Some Nitrosylsulphinate Radical-anions RN(SO₂⁻)O·

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Alkaline sodium dithionite reacts with solutions of C-nitroso-compounds to give stable radicals $RN(SO_2^-)O\cdot$, the e.s.r. spectra of which are tabulated.   With alkyl nitrites and with nitric oxide aqueous dithionite yields the nitrosyl-disulphinate radical-anion, $\cdot ON(SO_2^-)_2$ the e.s.r. spectrum of which is indistinguishable from that of the nitrosyldi-sulphonate radical-anion, $\cdot ON(SO_3^-)_2$ of Frémy's salt.

IN a recent communication [1] one of us mentioned that the reduction of 2-methyl-2-nitrosopropane in aqueous methanol by alkaline aqueous sodium dithionite yielded a radical stable over the pH range 4—10 having a_N 1·47 mT and g 2·0055 which was thought to be the nitrosyl sulphinate radical-anion (I; $R = Me_3C$) formed by the addition of the $(\cdot SO_2)^-$ radical-anion to the N=O double bond of the nitroso-compound [reaction (1)].

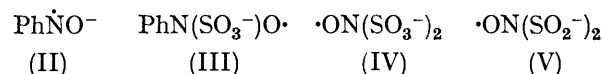$$RNO + (\cdot SO_2)^- \longrightarrow RN(SO_2^-)\text{--}O\cdot \qquad (1)$$
$$(I)$$
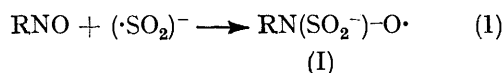
Many other tertiary aliphatic C-nitroso-compounds which we have had occasion to prepare [2] react in the same way.   Their e.s.r. spectra (Table 1) persist for several hours and do not exhibit further hyperfine splitting due to substituents present in the alkyl group R.

The spectra are weakened but not destroyed if their solutions are neutralised with acetic acid but are destroyed by the use of strong mineral acids.   Excess of dithionite destroys these e.s.r. signals and only the singlet of $(\cdot SO_2)^-$ (g 2·0057) then remains.

Similar spectra (Table 2) can be obtained from aromatic C-nitroso-compounds; these do exhibit hyperfine splitting due to the protons of the aromatic ring. On acidification of their solutions these spectra persist,

but become weaker at pH 4 and when the solutions are made alkaline again the signal strength increases.

$$\begin{array}{cccc} \text{Ph}\overset{\cdot}{\text{N}}\text{O}^- & \text{PhN(SO}_3^-)\text{O}\cdot & \cdot\text{ON(SO}_3^-)_2 & \cdot\text{ON(SO}_2^-)_2 \\ (II) & (III) & (IV) & (V) \end{array}$$

The spectrum of the radical-anion (I; $R = Ph$) was described by Russell and his colleagues [3] who obtained it by the dithionite reduction of nitrosobenzene in moist dimethyl sulphoxide or in dimethyl sulphoxide containing acetic acid.   The spectrum differs from that of the unstable nitrosobenzene radical-anion (II) which has a decidedly smaller a_N splitting constant and larger a_H (ortho and para) splitting constants than (I; $R = Ph$) and can only be obtained in strongly alkaline solution.[3-5] The spectra of the sulphinate radicals (I) can be obtained without the use of nitrogen.

More recently radical (I; $R = Ph$) has been described by Lakatos et al.[6] who have drawn attention to the similarity of the splitting constants of this radical to those of the sulphonate radical-anion (III).

When ethyl, or amyl, nitrite in aqueous methanol is treated with alkaline aqueous sodium dithionite a three line spectrum is obtained which, to within the experimental limitations of our instrument (10^{-3} mT), is superimposable on that of the well-known nitrosyldisulphonate radical-anion (IV) (i.e. Frémy's salt).   Our spectrum however must be that of the nitrosyldisulphin-

[1] W. A. Waters, *J.C.S. Chem. Comm.*, 1972, 1087.
[2] D. Mulvey and W. A. Waters, *J.C.S. Perkin II*, 1974, 666.
[3] G. A. Russell, E. J. Geels, F. J. Smentowski, K.-Y. Chang, J. Reynolds, and G. Kaupp, *J. Amer. Chem. Soc.*, 1967, **89**, 3821.
[4] C. J. W. Gutch and W. A. Waters, *Proc. Chem. Soc.*, 1964, 230.
[5] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.* (B), 1966, 903.
[6] B. Lakatos, B. Turcsányi, and F. Tüdös, *Acta. Chim. Acad. Sci., Hung.*, 1971, **70**, 225.

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TABLE 1

E.s.r. spectra of radical-anions

$$R^1 \diagdown \quad \diagup O\cdot$$
$$R^2\text{--}C\text{--}N$$
$$\diagup \quad \diagdown$$
$$X \qquad SO_2{}^-$$

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R¹	R²	X	a_N/mT	g Value	R¹	R²	X	a_N/mT	g Value
Me	Me	Me	1·47	2·0055	Me	Et	Cl	1·34	
Me	Me	Cl	1·37		Me	Et	Br	1·34	
Me	Me	CN	1·44		Me	Et	CN	1·42	
Me	Me	NO₂	1·37		Me	Et	NO₂	1·35	2·0059
Me	Me	OAc	1·36	2·0056					
Me	Pr¹	Cl	1·34	2·0053	Me	Buᵗ	Cl	1·35	2·0057
Me	Pr¹	Br	1·35		Me	Buᵗ	Br	1·34	2·0058
Me	Pr¹	NO₂	1·31						
Me	Pr¹	OAc	1·35		Me	Buᵗ	OAc	1·36	
Et	Et	Cl	1·33		C₆H₁₀ ᵃ		Cl	1·34	
Et	Et	Br	1·31		C₆H₁₀ ᵃ		Br	1·32	2·0057
Et	Et	CN	1·41	2·0058	C₆H₁₀ ᵃ		CN	1·42	2·0055
Me	Ph	Cl	1·31		C₆H₁₀ ᵃ		NO₂	1·31	2·0055
Me	Ph	OAc	1·34	2·0057	C₆H₁₀ ᵃ		OAc	1·35	
Me	H	Cl	1·34		C₅H₈ ᵇ		NO₂	1·32	2·0055
Me	Ac	Cl	1·35		Me	Cl	Cl	1·32	
Me	Bz	Cl	1·37		Me	Br	Br	1·32	
					Et	Br	Br	1·33	

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ᵃ C_6H_{10} = Cyclohexylidene.   ᵇ C_5H_8 = Cyclopentylidene.

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ate radical-anion (V). It can also be obtained by passing nitric oxide into aqueous sodium dithionite made alkaline with sodium carbonate. On acidification of these solutions the spectra of (V) persist even at pH 2.

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TABLE 2

E.s.r. spectra of radical-anions

$$Ar\text{--}N \diagup O\cdot$$
$$\diagdown SO_2{}^-$$

a/mT

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			a/mT			Overall	g
Ar	a_N	a_{o-H}	a_{p-H}	a_{m-H}	a_N	width	Value
C₆H₅	1·18	0·24	0·24	0·09		3·28	2·0054
p-ClC₆H₄	1·16	0·26		0·10		3·04	2·0055
2,4,6-Cl₃C₆H₂	1·25			0·06		2·64	2·0060
p-BrC₆H₄	1·16	0·25		0·09		3·04	2·0056
p-EtOCOC₆H₄	1·11	0·25		0·10		2·90	2·0055
p-H₂NC₆H₄	1·23	0·25		0·07	0·12	3·37	2·0050

Equations (2)—(5) satisfactorily explain the reactions of the alkyl nitrites; (4) and (5) resemble the reactions between nitric oxide and free radical-anions.

$$(S_2O_4)^{2-} \rightleftharpoons 2(\cdot SO_2{}^-) \qquad (2)$$

$$RO\text{--}NO + (\cdot SO_2)^- \longrightarrow RO^- + NO + SO_2 \qquad (3)$$

$$NO + (\cdot SO_2)^- \longrightarrow O\text{=}N(SO_2{}^-) \qquad (4)$$

$$O\text{=}N(SO_2{}^-) + (\cdot SO_2)^- \longrightarrow \cdot ON(SO_2{}^-)_2 \qquad (5)$$

Since the electrostatic effects of the $SO_3{}^-$ groups in (IV) and the $SO_2{}^-$ groups in (V) upon the nitrosyl group N–O· must be qualitatively similar it was expected that the hyperfine sp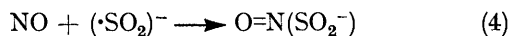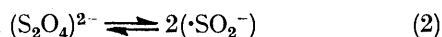litting constants and the g values of the e.s.r. spectra of the radicals (IV) and (V) would be similar too, but it was not anticipated that we would not have succeeded in distinguishing between them.

EXPERIMENTAL

The preparations of the aliphatic nitroso-compounds have been described recently.[2] The aromatic compounds were made by the customary route. *Ethyl* p-*nitrosobenzoate* does not appear to have been characterised hitherto. Its dimer crystallises from alcohol in yellow needles which at 81° melt sharply to the blue-green monomer (Found: C, 60·3; H, 5·3; N, 7·9. $C_9H_9NO_3$ requires C, 60·3; H, 5·1; N, 7·8%).

To obtain the radical-anions an aqueous solution of sodium dithionite containing sodium carbonate (pH *ca.* 9) or sodium hydroxide (pH *ca.* 11) was added dropwise to dilute solutions of the nitroso-compounds in methanol so that the mixtures still remained pale blue after storage for a few minutes. If necessary a little water was added to dissolve precipitated sodium salts. The free radicals could successfully be prepared under nitrogen, but this procedure had little advantage. The e.s.r. spectra were observed with a Varian E4 spectrometer and were calibrated by comparison with Frémy's salt (a_N 1·309 mT; g 2·0055).[7] The splitting constants in individual spectra could be measured to ±0·005 mT but to take account of solvent effects in the varying methanol–water mixtures which have been used they are reported in the Tables to ±0·01 mT only.

[7] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2467.