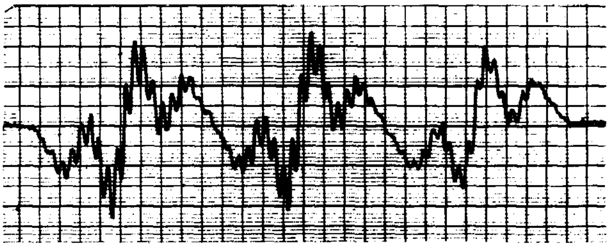


is a general reaction during photolysis of monomeric

C-nitroso compounds.

Typical primary, secondary and tertiary nitrosoalkanes and nitrosobenzene have been studied. Some of the signals could be identified by comparison with the e.s.r.-spectra of nitroxide-radicals, already prepared by oxidation and reduction methods (3, 4, 5), as indicated in the Table and in figures 1 and 2.

FIG. 1. E.S.R. spectrum of di-cyclohexylnitroxide. Each of three primary lines is split in three lines by the two α-protons. The hyperfine structure is due to interaction with the β-protons.



The photolysis can already be achieved with light of a wavelength beyond 660 nm (transmitted by a Schott-Jena RG-8 filter). Monomeric RNO has an optical absorption band in this wavelength region ($\pi^* \leftarrow n$ transition with $\lambda_{max} \approx 680$ nm). For nitroso-alkanes monomer-dimer equilibria have been established (6):

$$2\ RNO \rightleftarrows (RNO)_2$$

and for dimers no visible or near-infrared absorption bands are known.

Primary and secondary nitroso-alkanes are known to exist almost entirely in the dimeric form in solution at room-temperature and therefore no e.s.r. signal is found after irradiation with red light. Only at higher temperatures, when the monomer-dimer equilibrium is shifted towards the monomeric form, the e.s.r. signal of the dialkylnitroxide is obtained. This indicates that upon irradiation with red light, only the monomer will give rise to the formation of a nitroxide. Tertiary nitrosodimers, dissolved in 2-methyltetrahydrofuran, are considerably dissociated and consequently (stable) nitroxide-radicals are formed upon irradiation with red light in the temperature region from -100°C up to +60°C. Although exclusively monomeric nitrosobenzene has an absorption maximum at λ = 750 nm it gives, in contrast to the nitroso-alkanes, no formation of nitroxide-radicals with red light, and the formation of diphenylnitroxide can be achieved only with UV-light.

This difference in response towards the wavelenght was used to produce mixed alkyl-aryl-nitroxides. Upon irradiation of a solution of 2-methyl-2-nitrosopropane and an excess of nitrosobenzene with red light the signal of t-butylphenylnitroxide was obtained (fig. 2c). However, with less nitrosobenzene the di-t-butylnitroxide was also formed (fig. 2b).

FIG. 2a. E.S.R. spectrum of di-t-butylnitroxide.

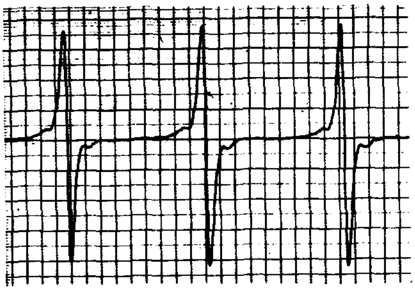


FIG. 2b. E.S.R. spectrum of di-t-butylnitroxide and t-butyl-phenylnitroxide, obtained by photolysis of a mixture of t-nitrosobutane and nitrosobenzene.

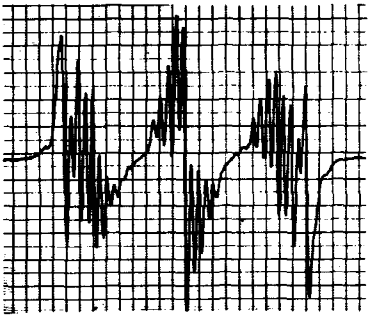
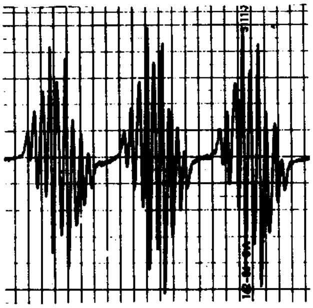
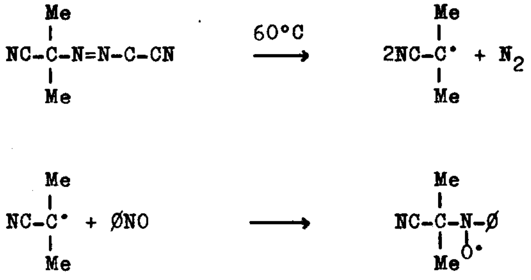


FIG. 2c. E.S.R. spectrum of t-butylphenylnitroxide, obtained by photolysis of t-nitrosobutane and an excess of nitrosobenzene.



The fact that the photochemical product ratio is determined by the ratio of the concentrations of nitroso-alkane and nitrosobenzene indicates that nitroxide formation depends on the probability of the excited nitroso-alkane RNO^* or the alkyl radical $R^\cdot$ to meet a molecule of nitroso compound. The photo-reaction can only be started by the monomeric nitroso-alkane and from this it can be concluded, that a relatively long-living intermediate, arising from the nitroso-alkane, must be present after excitation by red light.

It is known that a nitroxide is formed when alkyl-radicals add to a nitroso compound (7), which was confirmed by us in the thermal reaction of azo-bis-isobutyronitrile (AIBN) with nitrosobenzene:



$$\mathrm{NC{-}C(Me)_2{-}N{=}N{-}C(Me)_2{-}CN} \xrightarrow{60°C} \mathrm{2NC{-}C^{\cdot}(Me)_2} + N_2$$

$$\mathrm{NC{-}C^{\cdot}(Me)_2} + \text{ØNO} \longrightarrow \mathrm{NC{-}C(Me)_2{-}N(O^{\cdot}){-}Ø}$$

The reaction of an excess of AIBN with nitrosobenzene has been investigated by Gingras and Waters (8). They found no nitroxide, but obtained a yield of 75% of the di-t-alkyl--phenylhydroxylamine, probably formed by addition of a second radical to the O-atom of the intermediary nitroxide.
These data indicate that an alkyl radical is a possible intermediate in the photo-reaction:

$$\mathrm{RNO} \xrightarrow{h\nu} \mathrm{R^{\cdot}} + \mathrm{NO}$$
$$\mathrm{R^{\cdot}} + \mathrm{RNO} \longrightarrow \mathrm{R_2NO^{\cdot}}$$

On the other hand a long-living excited state RNO^* can also be considered as being responsible for the reaction with another molecule of nitroso compound:

$$\mathrm{RNO} \xrightarrow{h\nu} \mathrm{RNO}^*$$
$$\mathrm{RNO}^* + \mathrm{RNO} \longrightarrow \mathrm{R_2NO^{\cdot}} + \mathrm{NO}$$

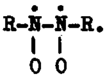
The same two possibilities have been discussed in the gas-phase photolysis of trifluoronitrosomethane (9). So far a decision between these two alternative mechanisms on the basis of the available data is not possible.

TABLE

E.S.R. SPECTRA OF NITROXIDES

formed by photolysis of nitroso compounds in o-xylene

R_1	R_2	Splittings (in gauss)								
		our values				literature				reference
		a_N	a_H	$a_{o,p}$	a_m	a_N	a_H	$a_{o,p}$	a_m	
Ø	Ø	9,7		1,9	0,8	9,73		1,91	0,82	(3)
$-C(Me)_3$	$-C(Me)_3$	15,7				15,5				(4)
$-C(Me)_2CH_2OAc$	$-C(Me)_2CH_2OAc$	15,2								
$-C(Me)_3$	Ø	12,4		2,0	0,9	13,3		1,8	0,9	(4)
$-C(Me)_2CN$	Ø	11,3		2,3	0,9					
$-C(Me)_2CH_2OAc$	Ø	12,6		not determined						
cyclohexyl-	cyclohexyl-	14,6	4,4			for R_1=R_2=isopropyl= 15,3	4,47			(4)
Ø$-CH_2-$	Ø$-CH_2-$	15,0	8,9			17,0	10,0			(5)
1-acetoxy-cyclohexyl-	1-acetoxy-cyclohexyl-	13,5								

Our results are at variance with those of Theilacker et al. (10), who recently reported that 1-acetoxy-2-methyl-2--nitrosopropane and nitrosobenzene are converted into dimeric biradicals,  $R-\underset{O}{\overset{\bullet}{N}}-\underset{O}{\overset{\bullet}{N}}-R$. However, no radical signals appear in these compounds, when they are carefully purified by GLC and kept in the dark.

All starting compounds were prepared according to known methods (6, 10, 11). The e.s.r.-spectra were measured using a Varian V 4502 e.s.r. spectrometer with 100 kc/s modulation along with a V 4531 multipurpose cavity and a variable temperature accessory, financed by the Stichting voor Scheikundig Onderzoek in Nederland.

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Note.

While this manuscript was complete, we noted a publication by Strom and Bluhm (12) on the formation of nitroxides under the influence of UV-light.

In our next paper on the subject we shall comment on these results.

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