

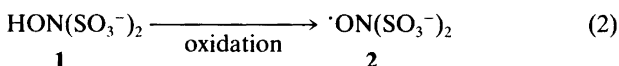
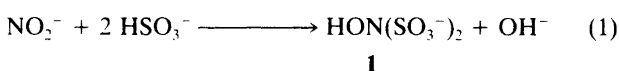
Radicals Formed in the Reaction between Some Alkyl Nitrites and Sulfite Ions Studied by EPR Spectroscopy

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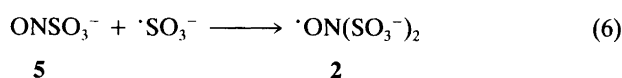
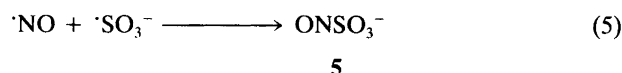
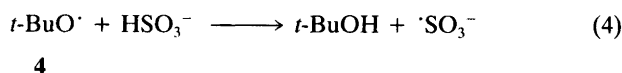
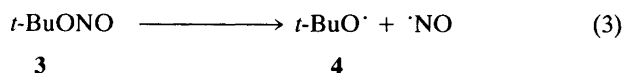
Previous EPR experiments^{1,2} have shown that the nitroso-disulfonate anion radical (Fremy's salt) (**2**) is formed in the reaction between nitrite and bisulfite anions, present in aqueous solutions of Na₂SO₃,³ eqns. (1) and (2).



The oxidation of the hydroxylamine (**1**) was performed with Ce⁴⁺ ions in acidic media,¹ or with O₂ in an alkaline aqueous solution, the latter method giving rise to more stable radicals (**2**).² It has now been found that the nitroso-disulfonate anion radical (**2**) is formed in high yield in the reaction between a number of alkyl nitrites and bisulfite ion without the addition of oxidizing reagents. Fig. 1 shows the EPR spectrum of the radicals obtained about 20 min after mixing 0.1 ml of *t*-butyl nitrite, 0.4 ml of methanol, 0.1 ml of 0.2 M NaOH and 0.1 ml of 0.01 M Na₂SO₃. The spectrum recorded at high amplification, exhibits the three-line system of **2**: *a*_{N14} = 1.3 mT, *g* = 2.0054, together with eight satellite lines which originate from the interaction of the unpaired electron with ¹⁵N (*I* = 1/2) and ³³S (*I* = 3/2) nuclei, the natural abundance of which are 0.37 and 0.76 % (*a*_{N15} = 1.80 mT, *a*_{S33} = 0.12 mT). Of the twelve ³³S lines, six are obscured by overlap from the three ¹⁴N lines. The coupling constants and *g*-value are in conformity with those obtained for a sample of Fremy's salt dissolved in an alkaline water solution.⁴ Identical results were obtained with NaHSO₃ (38 % in H₂O). The reaction was performed in a slightly alkaline medium in order to secure the stability of the radicals formed.

In addition to the spectral lines of radical **2**, Fig. 1 shows the presence of another radical species **R** that exhibits an interaction between the unpaired electron and one ¹⁴N nucleus and two equivalent hydrogen nuclei: *a*_N = 1.2 mT, *a*_H = 0.5 mT. The *g*-value of this radical is somewhat larger

than that of **2**, i.e. 2.0058. The same radical spectrum was obtained when the reaction was performed in methanol-*d*₄, or ethanol. No radicals of type **R** could be detected when the reaction was carried out with ethyl or butyl nitrite. In those cases the EPR spectra were completely dominated by the line-systems of radical **2**. The following reactions are suggested to be involved in the formation of radical **2** [eqns. (3)–(6)].



t-BuONO (**3**) is slowly split into nitric oxide and *tert*-butoxyl radicals (**4**) that abstract the hydrogen atom of bisulfite with the formation of the sulfite anion radical [•]SO₃[−] [eqn. (4)]. Reaction with nitric oxide gives the nitroso compound **5** [eqn. (5)]. Addition of a further [•]SO₃[−] radical to **5** gives the observed nitrosodisulfonate anion radical (**2**).

The aminoxyl radical **R** (Fig. 1) is formed by trapping of a primary radical of structure [•]CH₂R'. The latter radical is very probably not formed by abstraction of a hydrogen atom from the solvent alcohols, since the same 3 × 3 (1:2:1) spectrum was obtained in methanol, methanol-*d*₄ and ethanol. It is possible that the *t*-BuO[•] radical (**4**) abstracts a hydrogen atom from one of the methyl groups of **3** with the formation of the carbon-centered radical **6**, which is trapped by the nitroso compound **5** to give the aminoxyl radical **7**, eqn. (7).

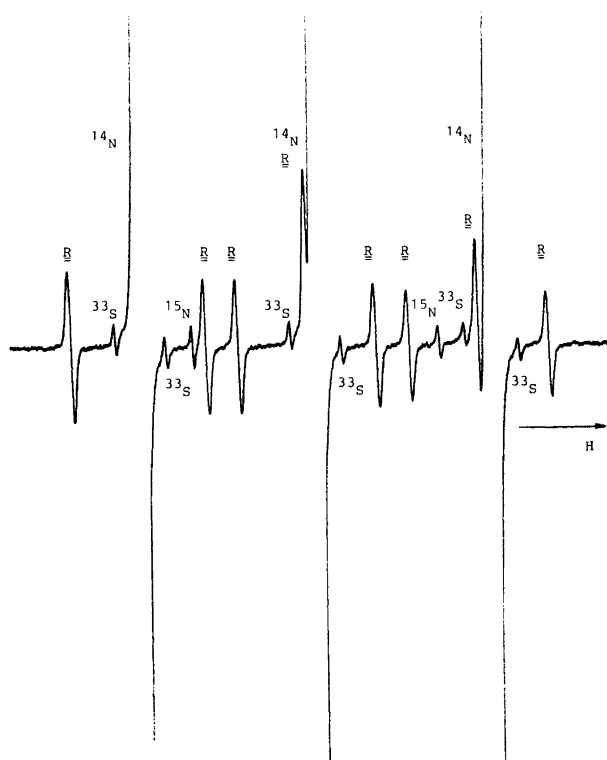
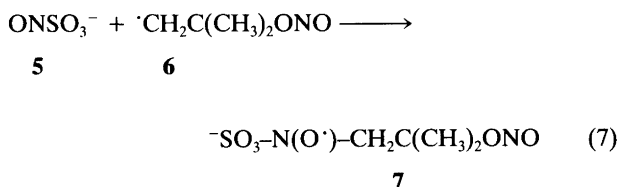
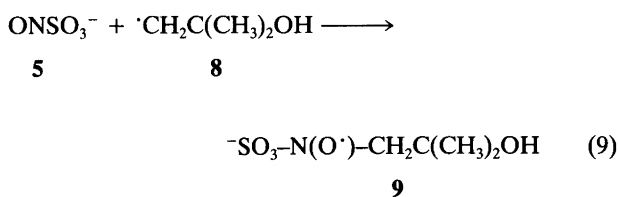
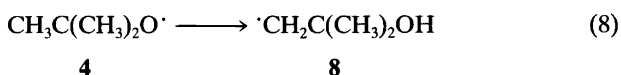


Fig. 1. EPR spectrum of the radicals formed in the reaction between *t*-BuONO and Na₂SO₃. The spectrum is an overlap of the line-systems of $\cdot\text{ON}(\text{SO}_3^-)_2$: three ¹⁴N lines and eight satellite lines from the natural abundance of ¹⁵N and ³³S nuclei, together with the lines of the aminoxyl radical **R**: 3 × 3 (1:2:1).



However, it is not clear why *t*-BuO \cdot radicals should abstract hydrogen atoms from *t*-BuONO (**3**) and not from solvent molecules such as methanol. An alternative explanation of the experimental findings might involve a rearrangement of the *t*-BuO \cdot radicals according to eqn. (8), a reaction path which seems not to have been reported so far,



followed by trapping of radical **8**. *t*-BuO \cdot radicals are known to undergo β -scission to form acetone and methyl radical.⁵ However, no CH₃ \cdot radicals were trapped in the reactions described here.

Aminoxyl radicals formed by trapping of carbon-centered radicals produced in the abstraction of hydrogen atoms from a tertiary butyl group often exhibit non-equivalent methylene hydrogens combined with line-width variations due to steric hindrance.^{6,7} No such anomalies could be observed in the spectrum of radical **R**, a finding that is consistent with the formation of a relatively small and non-bulky aminoxyl radical such as **7** or **9**.

The absence of radicals corresponding to the species **R** in the reaction with butyl nitrite might be connected with the inability of the BuO \cdot radical to abstract hydrogen atoms from H-C groups, or undergo a rearrangement analogous to that of *t*-BuO \cdot [eqn. (8)]. On the other hand, the BuO \cdot radicals are able to abstract hydrogen atoms from bisulfite in a reaction analogous to that of eqn. (4), since the nitrosodisulfonate anion radical (**2**) is also formed in high yield in the reaction with butyl nitrite.

The radical $\cdot\text{SO}_3^-$ is labile, but has been recorded by EPR spectroscopy in flow systems,⁸ in which the radical is continuously produced by abstraction of the hydrogen atom from HSO₃⁻ by $\cdot\text{OH}$ radicals generated in a Fenton reaction, or in the cleavage of H₂O₂ by UV light. The $\cdot\text{SO}_3^-$ radical is considered to be unable to abstract hydrogen atoms from hydrocarbon compounds, since the S-H bond expected to be formed in this process is much weaker than the C-H bond.³ For similar reasons, nitric oxide seems not to be able to perform hydrogen abstraction from hydrocarbon compounds.

Nitric oxide is known to play various important biological roles.⁹ In view of these findings, it would be interesting to apply the EPR technique to the study of reactions that involve $\cdot\text{NO}$. However, this relatively stable radical cannot be directly detected in aqueous solutions owing to its very short relaxation time. Furthermore, nitric oxide does not add to nitroso or nitrone spin traps to give aminoxyl radicals.

The experiments that gave rise to the aminoxyl radicals **2** and **R** can be considered to represent a very special form of spin trapping. Evidently, the radical species to be trapped constitutes the stable component, whereas the 'spin traps' are reactive and short-lived reagents. Whether such trapping systems might be of a practical value for the study of nitric oxide remains to be seen.

Finally, it should be mentioned that $\cdot\text{NO}$ has been used as a spin trap for a number of different short-lived radicals. These reactions gave rise to aminoxyl radicals detectable by EPR spectroscopy (Rockenbauer *et al.*¹⁰⁻¹²).

Experimental

The EPR spectra were recorded using a Varian E-9 spectrometer at 20°C with a microwave power of 1-2 mW and a 100 kHz modulation amplitude of 0.02 to 0.05 mT.

SHORT COMMUNICATION

Estimation of hyperfine splitting constants and *g*-factors were performed as described elsewhere.¹³ The chemicals used were obtained from Fluka AG or Aldrich Chem. Co., and were used as supplied.

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