

SPIN TRAPPING REACTIONS WITH NITRIC OXIDES IV. REACTIONS WITH OLEFINS

Antal Rockenbauer*, Miklós Győr and Ferenc 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: Electron Spin Resonance spectra of nitroxide radicals formed in the nitrogen oxide olefin systems (isobutylene, styrene and α -methylstyrene) have been investigated. The primary reaction step is the formation of alkyl radicals by the addition of nitrogen dioxide to the methylene carbon of olefins. The nitric oxide scavenges two alkyl radicals. In styrene and α -methylstyrene nitroxide diastereomers with different rates of formation and termination have been observed.

In the preceding papers of this work, we investigated the spin trapping reactions of nitric oxides with photochemically generated alkyl, alkoxy and peroxy radicals¹⁻³. In this paper the reactions of olefins and nitrogen oxides will be discussed. These reactions were extensively studied by Brown⁴, who applied classical analytic procedures in order to identify the major reaction products. He found the radical initiation was made by nitrogen dioxide



and the alkyl radicals reacted with nitric oxide:



The nitroso (pseudonitrosite) was supposed to react with either NO or R[·] by reactions:

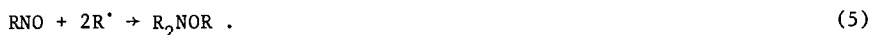


and



Brown identified the oily primary product with the yield of 66 % as the (RNOR)₂ dimer. Though trace amounts of nitrogen dioxide can induce radical formation, the high yield of conversion of isobutylene can only take place, if NO is simultaneously converted into NO₂. This conversion was supposed to be catalysed by the homolytic or heterolytic decomposition products of R(NO)ONO.

Phillips and Coyne also studied the isobutylene-nitric oxide system⁵ and found a new major crystalline product identified as tris (nitro-t-butyl)hydroxylamine, which can be formed by reactions



In order to obtain supplementary information about the above reaction scheme, we investigated the Electron Spin Resonance (ESR) spectra of radicals appearing in the olefin-nitric oxide system.

The same experimental apparatus (JEOL-JES-FE-3X spectrometer) and the same technique of generating nitric oxide was applied as earlier¹. Computer program was written for a KFKI (Hungary) made minicomputer (EMU-11) in order to interpret spectral superpositions and also the patterns of naturally abundant C¹³ satellites. Different olefins (styrene, α -methylstyrene and isobutylene dissolved in benzene) were deaerated and the ESR spectra were recorded at various times after admitting nitric oxide into the solvent.

In all cases, the spectra observed can be described by the characteristic g values ($g = 2.006$) and nitrogen couplings ($a_N = 1.5$ mT) of the dialkylnitroxides³ (see Table 1). When only trace amount of NO_2 was present, the build up rate was slow at the beginning and accelerated later. If oxygen was admitted into the reactor, where nitric oxide was generated, the build up rate of nitroxide radicals increased. These observations support the results of Brown⁴, namely the radicals are initiated by NO_2 and the transformation of NO into NO_2 is catalysed by intermediate products.

The structure of R' primary alkyl radical can be elucidated from the hydrogen splittings of the major nitrogen triplet in the spectra of nitroxide radicals. If the unpaired electron is localised on a tertiary carbon, no large splitting (larger than 0.1 mT) is expected, if it is localised on secondary carbon a 1:2:1 splitting of at least 0.3 mT separation should appear in the spectra of $\text{R}_2\text{NO}'$ radical. We observed hydrogen splittings of this magnitude only in the styrene- NO system, while in isobutylene and α -methylstyrene only small hydrogen splittings were found (see in Table 1). Consequently, the NO_2 attack takes place on the methylene carbon in the case of the investigated olefins.

Table 1: ESR parameters for radicals $\text{O}_2\text{N}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{R}_1}{\underset{\text{R}_2}{\text{C}}}-\overset{\text{O}\cdot}{\text{N}}-\overset{\text{R}_1}{\underset{\text{R}_2}{\text{C}}}-\overset{\text{H}}{\text{C}}-\text{NO}_2$

R_1	R_2	g	a_N	$a_H(\text{C}_\alpha)^a$	$a_H(\text{C}_\beta)^a$	$a_{\text{C}^{13}}$				$a_{\text{O}^{17}}$
						C_α	R_1	R_2	CH_2	
Me	Me	2.0061	1.456	-	0.047 (4)	0.53	0.41	0.41	0.44	b
H	Ph	2.0059	1.496	1.196 (2)	0.06 (2)	0.52	-	c	0.83	b
		2.0059	1.431	0.686 (2)	0.05 (2)	c	-	c	c	b
Me	Ph	2.0057	1.485	-	0.054 (2)	0.54	0.43	c	0.92	1.977
		2.0058	1.475	-	0.045 (2)	0.54	0.54	c	0.70	b

The hyperfine couplings are given in mT units

^anumber of equivalent hydrogens is given in parenthesis; ^bnot detected; ^cnon-resolved

As it can be seen from the data of this Table, the persistent radicals detected by ESR are nitroxide radicals with the structure $\text{R}_2\text{NO}'$. They can be formed by two consecutive alkyl radical scavengings, first a nitroso is formed by reaction (2) and then the nitroso traps the alkyl radicals:



Since no radicals of aminyl type were observed, reaction (4) can be ruled out. Moreover, the $\text{R}_2\text{NO}'$ radicals for tertiary alkyl groups are stable against autotermination and dimerisation like the spin label compounds of analogous structure⁶, and the molecular weight measurements of Brown were not accurate to make distinction between monomers and dimers⁴, and we think that the major primary product in the olefin nitric oxide system is not the $(\text{RNO})_2$ dimer, but the $\text{R}_2\text{NO}'$ nitroxide radical. This conclusion is in agreement with the result of Phillips and Coyne⁵, since the nitroxide radical can react with a further alkyl radical, which reaction can produce a hydroxylamine compound:



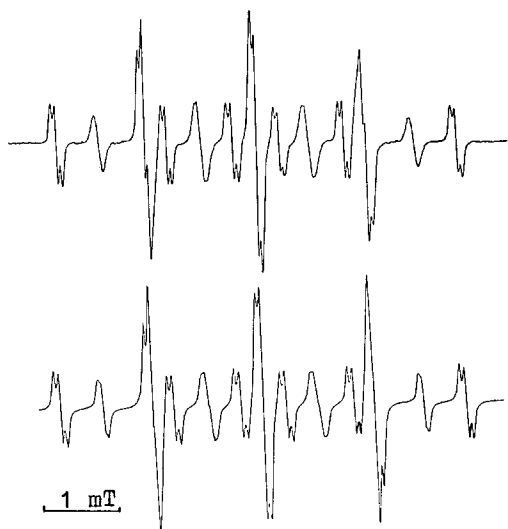


Figure 1: Experimental (top) and computer simulated (bottom) ESR spectra in the styrene-NO system. The signals of radical I ($g = 2.0059$, $a_N = 1.496$ mT, $a_{2H} = 1.196$ mT and $a_{2H}^2 = 0.06$ mT) and radical II ($g = 2.0059$, $a_N = 1.431$ mT, $a_{2H} = 0.686$ mT and $a_{2H}^2 = 0.05$ mT) are mixed in the ratio 1:0.65.

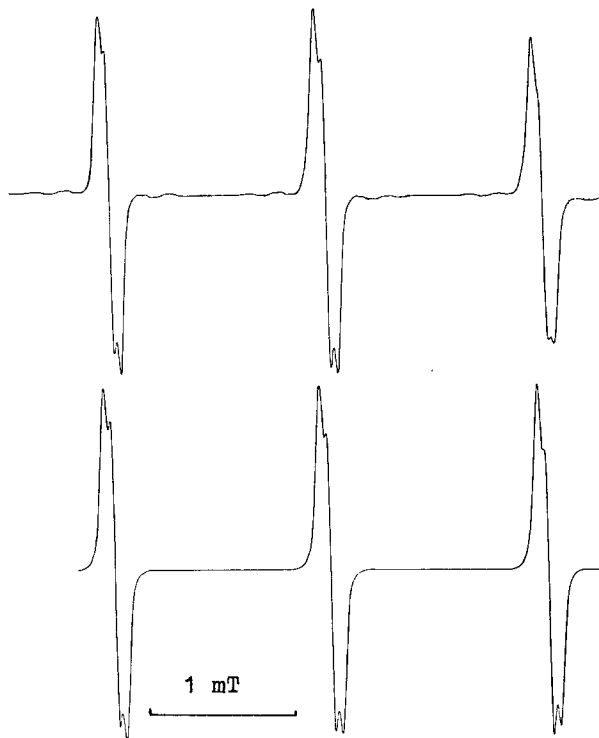


Figure 2: Experimental (top) and computer simulated (bottom) ESR spectra in the α -methylstyrene-NO system. The signals of radical I ($g = 2.0057$, $a_N = 1.485$ mT, $a_{2H} = 0.054$ mT) and radical II ($g = 2.0058$, $a_N = 1.475$ mT and $a_{2H} = 0.045$ mT) are mixed in the ratio 1:0.33.

The trapping of alkyl radicals in the systems of styrene and α -methylstyrene yields to the formation of diastereomer, which is reflected in the superpositional character of spectra in Figures 1 and 2. In styrene, similarly to the case when alkyl radicals were generated in ethylbenzene by hydrogen abstraction¹, the radicals with larger α -hydrogen couplings are formed in a larger concentration. With similar arguments used in Paper 1, we assign this radical to the diastereomer with identical chiral centers. After one day storage, the concentration ratio is shifted strongly in favour of this diastereomer, which shows the significant stereoselectivity of autotermination of nitroxide radicals. Unlike to the radicals observed in ethylbenzene¹, the nitrogen coupling constants are also different for the stereoisomers, which can be explained that the electron acceptor power of NO_2 groups is affected by the molecular geometry. In the α -methylstyrene-NO system, where no large hydrogen couplings exist, the asymmetry of three main nitrogen lines also shows the presence of diastereomers (Fig.2). Similarly to the system of styrene-NO, here also the more abundant stereoisomer has the larger couplings for C^{13} and hydrogen of the methylene group and for the nitrogen. Presumably, this species can be assigned to the diastereomer with identical chiral centers in both cases. In the α -methylstyrene-NO system, large radical concentration can be achieved, which

afforded the detection of naturally abundant O^{17} satellite lines⁷.

Additional consequence of chirality is the non-equivalent coupling of methylene hydrogens in styrene and α -methylstyrene (only a splitting due to two protons was resolved), while in isobutylene the nitrogen lines were splitted by four equivalent hydrogens.

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