Spin Adducts Formed from Nitroso Spin Traps and Dithionite

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In aqueous solutions of sodium dithionite, nitroso spin traps form stable nitroxide spin adducts $RN(O\cdot)SO_3^-$ as proven by their ^{17}O hyperfine structure, rather than sulphur dioxide anion radical adducts, $RN(O\cdot)SO_2^-$, as has been reported.

In several earlier publications,[1—3] a remarkable similarity of hyperfine coupling constants for nitroso compound spin adducts of the sulphur dioxide anion radical $[RN(O\cdot)SO_2^-]$ and the sulphur trioxide anion radical $[RN(O\cdot)SO_3^-]$ was reported. Mulvey and Waters also observed that Fremy's salt $[\cdot ON(SO_3)_2]^{2-}$ and the nitrosyldisulphinate anion radical $[\cdot ON(SO_2)_2]^{2-}$, formed by the reaction of nitrogen monoxide in alkaline sodium dithionite solution, had indistinguishable hyperfine coupling constants.[2] Although Lakatos *et al.* reported very small differences in the temperature dependence of

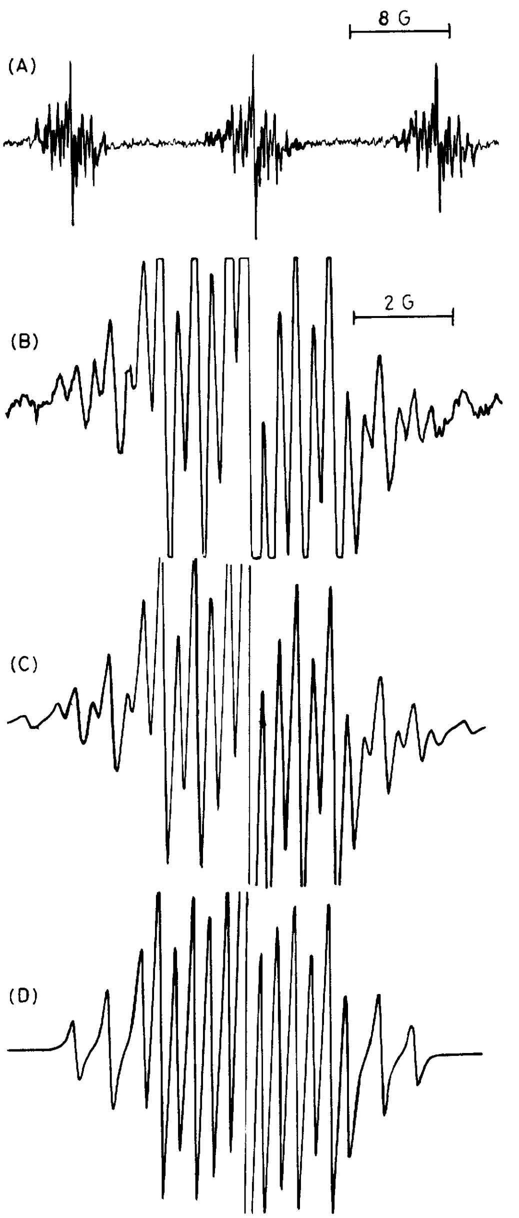

Figure 1. E.s.r. spectrum of the tNB radical adduct formed in alkaline sodium dithionite solution containing 56.3% $H_2{}^{17}O$ (16 mM tNB, 2.3 mM $Na_2S_2O_4$, 40 mM NaOH). (A) Complete spectrum. Spectrometer settings were: microwave power, 2 mW; modulation amplitude, 0.13 G; gain, 4 × 10^4; time constant, 0.25 s; sweep rate, 5.0 G min^{-1}. (B) Central component of the spectrum: microwave power, 2 mW; modulation amplitude, 0.13 G; gain, 2 × 10^5; time constant, 2 s; sweep rate, 0.63 G min^{-1}. Only the central component is shown. (C) Computer simulation of the tNB/$\cdot SO_3^-$ adduct. Parameters: $a(^{17}O) = 0.67_5$ G and 55% ^{17}O-content (I = 5/2), corresponding to an amplitude ratio (highest peak) of 23:75:61:100 for the species containing three, two, one, and no ^{17}O-atoms, respectively. (D) Computer simulation of the tNB/$\cdot SO_2^-$ adduct. Parameters: $a(^{17}O) = 0.67_5$ G and 68% ^{17}O-content, corresponding to an amplitude ratio (highest peak) of 75:71:100 for the species containing two, one, and no ^{17}O-atoms, respectively.

the $\cdot SO_2^-$ and $\cdot SO_3^-$ spin adducts with nitrosobenzene,[3] it remained unclear to us whether those spin adducts were really two different species or not. We therefore decided to study ^{17}O-labelled sulphur dioxide anion radicals and sulphur trioxide anion radicals, as the additional ^{17}O splittings would undoubtedly prove the structure of these spin adducts.

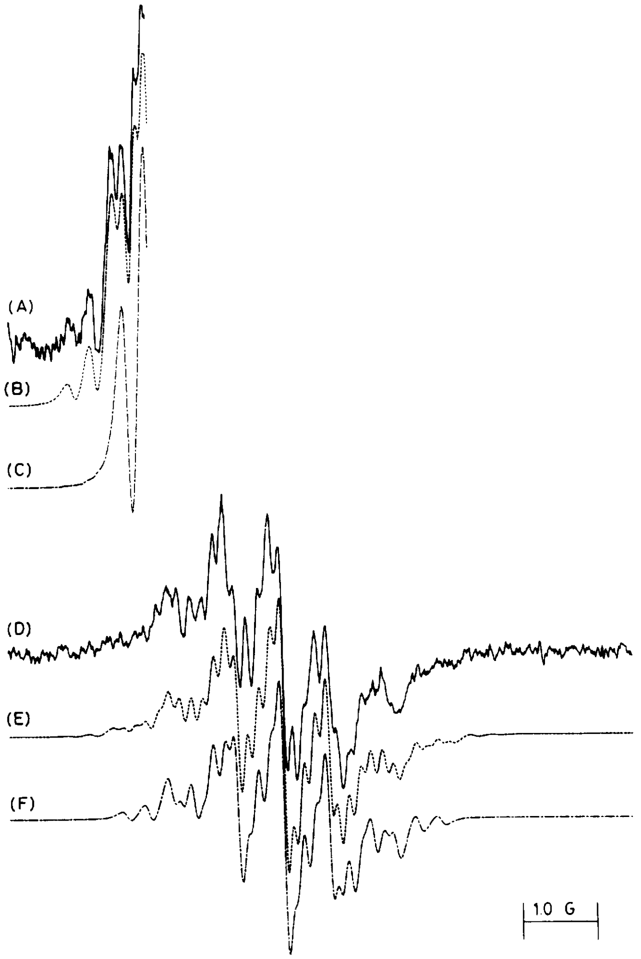

Figure 2. E.s.r. spectrum of the DBNBS radical adduct formed in sodium dithionite solution containing 58.7% $H_2{}^{17}O$ (200 mM DBNBS, 20 mM $Na_2S_2O_4$). (A) Experimental spectrum (outermost lines of the low-field component). Spectrometer settings were: microwave power, 1 mW; modulation amplitude, 66 mG; gain, 10 × 10^5; time constant, 32 s; sweep rate, 0.02 G min^{-1}. (B) Computer simulation of the DBNBS/$\cdot SO_3^-$ adduct. Parameters: $a\,(^{17}O) = 0.30$ G; a (H) = 0.63 G (2 protons) and 57% ^{17}O-content, corresponding to an amplitude ratio (highest peak) of 32:88:67:100 for the species containing three, two, one, and no ^{17}O-atoms, respectively. (C) Computer simulation of the DBNBS/$\cdot SO_2^-$ adduct. Parameters: $a\,(^{17}O) = 0.30$ G; a (H) = 0.63 G (2 protons) and 63% ^{17}O-content, corresponding to an amplitude ratio (highest peak) of 68:67:100 for the species containing two, one, and no ^{17}O-atoms, respectively. (D) Low-field component of the experimental spectrum. Spectrometer settings were: microwave power, 1 mW; modulation amplitude, 66 mG; gain, 10 × 10^4; time constant, 0.5 s; sweep rate, 1.25 G min^{-1}. (E) Computer simulation of the DBNBS/$\cdot SO_3^-$ adduct. Same parameters as in (B). (F) Computer simulation of the DBNBS/$\cdot SO_2^-$ adduct. Same parameters as in (C).

When sodium dithionite and the spin trap 2-methyl-2-nitrosopropane (t-nitrosobutane, tNB) were dissolved in nitrogen purged water and carefully handled in rubber sealed vials and flat cells, only a very weak e.s.r. signal could be obtained, although without the spin trap the single-line spectrum of the $\cdot SO_2^-$ radical was present.[4] However, when sodium dithionite was dissolved in air-saturated water and nitrogen purged immediately afterwards, the small amount of oxygen dissolved in water was sufficient to produce a strong e.s.r. signal when the spin trap was present.

To prove that the structure of the spin adduct is $Me_3CN(O\cdot)SO_3^-$,[5] we repeated the experiment dissolving the tNB and dithionite in ^{17}O-water (60% ^{17}O from MSD Isotopes) and obtained ^{17}O-couplings from three identical oxygen atoms. The results are in Figure 1. Figure 1A shows the complete spectrum. The coupling constant of the nitrogen is 14.7 G, the same as that Mulvey and Waters observed in their experiments.[2] Figure 1B shows the central component of the spectrum, and Figure 1C shows the best computer simulation for $Me_3CN(O\cdot)S^{17}O_3^-$. The statistical distribution of the four species containing three, two, one, and no ^{17}O-atoms was calculated using the binomial formula: c^3, $3c^2(1-c)$, $3c(1-c)^2$ and $(1-c)^3$, respectively, c being the ^{17}O enrichment of the mixture. In this simulation the ^{17}O coupling constant is 0.67_5 G and the concentration of the ^{17}O isotope in the adduct is 55%. Thus, the isotope exchange in the solvent (60% ^{17}O) was almost complete. The outermost lines in Figure 1C are clearly visible. The alternative structure $Me_3CN(O\cdot)SO_2^-$ would yield an e.s.r. spectrum containing only 11 lines that are derived from ^{17}O (best fit for 68% ^{17}O, Figure 1D). Since a ^{17}O content higher than the 56% of the water can never be obtained, the $\cdot SO_2^-$-adduct can be excluded. ^{13}C- and ^{33}S-satellite peaks have small hyperfine couplings and do not interfere with the outermost ^{17}O-lines. The ^{13}C- and ^{33}S-satellite peaks were assigned and their coupling constants were measured: a (^{13}C) = 4.0 G and a (^{33}S) = 1.6 G (G = 10^{-4} T). We therefore assign the observed species as the $\cdot SO_3^-$ adduct.

In the case of the nitrosobenzene adduct of the sulphur trioxide anion radical,[3] it is not possible to do this experiment because the contribution of five aromatic protons to the hyperfine structure renders the e.s.r. spectrum very complicated,[3,6] making the essential outer lines of ^{17}O too weak to be detected. Therefore, we decided to use the spin trap 3,5-dibromo-4-nitrosobenzenesulphonic acid (DBNBS) instead because it has only two aromatic protons, and its good solubility in water leads to spectra with a very high signal-to-noise ratio. In addition, the spectrum of its sulphur trioxide anion adduct has been reported recently.[7,8] Its e.s.r. spectrum consists of three multiplets separated by a nitrogen splitting constant of 12.7 G. In order to show the details, we expanded the low-field multiplet, which has the best spectral resolution. The results are shown in Figure 2. Figure 2A shows the outermost lines of the low-field component at high gain. Figure 2B is the computer simulation for the $\cdot SO_3^-$ adduct (best fit with a ^{17}O content of 57%). Figure 2C shows the best obtainable simulation for the $\cdot SO_2^-$ adduct. It is clearly evident that only the simulation in Figure 2B fits the experimental spectrum reasonably well. Figure 2D shows the low field component of the spectrum, Figure 2E the computer simulation for the $\cdot SO_3^-$ adduct, and Figure 2F the computer simulation for the $\cdot SO_2^-$ adduct. The splitting constants are a(H) = 0.63 G (2 *meta* protons) and a (^{17}O) = 0.30 G. The ^{17}O contribution in Figure 2E is 57%, while it is 63% in Figure 2F. The largest difference in hyperfine splittings between spin adducts of $\cdot SO_2^-$ and $\cdot SO_3^-$ as reported by Lakatos *et al.*[3] was only 0.2 G and could well be within experimental error.

The reported identity of the hyperfine couplings of spin adducts of $\cdot SO_3^-$ and $\cdot SO_2^-$ appeared to be a severe limitation of the spin-trapping technique, because different oxy-sulphur radicals could not be distinguished by spin trapping. Instead, the $\cdot SO_2^-$ radical apparently does not add to the nitroso bond at rates sufficient to form detectable spin adducts. Attempts to form radical adducts of $\cdot SO_2^-$ by its addition to the nitrone double bond of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) have also been unsuccessful, although $\cdot SO_3^-$ forms a very persistent radical adduct.[9] Addition of $\cdot SO_3^-$, but not $\cdot SO_2^-$, to carbon–carbon double bonds has also been reported.[10] In conclusion, $\cdot SO_3^-$, and not $\cdot SO_2^-$, is the species responsible for forming radical adducts in solutions of dithionite, contrary to previous reports.[1—3] The detection of $\cdot SO_3^-$ radical adducts in such solutions is in large measure a reflection of the persistence of this class of nitroxides, of which Fremy's salt is the best known example.

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