Appendix A

The line width ($1/T_2$) in radians per second of an observed resonance that is broadened by rapid exchange between two sites A and B is given by[25]

$$\frac{1}{T_2} = \frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}} + p_A{}^2p_B{}^2(\omega_A - \omega_B)^2(\tau_A + \tau_B) \quad (25)$$

Assuming that the transverse relaxation times T_{2A} and T_{2B} are equal, and using $p_A + p_B = 1$ and $p_A/p_B = \tau_A/\tau_B$, then eq 25 reduces to

$$\frac{1}{T_2} = \frac{1}{T_{2A}} + p_Ap_B{}^2(\omega_A - \omega_B)^2\tau_A$$

Substituting $\tau_A = 1/k_A$ gives

$$\frac{1}{T_2} = \frac{1}{T_{2A}} + \frac{p_Ap_B{}^2(\omega_A - \omega_B)^2}{k_A} \quad (26)$$

According to eq 26, the observed line width ($1/T_2$) is equal to the natural line width ($1/T_{2A}$) plus the exchange-broadened line width $p_Ap_B{}^2(\omega_A - \omega_B)^2/k_A$. Expressing chemical shift and line width in hertz (*i.e.*, $\omega = 2\pi\nu$) gives

$$\frac{1}{T_2} - \frac{1}{T_{2A}} = \frac{4\pi^2p_Ap_B{}^2(\delta_A - \delta_B)^2}{k_A} = \pi\Delta\nu_{1/2}$$

or

$$\Delta\nu_{1/2} = \frac{4\pi p_Ap_B{}^2(\delta_A - \delta_B)^2}{k_A}$$

where $\Delta\nu_{1/2}$ is the line width due to exchange in hertz.

Appendix B

The equilibrium constant for eq 2 may be written as

$$K = k_2/k_3 = \frac{[CH_3S^+(SCH_3)_2][CH_3SCH_3]}{[(CH_3)_2S^+SCH_3][CH_3SSCH_3]} = \frac{[CH_3SCH_3]^2}{[salt][CH_3SSCH_3]}$$

or

$$[CH_3SCH_3] = (K[salt][CH_3SSCH_3])^{1/2} \quad (27)$$

The concentration of methyl sulfide is also related to the exchanging chemical shift $\delta_{S(CH_3)_2}$ by way of the populations p_A and p_B and nonexchanging chemical shifts δ_A' and δ_B' of sites A and B. Thus

$$\delta_{S(CH_3)_2} = p_A\delta_A' + p_B\delta_B' \quad (28)$$

$$p_B = \frac{[CH_3SCH_3]}{[CH_3SCH_3] + [salt]} = \frac{[CH_3SCH_3]}{[salt]_0}$$

where $[salt]_0$ is the initial concentration of **1**. Substituting for p_B in eq 28 and using $p_A + p_B = 1$ gives

$$\delta_{S(CH_3)_2} = \delta_A' + \frac{[CH_3SCH_3]}{[salt]_0}(\delta_B' - \delta_A') \quad (29)$$

Substituting eq 27 in eq 29 and setting $\delta_B' = 0$ gives

$$\delta_{S(CH_3)_2} = \delta_A' - \delta_A'(K/[salt]_0)^{1/2}[CH_3SSCH_3]^{1/2} \quad (9)$$

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(25) S. Meiboom, Z. Luz, and D. Gill, *J. Chem. Phys.*, 27, 1411 (1957); J. A. Pople, H. J. Bernstein, and W. G. Schneider, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 10.

Electron Spin Resonance Study of Nitroxides Formed in the Reaction of Nitrogen Dioxide and Nitrogen Oxide with Styrenes

Leffert Jonkman,* Hans Muller, and Jan Kommandeur

Contribution from the Laboratory of Physical Chemistry, The University of Groningen, Bloemsingel 10, Groningen, The Netherlands. *Received February 8, 1971.*

Abstract: When NO_2 reacts with styrenes in the presence of nitrosobenzene, phenyl(1-aryl-2-nitroethyl) nitroxides (**3**) are formed through the reaction of β-nitroalkyl radicals **2** with nitrosobenzene. In the reaction of NO_2–NO mixtures with styrenes, bis(1-aryl-2-nitroethyl) nitroxides (**5**) are formed by the reaction of **2** with the α-nitroso-β-nitro addition products **4** of the styrenes. Both diastereomers of **5** (meso, and *d,l*) were observed with all styrenes investigated, except for those with ortho substituents. Dissociation of the dimer of **4** is found to be accompanied by decomposition of **4** into NO and the radical **2** with subsequent formation of the nitroxide **5**.

When nitrogen oxides react with olefinic substances, radicals are almost always formed. These radicals have in the past been interpreted to be charge-transfer complexes.[1-3] In a recent note[4] we have argued that these radicals are nitroxides and we reported the structure of a nitroxide formed in the reaction of NO_2 with styrene. We now present a more detailed account of the nitroxide formation in the reaction of NO_2 and NO with various styrenes of the general type **1**, in which Ar means a substituted phenyl nucleus.

We will first discuss the nitroxide formation in the reaction of NO_2 with styrenes in the presence of nitrosobenzene. Our experiments show that NO_2 reacts with styrenes to give a radical intermediate **2**; this β-nitroalkyl radical is trapped by nitrosobenzene to give the nitroxide **3** (Scheme I).

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(1) T. J. Schaafsma and J. Kommandeur, *J. Chem. Phys.*, 42, 438 (1965).

(2) A. Hudson, *Aust. J. Chem.*, 19, 1971 (1966).

(3) B. H. J. Bielski and J. M. Gebicki, *J. Phys. Chem.*, 73, 1402 (1969).

(4) L. Jonkman, H. H. Muller, C. Kiers, and J. Kommandeur, *ibid.*, 74, 1650 (1970).

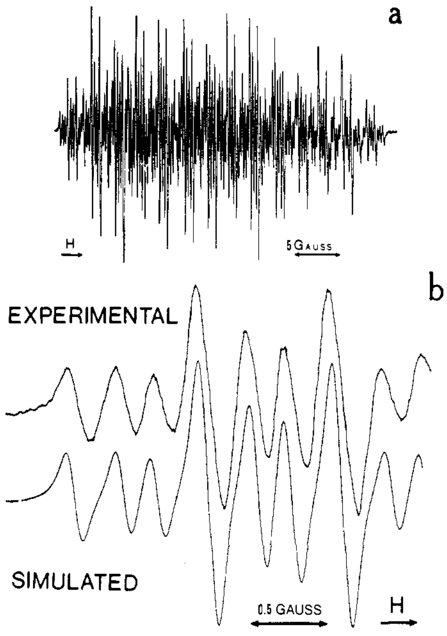
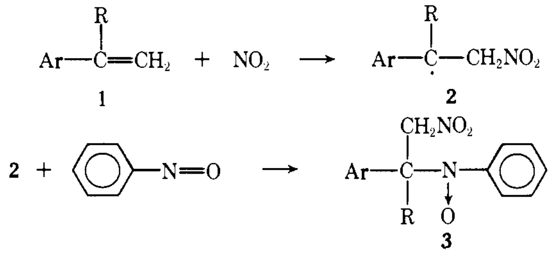


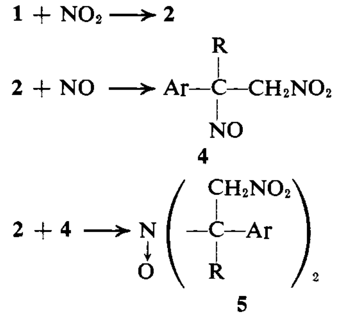
Figure 1. (a) The esr spectrum of the nitroxide **8d**. (b) The lowest field part of the spectrum of Figure 1a, together with its computer simulation.

Scheme I



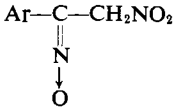
We will then show that in the reaction of NO_2 and NO with styrenes the nitroxides **5** are formed by reaction of the radicals **2** with the α-nitroso-β-nitro addition products of the styrenes (Scheme II). The formation of both diastereomers of **5** (meso and *d,l*) was observed with all styrenes with R = H investigated, except for those with ortho substituents, in which case one of the diastereomers appeared to be formed almost exclusively. The formation of **5** was sometimes accompanied by formation of iminoxy radicals **6** when R = H.

Scheme II

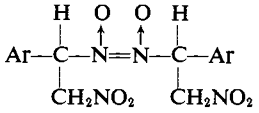


Since the results of the work of Fox, McRae, and Symons[5,6] with NO_2 and methyl methacrylate fit remarkably well in our picture of the reaction of NO_2 with styrenes, we will mention this analogy and make a proposal as to the structure of the paramagnetic product and the mechanism of its formation.

When R = H the α-nitroso-β-nitro addition products **4** dimerize to **7** and can then be isolated. We find that thermal decomposition of these dimers leads to the same nitroxides as found in the reaction of NO_2 and NO with the styrenes.



6



7

Nitroxides Formed in the Reaction of NO_2 with Styrenes in the Presence of Nitrosobenzene. It is well known that nitrosoalkanes react readily with various types of radicals to give nitroxides.[7-10] The same observation was made for nitrosobenzene.[7] The reaction of NO_2 with olefinic compounds is generally considered to proceed by a radical mechanism, involving initial formation of a nitroalkyl radical.[11] The nitroalkyl radical formation is such that the nitro group always becomes attached to the olefinic carbon bearing the most hydrogens. When NO_2 reacts with styrenes we consequently expect the β-nitroalkyl radical **2** to be formed.

In agreement with the foregoing we found that in the presence of nitrosobenzene these radicals are trapped (Scheme I) and intense esr spectra of the resulting nitroxides **3** are observed. In the case of styrene itself, the nitroxide formed is **8h**, the esr spectrum showing the following hfs parameters (in benzene): a_N = 10.2 G; a_H^{β} = 4.8 G (one proton); a_H(ortho, para) = 2.5 G (three protons); a_H(meta) = 0.87 G (two protons). Further interaction with γ protons is observed, but could not be interpreted because of insufficient resolution. The use of pentadeuteriostyrene (in which all phenyl protons are deuterated), leading to **8d**, yielded better resolution because of the absence of broadening by five phenyl protons (since $\mu_D = 0.15\,\mu_H$) and allowed determination of the hfs constants of the two γ-CH_2 protons, for which we found 0.54 and 0.32 G, respectively. The two γ protons are diastereotopic by the asymmetry of the α-carbon atom and thus magnetically inequivalent. The esr spectrum of **8d** is given in Figure 1, as is a picture of its lowest field part on an extended scale, together with a computer simulation of the latter; the parameters for the displayed simulation are: a_H(meta) = 0.87 G (two protons), $a_H^{\gamma_1}$ = 0.54 G (one proton), $a_H^{\gamma_2}$ = 0.32 G (one proton), and ΔH (line width) = 0.17 G.

In order to establish beyond doubt that we really have **8h** and **8d**, we prepared the parent amines **9h** and **9d** and oxidized them with 4-nitroperbenzoic acid. This procedure yielded exactly the same esr spectra as

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(5) J. A. McRae and M. C. R. Symons, *Nature (London)*, **210**, 1260 (1966).

(6) N. M. Fox, J. A. McRae, and M. C. R. Symons, *J. Chem. Soc. A*, 1773 (1967).

(7) J. Mason-Banus, *ibid.*, 4357 (1963).

(8) A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *Tetrahedron Lett.*, 2115 (1966).

(9) Th. A. J. W. Wajer, A. Mackor, and Th. J. de Boer, *Tetrahedron*, **23**, 4021 (1967).

(10) A. Mackor, Thesis, University of Amsterdam, The Netherlands, 1968.

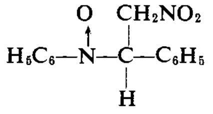
(11) H. Shechter, *Rec. Chem. Progr.*, **25**, 55 (1964), and references therein.

Table I. Hfs Parameters of the Nitroxide's Formed in the Reaction of NO_2 with Styrenes in the Presence of Nitrosobenzene[a]

Styrene used	Nitroxide formed	a_N	a_H^b	a_H^c (o,p)	a_H^d (meta)
Styrene	**8h**	10.2	4.8	2.5	0.87
α-Methylstyrene	**10**	10.7	*e*	2.3	0.85
2,4,6-Trimethylstyrene	**12**	10.8	10.0	2.5	0.85

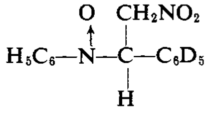
[a] All constants are in gauss; the solvent was in all cases benzene. [b] Interaction with one proton. [c] Interaction with three equivalent protons. [d] Interaction with two equivalent protons. [e] No β proton was present in this nitroxide.

reported above for **8h** and **8d**. As expected, the use of other styrenes leads to the same type of nitroxides. For some styrenes the esr parameters of the corresponding nitroxides are given in Table I. Although this method seems to give access to a multitude of nitroxides, at least in esr quantities, there are serious complications when there are alkyl groups adjacent to the double bond of the olefin used. In that case the olefin reacts readily with nitrosobenzene to give nitroxides, as was reported by Sullivan[12] for the case of tetramethylethylene with nitrosobenzene. The use of NO_2 then gives rise to a superposition of complicated spectra; because of this we were not able to get interpretable results with *aliphatic* olefins.



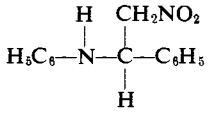
$H_5C_6-\overset{\overset{O}{\uparrow}}{N}-\underset{H}{\overset{CH_2NO_2}{C}}-C_6H_5$

8h



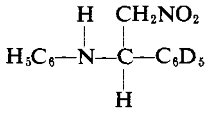
$H_5C_6-\overset{\overset{O}{\uparrow}}{N}-\underset{H}{\overset{CH_2NO_2}{C}}-C_6D_5$

8d



$H_5C_6-\overset{H}{N}-\underset{H}{\overset{CH_2NO_2}{C}}-C_6H_5$

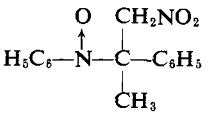
9h



$H_5C_6-\overset{H}{N}-\underset{H}{\overset{CH_2NO_2}{C}}-C_6D_5$

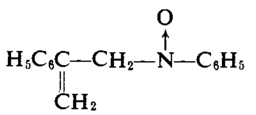
9d

We found that α-methylstyrene reacts with nitrosobenzene *via* Sullivan's scheme to yield **11**, the esr parameters (in benzene) being: $a_N = 9.8$ G; $a_H^\beta =$ 5.6 G (two protons); a_H(ortho, para) = 2.6 G (three protons); a_H(meta) = 0.85 G (two protons). The reaction rate, however, is much lower than with the aliphatic olefins. When the concentrations of α-methylstyrene and of nitrosobenzene were kept low and when NO_2 was introduced immediately after preparation of the solution, essentially no **11** was observed and the spectrum of **10** was obtained almost exclusively. The styrenes without an alkyl group attached directly to the olefinic double bond do *not* react with nitrosobenzene in the absence of NO_2. This is to be expected, since according to Sullivan's reaction mechanism these compounds cannot react with nitrosobenzene to give nitroxides.



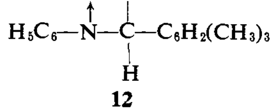
$H_5C_6-\overset{\overset{O}{\uparrow}}{N}-\underset{CH_3}{\overset{CH_2NO_2}{C}}-C_6H_5$

10



$H_5C_6\underset{\overset{\|}{CH_2}}{C}-CH_2-\overset{\overset{O}{\uparrow}}{N}-C_6H_5$

11



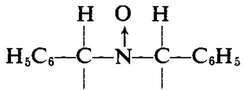
$H_5C_6-\overset{\overset{O}{\uparrow}}{N}-\underset{H}{\overset{CH_2NO_2}{C}}-C_6H_2(CH_3)_3$

12

Nitroxides Formed in the Reaction of NO and NO_2 with Styrenes. Results. We reported recently[4] that esr spectra obtained when NO_2 reacts with styrene can be attributed to the formation of two nitroxides: bis(1-phenyl-2-nitroethyl) nitroxide (**13**) and a nitroxide (**14**) which, according to its esr spectrum, resembled **13** very much. We gave a picture of the esr spectrum, together with the esr spectrum obtained when styrene-*ring-d*$_5$ was used. Part of our proof for the assignment of the structure **13** was formed by the fact that oxidation of bis(1-phenyl-2-nitroethyl)amine (**15**) as well as bis(1-(pentadeuteriophenyl)-2-nitroethyl)amine prepared according to the procedure of Worrall[13] gave esr spectra identical with those obtained in the reaction of NO_2 with styrene and pentadeuteriostyrene, respectively.

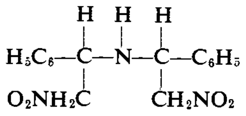
In addition to the above, we now report the following observations. When a 1:1 mixture of NO and NO_2 is used, the esr spectra become approximately *20 times more intense* than when NO_2 only is used. Rigorously purified NO by itself, however, *does not yield any paramagnetism* when added to (carefully deoxygenated) styrene.

The amine **15** can exist in the meso or the *d,l* diastereomeric forms. Although Worrall's procedure did not give both products in a pure state, a modified version of it permitted isolation and identification of both diastereomers (**15a** and **15b**). The detailed procedure can be found in the Experimental Section. Oxidation of amine mixtures with various **15a**:**15b** ratios always gave rise to esr spectra of **13** and **14** with the same **13**/**14** ratios.



$H_5C_6-\underset{O_2NH_2C}{\overset{H}{C}}-\overset{\overset{O}{\uparrow}}{N}-\underset{CH_2NO_2}{\overset{H}{C}}-C_6H_5$

13 and 14



$H_5C_6-\underset{O_2NH_2C}{\overset{H}{C}}-\overset{H}{N}-\underset{CH_2NO_2}{\overset{H}{C}}-C_6H_5$

15

All styrenes of the type **1** behaved in the same way toward NO and NO_2 as styrene itself. In all cases esr spectra were obtained showing the interaction of an unpaired electron with one nitrogen nucleus and two equivalent β protons (except, of course, for the case when R ≠ H). The esr spectra obtained from NO–NO_2 with 4-nitrostyrene and 4-methoxystyrene were also obtained after oxidation with 4-nitroperbenzoic acid of the reaction products resulting from the treatment with NH_3 of 4,β-dinitrostyrene and 4-methoxy-β-nitrostyrene, respectively. In Table II the hfs parameters are given of the esr spectra obtained with various styrenes and NO–NO_2. The spectra obtained with styrene, 2-methylstyrene and 2,4,6-trimethylstyrene are given in Figure 2. When NO–NO_2 reacts with a mixture of 2,4,6-trimethylstyrene and α-methylstyrene an esr spectrum is observed with $a_N = 15.6$ G and $a_H = 14.0$ G (one proton).

A feature sometimes observed when NO–NO_2 reacts with styrenes, especially when working in more polar solvents, is the existence of satellite spectra (besides the "main" spectra, given in Table II), consisting of three lines of equal intensities with a distance of about 31 G. These spectra are almost always very weak; only in the case of 4-nitrostyrene does its intensity reach the same order of magnitude as that of the spectrum given in Table II, while also further hf splitting of the three lines

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[12] A. B. Sullivan, *J. Org. Chem.*, **31**, 281 (1966).

[13] D. E. Worrall, *J. Amer. Chem. Soc.*, **49**, 1598 (1927).

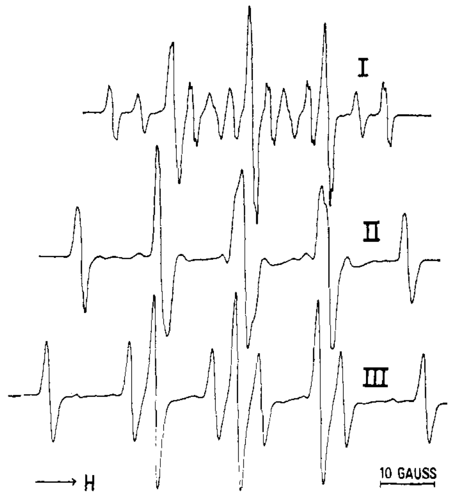
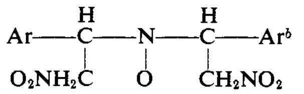


Figure 2. Esr spectra of the nitroxides formed in the reaction of NO–NO_2 with styrene (I), 2-methylstyrene (II), and 2,4-6-trimethylstyrene (III).

can be observed. The *g* value of these radicals is 2.0052 ± 0.0002.

Table II. Hfs Parameters[a] of the Nitroxides Formed in the Reaction of NO–NO_2 with Various Styrenes



$$\mathrm{Ar{-}\overset{H}{\underset{O_2NH_2C}{C}}{-}\underset{O}{N}{-}\overset{H}{\underset{CH_2NO_2}{C}}{-}Ar^{b}}$$

Styrene used	Nitroxide A $a_N{}^c$	Nitroxide A $a_H{}^d$	Nitroxide B $a_N{}^c$	Nitroxide B $a_H{}^d$
α-Methylstyrene[e]	14.7			
Styrene	14.9	11.4	14.5	6.6
4-Methylstyrene	15.0	12.0	14.3	7.0
4-Fluorostyrene	14.8	12.0	14.2	6.2
4-Chlorostyrene	14.6	11.5	14.2	6.5
4-Nitrostyrene	14.5	9.6	14.3	5.6
2-Methylstyrene	15.0	14.4		
2,5-Dimethylstyrene	15.2	14.3		
2,4-Dimethylstyrene	15.2	14.5		
2,6-Dimethylstyrene	14.9	19.7		
2,4,6-Trimethylstyrene	14.9	19.7		
2,4,6-Triisopropylstyrene	14.2	20.5		

[a] The solvent was in all cases benzene. The isotropic *g* values were 2.0059 ± 0.0002. All constants are measured at 20° and are given in gauss. [b] General structure of the nitroxide. [c] Interaction with one nitrogen. [d] Interaction with two equivalent protons. [e] No β protons are present in this nitroxide. Because of this A and B spectra will overlap and cannot be separated.

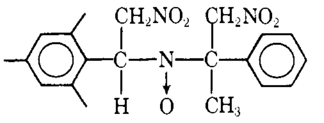
Nitroxides Formed in the Reaction of NO and NO_2 with Styrenes. Discussion. The hyperfine pattern and *g* values being consistent with this assignment, we attribute all spectra from Table II to the nitroxides of type **5**. The identity of these spectra with those obtained when the parent amine was oxidized provides complete evidence for this assignment.

We are now in a position to say something more about the mechanism of formation of these nitroxides. The experiments of NO_2 reacting with styrenes in the presence of nitrosobenzene showed already that NO_2 reacts with styrenes to give the radical **2**. Since NO by itself does not give any reaction, this must be the first step. Subsequent addition of NO to **2** gives rise to the formation of the α-nitroso-β-nitro addition products of the styrenes (**4** in Scheme II), which can be isolated as their dimers (see next sections). One expects these nitroso compounds to be able to trap the radical **2** to give the nitroxides **5** in the same way as nitrosobenzene traps **2** to yield **3**. The fact that NO_2 by itself also reacts with styrenes to yield the nitroxides **5** (but yielding a much lower concentration of **5** than with NO–NO_2) can be explained because even with rigorously purified NO_2 some nitroso compound is always formed, since some NO_2 will be reduced under the conditions of the reaction.[11,14]

The fact that oxidation of **15a** and **15b** yielded **13** and **14**, respectively, proves that the latter two compounds are the two diastereomeric forms of bis(1-phenyl-2-nitroethyl) nitroxide. In general, one now expects all nitroxides **5** to be formed in the two diastereomeric forms, the meso compound and the *d,l* pair. In the case of the nonortho-substituted styrenes the esr spectra indeed came out to be a superposition of two almost equally intense spectra, arbitrarily labeled A and B in Table II. With monoortho- and diortho-substituted styrenes, one spectrum always dominated (see also Figure 2). This indicates that here the formation of one of the diastereomers is strongly favored.

From Table II we further see that the value of $a_H{}^\beta$ depends strongly on the number of ortho substituents of the aryl groups. A quantitative interpretation of these phenomena will be given elsewhere.[15]

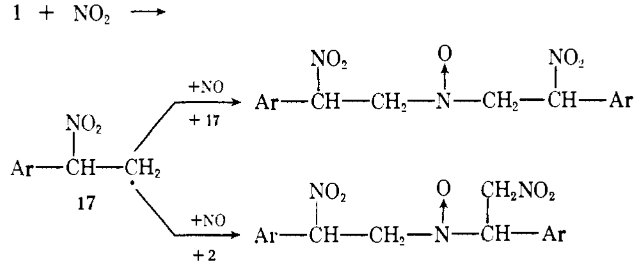
When NO–NO_2 reacts with a mixture of different styrenes according to Scheme II, one expects the formation of "mixed" nitroxides, together with the symmetrical ones. This is indeed found. A typical example is the esr spectrum reported above in the reaction of NO–NO_2 with a mixture of 2,4,6-trimethylstyrene and α-methylstyrene. This spectrum must undoubtedly be attributed to **16**.



16

It follows from our results that NO_2 attacks the β-carbon position of the styrene only. If the α-carbon position would also be attacked (Scheme III), the resulting α-nitroalkyl radicals **17** would in any case lead to nitroxides with more than two β protons. We never observed such nitroxides, not even as transient species. This is not surprising, since one expects the radical **2** to have a much lower energy content than **17**, since in the former delocalization of the unpaired

Scheme III



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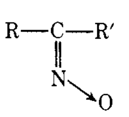
(14) H. Baldock, N. Levy, and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949).

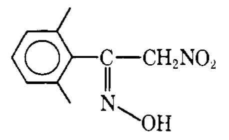
(15) L. Jonkman and J. Kommandeur, to be published.

electron over the adjacent phenyl nucleus can take place.

At the end of the Results we mentioned the appearance of satellite spectra, which in some cases accompanied the spectra of the nitroxides **5**. Since iminoxy radicals **18** have a nitrogen coupling constant of about 30 G and a *g* value of 2.0050 ± 0.0004, these satellite spectra are likely to belong to iminoxy radicals. In order to establish this point we prepared from the α-nitroso-β-nitro dimer of 2,6-dimethylstyrene the corresponding nitroxime (**19**) (see Experimental Section). Oxidation of **19** with lead tetraacetate gave the same esr spectrum as mentioned above for the satellite spectra. We conclude therefore these radicals to be iminoxy radicals with the general structure **6**. The formation of iminoxy radicals by oxidation of ketoximes is well established.[16-18]

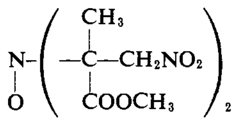


18



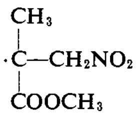
19

There is a striking analogy between our results with styrenes and NO_2 and the findings of Fox, McRae, and Symons with methyl methacrylate and NO_2.[5,6] In the reaction of NO_2 with methyl methacrylate and in dissociation experiments with the nitrosonitro dimer of methyl methacrylate in methylene dichloride they found the same nitroxides. Fox, *et al.*, suggested tentatively some structures for the main radical formed, based on a monomer-monomer mechanism and on addition of the monomer to methyl methacrylate, respectively. We suggest that the structure **20** is the correct one, and that it is formed by reaction of the nitroalkyl radical **21** with the nitrosonitro monomer **22**.



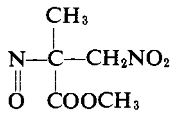
$$\underset{\displaystyle O}{\overset{}{N}}-\left(-\underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{C}}-CH_2NO_2\right)_2$$

20



$$\cdot\underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{C}}-CH_2NO_2$$

21



$$\underset{\displaystyle O}{\overset{}{N}}=\underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{C}}-CH_2NO_2$$

22

Thermal Decomposition of the α-Nitroso-β-nitro Dimers of Styrenes. When a NO-NO_2 mixture reacts with styrenes between −10° and room temperature one of the products formed is the blue colored α-nitroso-β-nitro addition product of the styrene **4**. When R = H, these products dimerize to the nitrosonitro dimers, which (at room temperature) are insoluble in the solvents used and can be isolated as white solids in yields up to 60%. The nitrosonitro dimers of styrene and 4-nitrostyrene have been reported before.[19-21]

When warmed to about 60° in polar solvents they dissolve slowly under dissociation, which is evident from the typical blue monomer color which appears. The dissociation is accompanied by the appearance of the esr spectrum of the nitroxides **5** (with R = H).

The most probable way of formation of **5** is loss of NO from the nitrosonitro monomer, followed by trapping of the resulting β-nitroalkyl radical by undecomposed nitrosonitro monomer.

Experimental Section

Melting points and boiling points are uncorrected. Nmr spectra were recorded on a Varian Model A-60D nmr spectrometer. A Varian Model E-3 epr spectrometer was used to obtain the esr spectra. The *g* values of the radicals were obtained by measuring against diphenylpicrylhydrazyl, which has a *g* value of 2.0036. To make sure that the measured coupling constants are correct, the scan ranges of the spectrometer were calibrated with the aid of an A.E.G. marginal oscillator (Type E 2307-97301/2), a proton probe, and an electronic counter (Hewlett Packard 5245L).

NO and NO_2. These gases were purchased from Matheson in stainless steel cylinders. NO was dried by passing the gas over phosphorus pentoxide and freed from NO_2 by passing it through an acetone-carbon dioxide trap. NO_2 was dried likewise and freed from NO by condensing it in an oxygen stream at −60°; subsequent removing of oxygen by condensing the NO_2 in an argon stream was undertaken in part of the experiments; since it turned out that the presence of oxygen did not have any measurable effect on the results, its removal was omitted in most of our work with NO_2.

Styrenes. All styrenes except those mentioned below were purchased from either K&K or Aldrich in the highest available grades. They were vacuum distilled before use and their quality was checked by nmr.

Preparation of Styrenes. A. 2,3,4,5,6-Pentadeuteriostyrene. Aluminium chloride (19 g) was added to a solution of hexadeuteriobenzene (10 g) (Merck AG, Darmstadt, 99%) in carbon disulfide (25 ml); after adding acetic anhydride (6 g) dropwise under vigorous stirring, the mixture was kept under slow reflux for 1 hr, and subsequently hydrolyzed, by pouring it onto crushed ice. The CS_2 layer was separated, washed with one 50-ml portion of 5% aqueous sodium bicarbonate and three 50-ml portions of distilled water, dried over anhydrous sodium sulfate, and distilled. The yield of 2,3,4,5,6-pentadeuterioacetophenone was 6.9 g (44%). Hexadeuteriobenzene (3.7 g, 37%) could be recovered and the synthesis could be repeated to obtain an additional 2.16 g of the ketone (total yield 59%).

A solution of the acetophenone (9 g) in anhydrous ether (20 ml) was added cautiously to a suspension of 1.1 g of lithium aluminum hydride in ether (25 ml) under rapid stirring; after refluxing for 2.5 hr the flask was cooled in an ice bath, and 10% sulfuric acid (25 ml) was added to hydrolyze the mixture. The ethereal layer was separated, washed with water, and dried. After evaporation of the ether some *p*-toluenesulfonic acid (0.2 g) and picric acid (0.05 g) were added to the residue. Distillation of this mixture at atmospheric pressure was performed. The distillate was freed from water and distilled under reduced pressure to yield 6.6 g (84%) of pentadeuteriostyrene. According to its nmr spectrum it was 95.5% deuterated at the phenyl ring.

B. **2,4,6-Triisopropylstyrene** was prepared according to ref 22.

C. *trans*-β-**Nitrostyrene**-*ring*-d_5. The procedure of Worrall[23] was used, but instead of "normal" benzaldehyde now benzaldehyde-*ring*-d_5 (Merck AG, 99%) was the starting material. The styrene thus obtained appeared to be at least 97% deuterated at the phenyl ring (by nmr).

Preparation of Amines. A. Phenyl(1-phenyl-2-nitroethyl)-amine. This compound was prepared according to Worrall[13] by the reaction of *trans*-β-nitrostyrene with aniline; nmr of the aliphatic protons (τ values): $-CH_2$, 4.65; $-CH$, 5.13 (solvent $CDCl_3$).

B. Phenyl(1-(pentadeuteriophenyl)-2-nitroethyl)amine. This was prepared analogous to the amine under A. Instead of "normal" β-nitrostyrene, *trans*-β-nitrostyrene-*ring*-d_5 was used in the preparation. Nmr showed that the phenyl ring attached to the ethyl group was 95% deuterated.

C. Bis(1-phenyl-2-nitroethyl)amine. Dry ammonia was slowly bubbled through a solution of β-nitrostyrene (1.0 g) in benzene (50 ml) at room temperature during 1 hr. The benzene was then removed by vacuum evaporation and the residue was kept at −15° until it solidified. It was recrystallized from hot cyclohexane (40

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ml). The yield of product, separated as long colorless needles, was about 80% with respect to β-nitrostyrene. The products obtained in this way proved to be, both from their nmr spectra and from the A/B ratio in the esr spectrum obtained on oxidation with 4-nitroperbenzoic acid, 1/1 mixtures of both diastereomers. Since the amine B crystallizes more slowly than A we could, by repeating the crystallization and by filtering off the crystals before it was complete, obtain a product enriched in A, while the amine obtained by vacuum evaporation of the filtrate was enriched in B. By repeating this procedure several times we obtained a sample containing 90% B and 10% A. *Anal.* Calcd for $C_{16}N_3H_{17}O_4$: C, 60.94; N, 13.33; H, 5.43. Found: C, 61.10; N, 13.16; H, 5.44. *Anal.* Found for a sample of pure A (obtained by repeated crystallization from ethanol): C, 61.01; N, 13.49; H, 5.37. The nmr spectra of the aliphatic protons of the diastereomers A and B proved to be ABC spectra, which were resolved by using the following deuterated species of the amine: bis(1-phenyl-1-deuterio-2-nitroethyl)amine and bis(1-phenyl-2-deuterio-2-nitroethyl)amine. The results are: diastereomer A (τ values), -CH-, 4.15; $-CH_2-$, 4.32 and 4.50; diastereomer B (τ values), -CH-, 4.62; $-CH_2-$, 4.56 and 4.44 (solvent $CDCl_3$).

D. Bis(1-(pentadeuteriophenyl)-2-nitroethyl)amine was prepared analogous to the amine under C, except that instead of β-nitrostyrene, β-nitrostyrene-*ring*-d_5 was used in the preparation.

Preparation of the α-Nitroso-β-nitro Dimers. These were prepared by passing $NO-NO_2$ in a 1:1 ratio through solutions of the styrenes in ether or benzene (concentrations about 10%) at 10°. The precipitates formed were filtered and washed thoroughly with the solvent, until no esr signal was detected in the wash liquid. They were dried at room temperature and stored at −30°. For a typical example (the dimer of 2,4,6-trimethylstyrene) we found: mp 133° dec; ir absorption (strongest) 1580, 1400, 1280, 1260, 1220 cm^{-1}. *Anal.* Calcd for $C_{22}H_{28}N_4$: C, 57.69; H, 5.77; N, 13.46. Found: C, 57.96; H, 5.92; N, 13.36.

Nitromethyl(2,6-dimethyl)phenylketoxime. The α-Nitroso-β-nitro dimer (5 g) of 2,6-dimethylstyrene was warmed at 100° in 10 ml of dimethylformamide during 20 min. After cooling, the resulting yellow liquid was poured into 50 ml of water. The solution was extracted twice with 20 ml of ether. The ether layers were combined, dried on Na_2SO_4, and evaporated. The resulting yellow syrup solidified after keeping it for some days in a refrigerator, and was then recrystallized from a 1:1 benzene–cyclohexane mixture, to give 0.3 g of white crystalline powder: mp 105° dec; nmr (τ values) 3,4,5-proton multiplet around 7.15; CH_2, 5.46; 2,6-methyls, 2.26; solvent, $CDCl_3$. *Anal.* Calcd for $C_{10}H_{12}N_2O_3$: C, 57.68; H, 5.82; N, 13.45. Found: C, 57.55; H, 5.83; N, 13.44.

Preparation of Esr Samples. A. NO_2 with Styrenes and Nitrosobenzene. A typical run was: about 1 g of the styrene and about 5 mg of nitrosobenzene were dissolved in about 10 ml of benzene. A small quantity of purified NO_2 gas was introduced through a capillary at temperatures ranging from 5 to 25°. Before esr measurement the samples were freed from oxygen by passing very pure nitrogen through the solution in the sample tube.

B. $NO-NO_2$ with Styrenes. About 1 ml of the styrene was dissolved in 10 ml of benzene or diethyl ether. At temperatures between −10 and 20°, NO_2 or a $NO-NO_2$ mixture was slowly introduced through a capillary. Usually minute amounts of gas were used.

C. Oxidation of Amines with *p*-Nitroperbenzoic Acid. Equal amounts of the amine and *p*-nitroperbenzoic acid, usually about 5 mg, were placed in the sample tube (quartz, inner diameter 2.8 mm). After addition of the solvent (0.4 ml, tetrahydrofuran or isopentane–ethanol in 3:2 ratio), the sample tube was warmed by holding it in water of 60° for 30 sec, while care was taken to keep the tube tightly shut. Subsequently some pure nitrogen gas was bubbled through the solution to free it from oxygen.

D. Dissociation of α-Nitroso-β-nitro Dimers of the Styrenes. The dimer (1 mg) was dispersed by mechanical and ultrasonic vibration in 0.2 ml of styrene in the esr sample tube. The tube was placed in the cavity of the esr spectrometer and immediately warmed up to a temperature between 50 and 80°. The development of the esr spectrum in time is studied. The solution gradually becomes green-blue and after about 3 min all dispersed dimer is dissolved. From this moment the green color starts to fade and the solution becomes pale yellow.

From comparison of the esr intensity of the maximum nitroxide concentration with samples of Würsters blue perchlorate of known susceptibility we determined the yield of the nitroxide formation to be about 1% with respect to the nitrosonitro dimer.