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Electron Spin Resonance Studies of the Nitroxide Radicals Formed in the Reaction between Nitrogen Dioxide and Dimethyl Sulphoxide

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Previous electron spin resonance (ESR) studies have demonstrated that free radicals are formed in solutions containing nitrogen dioxide NO_2 , and a variety of different organic substances.¹⁻³ Thus, the radicals observed with compounds containing the groups $-\text{CH}_2-\text{CO}-$, $>\text{C}=\text{CH}-\text{CO}-$, or $-\text{CO}-\text{CH}_2-\text{CO}-$ were found to be α -iminoxy and 2-iminoxy-1,3-dioxo radicals, respectively.² Identical radicals were also obtained in the reaction between 1,3-dioxo compounds and tetranitromethane.⁴ The radicals formed when NO_2 reacts with methyl methacrylate have been considered to be nitroxide radicals.^{2,5} The structure of the radicals observed in

solutions of NO_2 and a variety of olefinic substances seems not to be completely understood, even if there is strong evidence for the formation of an NO_2 -olefin π -complex.³

This note describes the ESR-spectra of the radicals formed in the light induced reaction between NO_2 and dimethyl sulphoxide. After bubbling NO_2 through dimethyl sulphoxide for about one minute, the sample was irradiated *in situ* in the ESR-cavity with UV light. Almost immediately, radicals appeared which exhibited the spectrum shown in Fig. 1a. Of the six main groups present the two outer groups were split into quartets (1:3:3:1) without any overlaps. The four central groups also showed a quartet splitting but in this case there was overlap from further lines. An experiment performed with Fremy's radical as an internal standard gave a g -value equal to 2.0059 for the observed radical.

The radicals could also be produced when dimethyl sulphoxide was diluted by solvents such as benzene, chloroform, or H_2O , prior to bubbling with NO_2 . No radicals could be detected when dimethyl sulphoxide was replaced by dimethyl sulphone, or when NO_2 was replaced by tetranitromethane; nor could any radicals be detected when NO_2 was replaced by NO purified from NO_2 by bubbling through an alkaline water solution.

When the radicals were prepared from dimethyl sulphoxide- d_6 the spectrum shown

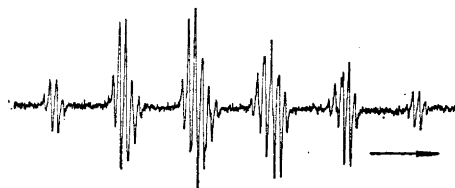


Fig. 1a. ESR spectrum of the radicals formed in the reaction between NO_2 and dimethyl sulphoxide.

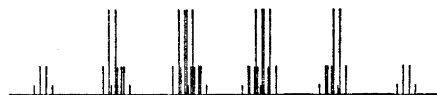


Fig. 1b. Reconstruction of the spectrum of Fig. 1a.

in Fig. 2 was obtained. The interpretation is straightforward and involves a main splitting into a triplet (1:1:1) evidently caused by the interaction of the unpaired electron with a ^{14}N nucleus. Each of the lines is further split into seven lines (1:3:6:7:6:3:1) by three equivalent deuterium nuclei. A very incomplete splitting of each of the 21 lines can just be observed under high resolution conditions.

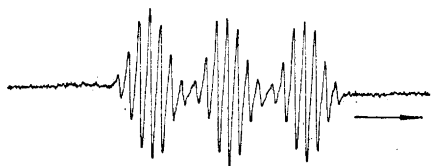
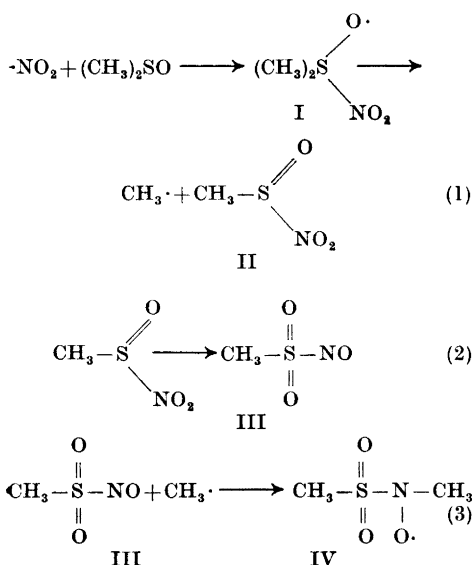


Fig. 2. ESR spectrum of the radicals formed in the reaction between NO_2 and dimethyl sulphoxide- d_6 .

By the use of these results the spectrum of Fig. 1a was analyzed and found to involve the following coupling constants: $a^{\text{N}}=12.2$ G, $a_1^{\text{H}}=11.0$ G (quartet: 1:3:3:1), $a_2^{\text{H}}=0.94$ G (quartet: 1:3:3:1); a reconstruction of the spectrum is shown in Fig. 1b. The findings imply that a nitroxide radical (IV) is formed which contains two non-equivalent methyl groups. The following reaction path is suggested



An intermediate compound,

$$\begin{array}{c}
 \text{O}\cdot \\
 | \\
 (\text{CH}_3)_2\text{S-OH}
 \end{array}$$

similar to I has previously been postulated in the reaction between hydroxyl radicals and dialkyl sulphoxides which leads to the formation of alkyl radicals in analogy with eqn. (1).^{6,7} The relatively large coupling constant $a_1^{\text{H}}=11.0$ G in the spectrum observed here indicates that one of the two methyl groups involved is situated directly on the nitrogen atom of the nitroxide group.^{6,8} Evidently, the methyl radical formed in eqn. (1) has been trapped by a nitroso compound. The latter class of compounds possesses scavenger properties for free radicals, and react to form stable nitroxide radicals (see Ref. 8). The nitroso compound III is very probably formed by the rearrangement of II according to eqn. (2).

An alternative mechanism might involve a direct intramolecular rearrangement of I to the observed radical IV without the presence of any free methyl radicals. However, this mechanism seems to be ruled

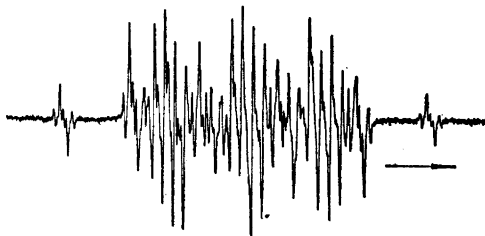


Fig. 3. ESR spectrum of the radicals formed in the reaction between NO_2 and a mixture of dimethyl sulphoxide and dimethyl sulphoxide- d_6 (1:1).

out by the following experiment. When the radicals were prepared from a mixture of dimethyl sulphoxide and dimethyl sulphoxide- d_6 (1:1) a number of new lines appeared in addition to the superposition of the two spectra shown in Figs. 1a and 2. The lines concerned were observed in the center of the two outer quartets of the spectrum of dimethyl sulphoxide, Fig. 3, and very probably originated from a radical species of the structure $\text{CD}_3\text{-SO}_2\text{-NO-CH}_3$, indicating an intermolecular cross-coupling according to the reaction scheme suggested above.

The exact role of the UV light is not known. It might involve the general activation of the reaction components, or the prevention of dimerization of the nitroso compound III to an inactive compound.⁸

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shown to contain simple phenethylamine derivatives.

The base fraction consisted of *N*-methylphenethylamine (I) and *N,N*-dimethylphenethylamine (II). The mixture was treated with ketene and then analyzed by combined gas chromatography-mass spectrometry. The retention times of II and of the acetyl derivative of I, as well as their mass spectra, were indistinguishable from those of authentic samples.

The main part of the alkaloid fraction consisted of a quaternary compound, a phenethyl trimethylammonium salt. This was isolated as the iodide (III), which was indistinguishable from an authentic sample (m.p., IR, UV, NMR).

10 kg of the fresh plant material afforded 1 g of III, 50 mg of I and 5 mg of II. Choline (0.3 g) was also obtained.

This seems to be the first time *N,N*-dimethylphenethylamine (II) and phenethyl trimethylammonium ion have been found in Nature.

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Studies on Orchidaceae Alkaloids

XV.* Phenethylamines from *Eria jarensis* Ames

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In most species of the genus *Eria* hitherto tested, a low alkaloid content has been detected.^{2,3} The first species investigated further, *Eria jarensis* Ames,** has been

* For paper No. XIV of this series, see Ref. 1.

** Collected in the Philippines by Miss Mary Fermin.